21ª RAU
REUNIÃO ANUAL DE
USUÁRIOS DO LNLS
22 E 23 FEVEREIRO 2011

RESUMOS

DE TRABALHOS CIENTÍFICOS

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21ª RAU - REUNIÃO ANUAL DE USUÁRIOS DO LNLS
21st Annual Users Meeting

22 E 23 DE FEVEREIRO DE 2011
February 22-23, 2011

Hotel Premium Norte
Campinas – SP, Brazil

LNLS

CNPEM

Ministério da
Ciência e Tecnologia

Agenda

22 de fevereiro	
08:30	**Recepção / Inscrições**
09:00	**Abertura** *Antônio José Roque da Silva* *Diretor LNLS*
09:15	**Status e perspectivas** *Yves Petroff* *Diretor Científico do LNLS*
09:45	**Projeto Sirius** *Antônio Ricardo Droher Rodrigues* *Coordenador do Projeto Sirus*
10:15	**Foto Oficial**
10:30	**Coffee Break**
10:50	**Plenária I** *Oleg Gang* *Brookhaven National Laboratory - USA*
11:40	**Plenária II** *Peter Cherepanov* *Imperial College of London-UK*
12:30	**Almoço**
14:00	**Sessões Temáticas I** *SAXS1 e SAXS2* (Sala 06) *LME* (Sala 09) *GM, SGM e SXS* (Sala 08) *MX1 e MX2* (Sala 02)
15:10	**Comunicações Orais** *Sessões Paralelas*

22 de fevereiro	
16:10	**Coffee Break**
16:40	**Sessões Temáticas II** *XAS e DXAS* (Sala 06) *XRF* (Sala 09) *XRD e XPD* (Sala 08) *MTA e LMF* (Sala 02)
17:50	**Comunicações Orais** *Sessões Paralelas*
18:50	**Sessão de Pôsteres** *Confraternização*

23 de fevereiro	
08:30	**Comunicações Orais** *Sessões Paralelas*
09:30	**Plenária III** *Vitali Prakapenka* *Argonne National Laboratory - USA*
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10:50	**Plenária IV** *Adam P. Hitchcock* *McMaster University – Canada*
11:40	**Discussão com Comitê de Usuários**
12:20	**Encerramento** *Resumo, avaliação e discussões*
13:30	**Almoço**

Comunicações Orais

22 de fevereiro	
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15h30	Crystallization and Preliminary X-Ray Studies of a New Acidic PLA2 from Bothrops moojeni Venom **Guilherme Henrique Marchi Salvador (pág. 06)**
15h50	Self-assemble properties of peptides: the Growth hormone releasing peptide (GHRP) case **Leandro Ramos Souza Barbosa (pág. 22)**
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15h30	Propriedades Eletrônicas e Estruturais de Filmes Nanoestruturados de ZnO **Talita Ströher Bürger (pág. 158)**
15h50	Superhydrophobic Al surfaces prepared by chemical surface functionalization of nano/micro structures **Daniel Eduardo Weibel (pág. 175)**
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	Métodos e Instrumentação (SALA 09)
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15h30	Testes de detectores de conversão direta do tipo APD no LNLS **Edson Massayuki Kakuno (pág. 112)**
15h50	An integrated image processing tool for strain mapping of thermomechanical SEM in situ experimentation **Ricardo Diogo Righetto (pág. 117)**
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17h50	Ionic photofragmentation of ClSO$_{2}$NCO in the S 2p, Cl 2p and S 2s regions **Angelica Moreno Betancourt (pág. 48)**
18h10	Estudo Teórico-Experimental da Fotofragmentação de Moléculas Pré-bióticas na Região da Valência **Manuela Souza Arruda (pág. 49)**
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	Geociência, Meio-ambiente e Aplicações em Materiais Biológicos (SALA 9)
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	Matéria Mole e Fluídos Complexos (SALA 02)
17h50	Phase transitions in membrane of lipids **Barbara Bianca Gerbelli (pág. 92)**
18h10	Stability and structure of sodium caseinate emulsions **Maria Lidia Herrera (pág. 89)**
18h30	Sol-gel synthesis: effect of precursors on the microstructure of silica hydrogels **Roberto Jorge Candal (pág. 90)**

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23 de fevereiro

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8h50	Structural and dynamic analysis of the sweet orange Hsp90 using SAXS **Yuri Abreu Mendonça (pág. 16)**
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8h50	Observation of Ferromagnetism in PdCo Alloy Nanoparticles encapsulated in Carbon Nanotubes **Rogerio Magalhaes Paniago (pág. 150)**
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9h10	Synchrotron radiation techniques applied to the study of GexSi1-x nanoparticles embedded in silica **Antonio Augusto Malfatti Gasperini (pág. 195)**
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8h50	Mecanismo de fratura intergranular por queda de ductilidade em ligas Ni-Cr-Fe endurecidas por solição sólida **Jimy Unfried (pág. 106)**
9h10	Utilização de raios-X a baixo ângulo (SAXS) em estudo de ligninas de bagaço e palha de cana-de-açúcar submetidas a diferentes tipos de processamento **Priscila Maziero (pág. 101)**

RESUMOS CONVIDADOS

Structural biology of retroviral DNA integration

Peter P. Cherepanov

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Integrase (IN) is the essential retroviral enzyme that binds both ends of linear viral DNA and inserts them into a host cell chromosome. Although clinically useful inhibitors of HIV IN strand transfer activity were developed (1), their mechanism of action was not known. These small molecules bind at the IN active site only when the enzyme is engaged with viral DNA within the functional nucleoprotein complex, termed intasome. Thus, in order to learn the structural basis for strand transfer inhibitor action, it was imperative to obtain diffracting crystals of the functional IN DNA complex.

Following comparative analyses of a range of divergent retroviral IN proteins we identified the ortholog from prototype foamy virus (PFV) as a promising model for detailed structural studies. Crucially, PFV IN was sensitive to clinical HIV strand transfer inhibitors (2). Using oligonucleotides mimicking viral DNA ends and wild type PFV IN we were able to obtain high quality crystals of the PFV intasome. Semiautomated screening, which afforded testing over 40,000 individual crystallization conditions, was vital to identification of the useful crystal form. The structure revealed for the first time the organization of the intasome comprising an IN tetramer assembled on a pair of viral DNA ends and the fully ordered IN active site (3).

Further work resulted in structural characterization of the PFV intasome engaged with target DNA and provided snapshots of the key intermediates of the retroviral integration process, elucidating the mechanics of the retroviral integration machinery (4). Soaking intasome crystals in the presence of HIV IN strand transfer inhibitors, such as raltegravir and elvitegravir, revealed how these small molecules bind at the IN active site and inactivate the viral nucleoprotein complex (3,5). The PFV structures furthermore helped us to explain the major raltegravir resistance mutations in HIV IN (5). This wealth of new structural information will aid the development of the secondgeneration HIV IN inhibitors with improved resistance profiles.

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Nanoscale systems assembled with DNA: from principles to rational design

Oleg Gang

Incorporation of biomolecules with specific recognitions into nano-object design provides a unique opportunity to establish highly selective and reversible interactions between the components of nanosystems. The interaction encoding can tremendously expand the concept of self-assembly by providing programmable instructions for the formation of structures from the multiple types of components. Our work explores how DNA can be engaged in the encoded interactions between inorganic nano-components, and how the morphology of self-organized structures can be regulated. By tailoring interplay of specific recognition interactions and non-specific physical effects, we have demonstrated an ability to control assembly kinetics, clustering, and ordering of DNA-capped nanoparticles, as well as we have probed an assembly behavior in-situ using synchrotron based x-ray scattering methods. I will discuss our recent progress in understanding the principles of programmable assembly and effects associated with polymeric nature of DNA and nano-object anisotropy. I will review approaches developed in our group for the rational fabrication of nanosystems with well-defined architectures, including 3D superlattices, finite size clusters of nanoparticles and switchable assemblies. Applications of these classes of systems for biosensing and for nano-optics will be also discussed.

Thickness and Clapeyron slope of the post-perovskite boundary

Vitali B. Prakapenka

The thicknesses and Clapeyron slopes of mantle phase boundaries strongly influence the seismic detectability of the boundaries and convection in the mantle. The unusually large positive Clapeyron slope found for the boundary between perovskite (Pv) and post-perovskite (pPv) (the ‘pPv boundary’) would destabilize high-temperature anomalies in the lowermost mantle, in disagreement with the seismic observations. IN this talk, we report the thickness of the pPv boundary in $(Mg_{0.91}Fe^{2+}_{0.09})SiO_3$ and $(Mg_{0.9}Fe^{3+}_{0.1})(Al_{0.1}Si_{0.9})O_3$ as determined in a laser-heated diamond-anvil cell under in situ high-pressure (up to 145 GPa), high-temperature (up to 3,000 K) conditions. The measured Clapeyron slope is consistent with the D″ discontinuity. In both systems, however, the pPv boundary thickness increases to 400–600 ± 100 km, which is substantially greater than the thickness of the D″ discontinuity (<30 km). Although the Fe^{2+} buffering effect of ferropericlase could decrease the pPv boundary thickness, the boundary may remain thick in a pyrolitic composition because of the effects of Al and the rapid temperature increase in the D″ layer. The pPv boundary would be particularly thick in regions with an elevated Al content and/or a low Mg/Si ratio, reducing the effects of the large positive Clapeyron slope on the buoyancy of thermal anomalies and stabilizing compositional heterogeneities in the lowermost mantle. If the pPv transition is the source of the D″ discontinuity, regions with sharp discontinuities may require distinct compositions, such as a higher Mg/Si ratio or a lower Al content.

Combined HRTEM and STXM-NEXAFS study of a patterned CNT

Adam P. Hitchcock

High-resolution transmission electron microscopy (HRTEM) and scanning transmission X-ray spectromicroscopy (STXM-NEXAFS) were used to evaluate the electronic, structural and chemical changes induced by irradiating a carbon nanotube at different ion/electron doses. The NEXAFS spectra recorded on the pristine CNT show strong Ē-polarization dependence (linear dichroism) due to the anisotropy of the electronic structure. For increased irradiation time the Ē-polarization dependence decreases due to creation of sp2 defects. Local defect densities can be evaluated by the spatial distribution of the p* intensity.

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Parte VII Métodos e Instrumentação

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Parte I

Biologia Estrutural

Structural characterization of Ohr (Organic Hydroperoxide Resistance Protein) from *Xylella fastidiosa* in oxidized conformation.

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The protein Ohr (Organic Hydroperoxide Resistance) is a Cys-based, Lypoyl-dependent peroxidase that plays an important role in the bacterial defense against organic hydroperoxide insult. This gene is present exclusively in prokaryotes and the protein possesses an alfa/beta fold that is not observed in the structure of other antioxidant enzymes as Peroxiredoxins and Glutathione Peroxidases. We previously determined structure of Ohr from *X. fastidiosa* and showed that the over-oxidized and reduced forms are in the closed conformation, in which a residue of arginine (Arg19) points toward the peroxidasic cysteine (Cys61), probably stabilizing it in a thiolate (RS^-) form. It was proposed that during the catalytic cycle (reduction of an organic hydroperoxide) the loop containing Arg19 detaches, releasing the product formed and the Ohr adopt the open conformation (oxidized, disulfide form). The determination of the Ohr structure from *X. fastidiosa*, in the open conformation may be helpful to understand the dynamic of the conformational changes of the protein during the catalytic cycle. Ohr was crystallized after treatment with diamide using sodium citrate (0.4 M) as precipitant in a sodium cacodylate buffer (0.1 M) at pH 6.0. Its diffraction patterns extend to 2.15 and the crystal diffracted belongs to space group C121 with the unit cell parameters a= 87.813, b= 83.693 and c= 60.766 . The crystal structure was solved by molecular replacement methods using the coordinates of a previous structure determined of the Ohr itself in an over-oxidized conformation (PDB: 1ZB9). At the moment, the refinement of the new structure is being performed.

Acknowledgements: This work was supported by FAPESP and CNPq (INCT Redoxoma)

Structural characterization of the Thioredoxin reductase 2 protein from *Saccharomyces cerevisiae*.

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In *Saccharomyces cerevisiae* the mithocondrial thioredoxin system composed by thioredoxin (Trx3), thioredoxin reductase (TrxR2) and NADPH acts as a disulfide reductase system that can protect the cell against oxidative damage. The interaction between thioredoxin-reductase and thioredoxin generally presents specie-specificity, where *S. cerevisiae* thioredoxin reductase 1 is able to reduce any *S. cerevisiae* thioredoxin (Trx1/Trx2/Trx3) but it fails to reduce human and *E. coli* thioredoxin counterparts and enzymatic assays have shown that there exists a difference between the catalytical efficiency to which thioredoxin reductase reduces each thioredoxin. Further understanding about the structure from TrxR2 may assist us in the comprehension of mechanisms involved in antioxidant defense and protein-protein interaction during catalysis. We have conducted the initial screening of TrxR2 using the LNLS automated crystal screening facility and after optimization of some conditions through the Reichert method several crystals have been obtained. Data collected at the LNLS MX-2 beamline has shown crystals that have diffracted at 1.9 resolution from the condition containing 100mM Bis-Tris/HCl pH 6.35; 25% Peg-3350; 200mM (NH_4)sulfate. The crystals belong to the space group P1 with unit cell parameters a = 64,58; b = 74,31; c = 79,13 . Molecular replacement using the coordinates from Thioredoxin reductase 1 from *Saccharomyces cerevisiae* and structure refinement have given us a Rfactor = 0,198 (Rfree = 0,249).

Acknowledgements: This work was supported by FAPESP.

Structural Study of Amyloid-like Proteins in Solution

Sales, E.M.[1], Damalio, J.C.P.[2], Barbosa, L.R.S.[3], Araújo, A.P.U.[2], and Itri, R.[3]

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Septins are GTP-binding proteins that were originally discovered in the budding yeast *Saccharomyces cerevisiae* cell division cycle forming 10 nm wide filaments that had to main functions: scaffold protein-protein interactions and act as diffusion barriers regulating the intracellular localization of proteins. They are largely found in neurodegenerative pathologies such as Parkinson, Alzheimers diseases and also solid tumors, forming highly organized fiber-like aggregates known as amyloid fibrils that are mostly composed by cross-β sheets.

In the present work, we used SAXS to investigate the formation and evolution of these aggregates at the influence of parameters such as temperature and concentration. We performed measurements with the entire Septin 2 protein (SEPT2) and only with the GTPase domain of Septin 2 (SEPT2G) at 1, 2.5 and 5 mg/mL concentrations and temperatures of 28, 37 and 46^oC.SAXS results indicate that, at the lowest temperature, there is already a coexistence of two distinct cylinders for both studied proteins. For SEPT2 at the lower concentration and temperature, the length of the smaller cylinders amounts to 170 , whereas the cross-section is approximately 60 wide; for the larger cylinders the measurements were of 420 and 300 , respectively. Increasing the temperature, it is possible to observe that the amount of thinner cylinders diminishes from 42 to 11%, indicating that the aggregate grows with the temperature.

Concerning SEPT2G, the SAXS data analysis reveals that for the lowest concentration and temperature, the cylinder cross-section radius and the length are equal to 30 and 180 , respectively; whereas for the larger cylinder we found 170 and 430 for the cylinder cross-section radius and length, respectively. Increasing the temperature, the scattered intensity contribution of small cylinders goes from 46 to 16%. For SEPT2G the effect of concentration was also observed and with the increasing of the concentration was possible to observe that not only the amount of small cylinders decreases but there is a formation of longer cylinders. We are now performing DLS measurements to better understand the bigger cylinders that form the aggregates, once that their lengths are on the edge of the SAXS technique. Nevertheless, our preliminary results indicate the presence of a small fiber coexisting with larger aggregates in solution, for both proteins.

Acknowledgements: FAPESP and CNPq for the financial support.

Crystallization and Preliminary X-Ray Studies of a New Acidic PLA2 from Bothrops moojeni Venom

Salvador, G. H. M.[1], Marchi-Salvador, D. P.[2], Silveira, L. B.[3], Soares, A. M.[3], and Fontes, M. R. M.[1]

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Phospholipases A2 (PLA2s) are small calciumdependent proteins that cause the liberation of fatty acids and lisophospholipids by hydrolysis of membrane phospholipids. These enzymes are largely studied because of the various pharmacological effects they play in envenomation by snake bites. BmooPLA2-I is an acid, non-toxic and catalytic phospholipase A2 isolated from Bothrops moojeni snake venom which exhibits inhibitory effect on platelet aggregation, immediate decrease in blood pressure, inducing edema at low concentration and an effective bactericidal effect. BmooPLA2-I was crystallized and X-ray diffraction data were collected to 1.9 resolution using a synchrotron-radiation source. The crystals belong to C2221 space group with unit-cell parameters a=39.3, b=54.2, c=90.6 . Preliminary analysis indicates the presence of one molecule in the asymmetric unit which is in agreement to non-denaturant electrophoresis experiments. The molecular replacement solution of BmooPLA2-I also indicate the monomeric state displaying similar conformation to the acid PLA2 form B. jararacussu (BthA-I). This comparative study may bring important insights into functional aspects of this class of proteins.

Acknowledgements: Financial support: FAPESP, CNPq and LNLS.

Small angle X-ray scattering studies of the cellulolytic enzymes with potential to hydrolyse sugarcane biomass

Oliveira Neto M.[1], Rosseto, Flávio R.[1], Serpa, V.I.[1], Colussi,F.[1], Voltatódio, M. L.[1], A. F. Craievich[2], and Polikarpov, I.[1]

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Concern for the environment, plus the depletion of fossil fuels has generated great interest among various sectors of society, making the ways of producing biofuels more affordable and efficient. The use of ethanol from renewable raw materials, such as sugarcane bagasse, represents a potential alternative source of energy, and it has been considered feasible and promising in Brazil. However, to make possible the use of biomass it is necessary to degrade cellulose, a constituent of the cell wall, to fermentable sugars. One form of degradation is the enzymatic hydrolysis, which is quite advantageous in many respects, especially as regards the use of "green chemistry". However, the use of enzymes for this purpose still presents high cost, which has led to more studies to make cellulosic ethanol economically viable. The structural knowledge of the enzymes as well as the interaction of these with the pretreated bagasse from sugarcane during the hydrolysis is extremely important. Small angle X-ray scattering (SAXS) is available for this purpose. Until the moment, any intact structure of cellulases was solved by crystallography or NMR. SAXS is able to give structural parameters about intact structures, as radius of gyration, maximum diameter, shape and relative position of the domains. SAXS studies have been done with cellobiohydrolase I and II from *T. harzianum* and with beta-glucosidase from *A. niger* . These study aims at understanding the molecular basis of the functioning of enzymes for application in the production of bioethanol from sugarcane bagasse.

Acknowledgements: This work was supported by FAPESP

Caracterização de celulose cristalina obtida a partir do bagaço de cana-de-açúcar

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O estudo de nanofibras de celulose atuando como fase de reforço em materiais se iniciou há aproximadamente 20 anos. Essas nanofibrilas de celulose retêm propriedades muito importantes e a principal razão de se utilizar nanocristais de celulose como agente reforçante em polímeros ou outros materiais, é que esses podem potencialmente explorar a rigidez e resistência das fibrilas em prol da otimização do compósito final. Considerando que o bagaço de cana-de-açúcar possui uma estrutura hierárquica fibrosa, pode-se tratá-lo de forma a romper com essa hierarquia, liberando a celulose cristalina. O módulo cristalino desses cristais no formato bastão é, segundo estudos, 138GPa, e considerando o módulo específico, que inclui a resistência do material normalizada pela sua densidade, esse valor se torna ainda mais alto, superando o do aço. No contexto da biorefinaria, o reaproveitamento da celulose cristalina busca agregar valor a esse resíduo da produção de etanol de segunda geração, permitindo em um futuro próximo, que o método se torne ambientalmente e economicamente viável. Neste trabalho, foram realizados estudos de caracterização de celulose cristalina. Inicialmente foi feito pré-tratamento do bagaço com posterior reação alcalina para remoção de lignina. Posteriormente foi realizada hidrólise enzimática desse bagaço seguida de uma hidrólise ácida branda, obtendo-se assim uma suspensão, formada por nanocristais de celulose. Esta suspensão foi investigada por espalhamento de raios-x a baixo ângulo (SAXS) e por espalhamento de luz dinâmico (DLS). Foi estudada também a cristalinidade desse bagaço após as etapas de pré-tratamento e hidrólises, além da interconversão das formas cristalinas utilizando o processo de mercerização alcalina.

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Molecular dynamics of a group II mutant periplasmic-binding protein: implications on movements for opening, closing and interaction with ligand

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Periplasmic-binding proteins (PBPs) in bacterial ABC transport systems have been studied functionally and structurally by our group and have shown higher stability of their flexible domains in the presence of their respective ligands (Balan et. al., 2006; 2008). PBPs comprise a structural classification depending on the number of interdomain connections they have: group I contain PBPs with 3 interdomain connections; group II with 2 and group III with a single α-helix connecting both domains. The PBPs studied in our group so far belong to the group II and molecular dynamic (MD) simulations have been applied using the crystallographic structure of the molybdate-binding protein ModA of *Xanthomonas axonopodis* pv. *citri* (*Xac*) (Balan et. al., 2006), to describe for the first time the kind of movements performed by PBPs of the group II in the presence and absence of the ligand. On the other hand, mutants of the ModA protein allowed the identification of a novel interaction region between domains that seems to be important for the binding function. Moreover, spectroscopic analyses by circular dichroism, fluorescence and structural characterization showed a different behavior of the mutant when compared to the native protein (*in prep*). In the same way, 50 ns simulations were performed using the structure of the ModA-mutant protein (pdb code: 3ZGZ) containing the residue D59 mutated for an alanine. The results showed that the binding and release mechanism of group II PBPs needs the coupling of two kinds of movements to compensate the limited flexibility of these structures. The presence of the mutation was not important for the movement of the domains but for maintaining of the ligand inside the pocket. The increasing of the secondary structure content of the ModA-mutant protein when compared to the native protein by circular dichroism was also observed in the simulations. It was possible to conclude that this effect is due to an increasing of the compactness and interactions in the structure when the mutation is present, explaining the incapability of ligation of the mutant in the experimental assays.

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Affinity and specificity of ABC transporter periplasmic-binding proteins involved with sulfur assimilation in *Xanthomonas axonopodis* pv. *citri*

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Sulfur is an essential element for bacterial growth and may be assimilated from a range of sources. Cysteine is the preferred source of sulfur for *Escherichia coli* and many other bacterial species. In *E. coli* , genes involved in sulfate and sulfonate compounds are clustered in a *cys* regulon which includes all the enzymes for sulfur assimilation as well as three ABC transporter systems: SsuABC for alkanesulfonates, SbpCysUWA for sulfate and TauABC for taurine. In this work we show that the phytopathogenic bacteria *Xanthomonas axonopodis* pv. *citri* presents not three, but four ABC transporters related to sulfate or sulfonate compounds assimilation, and make a comparative structural and functional characterization of them. Using bioinformatics tools, molecular modeling and molecular dynamic analysis, we show what are the main differences and similarities among the proteins that are responsible for the affinity and specificity of the systems. Affinity for the different ligands is determined essentially by size and presence/absence of apolar residues in the ligand-binding pocket and not charges. On the other hand, all the proteins conserved the residues involved in the sulfate coordination, which suggest some evolutionary relationship. The sulfate-binding protein is the most conserved of the proteins when compared with the orthologs identified in other bacterial species. In addition, molecular dynamic analysis were performed for the four proteins, which belong to group II of periplasmic-binding proteins, in other to characterize the important movement of opening and closing of the domains for capture and liberation of the ligands. The results showed that although both domains suffer conformational changes, one of them is responsible for the movements that will lead the ligand to the permease protein at the membrane. Key words: ABC transporters, sulfur, *citri* regulon, periplasmic-binding protein

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Mixed Disulfide Protein Complexes Between Thioredoxin and Peroxiredoxin

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Peroxiredoxins (Prx) are ubiquitous proteins that are able to decompose hydroperoxides using very reactive cysteines. Prx disulfides are frequently reduced by thioredoxin (Trx), an enzyme that possesses two highly conserved redox-active cysteine residues in the Cys-X-X-Cys motif. Trx use the N-terminal thiol to reduce the disulfide bridge of the target proteins, releasing a protein thiol and forming a transient mixed disulfide bridge with a cysteine residue of the target. Then the C terminal thiol of Trx Cys - X - X- Cys motif attacks the mixed disulfide bridge, releasing the reduced target and oxidized Trx, with an intra molecular disulfide bridge. Therefore, substitution of specific cysteines by serines can stabilize protein complexes linked by mixed disulfides. Despite the importance of the Prx and Trx in the cellular redox control, the molecular mechanisms of electron transfer between these enzymes and the events involved in establishment of these protein complexes remains poorly understood. Therefore, the *Saccharomyces cerevisiae* cytosolic Prx isoforms Tsa1 and Ahp1 and their mutants Tsa1^{C170S} and Ahp1^{C120S} were expressed and oxidized by DTNB, diamide or peroxides. To assay complex formation, equivalent amounts of oxidized Prx were reacted with reduced Trx1^{C33S} and the results were evaluated by non reducing SDS PAGE. Our data revealed that the only Tsa1-Trx1^{C33S} and Ahp1-Trx1^{C33S} combinations were able to form stable proteins complexes, but only when hydroperoxides were used to oxidize Prx. At the present, efforts are directed to characterize these complexes by means of mass spectrometry and X-ray crystallography.

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Estudos estruturais e funcionais das NEPs (*Necrosis and Ethylene inducing Proteins*) de Moniliophthora perniciosa, o fungo causador da doença Vassoura- de-bruxa em cacau

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A Vassoura-de-Bruxa é uma doença devastadora e de grande impacto econômico para a cacaiultura o Brasil e América Latina. A doença, a qual é causada pelo fungo *Moniliophthora perniciosa*, possui uma fase inicial com sintomas de hiperplasia e hipertrofia dos tecidos (Vassoura verde) e uma fase final caracterizada pela necrose total dos ramos infectados (Vassoura seca). Estudos de genômica e transcriptômica do fungo revelaram a presença de tr ês proteínas pertencentes à família das NEPs (*Necrosis and Ethylene inducing Proteins*). Proteínas desta família foram descritas como toxinas com capacidade citolítica e indutoras de morte celular através da formaç ão de poros e destruiç ão da membrana citoplasmática. Com o intuito de se entender a importância das três isoenzimas das NEPs de *M. perniciosa* para o processo da doença, estudos de RNAseq e PCR quantitativo foram feitos dos diferentes estágios da doença, indicando uma variaç ão da express ão das mesmas. Em paralelo, as três proteínas foram clonadas e expressas em sistemas heterólogos. A isoenzima MpNEP2 teve sua estrutura elucidade por cristalografia de proteínas e estudos de mutagênese apontam para resíduos importantes para o processo de necrose.

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Circular Dichroism Spectroscopic Analysis of the human RPL10 protein expressed in bacterial culture at low temperature.

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The ribosomal protein RPL10 belongs to the L10 family of ribosomal proteins, which is highly conserved from yeast to humans. The presence of the RPL10 protein is necessary for joining the 60S and 40S subunits in a late step of the initiation of mRNA translation. Although the exact extra-ribosomal functions of RPL10 are not yet fully understood, it has been identified as a putative tumor suppressor. The crystal structure of the core domain region (Phe34-Glu182) of this protein shows that it has secondary structure elements: beta-1, beta-2, alpha-1, beta-3, beta-4, beta-5, alpha-2, beta-6. In this study, the 680-bp human RPL10 cDNA was cloned into an expression vector (p1813) and the protein expressed in Escherichia coli strain. We then investigated the effect of growth temperature on the expression of the soluble form of the 24.5-kDa RPL10 protein. This protein was expressed in a soluble form in culture at temperatures of 25oC and 30oC for 16 h. The total production of RPL10 was 1.4 mg/mL of culture and the soluble fraction represented 34.5 percent of total RPL10. Structural analysis of the soluble protein fraction by circular dichroism showed that this protein has 24.8 percent of alpha helix and 43 percent of beta sheet. The data obtained with increase of temperature in the sample up to 90oC not showed significant alterations of structure secondary. The isodichroic points in the 200 to 206 nm had not detected confluence, suggesting that were probably no alterations in protein conformation. The RPL10 protein was sensible the addition of guanidine solution, with 70mM it lost of the alpha helix structure. In conclusion, the RPL10 protein expression in the soluble form in the bacterial cytoplasm own secondary structure and the analyses of thermal stability need studies with higher temperatures, above 100oC.

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Small-angle X-ray scattering studies of the DsbC protein from *Xylella fastidiosa*

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In Gram-negative bacteria, DsbC is a protein disulfide isomerase (PDI) which also shows chaperone activity, catalyzing the formation of native disulfide bonds, promoting the reactivation of denatured proteins and concurrently decreasing aggregation during its refolding. DsbC proteins play important roles in bacterial cell survival under oxidative stress conditions, suggesting their involvement in pathogenicity. In the present study we investigated the oligomeric assembly of recombinant DsbC from the phytopatogen *Xylella fastidiosa* (XfDsbC) under different oxidative conditions. To achieve this aim small-angle X-ray scattering (SAXS) experiments were performed, using recombinant XfDsbC in the presence or absence of the reducing agent tris(2-carboxyethyl)phosphine (TCEP). SAXS data were collected at LNLS in the beamline SAXS-1, with a sample-to-detector distance of 1101.5 mm, corresponding to a q range from 0.016 to 0.44 $^{-1}$. Data collection was carried out at 4C, with exposure time per frame varying from 60 s to 500 s according to the sample concentration and composition. After integration and averaging, structural parameters were estimated, including radius of gyration, maximum distance and distance distribution function. SAXS envelopes were recovered from the scattering curves and reported high resolution XfDsbC homologue structures were used as templates to model XfDsbC into the obtained SAXS envelopes. The results strongly suggested different XfDsbC oligomeric assemblies depending on the redox environment. The different oligomeric states of XfDsbC observed may be related to cell protection, patogenicity and enzyme activity efficiency. However the exact mechanism by which TCEP modulates DsbC assembly, as well as its implication in enzyme activity and cell survival remains to be elucidated.

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Estudos estruturais da Glutaminase Isoforma Kidney-type

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A proliferação celular em mamíferos é contolada por fatores de crescimento através de vias de sinalização específicas para os diferentes tipos celulares. Entretanto, em células tumorais, essas mesmas vias tornam-se constitutivamente acionadas direcionando, entre outros, a biossíntese de lipídeos, proteínas e ácidos nucléicos, indispensáveis para a proliferação celular. A multiplicação celular acelerada é associada à glicólise aeróbica, também conhecida como Efeito Warburg em que a maioria do carbono derivado do consumo de açúcar é secretado na forma de lactato. Somado ao Efeito Warburg, a glutaminólise auxilia as células tumorais a suprirem tanto a demanda por metabólitos do ciclo do ácido tricarboxílico, como por NADH e glutationa. Dessa maneria, tanto a glicólise aeróbica como a glutaminólise são mecanismos rápidos e eficientes na incorporação de biomassa em neoplasmas. Nosso estudo foca na enzima glutaminase, componente do primeiro passo da glutaminólise. Duas isoenzimas são expressas, a GLS1 e GLS2, sendo que a GLS1 formada por duas isoformas produtos de splicing alternativo (KGA Kidney type Glutaminase e GAC Glutaminase C). Segundo nossa hipótese de trabalho, a KGA é a enzima predominante durante o estado quiescente, provavelmente porque apresenta propriedades catalíticas que a torna de mais baixa processividade que a isoforma GAC. Visando um melhor entendimento destas propriedades, o objetivo deste trabalho é a determinação estrutural da enzima KGA, assim como a caracterização de sua atividade e estado oligomérico na presença/ausência do ativador fosfato.

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Structural and dynamic analysis of the sweet orange Hsp90 using SAXS

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The study of Hsp90 family proteins is widespread due to the key role they play in situations of infection and various types of stresses. Plants, being sessile, are much more vulnerable to stress factors, making the role of Hsps probably more relevant to protein homeostasis. Therefore, it is important to collect data on the structure and function of plant heat shock proteins in order to better formulate strategies to improve production by increasing resistance to both biotic and abiotic stresses. Following previous evidence that Hsp90 from Citrus sinensis (sweet orange) is one of the major factors in maintaining protein homeostasis in this important commercial plant, we took to investigate the structure and dynamic of this protein. The Hsp90 of sweet orange was cloned and expressed in E. coli and purified using an AKTA purifier device (GE Healthcare). The study of the effect of nucleotides on the conformation and function of Hsp90 by CD, intrinsic fluorescence and small-angle X-ray scattering are underway but preliminary results show evidence of conformation modulation by ligand. The SAXS experiments with the Hsp90 were performed at the SAXS1 and SAXS2 beamlines of the Brazilian Syncrotron Light Laboratory (LNLS). Measurements were performed with a monochromatic X-ray beam with a wavelength of 1.488. The samples were analyzed at a protein concentration of 2.2 mg/mL, in the absence of additives, in the presence of ADP, ADP βS, ATP and ATP γS. All the data were collected at a constant temperature of 25 degree C. Maximum sizes are given approximately 194 angstrons and radii of gyration around 58 angstrons for homologues of Hsp90 from other species. Our data indicate that the protein in the presence and absence of ligands shows a slightly conformational changes and variations in radius and maximum size. The molecular mass estimated was 164 kDa, in agreement with the value calculated using the ProtParam tool. These results can help to build a model of the action of Hsp90 which is dependent on the hydrolysis of ATP.

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Avaliação Funcional e Estrutural da Interação entre a Quinase de Adesão Focal e a Miosina Sarcomérica

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A tirosino-quinase de adesão focal (FAK) tem papel crítico na mediação da migração, sobrevivência e proliferação celular.Neste trabalho foi demonstrado que o domínio FERM da FAK medeia à interação com a miosina sarcomérica, sendo que esta interação leva a inibição da autofosforilação da FAK in vitro, enquanto que a ativação prévia da FAK reduz sua afinidade pela miosina. Ensaios de cross linking e posterior identificação por espectometria de massas demonstraram que esta interação ocorre através do subdomínio F2 do domínio FERM. Experimentos de microscopia confocal demonstraram que estas proteínas estão co-localizadas em cardiomiócitos de ratos neonatos e adultos. A interferência na interação FAK/Miosina pelo silenciamento gênico da miosina culminou com a ativação da FAK e o tratamento das células com o peptídeo FP-1, derivado do subdomínio F2 domínio FERM da FAK, levou a uma diminuição na interação com a miosina sarcomérica e ao aumento na ativação da FAK. O tratamento prolongado com FP-1 resultou em hipertrofia morfológica dos cardiomiócitos de ratos neonatos, efeito concomitante à ativação da via de sinalização Akt, TSC2 e S6Kinase. Tanto o silenciamento da FAK quanto o tratamento com rapamicina bloquearam a hipertrofia morfológica decorrente do tratamento com FP-1. Os dados deste trabalho indicam que a interação da FAK com a miosina sarcomérica é sensível ao estresse mecânico e que possui papel regulatório na manutenção da quiescencia basal da FAK e no controle das vias de sinalização mediadas por esta quinase, como a via de crescimento celular AKT/mTOR/S6Kinase, em miócitos cardíacos em cultura.

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Central domain deletions affect the SAXS solution structure and function of Yeast Hsp40 proteins Sis1 and Ydj1

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Ydj1 and Sis1 are structurally and functionally distinct Hsp40 proteins of the yeast cytosol. sis1 is an essential gene whereas the ydj1gene is essential for growth at elevated temperatures and cannot complement sis1 gene deletion. Truncated polypeptides capable of complementing the sis1 gene deletion comprise the J-domain of either Sis1 or Ydj1 connected to the G/F region of Sis1 (but not Ydj1). Sis1 mutants in which the G/F was deleted but G/M maintained were capable of complementing the sis1 gene deletion. To investigate the relevance of central domains on the structure and function of Ydj1 and Sis1 we prepared Sis1 constructs deleting specific domains. The mutants had decreased affinity for heated luciferase but were equally capable of stimulating ATPase activity of Hsp70. Detailed low resolution structures were obtained and the overall flexibility of Hsp40 and its mutants were assessed using SAXS methods. The results revealed that the G/F and G/M regions are not the only flexible domains.

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Understanding the oligomerization behavior of human dynein light chain Rp3

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Dyneins are molecular motors responsible for the retrograde transport of molecules and vesicles from the periphery to nuclear region of the eukaryotic cell. They are formed by a set of proteins including Dynein Heavy Chains (DHC), Dynein Intermediate Chains (DIC), Dynein Intermediate Light Chains (DILC) and Dynein Light Chains (DLC). This last group is responsible for targeting and attachment to the molecule or vesicle to be transported by this molecular motor. Many human DLC have been identified and characterized structurally and functionally showing that they are involved in diverse cellular pathways that may be involved or not with retrograde transport by the Dynein complex. In the present work the oligomeric behavior of the Dynein Light Chain Rp3, which has no previously reported structural data, was studied using the small-angle X-ray Scattering (SAXS) technique. Purified recombinant Rp3 samples, produced in *Escherichia coli* with and without His$_6$-tag, were analyzed under reducing conditions (5mM tris(2-carboxyethyl)phosphine (TCEP)) as the protein showed high instability under oxidative conditions. SAXS data were collected at LNLS in the beamline SAXS-1, with a sample-to-detector distance of 1174.9 mm, corresponding to a q range from 0.13 to 0.30 $^{-1}$. Data collection was carried out at 25C, with exposure time per frame varying from 60 s to 500 s according to the sample concentration and composition. After integration and averaging, structural parameters were estimated, including radius of gyration, maximum distance and distance distribution function. The resulting data strongly suggest that the Dynein Light Chain Rp3 was structurally folded and showed a concentration dependent oligomerization pattern as significative differences in the radius of gyration and anisotropy of the distance distribution function were observed among different concentration samples. Lower concentration samples (up to 2 mg/ml) appeared as dimers (supported by size exclusion chromatography data) whereas higher concentration samples indicated higher order oligomerization. It may also be possible that the His$_6$-tag favors protein oligomerization. SAXS envelopes were obtained from the scattering curves and we hope that the presented data may lead to a better understanding of the Rp3 structure and oligomerization pattern which is directly correlated to its function in the cell.

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Structural studies of 5 cerato-platanin orthologous from *Moniliophthora perniciosa*, the causal agent of witches' broom disease in cacao

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Cerato-platanin (CP) is a phytotoxic protein of about 12.4 kDa initially identified in culture filtrates of the ascomycete *Ceratocystis fimbriata f. sp. platani*, the responsible agent of canker stain disease. CP is also the founding member of the namesake protein family, which contains fungal-secreted proteins involved in various stages of the hostfungus interaction and act as phytotoxins, elicitors of defense responses and allergens. It has been suggested that this protein family has important physiological functions, including cell wall interaction and manipulation of the hosts defense system. However, the precise molecular function remains elusive. Its members have in common low molecular weights, a high percentage of hydrophobic residues and four conserved cysteine residues involved in the formation of two intramolecular disulfide bonds. Genomic-scale studies have identified at least five sequences in the *Moniliophthora perniciosa* genome encoding putative proteins similar to cerato-platanin proteins (termed MpCP1 to 5). This pathogen causes the main Latin Amarica fungal diseases of *Theobroma cacao* (cacao), the Witches broom disease. In order to contribute to the understanding of its molecular function(s) and help explain why the need of 5 different MpCPs in one organism, we are performing structural studies on variants of CP from *Moniliophthora perniciosa*, in combination with biochemical and functional data and the analysis of their expression levels throughout the pathogens life cycle.

*Juliana F. Oliveira and Mario R.O. Barsottini contributed equally to this work.

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Cancer and the glutamine addiction: Understanding the elevated glutaminolytic rates

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Recent findings in cancer biology point to the fact that the genes responsible for the control of the growing process, cellular division, adhesion, metastasis and programmed cell death are also involved on the metabolism control. Cell proliferation requires energy, nutrients, and biosynthetic activity to duplicate all macromolecular components during each passage through the cell cycle. Therefore, tumor cells present highly activated glycolytic pathway on the presence of oxygen (Warburg effect) and anaplerose of the tricarboxilic acid cycle dependent on glutamine. Tumor cells consume glutamine at unusual high rates, and its metabolism, called glutaminolysis, seems to be essential for the neoplastic transformation since its inhibition decreases cell proliferation. Very little is known regarding how signaling pathways and transcription activators can promote the glutaminase activation in cells. Ours results show that mammary cancer cells lines, namely SKBR3 and MBA-MD-231, as well as tumor tissues extracted from patients with breast cancer have higher levels of the mRNA for the glutaminase isoform GAC in relation to its splicing variant, KGA. Similarly, a tissue array analysis of several different cancer patients displayed an elevated level of the protein GAC in comparison to KGA. The working hypothesis is that GAC is amplified in cancer as it would correspond to a more active glutaminase isoform. Preliminary studies to determine why this isoform is overexpressed in cancer tissues led to the identification of Hur as a putative GAC mRNA binding protein, which, upon binding, would promote RNA stabilization and possibly control protein translation.

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Self-assemble properties of peptides: the Growth hormone releasing peptide (GHRP) case

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Growth hormone releasing peptide (GHRP-6: His-D-Trp-Ala-Trp-D-Phe-Lys-NH2) belongs to a class of synthetic growth hormone secretagogues (GHSs) that stimulate growth hormone (GH) secretion from somatotrophs in a concentration-dependent manner in several species and humans (1). Moreover, some studies suggest new potential therapeutical options for GHRP-6, such as the prevention and treatment of the heart failure (2,3), an effect that seems to be related to an enhanced nonischemic compensatory mechanism and mediated via specific GH secretagogue receptors. In the present work we studied the effect of concentration on the self-assemble properties of GHRP-6 using small angle X-ray scattering studies. To do so, we measure the SAXS curves of GHRP-6 at 5 different concentrations: 10, 20, 30, 50 e 70 mg/ml at pH 7.0 (phosphate buffer). We evidenced that at 10 mg/ml no aggregates could be evidenced in the SAXS curve. At 20 mg/ml, however, we could evidence the presence of a broad peak at q $\sim 0.076\ ^{-1}$. Such SAXS curve could be well modeled as a hollow cylinder with inner and outer radii equal to 30(2) and 65(3) , respectively. It was not possible to evaluate the length of such hollow cylinder, once it value was bigger then the maximum size that the SAXS experimental setup allows. Interestingly, increasing the peptide concentration from 20 to 30, 50 and 70 mg/ml, the structural parameters of the hollow cylinder remain the same. Nevertheless, we could notice the appearance of three peaks over the SAXS curves at 30, 50 and 70 mg/ml. According to the peaks position it was possible to infer that the cylinders are arranged in a hexagonal lattice with unity cell dimension, a, equals to 150 , for all studied systems. This work is still in progress.

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Parte II

Biologia Molecular e Química de Proteínas

Isolation of peptides and small proteins of soybean leaves from plants submitted to mechanical injury by two-dimensional electrophoresis gel

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The two-dimensional electrophoresis in polyacrylamide gel (2DE) is one of the main tools for proteomics to be able to separate with high resolution a large number of proteins from a complex sample and the possibility of doing gene expression analysis by comparing protein profiles of different physiological situations. However, this technique has limitations to detect peptides and proteins of low molecular weight that are of great biotechnological interest for use in plant defense. The aim of this work was to adjust methodologies for extraction and identification of peptides and proteins of low molecular mass, differentially synthesized by soybean plants subjected to abiotic stress using 2-DE. Leaves of soybean plants injured and not injured were powdered, homogenized with extraction buffer (Shen et al., 2002, with modifications), and centrifuged. The supernatant was precipitate by acetone/trichloroacetic acid (TCA). The precipitated proteins were washed with ice-cold acetone and resuspended in resolubilization solution. The samples were subjected to isoelectric focusing and the proteins separated by SDS-Tricine-PAGE, with modifications, were visualized by Coomassie brilliant blue G-250 staining. A set of proteins of low molecular weight and peptides were visualized by two-dimensional gel electrophoresis and some were differentially expressed between the different treatments, which are being analyzed by mass spectrometry. The adjustment of methodologies for proteomic analysis of peptides and proteins of low molecular mass by 2-DE appears to be very importance for future studies of plant proteomic and peptidomics. (EMBRAPA, CAPES, CNPq, FINEP, FAPEMIG). Shen et al. (2002), J. Biochem. 132,: 613-620.

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Citrus sinensis Cyclophilin modulates gene transcription associated with the citrus canker development

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Xanthomonas axonopodis pv. *citri* (Xac) utilizes the type III effector protein PthA to promote citrus canker. PthA proteins are targeted to the nucleus to modulate transcription of host genes. We observed that PthAs interacted with a *Citrus sinensis* cyclophilin (Cyp) in two-hybrid and pull-down assays. Citrus Cyp shows peptidyl-prolyl cis-trans isomerase (PPiase) activity and is 84% identical to ROC1, an *Arabidopsis thaliana* Cyp required for the activation of AvrRpt2 inside the host cell. The interaction of PthA with citrus Cyp was abolished in the presence of Cyclosporin A (CsA), an inhibitor of cyclophilins, indicating that PthAs bind to the active site of Cyp. The role of citrus Cyp on PthA-dependent gene expression was investigated. Interestingly, we observed that CsA and PthA2 induced a similar pattern of transcriptional change in citrus, suggesting that PthA2 inhibits the activity of Cyp *in vivo*. Furthermore, the citrus Cyp complemented the phenotypes of the *cpr1* and *ess1* mutations in yeast, two cyclophilins that play roles in transcriptional regulation and cytokinesis. In yeast, Ess1 binds to and isomerizes proline residues of the C-terminal domain of RNA polymerase II affecting transcription elongation and termination. These results strongly support the notion that PthAs require the function of cyclophilins for its activity.

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PthA from *Xanthomonas citri* interacts with Citrus MAF1, a negative regulator of RNA polymerase III

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Citrus canker disease is caused by the bacterium *Xanthomonas axonopodis* pv. *citri* (Xac), whose the major effector protein is PthA, required to elicit citrus canker. To gain insights into the molecular mode of action of PthA, a two-hybrid screen was performed to identify citrus proteins that interact with the PthA4 variant. Among several citrus proteins with functional DNA and/or RNA binding domains associated with transcription control, we selected a protein named MAF1 for further studies. In yeast and human, MAF1 is the only known global and direct Pol III transcription repressor that mediates numerous stress signals. In eukaryotic cells, Pol I and Pol III are responsible for the synthesis of the RNA species involved in ribosome biogenesis and the process of translation. This information is compatible with data from our laboratory showing that transient expression of PthAs in citrus cells significantly alters the transcription of host genes associated with cell division and ribosome biogenesis. The yeast MAF1 function is regulated by the opposing actions of PKA and PP2A. We show here that citrus MAF1 is a dimer in solution, however, only the monomer is phosphorylated by PKA. In addition, the citrus MAF1 protein was able to complement the yeast *maf1* mutant phenotype, strongly indicating that it represses tRNA transcription *in vivo*. Thus, since PthA up-regulates a number of genes involved in ribosome biogenesis, we hypothesize that it may displace MAF1 from the RNA pol III complex, thereby allowing RNA pol III-mediated transcription.

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Functional characterization of a *Citrus sinensis* Cyclophilin

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Cyclophilins are known to exhibit peptydil-prolyl-cis-trans isomerase (Ppiase) activity and to bind the immunosuppressive agent cyclosporine A (CsA). We have previously isolated and crystallized a cyclophilin (CYP) from Citrus sinensis that interacts with the effector protein PthA from *Xanthomonas citri*, the bacterial pathogen responsible for the citrus canker disease. The crystal structure shows that CsCYP has some unique features: a divergent loop between residues 48 and 54 (KSGKPLH); two conserved cysteine residues (Cys^{40} and Cys^{168}) in close proximity (5.4) and two other conserved residues, His^{54} and Glu^{83}, the latter thought to stabilize the loop. This loop is also suggested to be part of an ATP binding site. We believe that these unique features might play an important role in the regulation of the enzyme activity trough an oxi-redox mechanism. Here we show that CYP display Ppiase activity *in vitro* and is inhibited by CsA, PthA and oxidizing agents, including $CuSO_4$. Moreover, we present evidence indicating that CYP interacts with the C-terminal domain of the RNA Polymerase II and binds ATP *in vitro*. Taken together, these results suggest an involvement of CYP in transcriptional regulation.

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Enhancement of citrus resistance to *Xanthomonas axonopodis* pv. *citri* by overexpression of Citrus MAP kinase and WRKY genes

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The production of citrus fruits has been constantly threatened by the bacterium *Xanthomonas axonopodis* pv. *citri* (Xac), the causal agent of citrus canker. The disease is characterized by pustule-like lesions on leaves, fruits and branches. Nowadays, principals measures applied for controlling citrus canker are the immediate destruction of infected trees followed by quarantine restrictions that are enforced to prevent the spread of the pathogen. These measures have generated significant losses to the citrus growers. The present work proposes to develop citrus plants resistant to Xac. The aim was to overexpress two citrus genes previously identified in our microarray study as induced during a resistance reaction against *Xanthomonas axonopodis* pv. *aurantifolii* (Xaa) in sweet orange. The genes are related to a Mitogen-Activated Protein Kinase (MAPK) and to a WRKY factor that have been shown in other plants to mediate basal defense against pathogens. Transgenic plants of Troyer citrange overexpressing the *mapk* or the *wrky* gene were obtained by Agrobacterium tumefaciens-mediated transformation. The gene constructs consisted of the *mapk* or *wrky* gene cloned downstream of a Xac-inducible promoter, and the selection genes *nptII* with the Nos terminator. Initial challenging of the kanamycin-resistant plants with the pathogen showed that both MAPK and WRKY-transformed plants exhibited normal vegetative development and displayed increased tolerance to the pathogen, as revealed by the significant reduction on the severity of lesions. To our knowledge, this is the first report of a genetic transformation of citrus plants using a pathogen-inducible promoter and the *mapk* and *wrky* genes. Moreover, the data presented show that overexpression of the *mapk* and *wrky* reduces the susceptibility of citrus plants to the canker bacteria. Overexpression of MAP kinase and WRKY genes in Troyer citrange increased resistance to *Xanthomonas axonopodis* pv. *citri*

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Search of Cytosolic Thioredoxin Peroxidase II (cTPxII) Biological Partners United by Mixed Disulfides in *Saccharomyces cerevisiae*

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Thioredoxin peroxidases (TPx) are highly conserved proteins throughout the evolution in all kingdoms. The majority of TPx are homodimers and the enzymatic mechanism relies on a cysteine, (CysP-SH), to reduce peroxide substrates. Following oxidation of CysP (CysP-SOH) by the peroxide, a second cysteine (CysR-SH - resolving cysteine) forms a disulfide with the CysP and is required to complete the catalytic cycle. Recently it was described in *Schizosaccharomyces pombe* a transient interaction among TPxI and the MAPK Sty1 when the cells are challenged to H_2O_2 stress. Curiously, CysR to Ser substitution resulted on a stable TPx-Sty1 complex. *Saccharomyces cerevisiae* presents five isoforms of TPx. Although two cytosolic isoforms (cTPxI and cTPxII) share 86% of identity and 96% of similarity, some evidences suggest that both proteins have non-redundant cellular roles and must interact with different biological partners. Aiming to examine different features among cTPxI and cTPxII, we have modeled cTPxII using the coordinates of cTPxI. The results revealed striking differences on the quaternary structures between the two proteins. In order to investigate cTPxII biological partners we generated the cTPxII$_{C170S}$ mutant and standardized methodologies for pull down assays including yeast total soluble extract of ΔcTPxII strain and cTPxII$_{C170S}$ by oxidative stress. The mixed disulfide bond complexes were visualized by SDS-PAGE and analyzed by ESI Q-TOF mass spectrometry at LNBio. Until now our most restricted analysis appointed cTPxI, which has already been detected in large scale works, and an uncharacterized membrane protein (YM057) as possible biological partners of cTPxII$_{C170S}$.

Acknowledgements:

BUSCA DE PARCEIROS DE INTERAÇÃO DA ENZIMA GLUTAMINASE

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Células tumorais apresentam uma autonomia metabólica aumentada em comparação a células não-transformadas, incorporando nutrientes e metabolizando-os através de vias que suportam o seu crescimento e proliferação. Os trabalhos clássicos em metabolismo de células tumorais se focam na questão da bioenergética, particularmente no aumento da glicólise e supressão da fosforilação oxidativa (o efeito Wargurb). Entretanto, as atividades biossíntéticas requeridas para a geração de células filhas são igualmente importantes para o crescimento do tumor e somente nos últimos anos que estas vias têm sido trazidas à tona. Este trabalho enfatiza o estudo da enzima glutaminase, a qual processa glutamina em glutamato para posterior produção de alfa-cetoglutarato pela enzima glutamato desidrogenase, reabastecendo o clico do TCA e suportando seu funcionamento e geração de metabólitos essenciais para a síntese de macromoléculas. Duas isoenzimas são produzidas por dois genes, a glutaminase liver-type (LGA) e a glutaminase kidney-type (KGA), sendo também já descritas isoformas produzidas por splicing alternativo destes genes. Estas proteínas apresentam outros domínios além do catalítico, assim como repetições do tipo ankirin, sabidamente envolvidos em contatos proteínas-proteínas. Na busca por parceiros de interação da KGA através de ensaios de pull-down e caracterização, por espectometria de massas, de bandas diferenciais em gel de SDS-PAGE, identificamos a enzima aldolase A como provável candidato, sendo uma enzima da via glicolítica que converte frutose 1-6-bifosfato em dihidroxiacetona fosfato e gliceraldeído 3-fostato. Além de sua função enzimática, vários papéis não catalíticos já foram descritos, alguns deles envolvidos na formação de filamentos actina e de vesículas endocíticas, via interação com diferentes proteínas. Estas múltiplas interações colocam a enzima aldolase A como uma importante scaffold, chave para diferentes processos celulares.

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Analysis of Molecular Interactions by ESI Q-TOF Mass Spectrometry of *Saccharomyces cerevisiae* Cytosolic Thioredoxin Peroxidase I (cTpxI) in Response to H_2O_2

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Reactive Oxygen Species (ROS) are potent oxidant capable of damaging all cellular components including DNA, protein and membrane lipid. Although, eukaryotic cells produce H_2O_2 to mediate several transduction pathways related to proliferation, differentiation and cell migration. H_2O_2 is an important intracellular messenger that modifies the enzymatic function of several proteins, especially cysteine. To maintain REDOX imbalance, aerobic organisms are equipped with an array of defense mechanisms, among them, the thioredoxin peroxidases (TPx) have been known to metabolize H_2O_2 and alkyl hydroperoxides using reactive cysteines named peroxidatic cysteine (Cys_p) and resolving cysteine (Cys_r). In baker yeast, five TPx isoforms have been described: three are cytosolic, one is mitochondrial, and another is nuclear. Isoform orthologs are found in mammalian, thus, these unicellular organisms serve as a good model for TPx expression and regulation studies. In eukaryotes, TPx activity has been related to different cellular processes such as cell differentiation, H_2O_2 signaling, and apoptosis. Recently was described in *Schizosaccharomyces pombe* a transient TPx protein complex with the MAPK Sty1 when cells are challenged to H_2O_2. Cys_r to Ser substitution resulted on a stable TPx-Sty1 complex, revealing that the complex is stabilized by TPx Cys_p. The representative of *S. pombe* TPx in *Saccharomyces cerevisiae* is cTPxI and the present work aims the searching of cTpxI biological partners in response to increase of H_2O_2 levels that are able to establish interactions *via* disulfide bonds. At the present cTPxI was expressed as recombinant protein carrying Cys_r (cTPxI^{c170S}), purified by IMAC, treated with DTT, incubated with crude protein extracts of yeast ΔcTPxI and challenge to H_2O_2 to promote complexes formation. The results were detected by non reducing SDS PAGE using silver staining and submitted to analysis by ESI Q-TOF mass spectrometry and processed using MASCOT MS/MS Ion Search. The preliminary analysis indicates interactions of cTPxI with integral membrane protein that may promote secretion of certain hexose transporters (GSF2), protein integral to the mitochondrial membrane that has a conserved methyltransferase motif (OMS1p) and a kinase HSL1(Histone Synthetic Lethal) involved in the morphogenesis and septin checkpoints, which has already been identified as a cTPxI^{c170S} biological partner in previous works of large proteomic scales.

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SsuD protein from *Xanthomonas axonopodis* pv. *citri: what is it function?*

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The *ssuD and ssuE genes belong to the same operon that encodes the ABC transporter for alkanesulfonates in Xanthomonas axonopodis pv. citri. According to literature, the SsuD and SsuE are the monooxigenase and the oxidoreductase proteins, respectively, responsible for the conversion of the alkane in sulfite. As a monooxigenase, SsuD should produces aldehyde and sulfide after the oxydation of the alkanesulfonate in presence of reduced flavine mononucleotide (FMNH2). In order to prove its function and define how it works, we performed experiments involving bioinformatics tools, molecular modeling, and spectroscopic experiments. The bioinformatics results have shown that SsuD presents higher amino acid sequence identity with oxidoreductases than monooxygenases. This result was supported by the structural model of the protein built from the structural coordinates of the oxidoreductase of Salmonella typhimurium (PDB code 3ERP), which showed 58 % of sequence identity. In addition, the protein showed conserved residues in oxidoreductases proteins. After expression and purification of a recombinant protein in cells of Escherichia coli BL21 (DE3), the protein was submitted for spectroscopic analysis. Circular dichroism experiments revealed a folded protein with secondary structure content similar to the oxidoreductases formed by TIM barrel structures that suffer small changes in presence of alkanesulfonates and other ligands tested. The thermal stability and behaviour in different pH was also tested using CD and fluorescence. Crystallization tests produced small crystals and needles under refinement in the presence alkanesulfonates, Hepes and Mes, and in a range of pH from 6 to 8.*

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Evaluation of Penicilium Echinulatum secretome through Shotgun Proteomics

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Penicilium echinulatum has been considered a promising fungus based on the high level secretion of cellulolytic enzymes. However, the enzymatic repertory of this filamentous fungi is far to be well understood. The characterization of secretome proteins, being them part of the cellulolytic complex or accessories proteins, may provide promising insights for production of better enzymatic cocktails for biomass conversion. Aiming at to investigate the hydrolytic repertory of P. echinulatum, the fungus was grown in five different culture conditions regarding their carbon sources: crude bagasse, micropulverized cellulose and bagasse derived from three pretreatment processes, such as steam-explosion and alkali delignification treatment, sulfuric acid treatment and hydrothermal treatment. The hydrolytic activity of P. echinulatum supernatant was tested on several commercial polysaccharides, which evidenced the fungus enzymatic arsenal, which includes endoglucanases, beta-glucosidades, cellobiohydrolases, xylanases, pectinases and others hydrolytic enzymes not expected, such as alpha-amylase. The secretome profile of P. echinulatum was evaluated through LC- MS/MS shotgun analysis. The Mascot-Ions-Search against Fungi database allowed the identification of over 100 proteins matches and revealed peptides from different GHs family members, accessory proteins, including swollenin and acetyl xylan esterases, and a number of hypothetical proteins. It is interesting to highlight that the hydrolytic activity found from assays using commercial polysaccharides corroborate with the proteomic data. For instance, the highest hydrolytic activity in PNPG (p-nitrophenyl-glucopyranoside) was found from enzyme source derived from crude sugarcane bagasse and micropulverized cellulose, in which LC-MS/MS data shows proteins from GH3 family (beta–glucosidases). Similar results were found using PNPC, CMC, beta-glucan, pectin, xylan and others substrates and correlated GH counterparts were identified by LC-MS/MS. These results showed that our approach based on the use of different growth conditions, secretome shotgun analysis and comprehensive biochemical characterization, represents a powerful tool to reach a wider knowledge about P. echinulatum enzymatic repertory and better understanding of plant cell wall degradation mechanisms used by filamentous fungi.

Acknowledgements:

Coptotermes gestroi ***digestomic repertory involved in lignocellulosic bioconversion***

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Termites are known by wood feeding skills. Their gut environment is capable to breakdown lignocellulosic materials into monosaccharides with 90% of efficiency, mainly because they possess an enzymatic armory of glycosyl hydrolases (GHs) and accessory proteins (APs) named Digestome. Costa Leonardo & et. al., (2010) has generated a high throughput metatranscriptomics sequencing of termite Coptotermes gestroi, on 454 GFLX (Roche) platform, intend get information about caste differentiation and termites biology. The our goal was identify GHs and APs in Coptotermes gestroi 454-metatranscriptomic databases, throughout a gene discovery approach, and gene cloning for heterologous expression. The main purpose is gather knowledgment about the genomic repertory involved in biomass conversion, aiming at, not only, foresee novel enzymes for lignocellulosic bioethanol production. C. gestroi 454-metatranscriptomic databases has about 400 MegaBases sequenced grouping in 110.000 contigs. This databank was blast against Carbohydrate Active Enzymes Database (CAZY) and NCBI Database generating about 800 hits with similarities with GH's and AP's. Database generating about 800 hits with similarities with GH's and AP's. Among these hits, ten ORFs were selected as targets for cloning and heterologous expression. Thus, we designed primers to amplification this metagenomics genes and cloning in pET-28a vector expression. Putatives GH1, GH9, GH16, Laccase and Feruluyl Esterase (FAE) endogenous genes from C. gestroi and GH10 from symbiotic protozoan were cloned in pET-28a and sequencing for inserts confirmations. For cloning of putatives GH5, GH7, GH11, GH45 primers were designed. Further studies on expression, purification and functional characterization are needed to apply these recombinant enzymes in a biomass hydrolysis process and get insights into termites digestome and biology.

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BIOCHEMICAL AND BIOPHYSICAL CHARACTERIZATION OF A NOVEL HYPER THERMOSTABLE LAMINARINASE FROM THERMOTOGA PETROPHILA

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Laminarinases are highly specific enzymes that catalyse the hydrolysis of β-1,3-glucan. This is an important polymer found in algal, fungal, and plant cell walls, which have several biotechnological applications. Herein we describe the cloning of the gene in pET28a, expression in E. coli, purification and characterization of an endo-β-1,3-glucanase from hyperthermophilic bacterium T. petrophila. The recombinant enzyme showed a superior activity on laminarin and β-glucan from barley within a set of 17 substrates. Biochemical characterization revealed an optimum activity around pH 6.0 and 85°C. It also showed insignificant loss of activity after incubation for 16 hours at 70°C. Based on the analyses of the enzymatic hydrolysis through capilar electrophoresis, using APTS labeled saccharides, this enzyme is able to hydrolyze only oligosaccharides with more than three glucopyranosyl moieties, and preferentially releases laminaribiose and laminaritriose as major products. The far-UV circular dichroism spectrum showed a negative band near 216 nm, which is typical of βstructure, and an intense positive band at 230 nm which may be associated with the tyrosine residues. Thermal denaturation studies monitored by CD intensity changes indicated a melting temperature of 95°C that corroborates the functional data. The analysis of Laminarase by SAXS displayed a three domain structure, composed by two carbohydrate binding domains (CBD) and catalytic domain (CD).

Acknowledgements:

Prospection of enzymes involved in degradation of lignocellulosic biomass from a metagenomic library derived from sugar cane plantation soil.

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Metagenomics is a new area of investigation, which makes use of molecular biology's tools aiming to access the genome of uncultivable microorganisms. These microorganisms represent a wide source of biodiversity for isolation of new enzymes with potential applications in biotechnology, including cellulases and hemicelullases, which are key components for bioconversion of lignocellulosic biomass into biofuels production. Despite the complexity involved in the purification of nucleic acids from soil, the steps for generation of a metagenomic DNA library were based on the same procedures applied for cloning of genomic DNA from cultivable microorganisms. Endonuclease restriction analysis of the clones from the metagenomic libraries allowed not only the visualization of differences in cleavage pattern, but also the determination of inserts size, which on average was 2,4 Kb. Aiming to evaluate the biodiversity of microorganisms that were present in the cloned library, some clones were selected and had its inserts mapped by sequencing. The results of DNA sequencing was compared with the database from NCBI through tblastx analysis. The comparisons showed a great diversity of inhabitant microorganisms derived from sugar cane plantation soil, including members from Bacteria and Archea domains and different phyla, for example, Proteobacteria and Actinobacteria. The metagenomic DNA extracted from the soil sample were used as a template for a PCR using primers for conserved regions from 16S rRNA gene, which validated the library as adequate for prospection of new genes. It was also performed another PCR, using degenerate primers for amplification of xylanases genes from the metagenomic libraries. DNA fragments with approximately 300 bp were amplified and sequenced. Based on Blasts searches in NCBI database, it was confirmed that the DNA fragments represent portions of new xylanases genes. New primers were design with the purpose to achieve the whole sequence of the genes. Once the complete gene sequences are achieved, genes will be cloned for heterologous expression and characterization of new enzymes.

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The secretome analysis reveals molecules associated with migration in tumorigenic cells.

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Molecules in the extracellular milieu can be considered as a component of degradome, secretome or proteolysome. The identification of these molecules can reveal the functional stage of proteome, since most of them can have additional functions when they are bioactive as modulators of the tumor development such as inducing migration and proliferation. Proteases are the main responsible for this signaling circuit at the cell surface and in the extracellular matrix. The activity of several proteases can be induced by phorbol-ester (PMA). Thus, to study whether the response of proteases in subproteome composition of tumorigenic and non-tumorigenic is related to the cell ability to develop tumor, these cells were treated with PMA and the proteins and peptides released to media were evaluated by mass spectrometry. We found that secreted, membrane-bound and extracellular matrix proteins as well as endogenous cleavage peptides such as syndecan-1, Notch precursor, sodium channel protein, calcium-dependent secretion activator, cadherin-3 and desmoglein-3 were differentially released or shed in tumorigenic and non-tumorigenic cells by PMA treatment. These results suggested the extracellular subproteome composition differs among the tumorigenic and non-tumorigenic cells treated or not with PMA and the identified proteins and peptides could be potential candidates for cancer regulation.

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Parte III

Ciência Atômica e Molecular

($1s,2p_{1/2}$) and ($1s,2p_{3/2}$) resonant Raman scattering processes in Ti

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Resonant inelastic scattering (RIXS) or resonant Raman scattering of x–rays is a second order process which can be visualized as an x–ray absorption process followed by an x–ray emission one. The latter transition assumes that a radiative decay channel takes place, whereas in the case of a non–radiative event an Auger electron is emitted. The virtual intermediate state consists of a core–hole in a deep lying atomic shell and an electron promoted into an empty state above the Fermi level. Resonance excitation occurs when the energy of the incident photons is tuned below or closely above the core ionization threshold.

In this work we present a high resolution study of the main fingerprints of RIXS processes at the K–edge of Ti, namely the linear dispersion of the red–shifted Raman line (Raman Stokes–line) and the subnatural narrowing of the RIXS peak in the vicinity of the K–ionization threshold. Special attention was put in separating the contribution of the two Raman lines $2p_{3/2} \rightarrow 1s$ *and* $2p_{1/2} \rightarrow 1s$.

Measurements of resonant x–ray Raman spectra in Ti involving ($1s,2p_{1/2}$) *and* ($1s,2p_{3/2}$) *electronic transitions were performed at the D12A–XRD1 beamline using a high resolution inelastic x–ray scattering spectrometer. RIXS spectra were measured for different incident energies across the K absorption edge.*

The measured energy dispersion of the RIXS peaks can be well reproduced by the theoretical single electron model by Eisenberger et al. [1] after accounting for instrumental resolution effects. A subnatural narrowing effect at an excitation energy near the K edge was observed and its relative position is in accordance with the model by Gel'mukhanov and gren [2].

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[2] F. Gel'mukhanov and H.A. gren, Phys. Rep. **312** *87 (1999).*

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Produção de Filmes de Compostos Orgânicos Utilizando a Técnica Wet Powder Spraying.

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Existem alguns modelos que tentam explicar como biomoléculas mais simples (por exemplo, os aminoácidos que são à base das proteínas dos seres vivos) teriam sido formadas. Um dos modelos que tentam explicar esta evolução propõe que a vida na Terra tenha sua origem no espaço, sendo que estas biomoléculas teriam sido formadas no espaço e trazidas para a Terra pelos impactos de cometas e meteoritos. Esses compostos orgânicos são simplesmente moléculas com o átomo de carbono, que pode se combinar em longas cadeias. Os cometas possuem uma parcela significativa de material orgânico. Já foram encontrados desde elementos leves como C, H, O e N até moléculas como cianeto de hidrogênio (HCN), formaldeído (H_2CO), pirimidinas, polímeros etc. Como os cometas perdem grãos ao entrar em contato com a atmosfera terrestre eles podem ter desempenhado um importante papel de fontes de moléculas orgânicas para desenvolvimento da vida na era primitiva. Esse modelo tem sido reforçado pela astronomia observacional, que apresentou nos últimos anos resultados em relação à descoberta de moléculas complexas. Desta forma, a produção de filmes orgânicos e sua interação com a radiação VUV estão relacionadas com o estudo da origem da vida na Terra, que corresponde a um tema de grande interesse na comunidade acadêmica. Este trabalho tem como objetivo principal relatar a produção de filmes do composto orgânico L-alanina através do método wet powder spraying (WPS), que corresponde a uma técnica de deposição em fase condensada simples e de baixo custo, utilizando para a sua caracterização a espectroscopia FTIR. Estes filmes correspondem a materiais que possuem uma espessura quem podem variar na ordem de nanômetros a vários micrometros, e podem ser usado em diversas áreas da ciência. No presente estudo apresentamos o processo de produção filmes de L-alanina, ou ácido 2-aminopropanóico, ($C_3H_7NO_2$) com diferentes espessuras. Em particular apresentamos os espectros FTIR para filmes com espessuras de 5μm, 10μm e 20μm. O controle da espessura dos filmes é fundamental para a etapa posterior deste trabalho, que é o estudo da degradação desses filmes a partir da exposição à radiação VUV. (Apoio Financeiro: LNLS, CNPq, FAPESB, CAPES)

Acknowledgements:

X-ray photodesorption from methanol ice in protoplanetary disks

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The abundances of molecules and ions depend on the mechanisms of their formation and destruction that can occur both in the gas phase and in the condensed phase on grain surfaces. Photodesorption of grain surface species may explain the relative high abundances of gaseous neutral or ionic species detected in cold environments. X-ray photons from young stars are able to penetrate cold and dense regions inside protoplanetary discs, leading to molecular dissociation and desorption of photo-products from icy molecules on grain mantles. This paper aims to experimentally investigate the contribution of ion desorption from methanol ice stimulated by soft X-rays for producing chemically active ions in protoplanetary discs. The measurements were carried out at the Brazilian synchrotron light source (LNLS), using X-ray photons at the methanol O1s resonance energy (537 eV). Some possible pathways for the H^- *and* O^- *formation from singly charged desorbed ions are suggested. The photodesorption yields for positive and negative ions were determined and compared with previous results obtained using different ionization agents, such as electrons, heavy ions and photons at different energies. We also correlate our results to the ion production in protoplanetary discs.*

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Electronic properties of simple thiocyanate species using synchrotron radiation

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As part of a more general project aimed to the study of the structural and spectroscopical properties of thiocyanate species, we have been investigated the photoionization processes and photodissociation channels of different compounds belonging to this family.[1] The coalition of Photoelectron Spectroscopy (PES) and multicoincidence Time-Of-Flight (TOF)-based techniques seems to offer a most promising approach to a deeper understanding of the electronic structure and the ionic dissociation induced by photon absorption in the valence region. Furthermore, the development of a neon gas filter in the TGM line at the Brazilian Synchrotron National Laboratory (LNLS) now affords pure synchrotron radiation in the 12-21.5 eV range.Following this methodology, relatively simple species such as XC(O)SY (X= F, Cl and Y= Cl, CH_3*) have been already reported.[2-4] In this context, we present now a study of the photon impact excitation and dissociation dynamics of the* CCl_2FSCN *molecule. HeI photoelectron spectrum has also been measured and the assignments were made with reference to the results of the SAC-CI/6-311+G*. Along with these valence shell studies, the inner-shell electronic properties have been investigated, most specifically around the sulfur 2p and chlorine 2p edges. Total Ion Yield spectra (TIY) and multicoincidence techniques were applied. References: (1) Cortés, E.; Erben, M. F.; Geronés, M.; Romano, R. M.; Della Védova, C. O. J. Phys. Chem. A, 2008, 113, 564-572. (2) Geronés, M.; Erben, M. F.; Romano, R. M.; Della Védova, C. O.; Yao, L.; Ge, M. J. Phys. Chem. A 2008, 112, 2228. (3) Geronés, M.; Downs, A. J.; Erben, M. F.; Ge, M.; Romano, R. M.; Yao, L.; Della Védova., C. O. J. Phys. Chem. A 2008, 112, 5947. (4) Geronés, M.; Erben, M. F.; Ge, M.; Cavasso Filho, R. L.; Romano, R. M.; Della Védova, C. O. J. Phys. Chem. A 2010, 114 (31), pp 80498055.*

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Dissociative Photoionization of CCl_3SCN into the valence region and around sulfur 2p and chlorine 2p edges.

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Organosulfur compounds have attracted much attention and several outstanding reviews covering the chemistry of thiocyanates (RSCN) and isothiocyanates (RNCS) can be found in the chemical literature.[1-3] Simple alkylated species, (R= alkyl), are very well known molecules. Recently, we became interested in the CX_3SCN (X= H, Cl, F) molecules, in particular the inner shell electronic properties and the ionic fragmentation of photon excited CH_3SCN following S 2p excitation were studied by using synchrotron radiation.[4] The combination of PES and multicoincidence Time-Of-Flight (TOF)-based techniques seems to offer a most promising approach to a deeper understanding of the electronic structure and the ionic dissociation induced by photon absorption in the valence region.[5-7] Recently, we performed a study of the photon impact excitation and ionization dissociation dynamics of $CClH_2SCN$, by using a combined approach that includes the use of HeI photoelectron spectroscopy and of photoionization under the action of synchrotron radiation in the valence region. Following these studies, we report the photon impact excitation and ionization dissociation dynamics of CCl_3SCN in the 12-310 eV range. Total ion yields together with the PEPICO and PEPIPICO spectra were recorded at selected photon energies. Furthermore, the HeI photoelectron spectrum has been measured and the assignments were made with reference to the results of the SAC-CI/6-311+G.*

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Determination of the oxidation state by resonant-Raman scattering spectroscopy

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X ray fluorescence spectra present singular characteristics produced by the different scattering processes. When atoms are irradiated with incident energy lower and close to an absorption edge, scattering peaks appear due to an inelastic process known as resonant Raman scattering (RRS). In this process, the emitted photons have a continuous energy distribution with a high energy cut-off limit.

This work present results regarding the possibility of determining the oxidation state by resonant Raman scattering using an energy dispersive system. Pure samples of transition metals (Cu, Fe, Mn) and different oxides of them (CuO, Cu2O, Fe2O3, Mn2O3, MnO2) were irradiated with monochromatic synchrotron radiation below their absorption edges to inspect the RRS emissions.

The spectra were analyzed with specific programs using non-conventional functions for data fitting and a FFT smoothing procedure was applied. After smoothing, the RRS residuals are studied in order to detect variation with respect to the theoretical curve. These variations are closely related with the chemical environments of the absorbing element and can provide relevant structural information of the sample.

The changes existing in the RRS structure between pure elements and their oxides are clearly discriminated and suggest the possibility of structural characterization by means of resonant Raman scattering using an energy-dispersive system combined with synchrotron radiation.

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SPATIALLY RESOLVED RESONANT-RAMAN SCATTERING SPECTROSCOPY

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When atoms are irradiated by X ray photons different kinds of interactions take place: the photon can be absorbed by the photoelectric effect or can suffer a Rayleigh or Compton scattering. However, under resonant conditions, other low probability interactions can occur. One of these interactions is the resonant Raman scattering (RRS). The X ray resonant Raman scattering is an inelastic scattering process which presents fundamental differences compared to other scattering interactions between X rays and atoms; when the energy of the incident photon approaches from below to the absorption edge of the target element, a strong resonant behavior takes place contributing to the attenuation of X rays in matter.

It is well known that the use of synchrotron radiation in trace analysis by x-ray fluorescence (SRXRF) allows to reduce detection limits and to improve sensitivities. The intrinsic characteristics of synchrotron radiation (high intensity, polarization, natural collimation, etc.) and the construction of dedicated sources of synchrotron light make possible to improve detection limits for trace elements in several orders of magnitude.

The special characteristics of SRXRF combined with the structural information of RRS provide a unique opportunity of analysing oxidation state in several types of samples with spatial resolution. A special type of application is the analysis of biological samples, which includes surveys related to the human body. In particular the study of dental mineralized tissues.

In this work we present preliminary results of micro-RRS analysis with spatial resolution of dental tissues. Linear scannings were carried out covering different areas of a dental sample including dental calculus, i.e., root, dentine, enamel, and tartar. The experimental data required a complex and deep analysis. The preliminary results show clear variations of the RRS structures according to the position of irradiation opening the possibility of a precise structural analysis via Raman scattering combined with micro-XRF.

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Ionic photofragmentation of $ClSO_2NCO$ in the S 2p, Cl 2p and S 2s regions

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On the frame of a general project aimed to the elucidation of the photochemical and electronic properties of molecules containing the $XSO_2{}^-$ *group, with* $X =$ *halogen,*[1] *we present here the study of the electronic properties and the dynamic of the ionic photofragmentation of chlorosulfonyl isocyanate,* $ClSO_2NCO$*, in the S 2p, Cl 2p and S 2s regions. The Total Ion Yield (TIY) spectra of* $ClSO_2NCO$ *in vapour phase were recorded in the TGM beamline at LNLS between 100 and 300 eV, using the vacuum chamber for gaseous samples. Below the S 2p threshold, occurring at approximately 182.8 eV, the TIY spectrum presents a group of five well defined signals at 170.3, 171.6, 173.2, 174.2 and 175.6 eV and a shoulder at 176.9 eV.A single feature is observed at approximately 208 eV, below the Cl 2p threshold at 214.7 eV. The S 2s edge is also clearly observed as a broad signal at 239 eV. Almost every possible cationic fragment of the parent molecule is observed in the PEPICO spectra, although the relative abundances strongly depend on the excitation energy. The PEPICO spectrum taken at 110 eV, far below the first S 2p resonance, is dominated by a peak at 106 m/q, which corresponds to* SO_2NCO^+*. Also* M^+*,* $ClSO_2{}^+$*,* $SO_2{}^+$*,* SO^+*,* NCO^+*, among others, are discernable in the spectra. As the excitation energy reaches the S 2p resonance region, the* NCO^+ *and* SO^+ *fragments become more abundant, while at S 2p threshold energy the* S^+ *ion dominates the spectrum. In the PEPICO spectrum measured at 214.7 eV, at the Cl 2p threshold, the* Cl^+ *fragment is the most intense peak. Several double coincidences were detected in the PEPIPICO spectra, revealing different fragmentation mechanisms from a double charged molecular ion. The most important pairs of ions detected in coincidences were* Cl^+/SO_2NCO^+*,* $NCO^+/SO_2{}^+$*,* O^+/Cl^+*,* O^+/S^+*, and* N^+/S^+*.*

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Estudo Teórico-Experimental da Fotofragmentação de Moléculas Pré-bióticas na Região da Valência

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O estudo de moléculas pré-bióticas simples é de fundamental importância para entender a formação de moléculas orgânicas complexas, como os aminoácidos, as proteínas e as nucleobases presentes no DNA e no RNA. Uma hipótese para o surgimento das nucleobases é que elas teriam sido sintetizadas a partir de compostos orgânicos mais simples contidos em meteorito e asteróides que caíram na Terra.

Diversos experimentos demonstraram que é possível produzir moléculas pré-bióticas complexas a partir de moléculas mais simples em ambientes que simulam o meio inter estelar. Já foi observado, por exemplo, que quando aquecida e submetida à radiação ultravioleta a formamida produz as nucleobases purinas.

Assim, neste trabalho, realizamos um estudo teórico e experimental dos processos de fotoionização e fotofragmentação de moléculas pré-bióticas simples, importantes na síntese de biomoléculas complexas. Entre as moléculas escolhidas para este trabalho estão dois ácidos carboxílicos e uma amida, são elas: o ácido fórmico (HCOOH), o ácido acético (CH_3COOH) *e a formamida* (H_2NCHO).

Experimentalmente, coletamos dados da produção total e parcial dos íons destas moléculas em fase gasosa, em função da energia dos fótons, na região do ultravioleta de vácuo, entre 11 e 20 eV. Estes dados foram obtidos no Laboratório Nacional de Luz Síncrotron, com o auxílio de um espectrômetro de massa por tempo vôo. Os espectros de massa foram obtidos utilizando a técnica de coincidência entre elétrons e íons, PEPICO. Para um melhor entendimento dos caminhos de fragmentação destas moléculas fizemos uma análise teórica das fotofragmentações, utilizando a Teoria do Funcional da Densidade e a Teoria do Funcional da Densidade Dependente do Tempo. Com o auxílio do tratamento teórico, determinamos, por exemplo, quais os átomos e/ou moléculas são perdidos durante a fotofragmentação.

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INNER SHELL PHOTOEMISSION SPECTROSCOPY STUDIES OF A BISMUTH COMPLEX WITH MALEONITRILEDITHIOLATE (MNT) LIGAND IN THE S1s REGION

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Coordination compounds with polisulphurated ligands represent a very interesting class of inorganic complexes, due to their several applications as charger transfer salts on the development of high technology electronic materials as well on new molecular superconductors research. In this class of compounds the maleonitriledithiolate ligand (MNT) has been received great attention over the past decades due to its capacity of extending the π *electron delocalization among the entire molecule [1]. X-ray photoemission spectra were acquired in the S 1s region at the Soft X-Ray Spectroscopy Beam Line (SXS) at LNLS-Campinas for* $[NEt_4]_2[Bi_2(MNT)_3]Br_2$*. The compound has been synthesized following the literature [2-3]. It was introduced into the main chamber as a solid sample using a carbon sticky tape. The work pressure was kept at 4.0x* 10^{-8} *mBar. The spectral analysis of this compound has allowed us to identify all chemical elements present in the sample and the different chemical environments for sulphur in this complex.*

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Core-level Photoabsorption, Photoionization and Gas Emission in Sulfur-Containing Biomolecules Subjected to Ionizing Radiation

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Amino acids, peptides and proteins are highly susceptible to soft X-ray and electron beam irradiation, undergoing deep chemical transformations under prolonged or intense beam exposure. When subjected to ionizing radiation, these compounds may decompose through a number of pathways, including the release of gaseous species. We hereby report on the experimental determination of XPS and S 1s, N 1s and O 1s NEXAFS spectra of sulfur-containing amino acids, dipeptides and proteins. The XPS data were obtained at 2500 eV incident photon energy. The samples (powders) were deposited on a carbon sticky paper. In order to search for radiation damage effects, NEXAFS and XPS spectra were also obtained for the same samples, following electron beam (1 keV) or synchrotron radiation (zero order) irradiation. All measurements were made at the Brazilian National Synchrotron Radiation Laboratory (LNLS). Significant spectral changes were observed, particularly in the S 1s and N 1s NEXAFS spectra. During sample irradiation, several gaseous species (H_2, CO_2, CO, H_2S and others) were identified using a quadrupole mass spectrometer.

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Alteração de propriedades morfológicas e óticas de filmes calcogênicos pelo ultravioleta

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Tanto a estrutura de agregação atômica como as propriedades óticas como as propriedades óticas de filmes calcogênicos podem ser alteradas pela incidência de radiação.

As alterações foto-induzidas em filmes calcogênicos em ligas binárias e terceárias foram investigadas sob vários regimes de irradiação pela luz síncrotron na linha TGM do LNLS. Ambos os sistemas foram preparados por moagem mecânica em um moinho de bolas, depositadas como um filme fino em um substrato de vidro e posteriormente expostos à luz síncrotron na faixa do ultravioleta (12.0 a 40.0 eV). Posteriormente as amostras irradiadas e um grupo controle não irradiado, foram submetidas a análise por espalhamento Raman e por absorção ótica. Diferentes processos na transmitância do filme foram observado e interpretados pelo rearranjo sob diferentes regimes dependentes da dose indcidente.

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Excitação eletrônica na região de valência e na borda S 2p do enxofre da molécula de dimetildissulfeto, DMDS

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O dimetildissulfeto (DMDS, CH3SSCH3) é uma molécula fundamental no ciclo químico do enxofre entre os oceanos e a atmosfera, ciclo este de grande influência no clima na Terra [1,2] que contribui, inclusive na formação de chuva ácida . Esta molécula também pode ser vista como um protótipo para o estudo de ligações dissulfeto, de fundamental importância para a estrutura de diversas proteínas [3] Neste trabalho, o espectro de fotoabsorção (NEXAFS) da molécula do DMDS foi obtido na borda 2p do enxofre (160 190 eV) na linha SGM do LNLS. A força do oscilador foi determinada de modo absoluto a partir do espectro de fotoabsorção na região de 3 a 200 eV obtido por espectroscopia de perda de energia de elétrons em baixo ângulo de espalhamento (2^0), no Laboratório de Impacto de Fótons e Elétrons (LIFE) da UFRJ. A normalização do espectro de perda de energia foi realizada pela aplicação da regra de soma S(-2) [4], que está associada a polarizabilidade estática da molécula. Com este trabalho, estudamos o espectro eletrônico do DMDS tanto através de um método ótico quanto de um método de perda de energia de elétrons. Obtivemos pela primeira vez o espectro de NEXAFS na região do enxofre 2p, bem como o espectro de perda de energia no largo espectro de 3 a 200 eV, em que transições de valência ainda não caracterizadas pela literatura foram observadas. As seções de choque absolutas do espectro de NEXAFS foram determinadas para cada transicção, a partir do espectro absoluto de força do oscilador, obtido por impacto de elétrons.

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Description and performance of an electron-ion coincidence TOF spectrometer used at LNLS

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We report the characteristics and performance of a Time-of-Flight Mass Spectrometer (TOF-MS) for coincidence measurements between electrons and ions that has been developed jointly in Sweden and Brazil (1). The spectrometer, used for studies of inner-shell photoexcitation of molecules in the gas- phase, has been optimized by implementing ion and electron lenses to allow the use of relatively small diameter detectors. Simulations were performed to understand the lens performance and they show that ions (electrons) could be collected without angular discrimination with a maximum kinetic energy up to ten (two) times higher than without the lens actions. A rotary vacuum chamber allows the spectrometer axis to be positioned at different angles relative to the polarization vector of the excitation beam. An important characteristic of the apparatus is that the acquisition setup allows a multi-hit capability with 1 ns resolution. Hereby, PhotoelectronPhotoionPhotoion Coincidence (PEPIPICO) measurements can be performed on molecules containing two or more atoms of equal mass. A systematic study of the interaction region has been performed to determine the shape of the photon and gas beams. Measurements on molecular nitrogen demonstrate the spectrometers ability to resolve fragments with the same charge to mass ratio arriving within only a few ns. Simulations and experimental results of fragmentation of two singly charged cation nitrogen atoms agree, confirming that the spectrometer performance is well understood. (1) F. Burmeistera, L.H. Coutinho, R.R.T. Marinho, M.G.P. Homem, M.A.A. de Morais, A. Mocellin, O. Bjorneholm, S.L. Sorensen, P.T. Fonseca, A. Lindgren, A. Naves de Brito, J. Electron Spectrosc. Relat. Phenom., 180, Pages 6-13 (2010).

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Crystal Structure Determination of the Anhydrous Pseudopolymorphic Form of Doxycycline by Powder X-Ray Diffractometry Using Síncrotron Radiation

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Doxycycline is a broad-spectrum antibiotic with main application in the treatment of respiratory and urinary tract infections.[1] It is a very important drug due to its high efficacy, low rate of side effects and low cost of treatment. Nevertheless, it is subject to the polymorphism phenomenon, which may influence the pharmacokinetic properties like solubility and dissolution rate of a compound, affecting the bioavailability of the drug. Three solid forms of doxycycline are commercially available, i.e. monohydrated ($DOX \cdot H_2O$), hyclate ($DOX \cdot HYC$) and hydrochloride ($DOX \cdot HCl$), each of them with a different content of the active principle so that the use of the wrong polymorph may reduce its efficiency. Thus, it is imperative to identify and to quantify adequately the crystal form of this active pharmaceutical ingredient in medicine formulations. By knowing the single-crystal structure of a drug, it is possible to generate the powder X-ray diffraction pattern and use it for quality control purposes. When obtaining a single-crystal of a substance is not possible, an alternative way is to determine its crystal structure by powder X-ray diffractometry. This is the case for DOX, the anhydrous pseudopolymorphic form of $DOX \cdot H_2O$, which is may be formed by heating $DOX \cdot H_2O$ and is insoluble in all tested solvents. The hydrated form was heated to produce DOX, which was placed on a capillary tube and mounted on the D10B-XPD line of Laboratório Nacional de Luz Síncrotron. The measurement was undertaken with wavelength of 1.377 between 4 and 51 ^{0} with a step of 0.005. The time for step was normalized to obtain a constant value of 390.000 in the detector. The indexing was performed using the N-TREOR program, which is part of the EXPO2009 software package [2] used to solve the structure. The parameters were refined by the Le Bail method and the Simulated Annealing method was applied to adjust the atomic positions. The final structure was refined using the Rietveld method [3] with EXPO2009 software.

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Determination of the oxidation state by resonant-Raman scattering spectroscopy

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X ray fluorescence spectra present singular characteristics produced by the different scattering processes. When atoms are irradiated with incident energy lower and close to an absorption edge, scattering peaks appear due to an inelastic process known as resonant Raman scattering (RRS). In this process, the emitted photons have a continuous energy distribution with a high energy cut-off limit. This work present results regarding the possibility of determining the oxidation state by resonant Raman scattering using an energy dispersive system. Pure sam- ples of transition metals (Cu, Fe, Mn) and different oxides of them (CuO, Cu2O, Fe2O3, Mn2O3, MnO2) were irradiated with monochromatic synchrotron radiation below their absorption edges to inspect the RRS emissions. The spectra were analyzed with specific programs using non-conventional func- tions for data fitting and a FFT smoothing procedure was applied. After smoothing, the RRS residuals are studied in order to detect variation with respect to the the- oretical curve. These variations are closely related with the chemical environments of the absorbing element and can provide relevant structural information of the sample. The changes existing in the RRS structure between pure elements and their oxides are clearly discriminated and suggest the possibility of structural character- ization by means of resonant Raman scattering using an energy-dispersive system combined with synchrotron radiation.

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SPATIALLY RESOLVED RESONANT-RAMAN SCATTERING SPECTROSCOPY

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When atoms are irradiated by X ray photons different kinds of interactions take place: the photon can be absorbed by the photoelectric effect or can suffer a Rayleigh or Compton scattering. However, under resonant conditions, other low probability interactions can occur. One of these interactions is the resonant Ra- man scattering (RRS). The X ray resonant Raman scattering is an inelastic scat- tering process which presents fundamental differences compared to other scattering interactions between X rays and atoms; when the energy of the incident photon ap- proaches from below to the absorption edge of the target element, a strong resonant behavior takes place contributing to the attenuation of X rays in matter. It is well known that the use of synchrotron radiation in trace analysis by x-ray fluorescence (SRXRF) allows to reduce detection limits and to improve sensitivities. The intrinsic characteristics of synchrotron radiation (high intensity, polarization, natural collimation, etc.) and the construction of dedicated sources of synchrotron light make possible to improve detection limits for trace elements in several orders of magnitude. The special characteristics of SRXRF combined with the structural information of RRS provide a unique opportunity of analysing oxidation state in several types of samples with spatial resolution. A special type of application is the analysis of biological samples, which includes surveys related to the human body. In particular the study of dental mineralized tissues. In this work we present preliminary results of micro-RRS analysis with spatial resolution of dental tissues. Linear scannings were carried out covering different areas of a dental sample including dental calculus, i.e., root, dentine, enamel, and tartar. The experimental data required a complex and deep analysis. The prelimi- nary results show clear variations of the RRS structures according to the position of irradiation opening the possibility of a precise structural analysis via Raman scattering combined with micro-XRF.

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Elemental and structural x-ray microanalysis by confocal setup

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The confocal setup consists of x-ray lenses in the excitation as well as in the detection channel. In this configuration, a micro volume defined by the overlap of the foci of both x-ray lenses is analyzed. Scanning this micro volume through the sample, 1-3 dimensional studies can be performed. For depth profiling studies, only the scan of the confocal volume in the normal direction to the sample is required. An elemental analysis is obtained by the detection of the x-ray fluorescence produced in the confocal volume. In addition, Energy Dispersive X-Ray Diffraction analysis (EDXRD) in the confocal volume can be performed using a continuous polychromatic source and an appropriated fixed geometry based on a low divergence optic.

To implement the confocal setup, we used two monolithic semi-polycapillaries in the excitation and detection channel. The polycapillaries were made by means of drawing of multibundles of borosilicate glass capillaries in a heating furnace. The experiment was carried out at the D09B beamline of the Brazilian Synchrotron Light Laboratory (Laboratório Nacional de Luz Síncrotron, LNLS) using white beam. A silicon drift X-ray detector of 150 eV resolution at 5.9 keV was used for detection of scattered and characteristic photons. A mean spatial resolution of 90 micrometers for the three orthogonal axes was obtained. A detailed characterization of our confocal setup is described in this work. Elemental and structural x-ray microanalyses of stratified samples are shown.

Acknowledgements: We are grateful for the financial support of LNLS and CONICET for this project.

Parte IV

Geociência, Meio-ambiente e Aplicações em Materiais Biológicos

Potential Effects of Some Functional Food in Ovine Breeding: Analysis of Nutrition-Relevant Trace Elements in Sheep Serum by TXRF

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Recent advances in the studies on the effects of nutrition on genetic regulation, together with the increasing number of reports on the beneficial effects of herbal preparations led to the new concepts of functional food and personalized medicine. In this work, we investigated the potential advantages of using some functional food in sheep with the particular aim of increasing the natural defenses of animals to inflammatory and stress conditions. Serum analyses were performed in all animals at different times (before, 3 and 51 hrs after adrenocorticotropin hormone (ATCH)). We attempted to quantify elemental serum contents using synchrotron radiation total reflection x-ray fluorescence (SR-TXRF) at the Brazilian Synchrotron Light Laboratory. The analyses indicate that diet and ATCH activity cause significant quantitative variations in K, Ca, Cu and Zn concentrations. Unrelated to diet supplementation, a tendency to decrease K presence was observed for all animals 51 hrs after ATCH treatment. The average concentration of Ca showed a trend to decrease in animals treated with the extracts EA, AP and LD, while no significant variation was revealed for PO extract. Treatment with EA extract, but not with PO, AP and LD, resulted in a slight increase of Cu serum levels. These results were in accord with the biochemical analyses of serum ceruloplasmin in the same samples, suggesting that EA extract affects Cu metabolism. High inter-individual variation in Zn levels was found by SR-TXRF in all analyses animal groups, in agreement to conventional biochemical analyses. Our results indicate that diet supplementation can affect some serum microelement concentrations and further analyses will particularly investigate the physiological meaning of Ca and Cu variations.

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Elemental characterization of PM10 and PM2.5 by SR-XRF in Córdoba City, Argentina

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24-h samplings of PM10 and PM2.5 particulate matter have been carried out during the period July 2009-April 2010 at two places of Córdoba City, which are representative of different land use and human activities (Site 1: urban and Site 2: semi-urban). Measurements of total mass of PM2.5 and PM10 for the period show a positive and linear correlation between both fractions. Average ratio (PM2.5/PM10) for sites explored in this study was 0.62 approximately. The highest value in mass concentration for both fractions was found at the urban site. However, no significant temporal pattern or seasonal difference could be detected. The chemical compositions of aerosol particles were determined by synchrotron radiation X-ray fluorescence (SR-XRF) at the LNLS. The measurements were carried out using the D09B-XRF beamline. Aerosol samples were excited with both white and monochromatic excitation beam of 10 keV. The elemental composition was different in the two fractions: in the finer one the presence of elements with crustal origin is reduced while the anthropogenic elements, with a relevant environmental and health impact, appear to be increased. An important but unmeasured component is likely constituted by organic and elemental carbon compounds. In more detail, the highest contributions to the coarse fraction for both sites were from Al, Si, K Ca, Ti, Fe, Ba, Mn and Pb. Ni and Zn were found mostly in the fine fraction of the semi-urban site and S, V, Cr and Cu were found equally concentrated in both fractions. However, the urban site presented equally important contributions from S, V, Cr, Co, Ni, Cu and Zn. Multivariate analysis (Positive Matrix Factorization) of the SR-XRF data resolved a number of components (factors), which, on the basis of their chemical compositions were assigned physical meanings. Factor analysis was conducted with the two sizes aerosol composition data in order to identify anthropogenic and natural sources of the airborne particles. Preliminary results show that the coarse particles were mainly influenced by soil, resuspended dust, and metallurgical emission and fine particles were significantly attributed to several anthropogenic sources, such as motor vehicles, oil combustion, nonferrous metal source, and biomass burning.

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Atomic Signature of Pluripotent Stem Cells

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The mechanisms underlying pluripotency in embryonic and reprogrammed stem cells are unclear. In this work we characterized the pluripotent towards differentiated state through analysis of trace elements distribution using the Synchrotron Radiation X-ray Fluorescence Spectroscopy. Embryoid bodies derived from embryonic and induced pluripotent stem cells were irradiated with a spatial resolution of 20 m to make elemental maps and qualitative chemical analyses. Results show that these embryo-like aggregates exhibit self-organization at atomic level. Consistent elemental polarization pattern of S and P in both murine and human pluripotent stem cells were observed, indicating that neural differentiation and elemental polarization are strongly correlated.

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Study of structural characteristics of normal and neoplastic human breast tissues by SAXS

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Nowadays, the human breast tissues have been extensively studied because the large number of cases of breast cancer around the world. However, while the most researchers are focused to try to discover the genetic and epigenetic alterations that initiate and drive this neoplasia, a few of them are interested to identify the tissues structural changes due to cancer progression in order to achieve a early diagnostic of this pathology with consequent higher probably of cure for the patients. In this context, the use of the small angle x-ray scattering technique (SAXS) arises as an efficient tool to determinate supramolecular structures of human breast tissues. Therefore, this work aims to identify the structural features of normal and pathological human breast tissue and, to verify the potential of the SAXS scattering profiles in differentiating neoplastic breast tissues.

A total of 68 normal and pathological human breast samples were used in this work. The SAXS experiments were performed at the D02A-SAXS2 beamline in the National Synchrotron Light Laboratory (LNLS) in Campinas, Brazil. It was used an x-ray beam of wavelength 1.488 while the sample-detector distance was fixed in 1125mm, which allow to record the momentum transfer range $0.145\text{nm}^{-1} \leq q(= 4\pi.\sin\left(\frac{\theta}{2}\right)/\lambda) \leq 3.000\text{nm}^{-1}$ *on the two-dimensional detector. Each sample was irradiated on three places, one being on the central portion and the others adjacent to this, separated by 1mm. From analysis of the SAXS scattering profiles, we identify the presence of several peaks between* $q=0.29\text{nm}^{-1}$ *and* $q=1.17\text{nm}^{-1}$ *in all tissues corresponding to collagen-rich regions, moreover we found that the intensity and width of these peaks are lightly affected by the presence of the neoplasia. Concerning to the SAXS scattering profiles of normal tissue with adipose content, more two peak arise, one at* $q=1.4\text{nm}^{-1}$ *and other at* $q=2.7\text{nm}^{-1}$ *due to packing of triacylglycerols molecules, which are the main component of lipids. From the study of structural features throughout of a sample was verified that pathological samples present a non-oriented pattern of collagen fibrils.*

In this study it was observed that changes in structural features in neoplastic samples can be identified, e.g. peak intensity, peak width and collagen fibril orientation. Therefore, these results indicate the possibility of use the SAXS technique as a tool for assessing structural changes in human breast tissues.

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Identification of metabolites in the leaves of *Chrysophyllum gonocarpum* ***by NMR analyses***

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To contribute to the development of new methods for reducing the contamination of coffee beans with Aspergillus ochraceus and ochratoxin A, which is a toxin produced by this fungus, the selection of plants able to produce substances active against this microorganism was carried out in a previously performed study. To continue this study, the present work aimed to isolate and identify the substances in the methanol extract of barks from C. gonocarpum, which was one of the selected plants. Initially, the dry form of this extract was subjected to washes with solvents, resulting in three fractions: soluble in hexane, soluble in ethyl acetate and soluble in methanol. Since the last fraction was the most active and presented the greatest mass, it underwent several subsequent fractionations by column chromatography and by high performance liquid chromatography, which resulted in the purification of four substances. After analyses by ^1H *and* ^{13}C *nuclear magnetic resonance (NMR) spectroscopy, the following structures were attributed to these compounds: (7S*,8S*)-threo-1-C-syringylglycerol 4-O-B-D-glucopyranoside, (7R*,8R*)-threo-1-C-syringylglycerol 4-O-B-D-glucopyranoside, 4-O-B-D-glucopyranosil-3,3,4-di-O-methylellagic acid, 4-O-B-D-xylopyranosil-3,3-di-O-methylellagic acid. Further studies should be conducted to ascertain the effects these substances have on A. ochraceus.*

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SYNCHROTRON RADIATION USED TO DISTRIBUTION ANALYSIS OF TRACE ELEMENT IN PROSTATE TISSUES

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Many elements play an essential role in a number of biological processes by the activation or inhibition of reactions between metabolic enzymes. The determination of concentrations of trace and minor elements and their distribution in healthy and diseased tissue can potentially be exploited as diagnostic indicators of clinical conditions and may enhance better treatment and understanding of the pathogenesis of the underlying mechanisms involved. The aim of this work was to study the trace elemental distribution in normal prostate tissues. The measurements were performed exciting with a white beam and using a conventional system collimation (orthogonal slits) in the XRF beam line at the Synchrotron Light National Laboratory (Campinas, Brazil). The results showed that most elements analyzed presented non-uniform distribution for the different areas of the prostate examined.

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Elemental concentration analysis in Benign Prostatic Hyperplasia tissue cultures by SR-TXRF

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For several years now, people living in the surroundings of the Amazon Rain Forest have been using Orbignya speciosa (babassu), a Brazilian native palm tree, to treat inflammatory diseases as well as urinary symptoms. Metallic elements and their organic compounds have dynamic regulatory functions in cells. These elements take part in all metabolic processes, and they are components of different enzymes, catalyzing chemical interactions in living cells. It is now recognized that there is an association between the levels of certain trace elements in human tissue and the presence of various diseases. The prostate produces high levels of many these important biological substances. In this study, we established BPH tissue cultures and treated them with Orbignya speciosa (OSE),. The Total Reflection X-Ray Fluorescence spectroscopy using synchrotron radiation (SRTXRF) applied to these samples. The X-Ray Fluorescence measurements were performed at the X-Ray Fluorescence Beamline at Brazilian National Synchrotron Light Laboratory (LNLS), in Campinas, São Paulo. It was possible to detect the following elements: P. S. Cl. K. Ca. Fe. Zn. and Br. The students t-test technique showed the elements P, S and Zn presented statistical difference (alpha = 0.05) for most patients among the groups studied.

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Determination of trace elements in healthy and seborrheic keratosis skin samples by SRTXRF

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The aim of this work is to evaluate the concentrations of trace elements content in seborrheic keratosis (SK) skin lesions as well in normal skin and compare them. These data was acquired by Synchrotron Radiation Total Reflection X-ray Fluorescence (SRTXRF).This stage of research was supported by LNLS - Brazilian Synchrotron Light Laboratory in Campinas/São Paulo-Brazil. The collection of lesion and healthy skin samples, including papillary dermis and epidermis, from the same patient, has involved 5 males and females with ages varying from 34 to 80 years old. The results have shown the presence of P, S, Cl, K, Ca, Ti, Cr, Fe, Ni, Cu, and Zn in healthy skin. The comparison with lesion contents has revealed significant differences in contents of Fe, K, Cr, and Zn.

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Especiación de As por SR-TXRF-XANES en fracciones celulares de corteza renal de ratas de expuestas crónicamente a As

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La contaminación de agua con arsénico (As) es problema global que afecta la salud de millones de personas. El arsénico ingerido es absorbido en intestino y metabolizado en hígado y riñón, por lo que en sangre circulan varias especies como As(III), As(V), monometil arsénico (MMA(III) y MMA(V)), dimetil arsénico (DMA(III) y DMA(V)), que posteriormente son eliminadas por orina (principalmente). Utilizando técnica SR-XRF (línea D09B del LNLS) se han podido elaborar mapas de distribución de As acumulado en algunos órganos como hígado y riñón. Sin embargo, es relevante determinar las especies de As retenidas en los tejidos ya que la toxicidad del As es dependiente de su estado de oxidación y su metilación, siendo los estados +3 más tóxicos. Estos resultados son muy necesarios para lograr una adecuada relación dosis/efecto a fin de ajustar los diferentes modelos usados para estudiar los efectos nocivos de este tóxico ambiental. Para realizar estas determinaciones se ha implementado en la línea D09B del LNLS la metodología SR-TXRF-XANES. Considerando que las mitocondrias son la principal organela afectada por, se separaron diferentes subfracciones celulares a partir de corteza renal de ratas que bebieron agua con As(III), fueron liofilizadas y transportadas al LNLS para su análisis por SR-TXRF-XANES. Esta técnica permitó determinar que el estado de oxidación +3 es el más abundante. Concluimos que SR-TXRF-XANES será una herramienta muy valiosa en el estudio de la toxicidad del As.

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Efectos de arsénico o clorpirifos sobre la concentración de As y otros elementos en embriones y larvas de sapo común argentino Rhinella arenarum *expuestos durante su desarrollo*

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En la Patagonia Norte se produce la mayor proporción de peras y manzanas de exportación de la República Argentina y esto está asociado a un alto riesgo de contaminación hídrica con plaguicidas organofosforados. Esta situación es agravada por la presencia de un arco volcánico donde nacen algunos de los ríos cuyas aguas son usadas para consumo humano y el riego. Reporte aislados han mostrado una alta contaminación con de As en ríos que nacen en el arco volcánico de la Cordillera de Neuquén. Debido al fuerte impacto ambiental y sobre la salud humana de estos contaminantes se están determinando marcadoras de exposición y daño en la especie autóctona de sapo Rhinella arenarum (ex Chaunus arenarum). Esta especie ocupa una posición clave en la cadena trófica y es un interesante bioindicador del impacto ambiental de contaminantes. Se obtuvieron embriones de sapo por fertilización in vitro y se determinaron en laboratorio varios bioindicadores de exposición a concentraciones entre 0 y 25 ppm As, y 1 y 16 ppm clorpirifos. En LNLS se midió la concentración de As y otros elementos por SR-TXRF en los diferentes estadios embrionarios y de larva, de sapos expuestos a concentraciones ambientales de As y clorpirifos (1 y 2 ppm, y 2 ppm, respectivamente). No se encontró bioacumulación de As durante la etapa embrionaria. Sin embargo se observaron alteraciones en la concentración de otros elementos y estas alteraciones podrían estar relacionadas a la toxicidad de As y clorpirifos. El estado de larva fue alcanzado tras 8 días de incubación. Solamente se encontró bioacumulación de As en la etapa larval, que fue acompañada con alteraciones significativas de en la concentración de P, S, Cl, K. Para la detección de biomarcadores se requirieron dosis altas de As y clorpirifos (superiores a 15 ppm y 8 ppm, respectivamente), sin embargo, la técnica SR-TXRF permitió detectar alteraciones por exposición a dosis ambientales de ambos contaminantes.

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Caracterização por EXAFS do Gel Produzido pela RAA em Concreto

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A reação álcali-agregado (RAA) é uma interação que ocorre no interior poroso das estruturas de concreto, envolvendo água e agregados reativos contendo hidróxidos alcalinos. A reação produz um gel amorfo muito higroscópico e expansível que, se confinado na matriz de concreto pode gerar grande estresse mecânico e causar o aparecimento de rachaduras na estrutura. Há, portanto, grande interesse na compreensão exata da estrutura atômica desse gel amorfo, de maneira a auxiliar no desenvolvimento de métodos de reparo mais eficazes e/ou baratos que os atualmente disponíveis, bem como avanços tecnológicos que possibilitem a inibição completa da reação. Com esse objetivo, várias técnicas têm sido utilizadas para a caracterização estrutural do gel, por exemplo, através do estudo da função distribuição de pares (PDF) [1] e NMR [2,3]. Há ainda estudos teóricos que visam a elucidação dessa estrutura [4,5]. Neste trabalho, uma amostra de gel foi caracterizada por estrutura fina de absorção de raios X (EXAFS) nas bordas do potássio (3608 eV) e silício (1839 eV), com o objetivo de se estudar a ordem local ao redor desses átomos absorvedores. Foram obtidas informações a respeito da distância entre primeiros e segundos vizinhos, bem como ângulos de ligações químicas presentes no gel.

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Acknowledgements:

Evidences of the mechanism of As(III) immobilization on gibbsite by combining EXAFS and theoretical calculations

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The mechanism of aqueous As(III) species immobilization on gibbsite has been evaluated as a function of pH. Theoretical calculations and X-ray absorption fine structure spectroscopy (XAFS) were combined to elucidate the structure of arsenite surface complexes on synthetic gibbsite. Several adsorption sites have been evaluated using the self-consistent charge corrected density-functional based tight-binding (SCC-DFTB) method. The formation of bidentate-binuclear, bidentate-mononuclear, monodentate-mononuclear, and monodentate-binuclear complexes by means of both acid-base and non-dissociative mechanisms has been studied in detail. The SCC-DFTB calculations showed the bidentate-binuclear/acid-base complex as the most thermodynamically stable geometry for As(III) bonding to gibbsite surface, estimating As-O and As-Al distances of 1.75 and 3.24 , respectively. EXAFS results confirmed As(III) complexation to three oxygen atoms in the first shell, at a distance of 1.77 , and to two aluminum atoms in the second shell, at a distance of 3.21 , in a bidentate-binuclear configuration, at pH 5.0, 7.0 and 9.0. A monodentate-binuclear complex was shown to provide a minor contribution to As(III) sorption on gibbsite. Based on the results from theoretical calculations and experimental measurements it was demonstrated that inner-sphere complexation is the preferable immobilization mechanism for As(III) on gibbsite, in a pH range of 5-9. Therefore, the higher As(III) mobility in the environment, when compared to As(V), was suggested to be related to the feasibility of protonation of the bidentate-binuclear As(III) adsorbed complex. This protonation would restore the neutral H_3AsO_3 *molecule, which could be then released from the mineral surface. These results might be useful to predict and control arsenic mobility in aqueous environments, particularly where aluminum oxy-hydroxides are often found.*

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TRACE ELEMENT ANALYSIS IN HUMAN BLOOD SERUN OF PATIENTS WITH SICKLE CELL ANEMIA BY TXRF

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The determination of trace elements levels in physiological fluids is of considerable interest in clinical chemistry. Since it has been established this levels in human serum can be utilized as indicators for several pathological conditions, the simultaneous detection of certain elements in the serum offers a very interesting approach in the diagnosis and treatment of various diseases. Sickle cell anemia (SCA) is a blood disorder that affects hemoglobin, the protein found in red blood cells that help carry oxygen throughout the body. In this work we have analyzed serum samples from patients with SCA by using Total Reflection X-ray Fluorescence using synchrotron radiation (SRTXRF). The SRTXRF measurements were performed at the X-ray Fluorescence Beamline (D09B-XRF- LNLS) using a polychromatic beam. We have studied forty-three patients aged 18-50 years old, suffering from SCA and sixty healthy volunteers aged 18-60 years old. It was possible to determine the concentrations of the following elements: P, S, Cl, K, Ca, Fe, Cu, Zn, Br and Rb. Data were evaluated by using students t test (alfa = 0.05) between group of healthy subjects and group with SCA. It was observed that contents of the elements P, Cl, K, Fe, Cu, Zn and Br differed significantly (alfa = 0.05) between groups of healthy subjects and SCA. Moreover, there are evidences of an association among Fe, Cu and Zn in the SCA pathogenesis process.

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Structural characterization of novel catalysts based on iron oxides using the Rietveld method

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A promising catalytic application for destruction of organic contaminants in wastewaters is the combination of iron oxides and H_2O_2 *in a heterogeneous Fenton-like system. Herein, we report for the first time a highly reactive system based on heterogeneous Nb-peroxo complexes, produced by pretreatment of Nb-doped iron oxides with* H_2O_2*, for oxidation of organic compounds. The materials were characterized by powder X-ray diffraction, which was acquired at the National Laboratory of Synchrotron Light Brazil in a Bragg Brentano geometry using radiation of 1.23844 , parallel polarization correction and a graphite monochromator. Powder XRD patterns were acquired from 15 to 70° 2θ at a step width of 0.02°, 10 s per step. Silicon was used as an external standard. Rietveld refinement was performed with FULLPROF 2010 in order to estimate the structural parameters of each phase in the composites. The Rietveld refinement yielded a profile residual factor, Rp, of approximately 4.5% for each sample, indicative of good quality refined models. The pattern of pure composite before treatment with* H_2O_2 *shows diffraction peaks from hematite (91 wt.%) and maghemite (9 wt.%) and after* H_2O_2 *treatment these proportions practically does not change. Otherwise, the hematite/maghemite proportion is strongly affected by presence of niobium. The diffraction pattern of Nb-doped iron oxides before treatment with* H_2O_2 *mainly consists of hematite (32 wt.%) and maghemite (56 wt.%), whereas after treatment is constituted for hematite (51 wt.%) and maghemite (38 wt.%), suggesting the conversion of maghemite into hematite. The high content of maghemite in the Nb-doped iron oxides before treatment suggests that the Nb(V) ions can stabilize the maghemite structure. In addition these phase, it was observed diffraction peaks corresponding to* $FeNb_2O_6$ *with 12 and 11 wt. % in Nb-doped iron oxides before and after treatment, respectively. The pretreatment of composites with* H_2O_2 *strongly increases its catalytic activity for oxidation of methylene blue.*

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AVALIAÇÃO DA PRESENÇA DE METAIS PESADOS NOS LOCAIS DE DISPOSIÇÃO DE RESÍDUOS DA CIDADE DE CAMPINAS (SP) POR SR-TXRF: RESULTADOS PRELIMINARES

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O problema dos resíduos sólidos na grande maioria dos países vem se agravando como conseqüência do acelerado crescimento populacional, urbanização, desenvolvimento industrial e mudanças de hábitos de consumo. Dentre as inúmeras formas de disposição de resíduos, os aterros sanitários são hoje os mais indicados à realidade brasileira, tanto do ponto de vista técnico quanto de ponto de vista econômico. Suas características construtivas permitem minimizar os efeitos das duas principais fontes de poluição oriundas dos resíduos sólidos: o gás do aterro e o lixiviado. O objetivo principal deste trabalho é avaliar o teor de elementos traço em amostras de água subterrânea, água superficial e chorume advindos de locais de disposição de resíduos sólidos da cidade de Campinas, SP. As amostras de água subterrânea, superficial e de chorume foram coletadas nos Aterros Sanitários Delta, Santa Bárbara e Pirelli. No Aterro Delta e Santa Bárbara foram observados valores acima dos limites máximos permitidos estabelecidos pela CETESB para Cr (50 $\mu g.L^{-1}$*), Mn (400* $\mu g.L^{-1}$*), Fe (300* $\mu g.L^{-1}$*), Ni (20* $\mu g.L^{-1}$*) e Pb (10* $\mu g.L^{-1}$*) nas amostras de água subterrânea, enquanto que no Aterro Pirelli os elementos com concentrações acima do permitido foram: Mn, Fe, Ba (700* $\mu g.L^{-1}$*) e Pb. No Aterro Delta ainda foram observados valores acima do permitido estabelecido pela legislação CONAMA 357, nas amostras de água superficial, para os elementos Cr (0,05* $mg.L^{-1}$*), Mn (0,1* $mg.L^{-1}$*), Fe (0,3* $mg.L^{-1}$*) e Cu (0,009* $mg.L^{-1}$*), e nas amostras de chorume valores acima do permitido, também estabelecido pela resolução CONAMA 357, foram observadas para: Cr, Mn Fe, Ni (0,025* $mg.L^{-1}$*), Cu, Zn (0,18* $mg.L^{-1}$*) e Pb (0,01* $mg.L^{-1}$*). As amostras de chorume foram preparadas por duas metologias de extração, EPA 3050B, indicada para a determinação do teor ambientalmente disponível e a EPA 200.8 indicada para a obtenção do teor total. As concentrações de Cr, Ni, Cu e Pb obtidas foram superiores ao limite CONAMA 357 para a maioria das amostras coletadas em diferentes períodos (seco e chuvoso) e para as duas metologias de extração dos metais.*

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Determinação das prováveis fontes de emissão de material particulado na cidade de Limeira (SP) por SR-TXRF

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Os poluentes atmosféricos são responsáveis por diversos problemas ambientais, tais como chuva ácida e efeito estufa, causando diversos problemas à saúde humana, entre eles doenças respiratórias principalmente em idosos e crianças. Dentre esses poluentes, existe uma grande preocupação com o material particulado (MP), que por ser emitido por diversas fontes apresenta uma composição heterogênea. Desta forma, o presente trabalho teve como objetivo analisar quantitativamente o material particulado do município de Limeira (SP). As coletas de MP foram realizadas na estação meteorológica da FT (Faculdade de Tecnologia/ UNICAMP) com o uso de um sistema de amostragem de filtração sequencial. As frações, grossa e fina, do MP, correspondentes as frações inaláveis superior e inferior, respectivamente, foram coletadas em filtros de policarbonato colocados em série no amostrador. Após uma remoção em meio ácido, as amostras foram analisadas por SR-TXRF. Dentre os resultados obtidos, constatou-se que a maior contribuição para a formação do PM_{10} *é a fração grossa. Em todas as coletas realizadas o valor máximo estabelecido pela CETESB para o* PM_{10} *(150* $\mu g.m^{-3}$*) não foi ultrapassado. Com relação à composição do MP, foram detectados 16 elementos em ambas as frações: S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Ba e Pb. Segundo a USEPA o valor máximo permitido para a concentração de Pb no MP é de 0,15* $\mu g.m^{-3}$ *e neste trabalho estes valores também não foram ultrapassados em nenhuma das coletas realizadas. Empregando análises estatísticas multivariadas (componentes principais e cluster) foi possível determinar as prováveis fontes de emissão que contribuem na formação do MP. Para a fração grossa a principal fonte de emissão foi a ressuspensão do solo contribuindo com 57% na formação do MP, seguida da emissão veicular, com 30% e finalmente a industrial, com apenas 13%. Na fração fina do MP a principal fonte de emissão foi a poeira do solo, responsável por 79% da formação do MP, em seguida as emissões veiculares com 13% e, finalmente as emissões industriais com apenas 8%. Os valores obtidos neste trabalho foram comparados com os descritos por outros autores em outras localidades e apresentaram uma boa concordância.*

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Estudo preliminar do emprego da técnica de NEXAFS na borda S 1s no estudo da proteína ciclofilina associada com o cancro cítrico

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Espectros de fotoabsorção na região de Raios-X (NEXAFS) apresentam, além de um elevado caráter elemento-específico, forte dependência da ambientação química ao qual está sujeito o átomo cuja borda está sendo alvo de irradiação. Desta forma, podem fornecer informações relevantes sobre estado de oxidação e estrutura eletrônica da amostra. A potencialidade da técnica de NEXAFS na borda S 1s, para o estudo de sistemas biológicos, indo desde aminoácidos (cisteína, metionina) até proteinas e biomateriais em geral contendo o átomo de enxofre foi demonstrada recentemente. O cancro cítrico, causado pelo fitipatógeno Xanthomonas axonopodis pv. citri (XAC), constitui uma doença que afeta todos os cultivares comerciais de citros e é considerado uma das maiores ameaças à citricultura brasileira. No presente caso foram efetuados estudos espectroscópicos preliminares de amostras de uma ciclofilina de Citrus sinensis, associadas a esta patogenicidade. O interesse básico das medidas de NEXAFS consistiu em obter informações sobre o estado de oxidação dos átomos de enxofre se estas estão na forma reduzida ou formando pontes dissulfeto. Foram obtidos especteos da ciclofilina expressa em BL21(DE3) e em BL21 origami, cepa com ausência de tioredoxinas, favorecendo, portanto, a formação de pontes dissulfeto e estes foram comparados com espectros de amostras de cisteína e cistina, obtidos na mesma faixa de energia. Observou-se que os espectros das proteínas apresentavam uma maior semelhança com o espectro da cisteína, sugerindo que em ambos os casos a forma reduzida é no mínimo preponderante. Os resultados iniciais parecem promissores, no tocante ao uso da técnica de NEXAFS para a caracterização quanto à forma oxidada ou reduzida das proteínas. Considera-se desejável, portanto a continuidade dos trabalhos nesta linha, incluindo a obtenção de espectros de misturas de cisteina e cistina com diversas proporções relativas, bem como a obtenção adicional de espectros de ciclofilinas com uma estatística de contagem mais elevada.

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Análise de metais pesados em esgoto e lodo gerado em estações de tratamento, nos municípios de Jaguariúna e Campinas por SR-TXRF: resultados preliminares

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O rápido desenvolvimento urbanístico e industrial nas últimas décadas provocou alterações no meio ambiente, principalmente a poluição dos corpos dágua, causando danos à saúde da população. Os municípios de Jaguariúna e Campinas estão inseridos na RMC, uma das regiões mais dinâmicas no cenário econômico brasileiro, responsável por 2,7% do PIB nacional e 7,83% do PIB paulista. Portanto, visando estudar a influência antropogênica, foi avaliada a qualidade do efluente bruto e tratado e, do lodo gerado nas estações de tratamento de esgoto (ETE) empregando a técnica de SR-TXRF e os resultados comparados com os valores máximos permitidos (VMP) das legislações vigentes. Na ETE de Jaguariúna foram observados que as concentrações de Cr no efluente bruto estão acima do VMP (CONAMA 357) em dois dias de coleta (06 e 30/06/2009), enquanto que no efluente tratado, todas as concentrações estão abaixo do VMP . Para o Fe em todas as amostras de efluente bruto as concentrações estão abaixo do VMP (15 mg.L^{-1}*), entretanto no efluente tratado as amostras coletadas nos dias 06 e 30/06/2009 contém teores de ferro superior ao VMP, indicando que a ETE de Jaguariúna, está inserindo ferro durante o processo de tratamento. Os teores de Ba, Cu, Mn, Ni, e Zn , no efluente tratado estão abaixo do VMP indicando que estes podem ser lançados nos corpos dágua, sem prejuízos à qualidade ambiental. Na ETE de Campinas os teores de Cr estão acima do VMP (0,5 mg.*L^{-1}*) para o efluente bruto em três dias alternados, 10 e 24 de junho, e, 28/08/2009. Entretanto apenas a amostra coletada no dia 10/06/2009 apresentou concentração acima do VMP para o efluente tratado. O mesmo fato foi observado para o elemento Zn. No caso do Fe a mesma amostra citada acima apresentou concentrações que ultrapassaram o VMP, assim como outra amostra de efluente tratado coletada no dia 28/05/2009. Para o efluente bruto somente as amostras coletadas no dia 27 de junho de 2009 apresentaram concentrações acima do VMP. As concentrações de Cu, Mn, Ni e Pb ficaram abaixo do VMP, para o efluente bruto e tratado. Quanto as amostras de lodo coletadas na ETE de Jaguariúna os teores de Ba, Cr, Cu, Pb, Ni e Zn foram inferiores ao VMP estabelecido pela CONAMA 375, indicando a possibilidade de reúso do lodo gerado.*

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Avaliação de metais pesados em anéis de crescimento de árvores de Tipuana, nos passeios públicos da cidade de São Paulo (SP) empregando a SR-TXRF

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O alto consumo de metais em vários processos industriais tem implicado no descarte de grandes quantidades desses elementos no meio ambiente, somado a isso a emissão de poluentes na atmosfera por veículos automotores devem ser motivos de estudo e monitoramento. Atualmente muitos estudos utilizam os bioindicadores, plantas ou animais capazes de apresentar respostas qualitativas e/ou quantitativas, quando expostas a substâncias poluentes. As árvores registram e incorporam no seu lenho, desenvolvido ano após ano, as impressões do meio abiótico, tornando possível o estudo das diferentes alterações ambientais, entre elas a poluição, ocorridas ao longo da vida dessas árvores. A possibilidade de datação dos anéis de crescimento do lenho das árvores, aliando-se à aplicação das informações registradas em sua estrutura para estudos ambientais e históricos deu início à ciência chamada de dendrocronologia. A espécie selecionada, Tipuana tipu (Benth.) O. Kuntze está classificada na família Fabaceae (Leguminosae), é nativa da Argentina e Bolívia e foi introduzida no Brasil como ornamental. É uma das árvores mais comuns na arborização urbana paulistana e uma espécie de resistência. O presente projeto tem como objetivo principal determinar o teor dos metais pesados em amostras de anéis de crescimento de árvores da espécie Tipuana Tipu, previamente datados, coletadas em pontos estratégicos de São Paulo, como: Vila Pompéia, Bairro da Lapa e Butantã. Foram realizadas coletas da mesma espécie no Campus da ESALQ/USP em Piracicaba (SP), local de pouco acesso e com baixo fluxo de veículos. Após a datação dos anéis de crescimento as amostras foram submetidas a uma extração em meio ácido. Os elementos quantificados foram: S, Cl, Ca, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Ba e Pb. Nas plantas, teores de Pb, acima de 30 $\mu g.g^{-1}$ *são considerados como tóxicos e nos anéis de crescimento das espécies coletadas no Butantã, na cidade de Piracicaba (1998 a 2000) e na Vila Pompéia (1983 a 1985), os valores encontrados na espécie Tipuana foram superiores a este limite. Outros elementos como Cr, Ni, Cu, Zn e Ba também apresentaram concentrações elevadas consideradas acima dos normais. Os resultados preliminares indicam que a Tipuana pode ser utilizada como bioindicadora da contaminação ambiental.*

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Combining X-Rays and Neutrons to Shed Light in the Conformational Changes in L-Methionine

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In recent years crystalline amino acids have attracted a lot of attention due to their rich vibrational and structural properties [J. A. Lima Jr., et al, J. Raman Spect. 2008, 39, 1356; J. M. de Souza, et al., J. Phys. Chem. B 2007, 111, 5034; H. N. Bordallo, et al., J. Phys. Chem. B 2008, 112, 8748]. In addition, as a building block of proteins and peptides, amino acids are extremely important biological substances. Finally, understanding their ability to form polymorphs is a great challenge as it can later be extended to the design of smart materials. L-Methionine is an essential amino acid, important in the methylation process playing a key role in the immune system affected by HIV and other diseases [R. van Brummelen and D. Toit, Amino Acids 2007, 33,157; R. Pal, et al, J. Exp. Brain Res. 2007, 180, 765; E. Martignoni, et al, J. Neurol. Sci. 2007, 257, 31]. However very few studies of crystalline L-methione have been reported in the literature, thus very little is known about its physical properties. According to recent experiments, including Raman spectroscopy, thermal analysis, neutron diffraction and inelastic neutron scattering, changes in the conformational states of L-methionine induce a variety of structural arrangements between 220 and 340 K [J. Fischer, private communication; P.T.C Freire, private communication]. In order to analyse the structural arrangements of the intermediate conformational states high resolution X-ray measurements as a function of temperature are essential. Here we present the first results from X-ray synchrotron (LNLS-XPD) and neutron diffraction (IPEN) which combined to the previous results confirm that subtle structural changes in L-Methionine lead to a rich phase diagram in this important amino acid.

Acknowledgements:

Estudo de cartilagens e articulações por radiografia por contraste de fase com detectores de pixel Pilatus

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Neste trabalho apresentamos um estudo sobre a viabilidade da realização de imagens de cartilagens e articulações in vitro de pequenos animais e também de pequenos corpos de prova pelo método de Imagens Realçadas por Difração (IRD), utilizando um detector digital Pilatus 100K. A montagem experimental para a realização das IRD foi realizada na linha XRD2 do Laboratório Nacional de Luz Síncrotron utilizando um difratômetro de duplo eixo e dois cristais (monocromador e analisador) do tipo channel cut de Si (111) na reflexão (333) com uma energia selecionada de 10.34 keV. Nesta montagem a amostra era posicionada entre os dois cristais e o detector digital era posicionado Após o cristal analisador. Para a aquisição das imagens tanto a amostra quanto o detector eram deslocados simultaneamentes na frente do feixe por dois transladores lineares de alta precisão. Utilizando cristais de alta qualidade e com alta ordem, a rocking curve obtida girando o cristal analisador em torno do ângulo de Bragg apresentava largura angular a meia altura de poucos micro-radianos. Isto faz com que o cristal analisador funcione como um filtro angular permitindo que esta técnica obtenha imagens com alta resolução. Para obter todo o potencial do método de IRD o cristal analisador era deslocado de poucos micro-radianos fazendo com que as imagens obtidas não fossem mais realizadas com o analisador no máximo da curva, mas em diversas posições do flanco. Isto resultava em imagens com alta resolução de contraste o que torna as interfaces de tecidos fáceis de serem distinguidas. O resultado são imagens que apresentam realce nas bordas, sendo que para cada flanco da rocking há um realce de um dos lados da borda. Análises preliminares das imagens de pequenos animais mostram que devido ao grande tamanho do pixel do detector Pilatus (175 microns) não foi possível visualizar pequenas estruturas pois apesar da boa eficiência e velocidade do detector, este não apresenta resolução adequada para que se possam obter maiores detalhes nessas imagens.

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Estudo por XANES in-situ assistido por métodos quimiométricos de um catalisador a base de goethita na oxidação de metano

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A goethita é um dos óxidos de ferro mais estáveis e tem sido reportado como um catalisador ativo na oxidação de diversos compostos orgânicos. Sabe-se que durante estes processos catalíticos podem ocorrer alterações na estrutura do catalisador concomitantemente com a formação dos produtos. Neste trabalho, um catalisador a base de goethita foi avaliado in-situ durante a oxidação de metano através da espectroscopia de absorção de raios-X próximo da borda (XANES), fazendo uso de métodos quimiométricos para avaliar as transformações químicas ocorridas na estrutura do catalisador.A oxidação de metano foi conduzida em reator de fluxo contínuo em uma rampa de aquecimento de 25 a 800oC (10oC min-1). Os produtos da reação foram monitorados on-line por espectrometria de massas. O catalisador foi analisado in-situ por XANES na borda K do Fe. Os resultados da análise on-line por espectrometria de massas indicaram a produção de CO2 e H2O a partir de 400oC e a produção de CO e H2 a partir de 700oC. Análise de Fatores Evoluintes (EFA) indicou a presença de duas fases e sugeriu a existência de uma terceira. Utilizando a Determinação de Rank por Desvio Absoluto Médio (DR-MAD), foi confirmada a existência de três fases. Aplicou-se a análise por Resolução Multivariada de Curvas (MCR) para obter os perfis de concentração das espécies durante a reação e recuperar os espectros XANES puros de cada espécie. Os resultados de MCR indicaram que durante a reação a estrutura da goethita (fase 1) passou por uma pequena transformação, formando uma espécie intermediária não identificada (fase 2) e finalmente uma fase final (fase 3) contendo principalmente goethita e possivelmente pequena fração de maghemita. Os métodos quimiométricos foram essenciais para o estudo por XANES in-situ avaliação das transformações do catalisador durante a reação.

Acknowledgements: Ao Laboratório Nacional de Luz Síncrotron (LNLS), CNPq, Finep, Capes e Fapemig.

Use of in situ XANES on the evaluation of nickel doped Goethite as a catalyst for partial methane oxidation

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Partial methane oxidation is one of the most challenging research subjects nowadays. Due to the importance of the rational use of natural resources and the use of methane as a raw material on the production of several chemicals. In this work we present the use of in situ XANES technique for the evaluation of iron oxide doped with nickel (Gt-Ni10)acting as a catalyst on the partial oxidation of methane. XANES experiments were carried out using the facilities of the LNLS (Brazilian Synchrotron light Laboratory, Campinas). Goethite doped with 10

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Parte V

Matéria Mole e Fluídos Complexos

SAXS and XAFS characterization of Unimolecullar Micelles: Structure, Thermoresponsive supramolecular behavior, metal ions uptake.

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Soft matter materials are attractive because of their versatility as building blocks. Among them Unimolecular micelles are very attractive because of their stability, comparing with the traditional micelles. These structures can be synthesized capping a dendritic core having surface groups with different moieties. Here we present SAXS experiments on the molecular and supramolecular structure and the thermally induced changes observed in hyperbranched polyethileneimine(core)-palmitic acid(shell) (HPEI-C16) colloidal suspensions and thin films and SAXS, and XAFS data on transition metal salts loaded HPEI-C16. Suspension SAXS experiments were performed on HPEI-C16 samples. SAXS data of HPEI-C16 at 22C displays peaks indicating long range ordered with interplanar distances of 5.65 nm. The diagram also shows several equally spaced peaks indicating the lamellar structures. Thermal evolution of the line area indicates that the ordered phase vanishes around 30 C giving rise to a SAXS diagram typical for a colloidal suspension with bell-shaped Kratky plot indicating a globular structure. Further analysis shows a symmetric volume distribution for the particles with a polydispersity=2. Model analysis of the scattering curve demonstrated the core-shell structure of the micelle. Thermal evolution of the peak position indicates the occurrence of negative thermal expansion behavior. SAXS data of HPEI-C16 thin films displays similar diagrams, in agreement whit the previous experiments. Transitions metal (Cu,Co,Ni) salts were loaded on HPEI-C16 as sulfate salts. XAFS experiments were performed to gain insight about metal coordination in these structures.

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Investigating Protein-Surfactants complexes using Small Angle X-Ray Scattering

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Protein-surfactant interactions have both fundamental and applied interests. They play a significant role in the food industry, pharmaceutical industry, and, not the least, fabric and homecare detergent industry. Enzymes such as proteases, amylases, lipases, and cellulases are typically present in many detergency formulations. Furthermore, protein-surfactant interactions reveal new facets about the types of conformational changes that proteins may undergo in response to a changing environment. While both nonionic and ionic surfactants can increase the activity of lipases, ionic surfactants generally denature proteins at low concentrations through a combination of ionic and hydrophobic interactions. The classical model of protein denaturation by sodium dodecyl sulfate (SDS) is based on the pioneering work of Tanford and has been confirmed by more recent reports. In this model, individual SDS molecules at low surfactant concentrations first bind to a number of high-affinity sites, accompanied by a limited degree of structural change, followed by a plateau in the binding isotherm before a massive uptake of SDS occurs in a cooperative step. However, many details on binding and accompanying structural changes remain to be elucidated. Here it will be presented the results from two different investigations: the formation of protein-sufactant complexes between SDS and a simple α*-helix protein containing no cofactor, namely, the 86-residue four-helix bundle bovine acyl-coenzyme-A-binding protein (ACBP); and the SDS mediation of the aggregation of the 140-amino-acid protein* α*-synuclein (*α*SN), natively unfolded protein, which is related to the Parkinsons disease. For both cases [1,2] the combination of spectroscopy, chromatography, calorimetry, and small angle X-ray scattering (SAXS) provided a comprehensive structural and stoichiometric description of the protein-surfactant compexation.*

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Stability and structure of sodium caseinate emulsions

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Most dispersed multiphase systems are thermodynamically unstable per se and thus require stabilization. In the food industry sodium caseinate is widely used as an ingredient due to its functional properties, which include emulsification and gelation. The aim of the present work was to investigate the effect of sodium caseinate or sugar concentrations and fat phase composition on the stability and structure of emulsions formulated with a concentrated from fish oils, sunflower or olive oils as fat phase. The main mechanism of destabilization in a given formulation depended on NaCas concentration. Emulsions formulated with 0.5 and 1 % NaCas destabilized mainly by creaming. For the 2 % NaCas emulsion, both creaming and flocculation mechanisms, were involved while for emulsions stabilized by 3, 4 or 5 % NaCas the main mechanism was flocculation. When trehalose was added to emulsions, the rate of destabilization was markedly lower. The 5 % NaCas emulsion did not flocculate during a week at 22.5 ^0C*. Its back scattering remained unchanged during storage showing a great stability. This sample remained fully turbid and in the liquid state. SAXS patterns for emulsions formulated with 0, 20 or 30 % trehalose, 10 % CFO and 5 % NaCas were analyzed at 8* ^0C*. As was expected addition of sugar diminished the intensity of the signal since electron density of aqueous trehalose solutions increased with concentration and therefore there was less contrast. Values of q were 0.241, 0.248, and 0.252 nm*^{1} *for emulsions with 0, 20, and 30 % trehalose, respectively. Some aqueous phase components such as hydrocolloids proved to stabilize emulsions because they increase viscosity. The slightly increased of q values with trehalose addition might suggest that trehalose had an effect further than viscosity changes since the aggregation state of the protein changed with the aqueous phase formulation. These results were in agreement with the small particle size found when trehalose was added to aqueous phase. Changes in fat phase did not affect q values. However, patterns had different intensities and shapes. A deeper analysis of the scattering curves would provide more information about the internal organization of casein micelles.*

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Sol-gel synthesis: effect of precursors on the microstructure of silica hydrogels

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Sol-gel synthesis is an attractive route for the synthesis of new inorganic and hybrid materials, from ceramics to biocompatible soft inorganic gels. The properties of the final product can be tuned by controlling the solution parameters that rules the sol synthesis and the sol-gel transition. However a the relationship between synthesis and ageing parameters, microstructure and macroscopic properties is still not completely understood. Those relationships are fundamental for the synthesis of materials with controlled microstructure in the 1.0-1000 nm range. In this work we explore the microstructure-optical quality relationship of silica hydrogels prepared by hydrolysis of tetraethoxysilane in acid media, following the alcohol free procedure, with focus in the role of synthesis parameters: pH (2.5-7.1), total silica concentration (3.6 to 10.7 percentage) and additives. The obtained hydrogels have an amorphous nanoporous monolithic structure. The optical properties were evaluated by attenuance at 400 and 500 nm for samples aged 24 h in phosphate buffer (pH 6.5, 0.1 M). The microstructural characterization was performed by SAXS, (beam 2 of LNLS, wavelength=0.1488 nm, wave vector range: 0.09 - 2.2 nm-1 and sample stage in vacuum with mica windows). The log-log SAXS intensity plots are typical of the scattering from a mass fractal system. The fractal dimension (D) is estimated from the power-law decrease of the SAXS intensity in a q-range between the characteristic lengths of the fractal structure (R) and the characteristic length of the primary particles composing the structure (a). The values of the parameter a depend on synthesis pH but are independent of the silica concentration, whereas the values of D and R change significantly with silica concentration for a fixed pH. The difference observed in optical properties can be explained in terms of the fractal dimension and structure as both R and D decrease with increasing silica concentration indicating that smaller and less branched fractal structures produce lower light scattering in the visible range.

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Brewster angle microscopy and compressibility study of Langmuir monolayers

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The mechanical properties of liposome membranes are strongly dependent on type and ratio of lipid compounds, which can have important role in drug targeting and release processes when liposome is used as drug carrier. In this work we have used Brewster angle microscopy to monitor the lateral compression process of lipid monolayers on the Langmuir trough. The compressibility coefficient was determined at room temperature. The cholesterol fraction and the molar ratio of different lipids were studied by multivariate analysis to evaluate their impact on the compressibility coefficient of the monolayers. We observed that the same compressibility value can be obtained with different blend compositions, which is appealing for tailoring liposome carriers according to the application.

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Phase transitions in membrane of lipids

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Complexes of lipids and DNA can be used as model system for understanding biological processes and also for preparation of synthetic vectors for applications in gene therapy. Recently studies of X-ray diffraction on lipid lamellar samples containing DNA were performed using synchrotron light, revealing a hexagonal structure, and sometimes coexisting with a lamellar phase. This hexagonal structure can be interpreted in two ways: an inverse hexagonal phase of lipids with DNA encapsulated inside the cylinders of lipids or as a hexagonal phase of DNA intercalated in the host lamellar phase (Lα). From geometrical parameters we deduce the composition in volumetric fraction for each hypothesis and prepare samples with this composition. These samples were observed with polarized light microscopy to identify the mesophase (lamellar or hexagonal), and fluorescence microscopy to verify DNAs presence (labeled with fluorescent test). These observations showed a typical texture of a lamellar phase, with homogeneous fluorescence, confirming the presence of DNA between lipid bilayers. In addition, X-ray diffraction experiments were made in SAXS geometry, with samples encapsulated in glass capillaries. The results confirm the hexagonal structure with lattice parameter between a = 6.8nm and a=7.1nm, which corresponds to a lamellar periodicity D between D= (a $\sqrt{3}$)/2 = 5.9nm and D=6.1nm. This structure corresponds to a 2D hexagonal array of DNA rods, intercalated between the lipid bilayers. Samples with other compositions were prepared to explore the ternary phase diagram, and regions with lamellar phases coexistence were also identified, which just one fluorescent, indicating that DNA was incorporated only on one of the lamellar phases. In the following we are planning new experiments with suspended films of lipids, placed in a device with controlled humidity adapted to laboratory X-ray equipment (Nanostar-Bruker) and also to microscopy observations. The objective is to follow the transition from lamellar to hexagonal phase of lipids, using X ray grazing incidence and optical observations of texture.

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Estudo da interação entre a biomolécula DNA e membranas de lipídeos neutros

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O interesse de estudo neste trabalho é acerca da preparação e a caracterização de complexos de lipídios e DNA para analisar a organização supramolecular formada pelo encapsulamento do DNA em vesículas. As vesículas são preparadas a partir de lecitina de soja(Avanti Polar) através do método de depósito de filmes finos. É misturado o lipídeo com simulsol numa proporção de 70 % e 30 %. A mistura Lecitina Simulsol é solubilizada em ciclo-hexano $C\ _6H\ _{12}$*) e liofilizada para que se forme o filme, depois de ser liofilizado é então utilizado na preparação das amostras, que consiste em adicionar a água e soluções com a biomolécula. A biomolécula utilizada nesse trabalho são fragmentos de DNA adquiridos da Sigma, extraídos de timus de boi, e submetidos a sonicação para quebra da molécula em fragmentos de aproximadamente 150 pares de base que com esse comprimento pode ser interpretado como bastões rígidos. Variamos a concentração em massa de lipídeo desde 1 % á 2.5 %. E para amostras com a biomolécula foi utilizado soluções de DNA em água com concentrações equivalentes ao dobro da massa de lípideo correspondente a cada preparação, ie, 2 % á 5 %. O vetor de onda q do pico de espalhamento e fornece a distância interplanar entre as bicamadas. A análise dos complexos de vesículas - DNA foi realizado, nesta fase inicial, por indexação dos picos de difração. Picos de difração foram observados na região de baixo ângulo, indicando a formação supramolecular de longo alcance de ordenação. A partir da indexação de picos, um arranjo lamelar é encontrado indicando a formação de vesículas multilamelares. A peridodicidade lamelar encontrada é de 86,73 á 88,4 ,o que sugere fortemente que há incorporação de moléculas de DNA entre as camadas. Podemos concluir que a presença do DNA provocou a formação de vesículas multilamelares, e o seu encapsulamento entre as membranas do lipídeo. A perspectiva do projeto é investigar o diagrama ternário desse sistema.*

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Phase transitions in solutions of DNA fragments

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DNA molecule, is a semi flexible polymer that can be several meters long, in human cells. It is packed in a very small volume in the nucleus and goes through condensate phases depending on the cell life cycle. Therefore the DNA concentration in the nucleus is extremely high and its functionality is associated with its organization. DNA molecules in water solutions can show liquid crystalline mesophases such as cholesteric and hexagonal, revealing the self assembly properties of DNA. The objective in this work is study phases transitions that occur in solutions of DNA fragments, in function of DNA content and on ionic force. We combine polarizing and fluorescence microscopy and X-ray scattering techniques. The DNA is acquired by Sigma (calf thymus) and then is sonicated to obtain fragments of 150 base pairs (bp) that can be viewed as rigid rods. The solutions are prepared with ultra pure water, with concentrations varying from 100mg/mL to 550mg/mL. In polarized light microscopy, we observed a typical texture of a cholesteric phase for solutions with concentration above 100mg/mL, but with coexistence with an isotropic phase. These observations are combined with X-ray scattering to characterize the microscopical structure using samples encapsulated in glass capillaries. The mean distance between the DNA rods for each sample is determined for each sample, $D = 2\pi/q$*, where q is the wave vector of the peak scattering. For a monophasic solution, we expect D to be proportional to* $\phi^{-1/2}$ *, where* ϕ*, is the volumetric fraction of DNA. Extrapolating the D value for* $\phi^{-1/2} \rightarrow 0$ *we deduced the naked diameter of DNA to be (2.00 ± 0.41)nm. From the observation of textures we correlate the range of concentration corresponding to the isotropic, cholesteric and hexagonal phases, however we observe a large domain of coexistence of phases. Since DNA molecule has a negative charge, equivalent to 2e/bp, the dominant interaction between the rods is of electrostatic nature. Using monovalent salt, we plan to investigate the role of the electrostatic interaction on the isotropic-cholesteric phase transition, controlling the ionic force. The results obtained in this study are important for the interpretation of self-diffusion of DNA rods in anisotropic phases.*

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Parte VI

Materiais Estruturais e Aplicações na Indústria

Estudo microestrutural de catalisadores tipo Perovsquita para a produção de gás de síntese

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Óxidos cerâmicos com estrutura tipo perovsquita têm sido usados para diversos tipos de reações catalíticas em substituição aos catalisadores que contém metais nobres (Pd, Pt, Rh) como fases ativas, pois, entre outras vantagens, são bastante estáveis a elevadas temperaturas, resistentes a formação de coque e são menos onerosos. No presente trabalho foram sintetizadas perovsquitas pertencentes ao sistema $Ln_{2-x}M_xNiO_4$ *(Ln = Nd e Sm, M= Sr) visando utilizá-las como catalisadores para a produção de gás de síntese por reforma a seco (reforma do metano com dióxido de carbono). Tais materiais foram sintetizados por uma rota que faz uso de gelatina como precursor orgânico, a qual apresenta a vantagem de ser rápida, simples e de baixo custo, podendo substituir algumas rotas usuais de síntese. Através da análise microestrutural, foram investigadas a influência das substituições nos sítios A e B e das condições de calcinação (tempo e temperatura) para obtenção da fase perovsquita. De acordo com os difratogramas de raios-X, houve formação da fase perovsquita tipo Ruddlesden-Popper. As imagens SEM-FEG revelaram partículas com formas arredondadas, distribuição uniforme e tamanho nanométrico. Houve um aumento significante no tamanho de partícula nos pós calcinados por 6h. A porosidade observada foi proveniente da evolução dos gases formados com a decomposição da gelatina. Quando submetidos a reação de reforma a seco, os pós calcinados a temperaturas maiores foram mais ativos e resistentes a desativação.*

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Desenvolvimento de Nanoestruturas de ZnO para Aplicação em um Biosensor de Glicose.

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O Óxido de Zinco é um importante semicondutor que possui uma banda de energia proibida (gap) de 3,37 eV, isso o torna um material versátil e de considerável interesse em aplicações na área da óptica, na microeletrônica, fotocatálise e em sensores, devido à sua estrutura favorável e por possuir excelentes propriedades ópticas e fotocatalíticas [1]. ZnO nanoestruturado possui vantagens promissoras na aplicação em biosensores, por possuir alta área superficial, boa estabilidade química e rápida resposta eletroquímica [2-3]. Dentre os biosensores, destacamos aqui um dos mais populares, o sensor de glicose, o qual tem sido muito investigado devido a sua importância em aplicações clínicas. No presente trabalho será apresentado o desenvolvimento e a caracterização de filmes de ZnO nanoestruturados com o propósito de se construir um biosensor de glicose. Os filmes foram preparados sobre substratos diferentes (vidro, silício e aço inox), utilizando o método hidrotérmico. A DRX (Difração de Raios X) foi usada para fornecer a estrutura cristalina dos filmes enquanto que MEV (Microscopia Eletrônica de Varredura) foi empregado para avaliar a morfologia das nanoestruturas obtidas. O XPS (Espectroscopia de Fotoelétrons induzidos por Raios X) permitiu sondar o ambiente químico dos elementos presentes na superfície das amostras. Foi construído um biosensor de glicose utilizando um filme de ZnO, sobre o qual foi imobilizada a proteína glicose oxidase (GOx). Os resultados das medidas de voltametria cíclica (VC) mostraram que a GOx aderiu na superfície do filme, e que o sensor desenvolvido foi capaz de detectar a presença de glicose numa solução aquosa. 1- Huang, P. Xin, Z. Jumeng, W. Boxue, F ; Journal of Alloys and Compounds, 489, 614-619. (2009). 2- Wang, J.et al. Applied Physics Letters, 88, 233106 (2006). 3- WEI, A. et al. Applied Physics Letters, 89, 123902 (2006).

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Estudio Mn K y Ce L2-L3 XAS de nuevos materiales Mn-Ce óptimos para la eliminación de fenoles y otros compuestos orgánicos en aguas residuales

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En los últimos años los temas ambientales han adquirido gran relevancia dentro de las problemáticas que necesitan ser resueltas. El caso de los fenoles reviste singular importancia, debido a que son residuos industriales producidos en refinerías de petróleo, petroquímicas, pasteras y papeleras, de tintes y pinturas, de polímeros y plástica entre otras, y su presencia en aguas produce desde severos daños intestinales hasta la muerte. Es por ello que se han desarrollado una serie de nuevos materiales asociados a nuevas tecnologías para disminuir la concentración de fenoles en aguas residuales, los que han mostrado ser aptos para este propósito como para la eliminación de otros componentes orgánicos en aguas.

Tales materiales fueron preparados por co-precipitación de mezcla de soluciones acuosas de las sales metálicas en medio básico. El medio co-precipitante utilizado para una serie fue K(OH) y para la otra Na(OH). De esta manera se obtuvieron materiales con diferentes porcentajes relativos de Mn/Ce. Esta variación de relaciones induce la formación de diferentes fases y mezcla de las mismas, a la vez que produce variaciones en el estado de oxidación del Mn y del Ce.

Mediante estudios Mn K XANES se ha obtenido que el Mn se encuentra en estados de oxidación 3+ y 4+, y esto depende fuertemente del porcentaje de Ce presente en el catlizador. A la vez que se ha logrado determinar la relación relativa Ce3+ respecto de Ce4+ haciendo un estudio detallado de la región Ce L3 XANES. Se observó que el Ce tiene una valencia menor que en el CeO_2*, debido a que aumenta el número de estados desocupados 4f. Se obtuvo que la concentración de Ce 3+ depende de manera lineal con el porcentaje de Ce presente en la muestra.*

Estos estudios pueden ponerse en correlación con la actividad catalítica en la oxidación de fenoles, estudiando la electrónica involucrada sabiendo que la mejor actividad catalítica se presenta para los casos en que existe la mayor cantidad de iones Mn4+ y una relación Mn/Ce del orden de 1.

Acknowledgements:

Estudio de la densidad de estados desocupados Si 3p en óxidos mixtos mesoporosos soportados Si-Ti modificados con APTES

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Los óxidos mesoporosos tienen múltiples aplicaciones, y por ello la relavancia de la investigación básica en estos materiales. En nuestro grupo estudiamos este tipo de materiales, correlacionando las propiedades electrónicas con las propiedades fisicoquímicas que presentan.

En este trabajo, continuando una línea de investigación iniciada hace tres años(1), se muestran los resultados obtenidos del estudio de óxidos mixtos mesoporosos de Si-Ti soportados sobre Si, en diferentes concentraciones relativas, a la vez que se mantiene constante (20 por ciento) la cantidad de APTES (3-Aminopropyltriethoxysilane) presente en las paredes de los poros.

Mediante Si K XANES se obtuvo que la densidad de estados desocupados Si3p varía fuertemente de acuerdo a la concentración relativa Si/Ti. A menor concentración relativa, la densidad de estados es menor. Por otro lado, no se obtuvieron grandes variaciones entre la densidad de estados desocupados Si3p para el óxido SiO_2 *sin APTES y con APTES, lo que induce a idear un mecanismo de transferencia de carga compartido entre el Si y el Ti.*

P.C. Angelomé, L. Andrini, M.C. Fuertes, F.G. Requejo and G.J.A.A. Soler-Illia, Comptes Rendus Chimie, Vol. 13 (1-2), January-February 2010, 256-269.

Acknowledgements:

Utilização de raios-X a baixo ângulo (SAXS) em estudo de ligninas de bagaço e palha de cana-de-açúcar submetidas a diferentes tipos de processamento

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A predominância do uso de energia fóssil trará impactos negativos tanto a segurança energética como à sustentabilidade, portanto há uma necessidade em substituir estes combustiveis por combustíveis renováveis, como o etanol. No Brasil o etanol é produzido a partir da cana-de-açúcar e, apesar do constante crescimento da produção, as projeções indicam que a demanda será maior do que a capacidade produtiva. Neste contexto o uso dos próprios resíduos gerados na indústria sucroalcoleira, como o bagaço e a palha de cana, podem ser utilizados para obtenção e aumento de produtividade em etanol. Para a produção de etanol a partir de biomassa é necessário, separar as frações em lignina, celulose e hemicelulose. Uma das vantagens da bioconversão de lignocelulósicos para obtenção de etanol é a oportunidade de se criar biorefinarias. Ao produzir múltiplos produtos, uma biorefinaria pode tirar vantagem dos diferentes componentes da biomassa e produtos intermediários e maximizar o valor da matéria-prima. A lignina é um dos produtos gerados no processamento da biomassa que possui potencial para gerar quelantes, dispersantes e produtos de química fina. Poucos estudos avaliam as modificações da lignina quando a biomassa é submetida a processamentos, quer sejam eles, básicos, ácidos ou enzimáticos. Visando a utilização de lignina para geração de insumos químicos este trabalho tem como objetivo utilizar SAXS para avaliar as mudanças que ocorrem com ligninas de bagaço e palha de cana obtidas de diferentes processamentos. Comparando-se as ligninas de bagaço e palha para uma mesma condição de processamento pode-se afirmar que a superfície exposta ao solvente da lignina de bagaço é relativamente menor do que de palha. Os resultados demonstram, que dos pré-tratamentos avaliados, o ácido dluído possui maior influência na fragmentação da lignina em moléculas menores que contribuem para o aumento da flutuação de densidade eletrônica do solvente e uma área exposta ao solvente muito menor do que as demais ligninas obtidas de outros pré-tratamentos.

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INTERNAL RESIDUAL STRESSES IN SINTERED AND COMMERCIAL LOW EXPANSION Li_2O-Al_2O_3-SiO_2 (LAS) GLASS-CERAMICS

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Synchrotron X-ray diffraction analyses of internal residual stresses of newly developed LAS glass-ceramic produced by sintering and in commercial LAS glass-ceramic, CERAN, produced by the traditional crystal nucleation and growth treatments were performed. The measured internal stress is quite low for both glass-ceramics and can be explained by theoretical modeling if the high volume fraction of the crystalline phase (virgilite) is considered. The thermal expansion coefficient of virgilite was determined by high temperature XRD and dilatometry. The c-axis contracts with increasing temperature whereas the a-axis does not vary significantly. Using a modified Green model, the calculated critical (glass) island diameter for spontaneous cracking agreed with experimental observations. The experimental data collected also allowed the calculation of the critical crystal grain diameters for grain-boundary microcracking due to the anisotropy of thermal expansion of virgilite and for microcracking in the residual glass phase surrounding the virgilite particles. All these parameters are important for the successful microstructural design of sintered glass-ceramics.

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Desenvolvimento de uma instrumentação com temperatura e umidade controlada para análise morfológica por SAXS de compósitos eletroativos em função da tensão elétrica

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Este trabalho encontra-se no contexto das pesquisas envolvendo músculos artificiais. Alguns polímeros têm a capacidade de modificar suas dimensões e/ou forma em resposta a um estímulo elétrico. Entre estes polímeros eletroativos, os compósitos de polímero ionomérico e metal (IPMC) apresentam várias características estratégicas, pois são leves, macios e são ativados por voltagens entre 1 e 5V. O IPMC estudado é composto por Nafion, com espessura de 180μm e eletrodos de platina. O Nafion é um polímero perfluorado sulfonado, eficiente no transporte iônico. Essa eficiência é atribuída a domínios hidrofílicos que se organizam na forma de canais espalhados ao longo do filme. Cátions pequenos e grupos polares, como moléculas de água, migram facilmente por estes canais. Baseado nessa característica estrutural, quando um campo elétrico é ativado sobre o IPMC, cátions solvatados migram em direção do cátodo através desses canais. Em função do surgimento de uma diferença de concentração de água entre as faces da amostra, a que possui maior concentração de água sofre uma expansão, enquanto a outra contrai. Esta mudança de volume resulta no dobramento do material. O objetivo deste trabalho é avaliar como o diâmetro médio dos canais se modificam em função do estímulo elétrico e das condições de operação do atuador. Para isso, foi construída uma câmara com temperatura e umidade controlada, com janelas transparentes ao feixe de raio-X. No interior da câmara, foi instalada uma porta-amostra, cujas faces que prendem o material possuem eletrodos de ouro para permitir a excitação elétrica da amostra. A umidade foi controlada com soluções salinas e a temperatura com um banho termostatizado conectado a um trocador de calor de cobre, fixado próximo às amostras. A ativação das amostras foi realizada com um gerador de funções. A umidade foi monitorada com um termo-higrômetro digital e a temperatura, por um termopar. Os resultados preliminares apresentaram uma correspondência dos picos referentes aos canais ionoméricos, mas uma forte saturação causada pelos eletrodos de platina não permitiram uma análise mais precisa. Atualmente está sendo testada a eficiência de eletrodos com diferentes espessuras e composições. Entre os materiais estudados para compor estes eletrodos, eletrodos de polímeros condutores e eletrodos de ouro com espessuras bem finas estão se mostrando promissores.

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Soldagem por atrito com pino de juntas dissimilares Al-aço de chapas finas

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A soldagem por atrito com pino não consumível (SAPNC) é um processo já consolidado para a união de materiais de baixo ponto de fusão como alumínio e magnésio. Atualmente a sua aplicação em metais com pontos de fusão elevados, embora com sucesso, ainda é contraditória, devido principalmente ao elevado custo das ferramentas e sua limitada vida útil. Um novo caminho para a SAPNC é a soldagem de sistemas dissimilares, sendo a junção Al-aço de interesse particular devido ao desafio que este sistema representou por décadas. Múltiplas técnicas foram aplicadas para obter esta junção, sendo obtidos resultados moderados com a soldagem a laser, soldagem por ultra som e soldagem por explosão. Embora a literatura técnico-científica já apresenta trabalhos manifestando o sucesso da SAPNC nesses sistemas, duas características importantes para sua aplicação na indústria não são discutidas: a obtenção de juntas livres de defeitos e o aspecto superficial. No LNLS foram desenvolvidos parâmetros que permitem a soldagem de juntas dissimilares alumínio-aço de chapas finas com 2,0 mm de espessura mediante o processo SAPNC. O presente trabalho apresenta o estudo do efeito do deslocamento da ferramenta (offset) e a chapa de apoio (backing) na obtenção de juntas livres de defeitos, com aspecto superficial adequado. Para isto foram obtidas juntas soldadas dissimilares Al-aço mediante SAPNC empregando velocidade de rotação de 300 rpm, e velocidade de avanço de 150 mm/min. A ferramenta usada para a soldagem foi de WC-14Co com deslocamento (offset) variando de 0,5 a 2,0 mm, além de ser empregado backing cerâmico. Foi determinada a microestrutura ao longo da junta soldada e estudada a interface Al-aço, por meio de microscopia óptica (MO), microscopia eletrônica de varredura (MEV).

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Dissimilar welding of Inconel 625 to low carbon steel

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After two decades of development, friction stir welding (FSW) has become a joining alternative for aluminum alloys. Nowadays, a number of materials with high melting point are usually processed using FSW, including stainless steel, titanium alloys and Ni-base alloys. In addition, FSW has been shown to be a suitable alternative for joining systems with dissimilar metals and alloys systems which are difficult or impossible to weld by conventional welding. Cladding of dissimilar materials such as Ni-base alloys and steel has been widely used in chemical power plants, marine systems and oil exploration due to improvements in mechanical properties, particularly corrosion resistance. Inconel 625 is a Ni-base superalloy strengthened by a solid solution of molybdenum and niobium in its nickelchromium matrix. One of the most remarkable properties is that it retains high strength even at high temperature without any precipitation.

The current work was carried out to study FSW of Inconel 625 to low carbon steel in overlap join. An especial overlap joint configuration was used to develop weld parameter with several pin penetrations. Low carbon steel is the upper and bottom plate with an inclination of 0.1 with the Inconel 625 in the middle plate in the dissimilar joint. FSW overlap joints were performed using two rotational speeds and a travel speed de 100 mm/min. A polycrystalline cubic boron nitride (PCBN) tool was used, with a 24 mm shoulder diameter and 5.4 mm pin length.

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MECANISMO DE FRATURA INTERGRANULAR POR QUEDA DE DUCTILIDADE EM LIGAS DE Ni-Cr-Fe ENDURECIDAS POR SOLUÇÃO SÓLIDA

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A fratura intergranular por queda de ductilidade (FQD) é um tipo de falha que ocorre durante aplicação de processos de fabricação tais como soldagem, fundição e conformação plástica a quente em alguns materiais com estrutura cristalina cúbica de faces centradas (CFC), entre eles ligas de Ni, Cu e aços inoxidáveis. Este tipo de falha intergranular manifesta-se como uma redução considerável da ductilidade no intervalo de temperatura homóloga (TH) entre 0.5 e 0.8. Algumas características como grão grosseiro e contornos de grão lisos têm sido associadas a materiais que possuem baixa resistência à FQD. Pesquisas recentes associam à ocorrência de escorregamento ao longo de contornos de grão como o mecanismo preponderante e à presença de carbonetos de temperatura intermediaria do tipo M23C6 como um dos fatores mais influentes na ocorrência de FQD em ligas de Ni. Adições de elementos como Nb e Mo em ligas de Ni-Cr-Fe mostram-se como promissórias para aumentar a resistência a FQD; não obstante, o mecanismo fundamental operante na FQD não está esclarecido. Neste trabalho é estudado o mecanismo fundamental de FQD em ligas de Ni-Cr-Fe com e sem adições de Nb, Mo e Hf, mediante um ensaio in situ termomecânico acoplado a um microscópio eletrônico de varredura (MEV). Assim mesmo são discutidas suas relações com características metalúrgicas tais como modo de solidificação, morfologia de contorno de grão, precipitação e segregação de elementos na estrutura bruta de solidificação. Os resultados mostram que a adição dos elementos antes mencionados enriquece por segregação a região interdendrítica da estrutura de solidificação, aumenta a precipitação de carbonetos primários do tipo MX, modifica a morfologia dos contornos de grão, aumenta a resistência por solução sólida e modifica a estrutura bruta de solidificação de celular para colunar-dendrítica. É discutida a influência das características anteriores na resistência â FQD no intervalo de temperaturas entre 500 C e 1000 C e o proposto um novo mecanismo de ocorrência da FQD baseado em escorregamento dos contornos de grão similar ao proposto por Rachinger.

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Physical Simulation and Thermal-mechanical Materials Testing

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Physical simulators offer the ability to simulate real processes on a laboratory scale so that optimum operating parameters can be determined and then applied to the production process. It can also quickly develop processing maps for new materials and characterize stress/strain curves, strength at various temperatures, ductility, weldability, crack susceptibility, strain rate sensitivity as function of temperature, and more. The Gleeble® 3800 offers a wide range of testing capabilities for physical simulation. Capable of heating rates in excess of 10,000°C/s, stroke rates of 2000mm/s and static forces of 20 tons in compression or 10 tons in tension, the Gleeble installed at the LNLS is also equipped with a vacuum pump, quench systems for rapid cooling, a pyrometer for thermal control, and a variety of extensometers including a laser measurement unit. With its Mobile Conversion Units, the Gleeble can easily change its test configuration from tension/compression into torsion/tension/compression, with a maximum rotation speed of 1,500 rpm and torque readings of up to 56N.m.

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Parte VII

Métodos e Instrumentação

Spatial resolution of EPMA for the characterization of grain boundaries, precipitates and dendrites in Ni-Cr-Fe alloys

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Filler Metal 52 (FM-52) nickel alloy is susceptible to ductility dip cracking (DDC) when highly restrained components are welded. DDC occurrence depends on the chemical composition, segregation to grain boundaries, precipitation of intermetallic phases at both intragranular and intergranular regions, grain boundary morphology, etc [1,2]. Previous research suggests that DDC resistance of FM-52 can be improved by optimizing grain boundary morphology and second-phase precipitation during welding [1,2]. Consequently, it is interesting to know the relationship between chemical composition and grain boundary morphology in as-welded microstructures. In a recent study, it was observed that metallic additions to FM-52 induce changes in the tortuous character of grain boundaries [3]. In this work the spatial resolution of EPMA technique is studied, with the aim of developing a methodology for the characterization of grain boundaries, precipitates and dendrites in Ni-Cr-Fe alloys, in a submicron scale. Monte Carlo simulations are used to analyze the spatial distribution of K- and L-shell ionizations for Ni, Cr and Fe, when pure metals and alloys are irradiated with different beam energies. Complementarily, the accuracy of the chemical quantification of the alloys by EPMA is analyzed, in experiments performed with the same incident energies than the simulations. An energy dispersive system is used for the analysis through K lines, whereas a wavelength dispersive one is used in order to perform the analysis by means of L lines. Finally, the optimal experimental conditions are found for an accurate quantification of these alloys with the best spatial resolution possible.

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Testes de detectores de conversão direta do tipo APD no LNLS

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Neste trabalho reportamos os resultados de testes de detectores para raios x, de conversão direta, do tipo silicon avalanche photo-diode (Si-APD). Este tipo de detector é uma alternativa atraente aos detectores convencionais (cintiladores) de raios x, pois oferecem as seguintes vantagens: uma maior faixa dinâmica de operação, da ordem de 10^9 *e resolução em energias de 30 % a 50 %. Adicionado a isto, o know-how de construir detectores nos permitirá oferecer apoio técnico a qualquer instante. Atualmente dispomos de um aplificador de RF (home-made) de 3 estágios com um APD da Perkin Elmer: C30703F-200 de 10 x 10* mm^2*, com recursos provenientes do CNPq. Obtemos pulsos com largura da ordem de 5 ns e amplitude da ordem de 60 mVp para raios x de 5.9 keV (fonte de Fe55). Está previsto teste de homogeneidade da região sensível, medida de resolução em energias, teste de saturação, entre outros. Concomitantemente aos testes, estaremos realizando o desenvolvimento de hardware (amplificador de RF, fonte de alta tensão (HV), shaper amplifier, discriminador e contadores rápidos). Além da cooperação técnica com o grupo de detectores do LNLS, contamos com um aluno da graduação na condição de iniciação científica e bolsa concedida pela FAPERGS.*

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Standard Reference Materials for Powder Diffraction developed at IPEN/CNEN: comparison to NIST standards by high resolution diffraction at LNLS

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We are working in the development of standard reference materials for powder diffraction as substitute for the expensive NIST standards. The objective of this work is the production and characterization of a set of standard samples with equivalent properties to NIST standards but at lower costs. In order to fully characterize the standard materials and compare our standards to the NIST standards we performed high resolution diffraction measurements at the XPD beanline of LNLS for the two sets of standard materials, at the same conditions. The results show that our standard samples are fully equivalent to the NIST standards. The comparison of the FWHM vs 2θ plots for our samples compared to equivalent NIST samples show that our standards are completely equivalent to those produced by NIST. For line broadening analisys the NIST lanthanum hexaboride - LaB_6 *- can be substituted by our cerium oxide -* CeO_2 *- or yet ittryum oxide -* Y_2O_3*. For d spacing and quantitative analysis our alumina -* Al_2O_3 *can be considered better than the same material of NIST. For line position and breadth our Si standard material is similar to NIST Si standard. Some research laboratories in Brazil (public universities and research institutes) are already using our standard samples for routine diffraction procedures (neutron, Synchrotron and conventional X-rays).*

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Comisionamiento del espectrómetro de absorción de rayos-X in house R-XAS Looper de RIGAKU

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Se presentan resultados del comisionamiento del primer equipo in house para experimentos de absorción de rayos X instalado en el hemisferio sur. El espectrómetro recientemente adquirido e instalado en el Laboratorio de Absorción de Rayos X del INIFTA (CONICET y Dto. de Química, FCE, UNLP) presenta una gran versatilidad debido a la posibilidad de realizar experimentos en el modo transmisión y fluorescencia. Por otro lado, debido a la inclusión de siete diferentes monocromadores es posible realizar experimentos de absorción en la región que va desde los 5000 hasta los 25000 eV con diferentes características de flujo y resolución según la combinación escogida de rendijas, monocromador y detector empleados. En el presente trabajo se presentan los primeros resultados analizando las capacidades de dicho arreglo experimental para diferentes bordes de absorción, los que a su vez son comparados con resultados obtenidos en laboratorios de absorción de rayos X utilizando como fuente luz de sincrotrón.

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MEGACELL: A nanocrystal models construction software for HRTEM multislice simulation

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High Resolution Transmission Electron Microscopy (HRTEM) has become an important characterization technique for a number of groundbreaking scientific areas, as well as a fundamental tool for almost every development in nanoscience. However, differently from other imaging techniques such as SEM and AFM, the data extraction from phase contrast HRTEM images is not straightforward due to the complex image formation mechanism.

Multislice image simulation is a fundamental step in HRTEM data analysis that supports the atomic structure elucidation in an unambiguous way. It consists on the exit-plane wave function calculation after the incident electron wave function interaction with the crystalline structure projected potential. In addition, imaging distortions due to the lens system aberrations, microscope instabilities and image acquisition system properties are also included to reproduce the experimental imaging condition.

A difficult and time consuming procedure on HRTEM multislice simulation is related to the crystalline structure description for finite crystals as the atomic specie and position is required for each atom. This issue becomes critical for most of the real systems due to a combination of factors as: large number of atoms, crystal faceting, complex low-symmetry crystalline systems, high-order zone axes orientation. Therefore, here is presented a freeware package named MEGACELL, a nanocrystal model construction suite which supports the finite crystals HRTEM multislice simulation. Among a number of features, it allows the user to create both symmetrical and asymmetrical structures , which can be oriented at different zone axes. The data output can be either by a raw text data with each atom coordinates or adapted for input on some commercially available HRTEM multislice simulation softwares, such as JEMS.

HRTEM image simulation of finite crystals models generated by MEGACELL indicates its functionality for the evaluation of faceted nanoparticles structure and for retrieving 3D information on nanocrystals oriented attachment growth mechanism.

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Estudo comparativo in vitro da capacidade de corte e deformação de limas de níquel-titânio após o preparo de canais radiculares simulados

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O objetivo deste estudo foi comparar a capacidade de corte e deformação de dois tipos de instrumentos manuais de níquel-titânio (NiTi), após o preparo de canais radiculares simulados. Foram utilizados 20 blocos de resina fenólica contendo canais simulados com 75 . Os espécimes foram pesados para determinação do peso inicial. Em seguida, segundo o tipo de instrumento utilizado no preparo, foram divididos em 2 grupos: G1- limas manuais NiTi tipo K (15-40) acopladas ao sistema Endo-Gripper e G2 - limas manuais NiTi tipo K intercaladas com limas NiTi tipo H, da mesma forma que no G1. A avaliação da capacidade de corte baseou-se na perda de peso dos espécimes após o primeiro, segundo, terceiro, quarto e quinto usos. A análise da deformação dos instrumentos foi realizada por meio de MEV, antes do primeiro e após o quinto uso. Para tal, foram atribuídos escores de 1 a 4 em função da alteração da superfície do instrumento em 2 regiões: na ponta ativa e a 5 milímetros desta. Os dados foram submetidos à análise estatística (Teste t) e verificou-se que em ambos os grupos, ocorreu perda de corte em função do número de usos. Entretanto, não houve diferença significante (p¿0.05) do poder de corte entre os dois grupos avaliados. Quanto à deformação da superfície, houve diferença significante (p¡ 0.05) apenas em relação à região do instrumento, sendo estas mais acentuadas na ponta ativa do que a 5 mm desta região. Os grupos avaliados apresentaram comportamento semelhante quanto à perda de corte e deformação. O poder de corte diminuiu em função do número de usos. A ponta ativa dos instrumentos foi a região mais susceptível a deformações na superfície. (Apoio: FAPs - FAPESP N 2008/58713-4)

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An integrated image processing tool for strain mapping of thermomechanical SEM* in situ *experimentation

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The thermomechanical SEM in situ test of metal alloys performed at LNLS has required the development of specific tools for strain mapping in the micron and sub-micron scales. The currently available solutions are not fully integrated in the desired way. The high temperatures at which the tests are performed introduce severe noise and variable contrast conditions to the SEM images, and also make the use of speckles to track dislocations unsuitable. Conventional digital image processing techniques allow improvements in contrast and noise, as well as image registration to assure a same reference in the whole process of strain measurement. A Digital Image Correlation algorithm combines finite-elements and optimization concepts to mathematically model the displacements of pixels. A novel version of the DIC algorithm was implemented, which allows great flexibility in the choice of the mathematical models. By providing the output equations from DIC as input to deformation models, one can measure the strain suffered by each sub-region of the sample under in situ analysis with a very reasonable resolution. The user can analyze an arbitrary set of discrete images or a whole video, and tune several parameters of the processing in order to refine the results and visualization. The main advantage of this strain measurement system is the integration of different computational tools into a single package. Therefore, this software aids the analysis of thermomechanical properties by providing quantitative data for the temporal evolution of the strain and rotation tensors and their auxiliary components.

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Analise do perfil de linha e topografia com raios x em torno da nanoindentação em Si(100)

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Na avaliação de imperfeições em materiais monocristalinos com difração de raios x, existem duas técnicas principais: análise do perfil de difração e topografia . A análise do perfil de difração, ou rocking-curve, em geral com grande resolução angular sonda uma pequena área, enquanto a topografia fornece uma imagem da distribuição de imperfeições em uma grande área. Ambas sensíveis a tensões de deformação e rotação. A intensidade proveniente de toda a área iluminada pelo feixe incidente na amostra é registrada em um detector integrador, o que muitas vezes torna difícil associar quantitativamente a variação angular registrada as imperfeições presentes. Neste trabalho é apresentado um método que une as duas técnicas simultaneamente (rocking-curve imaging technique), com o objetivo estudar a região em torno de uma nanoindentação. Uma amostra de Silício (100) foi submetida a uma série de nanoindentações com ponta Bercovich e cargas de 500 mN e 150 mN, distantes 500 micrometro. O perfil de difração desta amostra foi obtido utilizando como detector CCD (resolução de 25 micrometros). Em cada ponto da rocking curve foi obtida uma imagem, portanto uma topografia. O experimento foi realizado na linha XRD2 do LNLS utilizando energia de 8 keV. O feixe incidente foi expandido usando um monocromador de silício (400) com duas reflexões assimétricas, de forma a iluminar uma maior área da amostra sem a necessidade de transladá-la. A análise das imagens e perfil de difração registrado em cada pixel está associado a pequenas regiões da amostra, permitindo identificar quantitativamente a existência de rotações e tensões em torno da região nanoindentada.

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Feasibility of pump and probe X ray diffraction measurements at LNLS

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Time resolved experiments with the pump and probe method are being performed at third generation synchrotron sources due to their specific bunch filling structure and high brilliance providing important information on the time scale of structural transformation at picosecond resolution. Aiming to introduce this important technique into a routine beamline at the future Brazilian third generation synchrotron facility Sirius (LNLS II), we have performed a feasibility study of implementing this type of experiment at the LNLS. Instead of using a complex and costly instrument as a high speed chopper we have used a gating method using the fast response of a pixel detector like the Pilatus 100K. In this way we were able to isolate a single pulse of X-rays from the LNLS ring operated in single bunch mode with the same frequency of our pump pulse that consisted of an 300 V electric pulse with 1ns length delivered by a pulse generator from Kentech Instruments, which also had a 1ns jitter that limited our time resolution. Our experiment investigated the ferroelectric response of a lithium niobate ($LiNbO_3$) single crystal under the effect of a pulsed electric field of the order of 3 kV/cm. The crystal was oriented in the (0 1 0) direction and set to diffract along the (0 3 0) and (1 2 2) reflections. By measuring the two theta angle and the rocking curve width of the Bragg peak with and without an electric pulse synchronized to the x-ray pulse we could follow the time evolution of the atom positions on the crystal. This measurement was repeated at different time delays between the electric pulse and the x-ray pulse at the sample position. The gating signal sent to the pixel detector and the gating signal sent to the pulse generator were synchronized and their time delay was controlled by a digital delay generator (DG535 Stanford Research Systems) which allows a delay resolution as small as 5 ps. The repetition rate was 1.4 kHz meaning that only one X ray pulse over 3293 from the single bunches passing through the bending magnet was detected and ensuring the total relaxation of the sample. The exposure time was of the order of 10 s, allowing the integration of over a thousand X ray pulses to create an image. Preliminary analysis of the data indicate that the electric field amplitude was not high enough to allow the observation of atom displacements within the limited beamtime allocated for this project. Nevertheless the implementation of the instrumentation was successful paving the way to other x-ray diffraction pump and probe measurements at LNLS and at the future Brazilian third generation synchrotron source Sirius.

Acknowledgements:

Laser Plasma Accelerators: Holographic Plasma Hybrid Case

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Inside a photocathode injector, an electron gun produce powerful ultrabright nanophotonics beams in dynamical phases through a)photonic FEL beam line design, b)a x-ray oscillator, c) an experimental stochastic temporal behavior measured by a magnetic spectrometer. Pulses of ultrafast laser hits plasmas bubbles. The collisions at high energies produce plasma waves that could accelerate electrons in a wakefield. But also produce holographic tools/artifacts: a multiwavelenght cell with intrinsic signals that govern the interaction inside each bunch of particles at Gev. Holographic environment needs a 2D reference simulation tool to build the ontology of the beam and the bunch of the particles in one nanobot group. We model a 6D nano-beam at environments of He/Ar plasmas orbit inside a plasma wakefield. Observation of toroidal nanobucklings assemble the stacks to fix instabilities that will be tunned by the interaction with the giant magnetic field plasma radiation ejected from galaxy center. The challenge is to catch up Tev through modelling an injection system with radio galaxy parameters which will be assembled into molecular machine drive by light in graphene meta-material.

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Sistema home-made STM para microscópio Nanoscope IIIa-Veeco

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A utilização de microscópios de tunelamento de elétrons-STM, requer altíssima qualidade e tempo na preparação de amostras, de pontas e da instrumentação. Muitas vezes a qualidade das amostras acabam frustrando a realização de medidas quando estas são colocadas no sistema de microscopia VT UHV STM, Omicron e que opera em ambiente de ultra alto vácuo-UHV. Não se consegue obter resultado algum mesmo após longo tempo de preparação. Uma solução seria a préseleção de amostras. Por esta razão implementamos um sistema para medidas por STM mas operando em pressão atmosférica, para ser acoplado sistema de microscópia Nanoscope IIIa, Veeco. Desta forma pretendemos ampliar as possibilidades do microscópio NSIIIa e ao selecionar as amostras mais promissoras, com melhores características no tunelamento, otimizar tempo e recursos do microscópio VT UHV STM Omicrom. Desta forma continuamos ao desenvolvimento de instrumentação em microscópios tipo SPM(scanning probe microscopy) no grupo de microscopia de tunelamento e força atômica-MTA do LNLS.

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Parte VIII

Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

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Structural properties and reduction behaviour of Pd/Ce-based mixed oxide nanotubes

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In the present work, 1 wt% Pd/ZCE and Pd/GDC mixed oxide nanotubes were synthesized following a very simple, high yield procedure and their properties were characterized by synchrotron radiation XRD, X-ray absorption near-edge spectroscopy (XANES) and scanning and high resolution transmission electron microscopy (SEM and HRTEM). In situ XANES experiments were carried out under reducing conditions in order to investigate the reduction behaviour of these novel nanotube materials. The Pd/CeO_2*-based nanotubes exhibited the cubic phase (Fm3m space group). The nanotube walls were composed of nanoparticles with an average crystallite size about 7 nm and the nanotubes exhibited large specific surface area (85* $m^2 g^{-1}$*). SEM and HRTEM studies showed that individual nanotubes were composed of a curved sheet of these nanoparticles. Elemental analysis showed that Ce:Zr:Pd or Ce:Gd:Pd ratios appeared to be approximately constant across space, suggesting compositional homogeneity in the samples. XANES results indicated that the extent of reduction of these materials is low and that the* Ce^{4+} *state is in the majority over the reduced* Ce^{3+} *state. Results suggest that Pd cations - most likely* Pd^{2+} *- form a Pd-Ce-Zr or Pd-Ce-Gd oxide solid solution and that the* Pd^{2+} *is stabilised against reduction in this phase. However, incorporation of the Pd (1 wt%) into the crystal lattice of the nanotubes also appeared to destabilize* Ce^{4+} *against reduction to* Ce^{3+} *and caused a significant increase in their reducibility.*

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Local structure study of Mn and V in spinel $\boldsymbol{Mn_{2-x}V_{1+x}O_4}$ series by high-resolution $\boldsymbol{K\beta}$ emission spectroscopy

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In the first row transition metals, high resolution X-ray $K\beta$ *spectra consist of main lines* ($K\beta_{1,3}$, $K\beta_5$) *and satellite lines* ($K\beta'$, $K\beta''$) *whose origin are related to spin coupling of 3p and 3d electrons or to ligand type. Relative variations of spectral parameters in different compounds are useful to characterize the main atom chemical environment, i.e., the oxidation states, the net spin in the valence band, and the occupation site.* $K\beta$ *spectra and their relation with the chemical environment have been quite studied for Mn compounds*[3,4,5] *and less for V compounds*[6]*. The spinel* $Mn_{2-x}V_{1+x}O_4$ *series with* $x = 0, 1/3$, *and 1, prepared by solid state reaction, were studied by Pannunzio-Miner et al.*[7] *using several techniques in order to explain their magnetic susceptibility and electrical properties behaviors. All the samples presented positive magnetoresistance (MR) at room temperature, in particular, the highest value (around 5%) was observed in the* MnV_2O_4 *sample. The electrical and magnetic transport was explained using a model of cation distribution where manganese was present as* Mn^{2+} *and vanadium as* V^{3+} *or* V^{4+}*, depending on the compound stoichiometry*[5]*.*

In this work, measurements of the V-$K\beta$ *and Mn-*$K\beta$ *X-ray emission spectra were performed using a high-resolution Johann-type spectrometer*[8] *at the D12A-XRD1 beamline at the LNLS. The spectral parameters dependences founded show that the Mn (V) atoms are in 2+ (3+ / 4+) oxidation states preferentially located at tetrahedral (octahedral) site. This results confirm the MR magnetic model of spinel* $Mn_{2-x}V_{1+x}O_4$ *series.*

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Advanced Magnetic Materials for Spintronics: Co-doped ZnO Systems

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Bulk $Zn_{1-x}Co_xO$ samples were synthesized via standard solid-state reaction route with different Co molar concentrations of 4, 8, 12, 15 and 21%. Fractions of the 4% sample was also annealed in a gaseous mixture of argon 95% and hydrogen 5% (hydrogenation processes). The crystal structures of the samples were characterized using x-ray diffraction (XRD). The microstructure and composition distributions were characterized by scanning electron microscopy (SEM) and energy dispersive x-ray (EDS) measurements. RAMAN scattering was used to study of the incorporation of dopants and the resulting lattice disorder of the host lattice. Co K-edge x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) was used to determine the valence state and to evaluate the environment of Co in the ZnO lattice. Changes in the density of defects were estimated by RAMAN and Photoluminescence (PL) measurements. Magnetic characterizations were performed using a superconducting quantum interference device (SQUID) magnetometer. The conjugated different techniques confirmed the Zn replacement by Co ions in the wurtzite ZnO structure, which retains a high crystalline quality. No segregated secondary phases neither Co-rich nanocrystals were detected. SQUID magnetometry demonstrates a paramagnetic Curie-Weiss behavior with antiferromagnetic interactions for the as-prepared samples and a coexistence of paramagnetic and ferromagnetic phases at room temperature for the hydrogenated samples. We discuss the observed room temperature paramagnetism of our samples considering the current models for the magnetic properties of diluted magnetic semiconductors.

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Study of Co doped SnO_2 films by grazing incidence x-ray absorption spectroscopy

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Diluted magnetic semiconductors (DMS) produced by doping transition metal ions into nonmagnetic semiconductors are of interest for potential applications in spin electronics. High temperature ferromagnetism has been reported in several oxide materials such as ZnO, TiO_2, SnO_2 doped with different transition metals (Co, Fe, Cu, Mn, etc.). The ferromagnetism is usually found in thin films, at doping levels below the percolation threshold for nearest-neighbour cation interactions. The results are not very reproducible, with different conditions and preparation methods leading to different moments or ordering temperatures. A careful examination of extrinsic effects, such as inhomogeneous dopant distribution it is necessary to understand the magnetic behaviours observed in these systems. In this regard, a clear understanding of the macroscopic magnetic properties requires a substantial knowledge of its dependence with layers thicknesses and the complex microstructural effects frequently localized at the interface with the substrate or the surface of the films. Such effects can be studied using experimental techniques able to peer selectively in the depth of the films such as X ray absorption spectroscopy with grazing incidence (GI-XANES) or performing angular scanning around the critical angle for the total reflection of X-rays. In the first case XANES spectra were taken for angles below total reflection, obtaining information about a superficial zone of the film (some nanometers), and for angles above critical angle bringing information about the inner layers of the films. In the case of angular scanning, through the angle-dependent fluorescence intensity measured, the composition, thickness and density of thin films and layers can be determined. In this work we present a Grazing-Incidence X-Ray Fluorescence (GIXRF) analysis of $Sn_{0.9}Co_{0.1}O_2$ films deposited by pulse laser deposition (PLD) on different substrates: $LaAlO_2$ (LAO) and $TiSrO_3$ (STO) and with different thickness: 100 and 1000 nm. The main purpose of this work is to study the depth distribution of dopant and the local structure around this for finally to find the relation between these features and magnetism.

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Graizing incident XRF and EXAFS study of $ZnFe_2O_4$ thin films

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Bulk $ZnFe_2O_4$ *crystallizes in the normal spinel lattice and it is antiferromagnetic with a Neel temperature of about 10K.* Zn^{2+} *occupies tetrahedral (A) sites and* Fe^{3+} *octahedral (B) ones. The magnetic structure and properties of the spinel-type oxides depend strongly on the relative strength of various superexchange interactions among the magnetic moments on A- and B-sites. Several works have demonstrated that when normal spinel ferrite* $ZnFe_2O_4$ *is nanosized, it displays a nonequilibrium cation distribution among their tetrahedral A and octahedral B sites that alters its long-range magnetic ordering and drastically enhances its magnetic response. X-ray absorption near-edge structure (XANES) technique together with simulations based on ab-initio XANES calculations such as code FEFF8.2 are powerful tools to identify the transferences of* Zn^{2+} *and* Fe^{3+} *from equilibrium to non-equilibrium state. On the other hand by glancing incident X-ray fluorescence (GIXRF), an optical flat sample is irradiated by the X-ray beam, using incident angles slightly smaller than the critical angle for the total reflection. Through angle-dependent fluorescence intensity measurement the composition, thickness and density of thin films and layers can be determined. Therefore, XANES combined with Grazing-Incidence X-Ray Fluorescence (GIXRF) is an interesting method to correlate the thickness-dependent electronic structure with magnetic properties. In this work, we present studies of* $ZnFe_2O_4$ *thin films, deposited by pulsed laser deposition using different oxygen partial pressure (between* 10^{-5} *and* 10^{-1} *mbar), combining XANES spectroscopy with GIXRF, to study the non-equilibrium cation site occupancy as a function of depth and how it affects the magnetic properties. Also, EXAFS measurements were performed to determine quantitatively the local environment of Zn and Fe ions. The samples were also magnetically characterized by SQUID.*

Acknowledgements:

EXAFS and XANES of $Ca_{2-x}Ce_xMnReO_6$ under pressure up to 1.2 GPa.

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EXAFS and XANES measurements at ambient pressure were investigated in order to determine the ReO6 and MnO6 octahedral coordination in the Ca2MnReO6 double perovskyte. The valence of Mn and Re was determined taken into account the MnO, MnO2, ReO2 and ReO3 calibrators. EXAFS pattern behavior of ReO6 and MnO6 octahedral was also investigated under hydrostatic pressure up to 1.2 GPa. A CuBe pressure cell with B4C anvils was used to applied pressure in situ. Our conclusions are that the both octahedral present a tilt under pressure without change its Re-O and Mn-O coordination distances.

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In-situ XANES studies of the reduction process of $Ce_{0.9}Zr_{0.1}O_2$ nanocatalysts

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Palabras clave: nanomaterials; XANES in situ; óxidos mixtos; Ce; Zr

The reduction of particle size to the nanometric level has put in evidence its influence in the structural, electronic and chemical properties of solids. Due to the fact that heterogeneous catalysis is related with surface structure and gas-solid or liquid-solid surface interactions, there is a strong influence of particle size in catalysts performances. In this work the objective was to study the interaction of Hydrogen (H_2) with the Ce-Zr mixed oxide with nominal composition $Ce_{0.9}Zr_{0.1}O_2$, synthesized via the nitrateαaminoacid combustion process using different αaminoacids. All the solids have nanometric particle size. Temperature Programmed Reduction (TPR) and in-situ XANES experiments near the Ce L_{III} edge were performed. In both experiments, the sample was heated with a temperature ramp of 10C/min in a flow consisted of Hydrogen (H_2) (5% mol) in Helium (He). The TPR experiments were carried out with a Micromeritics Autochem II 2920. The in-situ XANES experiments were carried out at the D06A-DXAS dispersive beamline of the Brazilian synchrotron Light Laboratory (LNLS), Campinas, Brazil. The D06A-DXAS dispersive beamline is equipped with a Si(111) monochromator and an image-plate detector to collect the absorption spectra. Besides, a mass spectrometer Quadrupole Mass Spectrometer QMS 422 Pfeiffer was connected to exhaust gases in order to register H_2 and water concentration during in-situ XANES experiments. The analysis of the experimental results allow to establish the influence of synthesis conditions on the temperatures of the beginning and end of the reduction process and the evolution of the ratio Ce^{3+}/Ce^{4+} during the reduction process. With this analysis, a better understanding of the reduction mechanism of the solids was achieved.

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Structural properties of LSC and BSCF for IT-SOFCs

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Mixed ionic-electronic conducting oxides (MIECs) based on transition metal oxides found application as cathodes in solid oxide fuel cells (SOFCs). The high working temperature of the SOFCs (900 to 1000º C) requires expensive materials to be used as collectors and interconnectors. Start-up and shut-down also reduces the SOFCs life span due to thermal stresses. So, great effort is dedicated to the research and development of new cathode materials that exhibit high electro catalytic activity for oxygen reduction reaction and high ionic conductivity at lower temperature (500-700º C) to be applicable to intermediate temperature SOFCs (IT-SOFCs). $La_{0.6}Sr_{0.4}CoO_{3-x}$ *(LSC) and* $Sm_{0.5}Sr_{0.5}CoO_{3-x}$ *(SSC) cobaltites and* $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$ *(BSCF) have been proposed as cathodes for IT-SOFC application. These materials show the perovskite-type structure* ABO_{3-x}*, where Sr replaces La in the A site of LSC, and Ba in BSCF. This substitution induces oxygen vacancies formation that is the responsible for the ionic conduction. Our investigation demonstrated that nanostructured LSC and SSC cathodes have better electric properties than microsized powders.*

In the present work, we studied the oxidation state of La and Co in LSC and Co and Fe in BSCF. The enhanced electrochemical performance of nanostructured LSC cathode may be due to a major concentration of O vacancies, induced by crystallite sizes in the order of 20 to 60 nm. We discuss the influence of crystallite size and synthesis methods on the oxidation state of Co in LSC and Co and Fe in BSCF powders, and relate these features to electrochemical performance. For this purpose, we synthesized submicron sized LSC y BSCF powders using the citrate complexation method, and nanosized LSC and BSCF using freeze-drying and gel-combustion methods.

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High-temperature synchrotron-XPD study on phase transitions in fine-grained dense ZrO_2-Sc_2O_3 ceramics sintered at low temperatures

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Solid-Oxide Fuel Cells offer clean conversion of chemical to electrical energy at high efficiencies. These electrochemical devices need high operating temperature (approximately 1000° *C) causing considerable disadvantages. One of the most important challenges in this field of research is the reduction of the operating temperature to intermediate values, typically 600-*800° *C. Among the electrolyte materials based on zirconia (ZrO_2) doped with aliovalents elements, the highest ionic conductivity is acquired for the system ZrO_2-Sc_2O_3. Thus, these ceramics are considered as promising candidates for intermediate-temperature devices. One of the main drawbacks that have limited the use of these materials is that there is a decrease in ionic conductivity associated with a cubic-rhombohedral phase transformation at around* 600° *C. The existence of rhombohedral phases, such as β, γ and δ, is a unique feature of ZrO_2-Sc_2O_3 and many efforts are focused on avoiding these low-conductivity phases. In earlier studies on nanocrystalline ZrO_2-Sc_2O_3 powders, we have determined by means of synchrotron-XPD that the phase diagram of this system, and so as the electrical properties, are strongly dependent on crystallite size. In a further work, we achieved fine-grained ceramics (with submicrometric average grain size) by low-temperature sintering (1050 to* 1350° *C) of nanopowders synthesized by gel-combustion and studied their crystal structure, finding that the phases of the dense ceramics may differ from the powder treated at the same temperature, mainly due to the presence of intergranular strains. In this work, we have investigated the phase transitions between room temperature and* 900° *C in fine-grained dense ZrO_2-X mol% Sc_2O_3 (X = 8, 9, 10) ceramics (above 95% of the theoretical) sintered at different temperatures from 1050 to* 1350° *C. The measurements were performed on both heating and cooling. The use of a high intense source was very useful to discriminate between cubic or tetragonal symmetries. The results showed that all the ceramics have cubic structure at high temperatures. The transition temperatures were accurately determined by monitoring the main Bragg peaks.*

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Aluminate-based high-k dielectrics: GISAXS and XRR

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In many applications, alloys of different materials are of great interest since alloying may allow tuning the material properties to the desired values for MOS technology. Examples are ternary high-k oxides or refractory metals. However, many of such systems can be metastable in a certain composition range and phase separation can occur during annealing at high temperature during device processing. Such phase separation has e.g. been found for ternary Hf-based silicates and aluminates. However, for the large majority of ternary high-k dielectrics, in particular rare-earth based oxides, phase separation has not been studied in detail. In addition, ternary refractory metal systems, as used as metal gate electrodes in semiconductor devices, can also show phase separation, which may alter their properties. This work is focused on the study of phase separation during high-temperature annealing with the aid of GI-SAXS on aluminate-based high-k dielectrics including HfAlOx. Shape, size and spatial correlation of composition variations are analysed in the thin films on (100)Si substrates. In addition, XRR is used to obtain thickness and roughness. The factors determining specific film morphologies and phase separation kinetics are addressed as function of thermal annealing in pure nitrogen and nitrogen+oxygen (5 percent).

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Local structure of Cr^{3+} and Zn^{2+} in Hydroxyapatite investigated by X-ray absorption spectroscopy

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The purpose of this work is the production of $Ca_{10}(PO_4)_6(OH)_2$, $Ca_{10-x}Zn_x(PO_4)_6(OH)_2$ *and* $Ca_{10-x}Cr_x(PO_4)_6(OH)_2$ *doped with different molar concentrations of* Zn^{2+} *and* Cr^{3+} *to investigate the local structural of Cr and Zn atoms. The X-ray absorption spectroscopy (XAS) technique allows obtaining more precise information about the local structure around the absorber atom. X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) results suggest one dominant coordination for incorporation of Zn and no evidence for other Zn containing phases. For Cr doped samples the oxidation from* Cr^{3+} *to* Cr^{6+} *is favored by increasing the doping concentration. Extended X-ray absorption fine structure (EXAFS) fitting revealed the* Zn^{2+} *incorporation into HAP host in the site* Ca_2 *with a tetrahedral symmetry with a four Oxygen at 1,96 and* Cr^{3+} *prefer replaces the site* Ca_2 *with first-shell coordination of six Oxygen at 1,92. However, a small amounts of* Cr^{3+} *in more regular VI fold coordination can also be found at the* Ca_2 *site.*

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X-rays characterization of structural properties and photoluminescence of pure and Eu^{3+} doped Y_2O_3 nanoparticles synthesized via proteic sol-gel method

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Yttrium oxide (Y_2O_3) is a crystalline material with body centered cubic structure, high melting point, optical transparency for a large range of wavelength and is considered to be one of the best hosts for lanthanide ions. Rare-earth doped samples present phosphor properties and are used in fluorescence lamps, plasma displays and radiation detectors. When produced as nanoparticles, these fluorescence materials can be combined with biological molecules resulting in bioconjugated material with potential application in imaging of biological system. The aim of the present work were the production of Y_2O_3 nanoparticles and the study of the correlation between synthesis procedure, structural features and optical properties of the rare earth doped materials. Y_2O_3 was prepared via a proteic sol-gel method with the particle size tailored through the control of the synthesis conditions. It was observed that samples prepared with $pH = 7$ can be crystallized at 350 °C, producing well dispersed nanoparticles with average size of 3 nm. Measurements of Extended X-ray Absorption Fine Structure (EXAFS) indicated that structural order of xerogel produced with $pH = 7$ was better organized than the structure of samples produced without pH control, confirming that these samples needed less energy to be crystallized in yttria cubic structure. Crystallized samples with small particle size presented a higher disorder degree. For Eu^{3+} doped samples, it was observed that Eu^{3+} ions tend to occupy the surface of the crystallites when the size of the particle was reduced from 7 nm to 4 nm. For 4 nm particles, it was also observed a blue shift of the band gap of this material, besides a lowering in the charge transfer process between the ion Eu^{3+} and its nearest neighbors. Also, through XEOL curves analysis, performed at the dopant edge, it was observed that the luminescence response does not depend directly on the X-ray absorption of the dopant.

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XEOL do $BaAl_2O_4$ dopado com európio

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O $BaAl_2O_4$ apresenta uma série de propriedades ópticas interessantes, sendo a mais surpreendente a fosforescência de longa duração, quando dopado com terra-rara divalente e trivalente. O desenvolvimento de uma nova rota de produção de materiais através da técnica sol-gel possibilita a produção de nanopós de $BaAl_2O_4$ usando temperaturas de calcinação mais baixas e tempos menores quando comparada com outras rotas cerâmicas como, por exemplo, a reação de estado sólido. Este trabalho tem como objetivo estudar o espectro de XEOL (X-ray Excited Optical Luminescence) do $BaAl_2O_4$ dopado com európio produzido através do método sol-gel protéico, bem como seu espectro de absorção de raios X. Neste trabalho foram produzidas amostras de $BaAl_2O_4$:Eu3+, todas na forma de pó, através do método sol-gel protéico, utilizando-se da água de coco processada como solvente de partida para preparação do sol. Todas as amostras produzidas foram analisadas através das técnicas de Difração de Raios X (DRX), Microscopia de transmissão eletrônica (TEM) e Espectroscopia de Fluorescência. As medidas foram realizadas utilizando luz síncrotron no Laboratório Nacional de Luz Síncrotron em Campinas, SP, utilizando a linha de espectroscopia de absorção de raios X de estrutura fina (D08-XAFS2) no modo de transmissão. A curva de absorção de raios X (XAS) e os espectros de luminescência devido a excitação com raios X (XEOL) foram coletados simultaneamente com o objetivo de acompanhar variações no espectro XEOL em função do tempo e/ou energia dos raios X incidentes nas amostras. Os materiais produzidos apresentaram fase cristalina única, confirmado por medidas de difração de raios X, e tamanho de partícula em torno de 80 nm, observado por microscopia de transmissão eletrônica. Resultados de espectroscopia de absorção de raios X mostram a absorção das bordas L_3 do Ba e a borda L_3 do Eu. O espectro XANES, medido no modo de transmissão, mostra dois picos característicos do Eu, indicando a presença do Eu tanto na forma reduzida (Eu^{2+}) quanto na forma Eu^{3+}. O espectro XEOL mostra uma banda larga em torno de 550 nm devido ao Eu^{2+} e um pico em torno de 620 nm devido à emissão do Eu^{3+}. Esses resultados indicam que a irradiação com raios X induz a redução de parte do Eu^{3+} para Eu^{2+}. Resultados preliminares mostram que a medidas que aumenta a intensidade de energia de raios X aumenta a quantidade de európio reduzido de Eu^{3+} para Eu^{2+}.

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Estudo dos octaedros MnO_6 e ReO_6 presentes na dupla perovskita Ca_2MnReO_6 por difração de raios X sob altas pressões

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Neste trabalho, apresentamos os resultados da análise do padrão de difração de raios X, obtidos para uma amostra de Ca_2MnReO_6 *submetida à pressão externa hidrostática de até 1,1 GPa e analisamos o comportamento dos octaedros* MnO_6 *e* ReO_6 *na matriz cristalina. A amostra* Ca_2MnReO_6 *tem uma estrutura do tipo dupla perovskita* ($A_2B'B''O_6$)*, onde o sítio B' é ocupado pelo Mn e o B"pelo Re, formando octaedros* MnO_6 *e* ReO_6 *num arranjo alternado. Em alguns casos, as duplas perovskitas podem ser descritas como sendo cúbicas Fm3m, no entanto, há casos em que as estruturas cristalinas das duplas perovskitas se apresentam distorcidas. A distorção pode ser causada pelo tamanho do raio iônico do átomo que ocupa o sítio A, da temperatura ou da pressão á qual a amostra está submetida. A estrutura oriunda deste ajuste é descrita como pseudocúbica, uma vez que a simetria cúbica Fm3m perde algumas de suas operações. Com a distorção da estrutura, a dupla perovskita apresenta uma simetria tetragonal I4/m e, incrementando ainda mais as distorções, a estrutura adquire uma simetria monoclínica P21/n. Assim, o estudo dos efeitos estruturais numa dupla perovskita, quando submetida á pressão hidrostática, permite estabelecer uma correlação entre as propriedades estruturais e as magnéticas.*

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X-ray excited luminescence and local structures investigations of the long-lasting phosphor $CdSiO_3$

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Cadmium silicate $CdSiO_3$ is a long lasting phosphorescent material with potential applications in phosphorescent paints and opto-electronic devices. This material presents monoclinic crystalline structure and light persistence of about 3 h in the visible region. In this work, we have studied the route of production and the phosphorescent properties of $CdSiO_3$ in pure state, doped with Mn^{2+}, Ni^{2+} and Cr^{3+}, and co-doped with (Mn^{2+}/ Cr^{3+}), (Mn^{2+}/ Ni^{2+}), (Ni^{2+}/ Gd^{3+}) and (Cr^{3+}/ Gd^{3+}). The powders were synthesized by a conventional solid-state method, using low-purity industrial precursors. The single crystalline phase $CdSiO_3$ was obtained after two milling for 72 h and two calcination stages at $1000^o C$/8 h. The inspection of the crystalline phases during the synthesis was performed by X-ray diffraction measurements (XRD). The optical and structural properties of the synthesized powders were studied via photoluminescence (PL), X-ray Excited Optical Luminescence (XEOL), X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (EXAFS). XEOL, XANES and EXAFS spectra were measured at the L_1, L_2 and L_3 Cd absorption edge, as well as at the K Si absorption edge and at the K absorption edge of the transition metals (Mn, Ni and Cr). The PL and XEOL emission spectra of the pure, doped and co-doped samples presented broad emission bands near 496 nm and 593 nm, with different relative intensities depending on the type of excitation. The valence of the dopants inserted in the host matrix was investigated by XANES. The valence states of Cr and Ni were determined as 3+ and 2+, respectively. For Mn, both 2+ and 3+ oxidation states were detected. EXAFS spectra showed that the distribution of coordination shells seems to be modified by the presence of each dopand. This work enabled the development of phosphors $CdSiO_3$ with blue ($CdSiO_3$ undoped), green ($CdSiO_3$:Ni^{2+}), orange ($CdSiO_3$:Mn^{2+}), pink ($CdSiO_3$:Cr^{3+}) and white ($CdSiO_3$:Ni^{2+}, Gd^{3+} and $CdSiO_3$:Cr^{3+}, Gd^{3+}) emission.

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Caracterización Ge-K y Se-K -XAFS de vidrios calcogenuros: Ge-Se y Ge-Se-Ag

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Los vidrios colagenuros han provocado gran inter és por sus características de baja atenuación óptica, fotodifusión, conducción iónica, etc.. En particular los sistemas AgX (Ge $_y$*Se* $_{1-y}$*)* $_{1-x}$ *(en fracción atómica) presentan notables propiedades de transporte. Vidrios con y* $\sim$ *0.25 se comportan como semiconductores para x menores que 0.08, mientras que para x mayores o iguales a 0.08 se convierten en conductores i ónicos rápidos.(1) Diferentes modelos han sido propuestos con el fin de explicar este drástico cambio. Dicho comportamiento ha sido atribuido a la separación de fases que tienen lugar en el vidrio. Para bajas concentraciones de Ag (x ¡ 0.08) se observa una fase rica en Ag inmersa en una matriz de bajo contenido de Ag, en tanto que para mayores concentraciones de Ag (x¿0.10) esta situación se invierte. (2) En el presente estudio se investigaron sistemas Ag* $H_x O$ *(Ge* $H_{0.25}OSe$ $H_{0.75}O$*)* $H_{1-x}O$ *(x = 0, 0.25) en comparación con Ag* H_8OGeSe $H_{2-x}O$ *empleado como compuesto cristalino patrón. Estos sólidos fueron sintetizados mediante la técnica de enfriado rápido desde el líquido, y previamente caracterizados por nuestro grupo empleando diferentes técnicas (DRX, SEM, SAXS, ME).(3, 4) Un conjunto de muestras de los materiales mencionados fueron estudiadas mediante Ge-K-XAFS y Se-K-XAFS con el objetivo de correlacionar el comportamiento eléctrico de estos sistemas con la estructura de corto rango en el entorno cercano del Ge y del Se. 1) Ureña María Andrea, Piarristeguy Andrea, Fontana Marcelo and Arcondo Bibiana; Ionic Conductivity (Ag+) in AgGeSe Glasses; Solid State Ionics, 176 (2005) 505-512. 2) B. Arcondo, M.A. Ureña, A. Piarristeguy, A. Pradel and M. Fontana; Homogeneous-inhomogeneous models of Agx(Ge0.25Se0.75)(100-x) bulk glasses;. Physica B 389 (2007) 77-82. 3) J.M. Conde Garrido, J.A. Rocca, M.Erazú, M.A. Ureña, M. Fontana, B. Arcondo; Analyses of intrinsic inhomogeneity and metal segregation in samples of AgGeSe glasses; Physica B: Condensed Matter, volume 404, 2009, pp. 2816 - 2818, doi:10.1016/j.physb.2009.06.083. (Elsevier Science, Holanda) ISSN 0921-4526. 4) B Arcondo, M A Ureña, J M Conde Garrido, J A Rocca and M Fontana; Characterization of Ag-Ge-Se bulk glasses by means of Mössbauer effect on 57Fe and 119Sn atomic nuclei; Journal of Physics: Conference Series 217 (2010) 012073*

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Dopping Effect on the Magnetic and Structural Properties in $Cu_{1-x}TM_xO$ (TM=Fe, Ni, Zn and Al) Systems

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Stoichiometric CuO is a Mott-Hubbard insulator with a gap of the charge-transfer type [1]. However, when the CuO structure has oxygen vacancies it presents semiconductors properties. when doped with others magnetic ions (3d transition metals or rare earth) in the semiconductor host it tend to Diluted magnetic semiconductors (DMS). Recently, Zheng et al. have observed the T_N *suppression of CuO doped with a non-magnetic* Li^{+1} *ion [2]. It is well known that this kind of doping create one hole in the valence band because the charge difference between* Cu^{+2} *and* Li^{+1} *ions. Magnetic order was shifted to around* $100K$ *at concentrations larger than* 16% *his suppression is believed to be due the different electronic structure of the* Li^{+2} *ion related* Cu^{+2}*. To test the role of the electronic structure in the magnetic ordering of CuO we have used the co-precipitation method to synthesize polycrystalline TM-doped CuO samples (MT=* Ni^{+2}*,* Fe^{+3}*,* Zn^{+2} *and* Al^{+2}*) [3]. The magnetic and structural properties of* $Cu_{1-x}MT_xO$ *samples have been investigated as function of doping concentrations(x). Magnetization measurement as function of temperature show that* T_N *is suppressed in the Fe-doped sample with concentration around* $x = 0,06$*. Surprisingly, for Ni-doped samples, TN seem to be unaffected by the TM substitution. To understand magnetization results were performed X-ray Diffraction (XRD) and X-ray absorption (XAS) analysis in regions near to magnetic transitions temperature (TN). The Rietveld analysis of the XRD pattern of NiO presents a low concentration near* 2% *of spurious phase NiO. Besides, the Rietveld analysis shows a small difference in occupation factor in TM site compared with the nominal value and small modifications in cell parameters was observed with decreasing of the temperature. The XAS results for TM ions K-edge show not larger modifications in the XANES profile. Therefore, the XANES results in the TM* $L_{2,3}$*-edge and O K-edge show significant modifications depending of the doping ion.*

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X-ray Excited Optical Luminescence (XEOL) of $CdWO_4$ scintillator at Cd L-edges and W $L_3 - edge$

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Scintillators are luminescent materials that efficiently absorb high-energy photons and then convert the absorbed radiation into visible light. Cadmium tungstate (CdWO4 CWO) is a well-known scintillator with high detection efficiency for X- and γ-rays. In view of its nonhygroscopic nature and high density, CWO is a suitable material for oil well logging, dosimetry and computer tomography applications. X-ray excited optical luminescence (XEOL) is an X-ray photon-in, optical photon-out technique that investigates the conversion of X-ray energy absorbed by a material into optical emission. The advantage of XEOL using synchrotron radiation is that one can monitor the scintillation intensity across an edge and it can be used to reveal the origin of the luminescence. In the present work, CWO ceramic powder was produced via solid state reaction using high purity precursors (CdO and WO_3). Optical characterization of CdWO4 scintillator using XEOL technique was performed at D04A-SXS and D08B-XAFS2 beamlines. SXS beamline operates with soft X-rays and was used for the measurements across Cd L2 and L3-edges (3727 eV and 3538 eV, respectively). XAFS2 beamline was used for the energy range across both Cd L1-edge (4018 eV) and W L3-edge (10207 eV). It was observed a broad band emission between 400 nm and 600 nm, with maximum at 490 nm which is the characteristic scintillation of CWO. The results in the excitation mode, that is, the total optical luminescence as a function of X-ray excitation energy, are compared with EXAFS spectrum and provided a further understanding about the scintillation mechanism in this material.

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Synchrotron Radiation X-ray multiple diffraction Study of Cu(II) Doped monohydrated L-Asparagine Single Crystals.

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The investigation of the amino acid crystals has attracted the attention of the scientific community in the latest decades. It is because these materials have a wide range of potential technological applications on pharmaceutical industry and electronic industry, including electro-optical devices. L-asparagine is one of the 20 protein-forming amino acids, playing a fundamental role in several biological mechanisms. Single crystals of monohydrated L-asparagine [C4N2O3H8.H2O] were grown fromaqueous solution by the slow evaporation method at constant temperature. CuCl2 was added to the growth solution to prepare Cu doped samples. X-ray multiple diffraction technique using synchrotron radiation at room temperature was used in the analysis of the Cu doped monohydrated L-asparagine crystal. The measurements show a doped crystal with the same orthorhombic structure as the undoped one. High resolution Renninger scans were carried out at the XRD1 station of the Brazilian synchrotron radiation facility (LNLS), Campinas, SP, Brazil The obtained diffraction results indicate that the Cu ions probably occupy interstitial crystallographic sites in the crystal lattice since changes in the intensity of a secondary peak were detected as well as the crystal quality has strongly bee affected by the Cu atoms incorporation in the doped crystal. Here, we propose the Cu ions occupy in L-asparagine the same crystallographic site position found in the previous work (Michael J. Colameri and Jack Peisach J. am. Chem. Soc. 1992, 114, 5335-5341) of Cu ions in L-histidine hydrochloride monohydrated structure showed.

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A synthesis of magnetic nanowires and their structural and magnetic characterization

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Abstract Pursuing the idea of the synthesis of magnetic nanostructures, we have explored in our laboratory (LSA) our own method for synthesizing nanowires of maghemite inside nanopores in an alumina substratex[1]. The first preliminary results indicate that the method is valid. AFM images show partial filling of nanopores. Magnetic measurements show clear differences that can be attributed to the existence of nanowires. We study those samples also by SEM/TEM techniques. We plan to use XAS technique (LNLS) to get information about local atomic coordination of iron atoms in nanowires and to link it with observed magnetic behavior and results coming from Mössbauer spectroscopy. We want to study nanowires formation as a function of crystallite size of precursor and diameters of nanopores as well. [1] The substrate was prepared in the LMBT, UNICAMP.

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XANES studies on zirconia-based materials for catalysis

Bacani, R.[1], *Martins, T. S.*[2], *Fantini, M. C. A.*[1], *Fuentes, R. O.*[3], *Prado, R. J.*[4], *Fábregas, I. O.*[3], *Acuña, L. M.*[3], *Andrini, L.*[5], *Muñoz, F.F.*[3], *and Lamas, D. G.*[3]

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Ordered mesoporous silica, with bi-dimensional hexagonal (SBA-15, MCM-41) structures are extensively studied since the 90s, but only few works dealt with ZrO_2 *ordered mesoporous structures for catalytic applications and, few research was reported for their use as anode in solid oxide fuel cells (SOFC). These systems may lead to better performance in the mass transport of fuel/oxidation agent, in the electron conductivity and charge transfer, due to an enhancement on surface area, aiming to achieve a lower operation temperature limit. These zirconia-based materials synthesized with polymer templates, the mesoporous network usually collapses due to the crystallization of the walls at low temperature (around 300°C). In our previous work, a silica palisade was added to the zirconia-based matrix to improve the mechanical stability. Although the final material has high superficial area (100*m^2/g*), this method was not enough to maintain the ordered mesoporous structure after the calcination at 540°C, a goal that has been pursued in our present research. In order to study probable changes on the Zr first shell coordination in pure* ZrO_2 *mesoporous samples due to the differences on the synthesis processes (hydrothermal treatment in Teflon autoclave at 80°C/48h and water vapor at 40°C/48h, calcination at 400°C in air and at 540°C in* N_2 *and air), XANES data were collect at Zr* L_2,L_3*-edges in the D04A/SXS-9197 beamline, using total electron yield detection. The results showed that a larger calcination temperature lead to a more ordered first Zr-O shell, but without any difference in the spectra that could be related to a specific zirconia nanocrystalline phase (cubic or tetragonal). In order to analyze the* Ce^{3+}/Ce^{4+} *ratio in* ZrO_2*-90%*CeO_2 *samples, prepared with a silica palisade, temperature-resolved XANES data were collected at the Ce* L_3*-edge spectra in the D06A/DXAS-10900 beamline. The experiments were performed under He/(5%)*H_2 *(flux of 20mL/min), detected through transmission mode in the temperature range of 25°C up to 500°C (ramp of 12.5°C). The results demonstrated that the increase of silica content (from 10 to 30 mol%) and the improvement on the superficial area promoted a higher reduction of* Ce^{4+} *under lower temperature.*

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Optical and Structural Properties of $Ca_2Al_2SiO_7$ studied by Synchrotron Radiation

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The $Ca_2Al_2SiO_7$, CAS, is an attractive material for optical application as phosphor or scintillator. This work aimed the structural and optical characterizations of pure, doped and co-doped systems by Ce^{3+} and Mn^{2+}. The synthesis of pure and doped $Ca_2Al_2SiO_7$ system was done by a new hybrid route, which combines the proteic sol-gel method with the solid state synthesis. In this synthesis route, coconut (Cocos nucifera) water is used as starting solvents for soluble reactants (calcium and aluminum nitrates). Different silicon sources were used in each of the methodologies. The single phase of CAS was identified by XRD and thermal analysis was used to complement. HR-TEM results indicated that the calcined powders are in the nanometric scale in the different synthesis route. The nanoparticles have a good crystallinity with typical inter planar distances of the $Ca_2Al_2SiO_7$. Optical properties of pure, doped and co-doped samples were studied by Optical Absorption (OA) and Phtoluminescense (PL) thechinques. According to the results obtained using OA, the optical band gap of the CAS system is $\sim$ 6 eV. With OA was possible to observe regions of Mn^{2+} absorption in the co-doped samples. The PL analysis showed that the co-doped system presented two wide emission bands. The first emission band was related to the Ce^{3+} emission and the second one was related to the Mn^{2+}. XEOL preliminary studies in SXS line indicated that in the K edge of Ca there is the main emission compared to K edge of Al and Si. This is related with the luminescent centers situated in Ca site. XEOL results confirmed PL analysis. In single bunch mode $Ca_2Al_2SiO_7$: Ce^{3+} showed that has a very short luminescence lifetime in order $\sim$ 30 ns. This material is among the fastest known scintillators. New studies will be done in the K edge of Ca, Si and Al to analyze the luminescent centers neighborhood, the lattice behavior dependence to silicon source and to dopants insertion. With the results a mechanism of luminescence for doped and co-doped CAS will be proposed.

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X-ray topographic investigation of growth defects of organics crystals

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We use Renninger scans (RS) of the X-ray multiple diffraction (XRMD) to determine the piezoelectric coefficients of the Fe-doped L-arginine.HCl. H_2O *(L-AHCl.* H_2O*:Fe) trough of the distortions produced in the unit cell under the influence of an applied electric field. The advantage of this technique is the possibility to obtain more than one piezoelectric coefficient from a single Renninger scan measurement. It was verified a decreasing in the coefficients of Fe-doped crystal* ($d_{22}=6.2(7)x10^{-10}CN^{-1}$) *when compared to the coefficients of the non doped crystal* ($d_{22}=2.2(3)x10^{-9}CN^{-1}$)*, due change in the ferroelectrics domains, caused by the presence of the* Fe^{3+} *ions in the structure that difficult the alignment with the electric field. It was possible also to obtain topography using XRMD technique, in one non doped L-arginine.HCl.* H_2O *crystal growth by slow evaporation. The topographies images were obtained under different positions of primary reflection and one secondary peak through rocking curve and RS, respectively. In these images were possible to visualize different contrast in both primary and secondary expositions. The advantage in study topography in condition of XRMD compared to conventional techniques is related to choice of any secondary plan inside crystal to study crystalline defects.*

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Síntese e Caracterização de Nano-ligas de $Co_{1-x}TM_x$ (Fe, Cr and Mn)

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As nanopartículas (NPs) obtidas pelo método de síntese utilizando precursores organometálicos têm sido alvo de grande interesse nos últimos anos, devido seu grande potencial no controle do tamanho, distribuição de tamanhos e morfologia, comparado a outros métodos encontrados na literatura. Os interesses nos estudos das nanopartículas metálicas em particular, estão relacionados às possíveis aplicações biomédicas, detecção química e no desenvolvimento de unidades de disco rígidos e ultra alta densidade [1,2]. Neste trabalho temos por objetivo estudar o processo de síntese, as propriedades estruturais e magnéticas de nanopartículas metálicas $Co_{1-x}TM_x$ *(MT= Fe, Cr e Mn). Resultados preliminares de magnetização Zero Field Cooling (ZFC) e Field Cooling (FC) para nanoparticulas de Cobalto e Cobalto dopado, mostram que as partículas não apresentam um comportamento superparamagnético, devido a uma possível interação dipolar que favorece uma aglomeração, fazendo com que se formem grãos compostos de várias partículas, observado por Microscopia Eletrônica de Transmissão (MET). Para entendermos melhor o processo de síntese, sistemas com diferentes concentrações de MT quanto de surfactante estão sendo preparados com o objetivo de minimizar esse de coalescência. Essas mudanças também podem influenciar no tamanho, distribuição de tamanho e morfologia. Resultados de difração de raios X juntamente com refinamento Rietveld mostram que as partículas possuem tamanho médio de 5nm, visto que para esse tamanho as partícula deveriam se comportar como um único monodomínio magnético. Devido as Nps se comportarem como pequenos ímãs, quanto maior seu tamanho maior a interação entre elas, modificamos então, os parâmetros de síntese, com objetivo de reduzir o tamanho juntamente com a introdução dos MTs como dopantes para possivelmente enfraquecer essa interação dipolar, devido as possíveis mudanças nas propriedades magnéticas e estruturais e muito possivelmente na distribuição. Além disso, os resultados mostram que as nanopartículas sofrem uma competição das fases cristalinas cúbicas e hexagonal do Co a depender da concentração e do dopante inserido na estrutura do Co. Referências: [1] Q. A. Pankhurst et al., J. Phys. D 36, R167 (2003); [2] S. Sun et al., Science 287, 1989 (2000).*

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Desenvolvimento de um Modelo Estrutural por SAXS de Materiais Híbridos Siloxano-Metacrilato

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Durante as duas últimas décadas, houve um crescente interesse no estudo de materiais híbridos orgânicos - inorgânicos pela indústria e grupos acadêmicos devido a suas potenciais aplicações e a possibilidade de controlar a síntese e as propriedades estruturais. Os híbridos orgânico-inorgânicos são materiais bifásicos, onde há uma interpenetração das fases em uma escala nanométrica. Eles são constituídos pela combinação dos componentes orgânicos e inorgânicos que, normalmente, apresentam propriedades complementares, dando origem a um material com propriedades diferenciadas daquelas que lhe deram origem. A parte orgânica do material híbrido confere aos nanocompósitos propriedades físicas ou químicas específicas tais como ópticas, elétricas, eletroquímicas, reatividade química ou bioquímica. Por outro lado, a parte inorgânica do material contribui no aumento da resistência mecânica e térmica, permite modular o índice de refração, podendo ainda conferir propriedades eletroquímicas, elétricas ou magnéticas interessantes. A síntese desses materiais via sol-gel é particularmente atrativa devido a simplicidade a versatilidade associada a este processo que permite incorporar facilmente componentes orgânicos em uma rede inorgânica sobre condições brandas. Uma família particularmente interessante de materiais híbridos são os siloxano-metacrilatos. A síntese de materiais monolíticos de boa qualidade e com propriedades interessantes requer um conhecimento preciso das propriedades nanoestruturais e do comportamento mecânico e termomecânico, pois estes exercem uma forte influância sobre a viabilidade da utilização desses materiais em dispositivos de engenharia. Neste trabalho tem-se como objetivo estabelecer correlações entre as condições de preparação, propriedades e a estrutura dos materiais resultantes utilizando SAXS e a partir disso desenvolver um modelo que represente a nanoestrutura desses materiais

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Observation of Ferromagnetism in PdCo Alloy Nanoparticles encapsulated in Carbon Nanotubes

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It is a technological challenge to implement nanodevices using carbon nanotubes with magnetic properties. In the other hand, Pd is an ideal candidate for contacts and it is also interesting for its chemical stability. Recent studies have shown the possibility of ferromagnetism in Pd nanoparticles [1]. Pd can be used as catalyst to grow carbon nanotubes only if it is combined with 3d transition metals (Fe, Co, Ni). Recently, we have observed ferromagnetism in PdCo alloy nanoparticles encapsulated in carbon nanotubes [2].

In this work we have grown carbon nanotubes with PdCo nanoparticles (average diameter of 80nm) with varying Co concentration using Plasma Enhanced Chemical Vapor Deposition (PECVD). This growth technique results in a forest with all nanotubes perpendicular to the substrate and the PdCo nanoparticle on top. The Co concentration was varied to verify its influence on the nanoparticle structure and magnetism. The crystalline structure was studied by High Resolution Transmission Electron Microscopy (HRTEM), Selected Area Electron Diffraction (SAD) and Electron Energy Dispersive X-ray Spectroscopy (EDS). The average magnetism behavior of the samples was analyzed by Vibrating Sample Magnetometry (VSM).

In order to confirm the contributions of both Cobalt and Palladium to the total magnetization, we have performed X-ray Magnetic Circular Dichroism (XMCD) measurements of all 4 samples. The XMCD experiments were done at beamlines SGM (near the Cobalt L2 and L3 edges) and SXS (Pd L2 and L3 edges) at the Brazilian Synchrotron Light Source (Campinas, SP) in total electron yield mode. Our results confirm the Pd contribution to the nanoparticle magnetism [2].

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An Efficient synthesis route of $Na_2V_6O_{16}nH_2O$ nanowires in hydrothermal conditions

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Recently, alkali-metal vanadium oxides bronzes have attracted much interest due to a wide range of application such eletrochromic devices, humidity sensor, etc. The main objective of this work is study the synthesis and characterization of $Na_2V_6O_{16}nH_2O$ *nanostructures using a simple and clean method. In a typical procedure, the mixed solution was prepared containing 0.06M of peroxovanadate with 12 ml of 0.1M NaOH solution. Then, this mixed solution was placed in a 100 mL hydrothermal cell to treatment in different temperatures and periods. The brownish-red precipitate was dried at 50 C for 24 h. X-ray analysis revealed only the formation of* $Na_2V_6O_{16}3.0H_2O$ *nanostructures independent of synthesis conditions. The water content in the as-obtained samples was confirmed by Thermal Gravimetric Analysis. The oxidation state and the local structure of vanadium atoms were obtained by measuring the X-ray absorption spectra at the V K-edge at the D04B-XAFS1 LNLS beam lines. From the analysis of the XANES spectra we observe only the presence of* V^{5+} *ions for the as-obtained samples. Although the* V_2O_5 *orthorhombic phase (used as reference compound) is composed of* VO_5 *octahedral units while* $Na_2V_6O_{16}nH_2O$ *(as-obtained samples) is composed of* VO_6 *octahedral units, the analysis of the pre-edge peak of these two samples shows that the local structure around vanadium atoms are quite similar. The high-resolution transmission electron microscopy (HR-TEM) provided by LME-LNLS shows that the as-obtained samples have a polycrystalline nature with uniform wire-like morphology with around 25nm of width and e and 5-15m of length.*

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Determinação do Tempo de Vida Radioluminescente de Cintiladores de Germanato de Bismuto Puros e Dopados com Terras Raras

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Neste trabalho estudamos os tempos de vida característicos de cintiladores de germanato de bismuto (Bi4Ge3O12) e sua dependência com o tamanho de partícula, natureza e concentração dos dopantes inseridos no material. As medidas de tempo de vida foram realizadas na linha XAFS-2 do LNSL em modo single bunch. No arranjo experimental, utilizamos uma fotomultiplicadora acoplada a um circuito de tempo de resposta rápida. A luz emitida pela amostra sob excitação era captada e o sinal era enviado da fotomultimplicadora para um osciloscópio, que por sua vez estava sincronizado ao pulso de raios-X. Uma das propriedades importantes de qualquer cintilador é o chamado tempo característico, definido como a constante de tempo da curva de decaimento da intensidade de emissão após cessar a excitação com raios X. Vários cintiladores comerciais apresentam pelo menos 2 tempos característicos indicando que os processos de emissão luminescente associado com a conversão da energia depositada pelo feixe de radiação na amostra em luz visível segue pelo menos duas rotas distintas. O valor do tempo mais longo normalmente define a aplicabilidade de um determinado cintilador. Cintiladores rápidos são bastante indicados para medidas de processos dinâmicos, como os existentes em uma colisão em física de altas energias, ou aplicações médicas em imagens, por exemplo. A radiação Sincrotron em modo single bunch é uma fonte de raios X bastante conveniente para caracterização destes materiais, pois fornece pulsos estreitos com energia de excitação sintonizável. Neste trabalho, investigamos o efeito da energia dos fótons de raios X sobre os mecanismos de decaimento da luz. As medidas iniciais com o monocristal de Bi4Ge3O12 resultaram em um tempo característico de cintilação em torno de 50 ns, medidos na borda de absorção do bismuto.

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Insight into the phase transition of Nb addition on TiO_2 nanoparticles

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Titanium dioxide (TiO_2) is one the most investigated metal oxides due to their unique properties and potential applications in photocatalysis [1], solar cells [2], gas sensors [3]. Despite variety of applications, most of these ones have their performance related to its crystalline structure, nanocrystal size and the morphology of the particles [4]. It is well known that TiO_2 crystallize in three differents crystalline structures: rutile, anatase and brookite, being rutile is the most stable phase. The compounds based on anatase structure have attracted more attention due the enhancement of catalytic activity and exhibits higher electron mobility [1]. On the other hand, the efficiency of these devices also can be improved through the introduction of cation doping into the TiO_2 network, such as Cu, Nb, among others [5]. In the case of Nb-doped TiO_2, which forms $Ti_{1-x}Nb_xO2+\delta$ solid solution, it has been observed an increase of the the gas sensitivity at lower working temperature and also a shorter response time [5]. Furthermore, it has been observed that the Nb addition in the TiO_2 lattice hinders the anatase to rutile phase transition and preventing its grain growth [6]. In this work, we report a local order structural studies of nanostructured TiO_2 and $Ti_{1-x}Nb_xO2+\delta$ compounds synthesized by using the polymeric precursor method. To study the influence of Nb ions addition on transition anatase to rutile phase, different characterization techniques such as differential thermal analysis, X-ray diffraction measurements, micro-Raman and XANES spectroscopy were apllied. The Ti K-edge X-ray absorption spectra were collected at the XAFS1 LNLS beam line. Based on the results obtained by these techniques, we can confirm that the addition of Nb on TiO_2 network inhibits the phase transition anatase rutile. Through to XANES results, the phase transition process could be accompanied more easily by the analysis of the post-edge region of the XANES spectra.

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Probing vacancies in undoped ferromagnetic CeO$_2$ thin films by XANES

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Room temperature ferromagnetism has been observed in undoped CeO$_2$ nanostructures as films, nanoparticles, nanobelts, and nanocubes [1]. The origin of this magnetism is still under debate, but recent experimental work and band structure calculations proposed that ferromagnetism observed in CeO$_2$ and several other undoped oxides is due to the existence of intrinsic point defects [2]. Most of these works explore the magnetism with a minimum concentration of defects, i.e., in the diluted defects limit. The magnetic interaction distance is arbitrarily established within percolation analyses. The onset for collective magnetic effects occurs (approximately) for more than 20 % defects in a cation sublattice having face-centered cubic symmetry, as in CeO$_2$.

In the present work we demonstrate that Ce L_{III} XANES measurements can be used to obtain the number of oxygem vacancies in non-stoichiometric CeO$_2$ films grown on Si by electrodeposition. To investigate the effects of the amount of vacancies above the percolation threshold concentration, the films were prepared under different growth conditions and also submitted to ion irradiations. In order to corroborate the results from XANES, whe compare them to those obtained from well-established XPS technique. The data show that starting from pristine CeO$_2$ films with negligible oxygen deficiency it is possible to obtain a significant increase of the saturation magnetization by increasing the Ce^{3+} concentration, i.e., increasing oxygen vacancies. Such behavior can be modeled by band structure calculations in the diluted defects limit [3], confirming a defect-induced origin for the ferromagnetism in undoped CeO$_2$, even above the percolation limit of magnetically interacting vacancies. In addition, we demonstrate that the presence of a certain degree of disorder does not inhibit the ferromagnetism.

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Estudo Estrutural de $LiCoO_2$

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Um dos materiais mais importantes e amplamente utilizados para aplicação como material catódico é o óxido de cobalto e lítio ($LiCoO_2$) *que foi inicialmente descrito por Mizushima et al.*[1]*. Este sólido, quando sintetizado a altas temperaturas, apresenta-se com estrutura hexagonal (estrutura lamelar) com um grupo espacial (R-3m)*[2]*. Estudos reportados por Bueno et al.*[3]*, analisando dois métodos de preparação distintos e usando radiação síncroton, propuseram a presença de uma fase espinélio (Fd-3m) juntamente com a fase lamelar (R-3m). Entretanto quando da sua preparação a temperaturas mais baixas, objetivando sólidos em escala nanométrica, há uma grande dificuldade de se realizar análises quantitativas, por meio de refinamento Rietveld, devido à similaridade das duas fases. Nesse trabalho, estudamos os compostos obtidos por uma metodologia alternativa á descrita anteriormente*[3]*, no qual osólido é obtido por combustão assistida por amido, que consiste da formação de um gel após a adição de quantidades adequadas de soluções aquosas de* $LiNO_3$, $Co(NO_3)_2.6H_2O$ *juntamente com uma dispersão aquosa de amido de milho. Em seguida, a dispersão é submetida ao ultra-som a uma temperatura de* 65^oC *por um período de 3 horas, o que dá origem a um gel homogêneo de coloração rósea. Esse gel então é aquecido ao ar nas temperaturas de 400, 500 e* 750^oC *por 16 horas originando sólidos escuros, com aspecto esponjoso e bastante finos. As amostras foram analisadas usando as facilidades do LNLS para linha XRPD (Proposta D10B XPD-9340), com experimentos a temperatura ambiente em dois comprimentos de onda diferentes, 1.62802 e 1,23868 e então analisadas por meio de refinamento Rietveld usando o programa GSAS. Os resultados indicam a presença das duas fases para temperatura a* 400^oC*, mas apenas uma fase (a hexagonal lamelar) a 500 e* 750^oC *juntamente com* Co_3O_4.

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Um estudo EXAFS da distribuição de cátions em nanopartículas de ferrita de Co

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A estrutura cristalina das ferritas é baseada numa rede cúbica de face centrada de íons de oxigênio, formando sítios tetraédricos (A) e sítios octaédricos [B], ocupados pelos íons do metal divalente e por íons de Fe(3+) [1]. Ferritas de Co em volume, normalmente exibem estrutura de espinélio inverso com os íons de Co ocupando os sítios B, e os íons de Fe3+ocupando os sítios A e B em proporção 50/50. Quando na faixa nanométrica, a distribuição de cátions em (A) e [B] pode apresentar significativas alterações, ocorrendo a ocupação parcial do sítio A por íons de Co. A distribuição de cátions em (A) e [B] depende das condições de preparação e do histórico de tratamento térmico do material [2,3]. As importantes propriedades estruturais, elétricas e magnéticas da ferrita de Co nanoestruturada, responsáveis por sua aplicação em várias áreas do conhecimento, são dependentes das interações magnéticas e da distribuição de cátions entre as duas subredes, sendo, portanto, de extrema importância o estudo rigoroso da relação cátions em (A) / cátions em [B]. Neste trabalho amostras de ferrita de Co obtidas por coprecipitação, com tamanhos de partículas entre 4 e 85 nm, foram analisadas por espectroscopia de absorção de raios X (EXAFS). A comparação dos resultados de XANES com simulações realizadas com o programa FEFF8.4 [4] indica, de maneira qualitativa, a ocupação parcial do sítio A por átomos de Co. A análise de dados EXAFS está em andamento e permitirá quantificar a distribuição de cátions nos sítios A e B.
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XANES and XRD study of $Pb_{1-x}R_xZr_{0.40}Ti_{0.60}O_3$ (R = La, Ba) ferroelectric ceramic materials

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Solid solutions of lead zirconate and lead titanate ($PbZr_{1-y}Ti_yO_3$ or PZT) represent an important technological family of ferroelectrics and antiferroelectrics whose properties and phase transitions have been extensively studied. These materials have been used as capacitors, actuators, transducers and electro-optic devices. At high temperature, these materials present a cubic perovskite (ABO_3) structure and on cooling below the maximum of the dielectric permittivity curve, they undergo a phase transition to a lower symmetry phase. It is well known that the substitution of Pb^{2+} by La^{3+} or Ba^{2+} atoms lead to a signiticative variation on electrical and structural properties of the $PbZr_{0.40}Ti_{0.60}O_3$ ceramic system. For samples containing a large amount of La^{3+} or Ba^{2+}, a transition from a normal to a relaxor ferroelectric behavior has been observed. From the structural point of view, a transition from a low to a high symmetric phase has been observed. In order to better understand the relaxor behavior observed with the substitution of Pb^{2+} by La^{3+} or Ba^{2+} atoms at the structure of $Pb_{1-x}La_xZr_{0.40}Ti_{0.60}O_3$ (PLZT) and ($Pb_{1-x}Ba_xZr_{0.40}Ti_{0.60}O_3$) PBZT ceramic systems, X-ray absorption spectra at the Ti K-edge and X-ray diffraction patterns were respectively measured as a function of the temperature. PLZT compositions with x varying from 0.0 to 0.21 and PBZT compositions with x varying from 0.10 to 0.50 were prepared by using a solid state reaction route. Ti K-edge X-ray absorption spectra were collected at the LNLS (National Synchrotron Light Laboratory) facility using the D04B-XAS2 beam line. X-ray powder diffraction measurements were carried out at different temperatures at the D10B-XPD LNLS beam line. XANES spectra at Zr L_{III}- and L_{II}-edge were also collected for PLZT and PBZT samples using the D04A-SXS-9162 beam line at LNLS. The analysis of these XANES spectra indicates that the local structure around Zr atoms is affected by the introduction of La or Ba atoms in PZT system. A relationship between the structural results and the dielectric properties will be discussed.

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Propriedades Eletrônicas e Estruturais de Filmes Nanoestruturados de ZnO

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O óxido de zinco (ZnO) é um material muito estudado em diversas áreas. O interesse por este óxido, nas suas formas nanoestruturadas, é crescente devido à sua versatilidade, com morfologias variadas e disponibilidade de fabricação simples e de baixo custo. A alta estabilidade química e térmica deste óxido permite ampliar o leque de utilização do mesmo, desde aplicações na indústria aeroespacial, desenvolvimento de sensores e catalisadores [1]. Nas aplicações em fotoquímica, como a degradação de corantes orgânicos, o ZnO tem se mostrado tão interessante quanto o TiO_2*, pois apresenta comparável habilidade na desintoxicação do meio através de mecanismos fotocatalíticos similares, e ainda, a vantagem de ser economicamente mais viável [2]. No presente trabalho foram desenvolvidos filmes nanoestruturados de ZnO, crescidos sobre substratos de alumínio e de grafite. Para a caracterização destes filmes foram utilizadas as técnicas de MEV (Microscopia Eletrônica de Varredura), Espectroscopia de UV/Vis, EXAFS (do inglês Extended X-ray Absorption Fine Structure), DRX (Difração de Raios-X) e XPS (do inglês X-ray Photoelectron Spectroscopy). O valor da largura da banda proibida do ZnO foi obtido por espectroscopia UV/Vis. As imagens de MEV revelaram as diferentes morfologias obtidas, que se apresentaram na forma de placas e colunas mais ou menos ramificadas. Os espectros de XPS apresentaram contribuições associadas às ligações Zn-O, características do ZnO, e Zn-OH. A análise dos dados de EXAFS mostrou a formação de duas fases (ZnO e* $Zn(OH)_2$*) que dependem do tratamento prévio do substrato.*

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REVESTIMENTO DOS POROS DE SBA-15 COM FILMES DE ESPESSURA CONTROLADA DE CeO_2

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Neste trabalho, em fase final de execução, apresentamos a síntese e caracterização de SBA-15[1] *modificada com filmes de CeO_2. Os filmes foram preparados pela impregnação de precursor metalorgânico de cério nos poros da SBA-15, seguido de tratamento térmico. O número de ciclos de impregnação-decomposição térmica resultou na obtenção de filmes de diferentes espessuras, como sugerem as análises de adsorção-dessorção de N_2 e SAXS.*[2] *Modificações em função do número de ciclos também foram observadas por espectroscopias Raman e UV-Vis, que indicam que CeO_2 encontra-se em dimensões nanométricas e tem valor de banda proibida variável entre 3,3 e 3,6 eV. PXRD permitiu a identificação do óxido de cério na fase fluorita e indicou um aumento do teor de CeO_2 após ciclos sucessivos de impregnação-decomposição térmica. Análise por TEM mostra que a estrutura da SBA-15 permanece intacta mesmo após o procedimento para a inserção do CeO_2 e corrobora com os resultados de fisissorção de N_2 e SAXS, indicando que o óxido semicondutor está presente dentro dos poros da SBA-15. A caracterização feita indica a possibilidade de controlar a espessura do filme de CeO_2 e, conseqüentemente, de variar a largura da banda proibida, o volume total de poros e a área superficial do material final apenas alterando-se o número de ciclos de impregnação-decomposição.* [1] *D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548.* [2] *P. F. Fulvio, S. Pikus, M. Jaroniec, ACS Appl. Mater. Inter. 2 (2010) 134.*

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Optical properties of polydisperse submicrometer aggregates of sulfur-containing zinc oxide consisting of spherical nanocrystallites

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Agglomerated spherical nanocrystals of sulfur doped ZnO were successfully prepared by homogeneous precipitation of ZnS followed by thermal treatment under oxygen rich atmosphere. The solids obtained were characterized by thermogravimetry (TG) and X-ray diffraction (XRD), by Raman, UV-vis diffuse reflectance (DRS) and luminescence spectroscopies and their morphologies were observed by transmission and scanning electron microscopies (TEM and SEM). Analyses results show the presence of ZnO and ZnS phases for the short time thermal treatments and only ZnO wurtzite phase for longer thermal treatments. However, all samples present Zn-S bonds as shown by Raman spectroscopy. The Zn-S bonds decreases the ZnO band gap energy (as verified by an UV-Vis absorption tail (DRS)) probably due to a VB offset. SEM and TEM confirm that S:ZnO is formed as aggregates of spherical nanocrystallites of 25 nm size.

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Refinamentos de Rietveld do oxalato de calcio monohidratado e estudo da transição de fase.

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Este trabalho descreve refinamentos usando o método Rietveld em dados de difração de raios X de um calculo renal monofásico de oxalato de cálcio monohidratado. Realizamos um estudo da transformação de fase do oxalato de cálcio monohidratado utilizando um tratamento térmico no calculo renal COM em 250^{O} *C e* 300^{O} *C. O resultado esperado deste recozimento seria a tranzição de faze do oxalato de cálcio monohidratado para oxalato de cálcio, resultando na perda de água na estrutura, e posterior mente em carbonato de cálcio, de acordo com a literatura, mas os resultados encontrados no refinamento Rietveld das temperaturas de* 250^{O} *C e* 300^{O} *C revelam que existe uma fase internediária não determinada que se modifica gradualmente com o tratamento térmico. Estamos interpretando essa fase como uma fase metaestável que não foi investigada até o momento.*

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Application of Rietveld analysis to determine cations distribution in cobalt ferrite by X-ray dispersion effects

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Magnetic nanoparticles have many applications ranging from medical and biological applications until magnetic fluids. All these applications depends on the magnetic properties which in turn depend on several factors, both external (such as size and shape of the crystallites) and internal (such as structural arrangement and atomic distribution). Cobalt ferrites have cubic spinel structure and the cations distribution can be represented by formula $(Co_{\delta}Fe_{(1-\delta)})[Co_{(1-\delta)}Fe_{(1-\delta)}]O_4$*, cations between parentheses are in tetrahedral sites and cations between bracket are in octahedral sites,* $\delta = 1$ *and* $\delta = 0$ *corresponds to cubic normal spinel structure and cubic inverse spinel structure respectively, for* $0 < \delta < 1$ *we have a cubic mixed spinel structure. We present cobalt ferrites* $(Co_xFe_{(3-x)}O_4)$ *nanoparticles synthesized by coprecipitation* $(x = 1.0)$ *and combustion reaction with urea as fuel* $(x = 1.2)$*. Co and Fe scattering factors are close and we used synchrotron radiation with energies 7.038 KeV, 7.112 KeV, 7.122 KeV (Fe absorption edge) and 7.718 KeV (Co absorption edge), collected at the x-ray powder diffraction (D12A - XRD1) beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil). With Rietveld refinement we made a phase quantitative analysis; for nanoparticle synthesized by coprecipitation just a single phase was obtained, while for nanoparticle synthesized by combustion reaction we found* Fe_2O_3*,* CoO *and* Co_3O_4 *as additional phases; because of these extra phases the value of x after the refinement was equal to* 1.0 *for* $Co_{1.2}Fe_{1.8}O_4$*. The distribution determined for cobalt ferrites nanoparticles characterized a cubic mixed spinel structure. With experiments on a vibrating sample magnetometer we compare the saturation magnetization of our samples with magnetization of unit cell calculated from the distribution determined by Rietveld analysis.*

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Production and characterization of Co clusters

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Cluster science corresponds to an active field of fundamental and applied research. The properties of sample are sensitive to the morphology, structure and chemical composition of the clusters. Here we present a general analysis of Co clusters with sub-10 nm diameters produced using the gas-aggregation technique. Such was realized by modifying a commercial sputtering system to include a high inert gas pressure chamber in front of gun that promotes cluster condensation due to the thermal cooling of the sputtered atoms via collisions with the gas. A substrate located near the exit of the chamber collects the material. There is no restriction as the material used to produce the clusters. For this study we chose Co. We analyze the morphology and structure of the clusters using high-resolution transmission electron microscopy (TEM) and small angle X ray scattering (SAXS). The mean cluster diameter is around 5 nm with dispersions lower than 30 %. Further analysis show that the clusters are granular with grains smaller than 2 nm. Using Rutherford Backscattering we estimate that the clusters are disposed on the substrate following a Gaussian distribution with the maximum of concentration in the middle and decaying exponentially, symmetrically, in all directions. Magnetic characterization was performed using regular magnetometry. Even though particles of such size tend to be paramagnetic at room temperature, we do observe hysteresis which can likely be attributed to aggregation effects between the clusters.

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Perspectives and preliminaries results for the study of multiferroics at the LNLS

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Multiferroic materials, where magnetism and ferroelectricity coexist and can be coupled, are of considerable interest today. In these materials, different magnetic interactions may lead to competing magnetic ordered states without inversion center, causing atomic displacements which also break the inversion center and leads to ferroelectricity. However, the atomic displacements expected in these ferroelectrics are very small, typically lying in the range of 10^{-3} *or less. Conventional crystallographic methods have not been sufficient in resolving the crystalline structures of the ferroelectric phases. We propose to develop a new crystallographic method at the Laboratório Nacional de Luz Síncrotron (LNLS) to be able to achieve the necessary sensitivity to resolve the small displacements that occur in these polar structures, involving the collection of amounts similar to so-called Friedel pairs. In our preliminary study, this nonconventional methodology with anomalous x-ray diffraction was employed to investigate such displacements in* $DyMn_2O_5$ *with giant magnetoelectric coupling and two distinct* Mn^{3+} *and* Mn^{4+} *sites. Intensity differences of a selected Bragg reflection were measured as the direction of electric polarization was switched by a poling field. A significant differential effect, which is strongly enhanced at energies near and above the Mn K edge, was observed near and below the ferroelectric transition temperature,* $T_c \sim 40$ *K. An upgrade in the proposed instrumentation and methodology is underway, which, we believe, will lead to a reliable and general method to investigate the minute polar displacement in multiferroic materials.*

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GISAXS, TEM and MEIS investigation of structural properties of Pb nanoparticles implanted in SiO_2/Si thin film

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Grazing Incidence Small Angle X-ray Scattering (GISAXS), Transmission Electron Microscopy (TEM) and Medium Energy Ion Scattering (MEIS) and Rutherford Backscattering Spectrometry (RBS) measurements are applied to characterize the thermal evolution of Pb nanoparticles (NPs) synthesized by Pb^+ *ion implantation into a 200 nm thick silica film over a Si (001) substrate. The implantation energy of 300 keV was selected in order to place the implanted ions in the central region of the film. Two sets of samples were prepared. In the first process the Pb ions are implanted to a fluence of* $\phi_1 = 1\times10^{16}$ *atoms/cm*^{2} *and submitted to a combination of a two-step annealing: (i) a low temperature long time aging treatment performed at 200 C for 100 h in open atmosphere, and (ii) a high vacuum furnace annealing (FA) for 1 h at 1100* ^oC*. In the second process, the Pb ions are implanted to a fluence of* $\phi_2 = 2\times10^{16}$ *atoms/cm*^{2} *and also submitted to the ageing treatment. These samples are FA at several temperatures: 500* ^oC*, 700* ^oC*, 850* ^oC *and 1100* ^oC *for 1 h. GISAXS measurement of the aged* ϕ_1 *samples showed showed a small and nearly angle-independent scattering intensity. This is likely due to a combination of the small NP sizes and to the small quantity of scattering material. The measurements performed on* ϕ_2 *samples show an increase in NPs size when submitted to the aging and also with increasing the FA temperature.*

RBS measurements and TEM observations from aged and FA ϕ_1 *samples show the formation of a dense Pb NP system exclusively at the interface, while the silica film recovers its pristine aspect. The shape of the interface located NPs from aged and FA* ϕ_1 *samples were characterized by plan-view and cross-section TEM observations. The TEM images show nanoparticles have a nearly hemispherical shape in the* SiO_2 *side and a pyramidal frustum shape in the Si matrix. Moreover, the pyramidal frustum facets are parallel to the (001) Si plane. The symmetry expected for this structure is confirmed by GISAXS measurements performed at different azimuthal angles. Complementary microstructural information comprising shape, mean size and number density of NPs will be further determined by MEIS measurements analysis. GISAXS results are still under analysis in order to obtain more accurate information about the NPs shape and their pair correlation function.*

Acknowledgements:

Magnetism in europium chalcogenides and IV-VI semiconductors heterostructures studied with x-ray diffraction and SQUID magnetometry

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IV-VI semiconductors like SnTe and PbTe are narrow gap semiconductors with NaCl structure, used in the construction of lasers and detectors in the infrared region. Europium chalcogenides (EuTe and EuSe) are wide gap semiconductors, with the same structure and close lattice parameter to the IV-VI semiconductors. These materials have attracted renewed attention since the observation of new absorption and photoluminescence lines, and of magnetic interlayer interactions in superlattices of EuTe/PbTe. This work will present the results of the structural and magnetic characterization of EuTe(EuSe) thin films, and EuTe/PbTe(SnTe) heterostructures, using x-ray diffraction techniques. The samples were grown by molecular beam epitaxy: EuTe, EuSe thin films; EuTe/PbTe(SnTe) superlattices; and EuTe quantum dots on SnTe matrices. Magnetic resonant x-ray diffraction was used to detect the magnetic ordering within the films and superlattices, and its temperature dependence. Grazing incidence x-ray diffraction and anomalous x-ray diffraction were used for the investigations of the quantum dots. Magnetometry (SQUID) measurements were also made and correlated with the structural characteristics of the samples.

Acknowledgements:

Optical spectroscopy and EXAFS characterization of Eu^{3+}:$LiLa(WO_4)_2$ single crystal fibers

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Eu^{3+}-activated scheelite-like double tungstates exhibit relatively good thermal and chemical stability, show strong absorption in the near-UV region with strong visible red emission. Therefore they are considered to be good host materials to design a several number of luminescent materials. In addition to the well know laser properties, single crystal fibers are also interesting because of their reduced cost of preparation and potential for nonlinear optical devices. The fiber shape is suitable to nonlinear optical interactions, whose efficiencies can be greatly enhanced by the long interaction lengths and tight beam confinement available in guided wave structures. In this work we report the investigation by optical spectroscopy and EXAFS of Eu^{3+}:$LiLa(WO_4)_2$ (Eu:LLW) single crystal fibers in different concentrations. The starting compounds $LiLa(WO_4)_2$ (LLW) and $LiEu(WO_4)_2$ (LEW) were obtained by solid state reaction from raw commercial reagents. The formation of both tungstates was confirmed through XRD analysis. The dopant concentration for crystal growth was obtained by mixing appropriated fractions of each tungstate. Single crystal fibers were grown Eu:LLW and LEW by the micro-pulling-down method in a resistive heating mode with pulling rates from 0.06 to 0.20 mm/min, in air atmosphere, and Pt-Au crucibles with 0.8 mm nozzle diameter. Transparent and uniform single crystal fibers up to 45 mm length were obtained. Site-selective excitation spectroscopy and EXAFS were used to investigate local disorder and substitution sites for Eu^{3+} and defect structures of the Eu:LLW crystal fibers. The narrow excitation and emission lines due to the $4f \rightarrow 4f$ transitions of Eu^{3+} in LLW offer an appropriate method for monitoring the different sites. Each line appearing in the excitation spectra of the $^7F_0 \rightarrow {}^5D_0$ transition corresponds to a different Eu^{3+} center since the transition between the nondegenerate $^7F_0$ and $^5D_0$ levels can have only one line per site. EXAFS data are under analysis. By our partial results we conclude that the Eu^{3+} ions occupy at least two different sites in Eu:LLW crystal.

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Magnetic properties of Gd_2CoGa_8 and Dy_2CoGa_8 investigated by resonant X-ray diffraction

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Intermetallic systems R_nTX_{3n+2} (R=rare earth, T= Co, Rh, Ir and X=In and Ga) belong to a family of materials with several interesting physical phenomena like unconventional superconductivity, heavy fermion systems, magnetic ordering and pressure induced superconductivity. The compounds with n=2, T=Co and X=Ga (R_2CoGa_8) can be viewed as alternating layer of RGa_3 and $CoGa_2$ along the c−axis. These compounds crystallize in a tetragonal structure with space group P4/mmm (No. 123). Our group has been extensively investigating the system R_2CoGa_8 with R=Gd-Tm using X-ray and neutron diffraction. In this work we report the results obtained for the system formed with R=Gd and Dy. Single crystals of Gd_2CoGa_8 and Dy_2CoGa_8 were grown by the self-flux method. These compounds have a magnetic propagation vector type $\boldsymbol{\tau} = (\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$. The sample were investigated by resonant magnetic X-ray magnetic diffraction at the L2 absorption edge of Gd (7.930 keV) and Dy (8.581 keV) at the beamline XRD2 (LNLS) using a four-circle X-ray diffractometer and a closed-cycle helium cryostat. To determine the direction of the magnetic moment about six magnetic Bragg peaks $(\frac{1}{2}\ \frac{1}{2}\ \frac{L}{2})$ for L= 9 to 19, were measured for each compound. Comparisons between observed intensities with calculated magnetic peaks have shown that the magnetic moment in Dy_2CoGa_8 compound is close to 20 degrees away of the c−direction. Performing these same preliminary analysis to Gd_2CoGa_8 we have found that the direction of the magnetic moment is at 45 degrees between the axis c and the ab−plane suggesting an isotropic magnetization. Measurements of magnetic peaks as a function of temperature showed a second order phase transition to an antiferromagnetic state with the Néel temperature $T_N \sim 22$ K for R=Gd and $T_N \sim 15$ K for R=Dy and a critical exponent β of approximately 0.35 for both suggesting a three dimensional Heisenberg system.

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Local environments of Fe in Fe_2Zr powders mechanically alloyed

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Local environments of Fe in mechanical alloyed Fe_2Zr powders was were systematically investigated using ^{57}Fe Mössbauer spectroscopy and extended X-ray absorption fine structure (EXAFS). Using the mechanical alloying technique, we have prepared a Fe-Zr alloy starting with a mixture of elemental iron and zirconium powders with a nominal composition of 66.7 at% of Fe and 33.3 at% of Zr. Mössbauer results at room temperature show that the sample (after 12 hours of milling) is basically composed by (Fe, Zr) nanograins embedded in paramagnetic amorphous matrix phase. Mössbauer results at 4.2 K show that the sample is magnetically ordered. On the other hand, the Fe-edge EXAFS data show significant modification on the Fe-short-range order due to the presence of Zr for the 12 h milled Fe_2Zr powders. The Fourier transform of the EXAFS oscillations curve for the Fe K-edges exhibits a broad main peak at about 2.05 . For this sample, the structural parameter values, such as coordination numbers, nearest distance and mean deviation of distances around of Fe atoms were obtained in the region of the main peak. To fit this spectrum, we assumed three sub-shells: Fe-Fe(1), Fe-Fe(2) and Fe-Zr within the main peak. These results are in good agreement with Mössbauer results.

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Parte IX

Superfícies, Interfaces e Nanossistemas

Extrinsic effect of ultraviolet light on hole transport materials used in OLEDs

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OLEDs are a promising technology in the improvement of display devices. Extrinsic degradation processes caused by environmental factors like sunlight on the different components of the devices constitute one of the most important limitations for the non extensive application of this technology. Due to the relevance of hole transport materials with respect to efficiency and stability of the OLEDs, we conducted a comparative study of degradation using UV radiation and intense sunlight on N, N '-diphenyl-N, N '-bis(1-naphthyl)-(1,1 '-biphenyl)-4, 4 '-diamine (NPB) and N,N'-diphenyl-N,N'-bis(3-methyl-phenyl)-l,l'biphenyl-4,4'diamine (TPD) films employing synchrotron radiation-based photoabsorption and photoemission techniques at carbon and nitrogen 1s edges at the SGM beam line from the Brazilian Synchrotron Light Source (LNLS). This degradation study simulates the possible effects on the device caused by a prolonged exposure to UV light and sunlight and the effects caused in the process of transport of charge carriers generated by the influence of the electric field to which the device is brought into operation. The results showed significant differences between exposed and non exposed NPB and TPD. Attenuation of peak intensities at C and N 1s transitions were observed for the exposed film, with loss of nitrogen in both molecules. This suggests changes in the chemical environment with damage of the pi-system of the molecule that might cause loss of hole transport properties and change in the glass transition temperature. These studies contribute for the understanding of the irradiation damage mechanisms in NPB and TPD.

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Funcionalização superficial seletiva de polímeros utilizando excitação monocromática de camada interna e exposição à atmosfera gasosa reativa.

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Estudos recentes [1] mostraram que em tratamentos de plasmas de baixa potência as espécies radicalares superficiais são geradas pela radiação VUV-UV e não pelos íons. A radiação Síncrotron oferece o potencial de utilização necessário, principalmente pelo intervalo de energia requerido (1 a 4 nm) para as excitações de elétrons de camada interna, além da possibilidade de extrema monocromaticidade. As superfícies de filmes finos (200 nm) de poliestireno (PS), polipropileno (PP) e polibutadieno (PBU) foram funcionalizadas seletivamente com a combinação de radiação Síncrotron monocromática e exposição à atmosfera de oxigênio. Os experimentos foram realizados na linha SGM, LNLS (bordas 1s do C e O). Espectros NEXAFS e XPS foram obtidos antes e após a irradiação em diferentes tempos e energias. Pela específica energia de excitação de camada-K, foi observada uma alta e eficiente funcionalização de grupos oxigenados. Quando PS foi excitado com a energia de transição do C 1s sigma de C-C, produziu-se uma extrema oxidação das camadas atômicas mais superficiais (70 por cento de grupos COO e C=O). Os resultados mostrados com PBU e PP estão em etapa de análise, porém pode-se afirmar perante os resultados obtidos com PS que mecanismos de dessorção estimulada Auger estão envolvidos no processo[2]. [1] M. Dhayal, M. R. Alexander and J. W. Bradley, Appl. Surf. Sci. 252 (2006) 7957. [2] D. E. Weibel, F. Kessler and G. V. S. Mota, Polymer Chemistry 1 (2010) 645649*

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Superhydrophobic Al surfaces prepared by chemical surface functionalization of nano/micro structures

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In recent years, a great deal of experimental and theoretical research has been devoted to the so-called superhydrophobic surfaces (water contact angles, WCA higher than 150 degree) with low hysteresis (drops roll off easily even at small inclinations) [1]. In the present work, superhydrophobic self-cleaning surfaces were prepared on treated Al substrates via chemical functionalization o micro/nano structures [2].

Superhydrophobic surfaces were produced on chemical etched Al substrates after anodization and final coating with Trimethoxypropylsilane (TMPSi) and PTFE using the Physical Vapor Deposition (PVD) method. Surface properties were measured by WCA, SEM, NEXAFS and XPS. NEXAFS spectra were obtained at the Brazilian Synchrotron Light Source (LNLS), Campinas using the SGM beam line. XPS spectra were obtained in a conventional electron spectrometer equipped with a high performance hemispherical energy analyser. SEM was evaluated by planar and cross-section images using an electron acceleration of 20 kV.

Prepared superhydrophobic surfaces showed WCA higher than 150 degree with very low hysteresis (lower than 3 degree). SEM images showed that the transition of superhydrophobic surfaces from high to low hysteresis was produced when a nanostructure (worn-like network) was formed superimposed to the microstructure. Without the nanoscale roughness, the water droplet has strong adhesion to the superhidrophobic surface. The low hysteresis obtained was magnified by the presence of a thin layer of a low surface energy chemical compound, a PTFE like over layer. NEXAFS and XPS analyses carried out on the functionalized Al substrates confirmed the presence of a thin layer resembling a PTFE polymer on top of the treated surfaces. Under those conditions, our prepared substrates were water repellent and presented self-cleaning conditions.

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PREPARAÇÃO E CARACTERIZAÇÃO DO CATALISADOR MODELO $Pd/Cr_2O_3/Ag(111)$

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A física de superfícies tem sido amplamente aplicada no estudo de catalisadores, porém a sua complexidade morfológica e estrutural constitui uma barreira para se obter um conhecimento detalhado das suas propriedades microscópicas, e o conseqüente desenvolvimento de novos catalisadores mais eficientes. Uma solução encontrada é a simplificação de um catalisador real, preparado na forma de um catalisador modelo, com a vantagem de ser compatível com as técnicas canônicas de física de superfícies. Os catalisadores modelo permitem a introdução de determinadas características estruturais em uma superfície de forma controlada, simplificando o catalisador real. Esta dissertação apresenta um estudo da estrutura atômica da superfície do catalisador modelo $Pd/Cr_2O_3/Ag(111)$. O catalisador modelo foi produzido por técnicas de deposição MBE, e as caracterizações foram baseadas em técnicas de Física de Superfícies, tais como, LEED, XPS, ARXPS, XPD. Até o presente momento não se tem conhecimento da caracterização deste catalisador modelo através da técnica XPD. Com as caracterizações foram determinadas a composição e a espessura dos filmes, bem como o grau de ordenamento da estrutura. A composição do filme foi determinada pela técnica XPS e sua espessura foi calculada com a técnica ARXPS. O ordenamento cristalográfico do filme foi averiguado com a técnica LEED. O estudo da estrutura cristalina da superfície foi realizado com a técnica XPD, e as simulações computacionais foram realizadas com programa MSCD. Com este estudo foi determinado que o Pd possui uma estrutura FCC, e que ocorre relaxação estrutural somente nas duas primeiras camadas atômicas do Pd. Evidências da formação de ilhas de Pd são também abordadas [1].

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Zn doped magnetite nanoparticles for hyperthermia therapy

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It has been demonstrated that ferrofluids can be used for localized hyperthermia treatment due to magnetic relaxation heating effects in the presence of a radiofrequency (RF) magnetic field[1]. Magnetic nanoparticles (MNP) relaxation can increase tumor temperature above 43° C and selectively kill tumor cells. One important feature of MNP for hyperthermia therapy is their specific loss power or specific absorption rate (SLP/SAR), which determines the heating rate during treatments. In this work Zn_x Fe_{3-x} O_4 $(0 \leq x \leq 0.5)$ *MNP in the form of powder and chittosan/aqueous ferrofluids were prepared. Mean sizes (> 40 nm) and compositions were envisaged to produce high SLP effects. To this end, Zn concentration was varied to optimize the saturation magnetization Ms. Materials were characterized with several techniques to determine their structural, microstructural and magnetic properties and correlate them with their SLP performance.* Zn_x Fe_{3-x} O_4 *nanoparticles were prepared by coprecipitation from* $FeSO_4/ZnSO_4$ *precursors in basic pH and studied by Mössbauer Spectroscopy, TEM, DRX, SAXS, XAFS, magnetic thermogravimetry, VSM and RF-SLP. The nanoparticles have cubic-type shape with mean sizes of about 50 to 100 nm, decreasing with Zn concentration. It was observed that* Zn^{2+} *replaces* Fe^{3+} *at tetrahedric sites of the spinel structure increasing the* Fe^{3+}/Fe^{2+} *ratio at the octahedric sites, similarly to what was reported for the bulk material; however, the highest Ms occurs at x = 0.1 0.2 (Ms of about 105 emu/g) instead of at x = 0.4 (bulk). The measured SLP values were in the range of 100 - 400 W/g.*

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Study of t Phase Transition on Composite Thin Films Formed by Silver Dispersed in Titania Matrix

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Composite thin films formed by silver dispersed in titania matrix have been deposited by sol-gel process in Pyrex substrates. The evolution of the structure and morphology of the films as a function of the preparation temperature were evaluated by X-ray diffraction, atomic force microscopy, electron diffraction and high-resolution transmission electron microscopy. Only amorphous and anatase phases were identified by XRD patterns, but TEM results show the presence of the anatase and rutile phases, where the rutile phase was not expected. Changes in diffraction pattern also were observed during HRTEM measurement, showing the sensitivity of these samples to the electron beam.

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Estudo da formação de $Cu_2(OH)_3Cl$ por DXAS in situ

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Os materiais inorgânicos micro e nanoparticulados desencadearam ao longo dos anos consideráveis investigações em função das suas propriedades eletrônicas, mecânicas e ópticas. Dentre estes materiais, o cobre tem sido aplicado em diversos campos da ciência, como em semicondutores do tipo-p feitos com óxido de cobre por possuir um band gap de 1,2 eV. Também tem sido aplicado em catálise, baterias, sensores de gás, biossensores e transistores [1-6]. Neste trabalho obtemos a formação de compostos nanoparticulados a base de cobre, monitorado através de espectroscopia de absorção de raios X in situ (XAS). O monitoramento in situ foi possível através do uso de um reator específico para este tipo de estudo, o qual permite acompanhar a formação de compostos de cobre em solução com resolução temporal. As medidas de XAS in situ foram realizadas na linha de luz DXAS do LNLS. Os particulados formados foram caracterizados por técnicas complementares, como a espectroscopia de fotoelétrons induzidos por raios X (XPS), difração de raios X (DRX) e microscopia eletrônica de varredura (MEV). Os resultados indicam a formação de um sólido contendo cobre ($Cu_2(OH)_3Cl$)*, um material polimorfo que cristalizou na forma de Atacamita e Paratacamita, com uma distribuição de tamanho na escala micrométrica.*

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Estudio de la adsorción de compuestos orgánicos quirales sobre catalizadores metálicos soportados

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Previamente estudiamos la estructura de catalizadores Pt-Sn obtenidos a partir de síntesis organometálica (OM) [1, 2]. Como una siguiente etapa para optimizar la síntesis y comprender el modo de acción de los catalizadores heterogéneos quirales a base de metales de transición soportados, se propone determinar la estructura superficial de los sistemas organobimetálicos generados utilizando espectroscopía de absorción de rayos X. Los compuestos usados son sustancias OM del tipo M-R_4 *(M: Sn, Ge y* R_4*: mentilo, butilo), empleadas para modificar las propiedades de catalizadores de Pt sobre sílice utilizados en reacciones de hidrogenación de interés en química fina, exigentes en selectividad. Los resultados EXAFS muestran una fuerte interacción de los compuestos OM con el Pt, el que es fuertemente dispersado por éstos, independientemente del tipo de grupo utilizado. En el catalizador monometálico de partida, el Pt forma clusters metálicos de 1 nm de radio. En los catalizadores OM se reduce fuertemente el número de coordinación Pt-Pt y aparecen enlaces Pt-C debido a la adsorción de los grupos metilo y butilo. En el caso de los catalizadores Pt-Ge, no se observa una interacción directa entre los metales similar a la observada en el caso del Sn [3], la que sería a través de los grupos mentilo y butilo.*

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Difusión de Co controlada en la nanoescala en matrices de Si monocristalino: estudios por HRTEM y GISAXS

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Debido a sus potenciales aplicaciones para el desarrollo de micro- y nanodispositivos en electrónica, existe un gran interés en el estudio de la formación, estructura y propiedades de siliciuros metálicos. En particular el $CoSi_2$ *ha sido ampliamente estudiado por su baja resistencia eléctrica, apropiada para ser incorporado así a dispositivos pequeños.*

Las muestras estudiadas consisten en películas delgadas de sílica amorfa conteniendo nanopartículas de Co, soportadas sobre sustratos de Si monocristalino con superficies externas paralelas a las familias de planos cristalográficos (100), (110) y (111). Resultados recientes de GISAXS muestran que luego de someter dichas muestras a un tratamiento térmico se promueve la difusión de Co desde la película de SiO_2 *hacia el interior del monocristal de Si, formando nanoplacas insertas que contienen Co, orientadas en la dirección (111) del monocristal. El análisis cuantitativo de los diagramas de GISAXS permitió la determinación del espesor medio y la dimensión lateral media de la nanoplacas, para las tres orientaciones del monocristal de Si. Por otro lado, mediante el empleo de HRTEM se pudo comprobar la presencia de nanoplacas finas de* $CoSi_2$ *insertas en el monocristal de Si, orientadas paralelamente a los planos (111), con una estructura coherente con la estructura cristalográfica de la matriz de Si.*

El conocimiento detallado de la estructura de las nanoplacas de $CoSi_2$*, así como también su orientación, morfología y naturaleza de la interfase* $Si/CoSi_2$ *de forma local y extendida a lo largo de toda la superficie del cristal, obtenido mediante el uso combinado de las técnicas de GISAXS y HRTEM resulta esencial para comprender la formación de* $CoSi_2$ *durante la difusión de Co en la matriz de Si y entender así sus propiedades de transporte.*

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Understanding the morphology of Gold@Gold(I)-Thiomalate Core-Shell Nanoparticles

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Gold nanoparticles are widely studied because they exhibit extraordinary properties that could have strong impact in different fields of science and technology. In particular, their small dimensions make it easy to incorporate them into biological systems, which are on the same size scale. Metal nanoparticles can be conjugated with small molecules for biomolecular targeting or recognition ligands allowing molecular specificity.

While it is easy to prepare stable thiol monolayer-capped nanoparticles soluble in organic solvents by using standard procedures such as the Brust-Schiffrin two-phase method, isolable, stable and water-soluble gold nanoparticles, a crucial property for possible application in biological systems, are more difficult to be prepared. In this work we study Au nanoparticles synthesized using the modified Brust method developed by Chen and Kimura, under conditions of incomplete reduction. The chemical nature and structure of the nanoparticles are characterized by using a multi-technique approach. The particles consist of 1nm in size gold metallic core and a stable shell of gold(I)-thiomalate layer. The described results give new insights in the synthesis and characterization of metal and core-shell nanoparticles[1].

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Análise química e morfológica do Si corroído por jato de plasma de SF_6 a baixa pressão

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A ascensão da tecnologia MEMS tem motivado diversos estudos sobre processos de corrosão do silício (Si) por plasma. Entre os processos de corrosão por plasma, a técnica de jato de plasma a baixa pressão é muito atrativa porque reduz os danos no substrato. Os substratos neste trabalho foram mascarados por estruturas de linhas com diferentes larguras processadas por filmes de Ni/Cr. Nos experimentos realizados, o substrato de Si fixado sobre o porta-substrato (aterrado) foi posicionado a uma distância de 50 mm do início do jato de plasma de SF_6*. A potência da descarga foi fixada em 150 W e a pressão total em 5,0 mTorr. A primeira corrosão foi realizada apenas com gás* SF_6*. Posteriormente, foram realizadas corrosões adicionando-se diferentes concentrações de* O_2 *(entre 0 % e 60 %) a mistura* $SF_6 + O_2$ *durante 10 minutos. Os resultados de MEV e de perfilômetro óptico mostraram que pequenas concentrações de oxigênio (20 % de* $_{O}2$*) na mistura com* SF_6 *apresentaram ótimas condições de trabalho com alta taxa de corrosão vertical de 1,4 m/min, boa anisotropia (88 %) e baixa rugosidade (25 nm), para aplicações em dispositivos na microeletrônica, vias transversais, trincheiras, etc. Para essa mesma condição, na superfície do Si foram verificados por XPS elementos como C, N, O, F e Si, apresentando uma menor contaminação por parte de C que provêm da pulverização do catodo oco.*

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Role of Cationic Gold on the Catalytic Activity of Al_2O_3-supported Gold for Carbon Monoxide Oxidation

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Since the catalytic activity of oxide-supported gold nanoparticles for carbon monoxide (CO) oxidation was discovered, those catalysts have been subject of an intense investigation. A number of variables have been proposed to play a role in the origin of the unexpected catalytic activity. Particularly, the oxidation state of gold in oxide-supported gold catalysts has been extensively investigated. Metallic gold, cationic gold and a mixture of both have been claimed to be necessary to catalyze CO oxidation. Nonetheless, the active site structure still remains unclear. In this work, we characterized coprecipitated Al_2O_3*-supported gold samples by temperature programmed reduction (TPR) and X-ray absorption near edge structure (XANES) spectroscopy, to investigate the oxidation state of gold in various* Al_2O_3*-supported gold samples that were active for CO oxidation catalysis. The sample was treated in a flowing mixture of CO and* O_2 *(total flow rate: 100 mL* min^{-1}*, 2% CO, 1.5%* O_2 *balance* N_2 *at 760 Torr) as the temperature increased linearly from 298 to 673 K. The results show the onset of catalytic formation of* CO_2 *at approximately 373 K, and the CO conversion reached 100 % when the temperature reached approximately 498 K. The TPR profile characterizing the* Au/Al_2O_3 *sample showed a peak at ca. 543 K attributed to the reduction of cationic gold to zerovalent gold. Bolstering these results, XANES spectra of a fresh sample showed features characteristic of cationic gold, while XANES spectra of hydrogen treated sample show features that resemble those of zerovalent gold. Because the temperature at which reduction of the gold occurred was higher than that at which the samples were catalytically active for CO oxidation, we conclude that at least some gold was cationic during catalysis, suggesting a possible role for cationic gold in the CO oxidation.*

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Crystal structure, local atomic order and metastable phases of zirconia-based ceramics for Solid-Oxide Fuel Cells

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Zirconia-based ceramics exhibiting the tetragonal and/or cubic phases have important technological applications because of their excellent electrical and mechanical properties. For example, ZrO_2*-based materials doped with oxides of divalent or trivalent cations are usually employed as solid electrolytes in Solid-Oxide Fuel Cells (SOFCs). Differently,* ZrO_2*-*CeO_2 *solid solutions are used as SOFC anodes and in three-way catalysis due to their excellent oxygen-storage capability.*

In the last years, our research groups investigated the crystallographic features of a number of ZrO_2*-based systems (*ZrO_2*-*CeO_2*,* ZrO_2*-CaO,* ZrO_2*-*Y_2O_3 *and* ZrO_2*-*Sc_2O_3*). We focused on the retention of metastable tetragonal forms in nanocrystalline solid solutions. These materials exhibit three tetragonal forms, all belonging to the* $P4_2/nmc$ *space group. The stable tetragonal form is called the t-form, which is restricted to the solubility limit predicted by the equilibrium phase diagram. The t'-form with a wider solubility, but unstable in comparison with the mixture of the t-form and cubic phase. Finally, the t"-form has an axial ratio c/a of unity, but with the oxygen atoms displaced along the c axis from their ideal sites of the cubic phase.*

In this presentation, we will review our main studies on this matter, performed by XPD and EXAFS at the LNLS. The use of a high intensity synchrotron source in XPD experiments allows the detection of small Bragg peaks, which are related to the displacement of oxygen atoms. By analyzing selected compositions in high-temperature XPD experiments, we investigated the influence of the crystallite size on the phase diagram of these ZrO_2*-based systems. It is particularly interesting the case of the* ZrO_2*-*Sc_2O_3 *system, which exhibits low-conductivity rhombohedral phases that can be avoided in nanopowders and fine-grained ceramics. We will also discuss our EXAFS results regarding the local atomic structure of these materials, which gave important information on the disorder in the oxygen sublattice.*

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Control of the physical properties of magnetic nanoparticles by structural manipulation

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This experiment intends to test the following hypothesis: Using a new synthesis method can produce magnetic nanowires with controlling their properties. In order to obtain the nanowires, different substrates are filled with hexaferrites nanoparticles (NP). The filling is made using a method developed by our group, whose report is in process of writing. Such method allows the synthesis of NP in situ, in the nanospace previously designed on the substrate. The hexaferrite NP are synthesized by Sol Gel method [1-3], and heat treatment under controlled atmosphere [4]. Such physical-chemical method ensures the synthesis of NP with crystallite size between 5 nm and 100 nm. The flexibility of the synthesis allows inducing structural changes that determine the physical properties of the nanowires obtained. Preliminary studies [4] show that the proposal method allows manipulating the occupation and the local symmetry of the iron ions in the crystals sites of the hexaferrite. The partial occupation and the local symmetry changes affect the superexchange interaction, and the magnetic order. Therefore, the control of some physical properties of the magnetic nanowire is possible. Using the LNLS facilities (line D10B XPD), the structural refinement of the NP hexaferrite will be done in order to correlate the crystal structure and physical properties.

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Controlling α-Fe_2O_3 nanoparticle formation using chelating agents

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In this work Fe_2O_3 powders were synthesized in nanoscale dimensions by co-precipitation method on the addition of two chelating agent (sucrose and glycerin) at different synthesis conditions (concentration and synthesis temperature). X-ray diffraction results added to the magnetism results show that the addition of organic precursor in the synthesis influence significantly on the control particles size and the sizes distribution (with average size around 6 nm). Therefore the nanoparticles prepared without organic precursor present average size of 75 nm and temperature-dependent field cooling magnetization showed that there was Morin transition. Besides, Rietveld refinement analysis added to image of Scanning Electronic Microscopy show that for low concentrations of sucrose the particles shape are changed of randomly form to rod-like (5x20 nm^2) and directed to a preferential growth in (110) crystalline plane confirmed by transmission electron microscopy. ZFC-FC magnetizations curves show that samples obtained in low temperature present a superparamagnetic behavior with blocking and irreversibility temperatures around 95 and 135K, respectively. We have concluded that the presence of sucrose in the synthesis inhibited the coalescence effect (CNPq, FAPITEC-SE).

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Energy dispersive X-ray Bragg-surface diffraction to study in-plane strain anisotropy due to re-crystallization in Fe$^+$ Implanted Si(001).

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Metal nanocrystal memory devices employing discrete charge traps as storage elements have attracted considerable research attention as promising candidates to replace conventional DRAM or Flash memories [1]. The advantages of metal nanocrystals (NCs) over their semiconductor counterparts (e.g., Si or Ge NCs) include smaller energy perturbation caused by carrier confinement, higher density of states, better size scalability, and design freedom of the work-function engineering to optimize device characteristics. In this context, cubic metallic to $\gamma - FeSi_2$ *is a potential material for this application due to its high density of d states at the Fermi level [2]. The X-ray multiple diffraction (XRMD), which is a very special technique for providing enough sensitivity for detecting subtle distortions in the lattice as those caused by an external stimulus. Recently [3], In-plane strain anisotropy was observed by the X-ray Bragg-surface diffraction technique in the silicon lattice surrounded by nanoparticles that were synthesized by an ion-beam-induced epitaxial recrystallization process of Fe-implanted amorphous Si layer. In this work an study of this anisotropy was performed using X-ray Bragg-surface diffraction as a function of enegy. High resolution transmission electron microscopy images have shown the occurrence of metallic spherical and plate-like* $\gamma - FeSi_2$ *nanoparticles in the implanted/recrystallized region with different orientations responsible for the strain anisotropy. The mappings of the (111) Bragg-Surface Diffraction (BSD) reflections in 6.63, 6.77, 8.5 and 11.3 keV show a clearly anisotropy between* ϕ*=0 and* 90^o *maps and also a marked broadening between Si (matrix) and implanted sample profiles.*

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In-situ XANES Studies of of $Ce_{0.9}Zr_{0.1}O_2$ Nanocatalysts for Total Oxidation of Methane

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The catalytic combustion of methane constitutes an alternative to conventional methane thermal combustion to produce energy. This method has the advantage to give the possibility of performing the oxidation reaction at lower temperatures, thus reducing the emissions of NO_x*. In recent years there has been growing global concern about the rapid increase in emissions of gaseous pollutants and greenhouse gases caused by the growth in energy demand. Under the Kyoto protocol, the reduction of hydrocarbons,* CO_2 *and* NO_x *emissions, and the increase of combustion efficiency, especially in the case of methane and natural gas, have become a central research topic. The aim of this work is to study the catalytic performance of Ce-Zr mixed oxides for the total oxidation of Methane with different techniques. All the solids of nominal composition* $Ce_{0.9}Zr_{0.1}O_2$*, have nanometric particle sizes, and were synthesized via the nitrate-*α*aminoacid combustion process using different* α*aminoacids. Catalytic studies were performed in a laboratory fixed-bed reactor in the traditional way. Besides, in-situ XANES experiments near the Ce* L_{III} *edge were carried out heating the sample with a temperature ramp of 10C/min and with a feed consisted of Methane(*CH_4*) (2% mol.) and Oxygen (*O_2*) (4% mol), in Helium (He). During these experiments, a mass spectrometer Quadrupole Mass Spectrometer QMS 422 Pfeiffer was connected to the exit in order to register the composition of exhaust gases. In-situ XANES experiments were carried out at the D06A-DXAS dispersive beamline of the Brazilian synchrotron Light Laboratory (LNLS), Campinas, Brazil. The D06A-DXAS dispersive beamline is equipped with a Si(111) monochromator and an image-plate detector to collect the absorption spectra. The comparison of traditional catalytic studies with in-situ XANES results allows following the evolution* Ce^{3+}/Ce^{4+} *ratio during the reaction rate at different temperatures and its importance in Methane molecule activation.*

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Imaging of strain in SiGe nanostructures by coherent x-ray diffraction

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Coherent diffraction imaging (CDI) has recently emerged as a technique with great potential for the 3-dimensional determination of atomic displacement fields inside nanocrystals [1]. This lens-less imaging method relies on the use of a coherent x-ray beam, whose wavefront has a well-defined phase relation that is preserved through the scattering process. Therefore, the complex valued wavefield holds the information on the exact position of the single scatterers.

We have performed here the first measurements of coherent X-ray diffraction from an ensemble of 130nm SiGe nanostructures at beamline XRD2. Complete 3D X-ray maps of the (004) and (113) reflections were obtained using a 2-dimensinal 100K Pilatus single photon detector.

We present the first attempts to retrieve the strain inside these SiGe nanostructures and compare the results with finite element methods.

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Acknowledgements:

Synthesis of Gold Nanoparticles by Direct Sputtering Deposition onto Liquids Substrates

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The sputtering of Au targets onto castor oil and ionic liquids (ILs) generates stable spherical gold nanoparticles (AuNPs) of 2.4 to 4.6 nm. On the castor oils, the AuNPs size increases with the discharge voltage and the mechanism of nucleation and growth are related with the energy of the atoms/clusters ejected from the target. The sputtering of gold foil onto 1-n-butyl-3-methylimidazolium tetrafluoroborate, hexafluorophosphate, bis(trifluoromethylsulfonyl)amide or tris(fluoro)tris(perfluoroethane)phosphate ILs generates stable and well-dispersed AuNPs of 3-5 nm under conditions of 40 mA, 335 V and 2 Pa Ar work pressure. The size and size distribution of these Au nanoparticles depends on various experimental parameters, particularly the surface composition of the IL and less so the surface tension and viscosity. Under the experimental conditions used here, both nucleation and NP growth seem to occur on the IL surface and the NP size changes with the changes in the IL surface composition, especially with the increase of the fluorinated content. Moreover, the NP size is independent of sputtering time but does depend on the discharge current. When higher discharge currents are used, more gold atoms hit the ionic liquid surface per unit time, changing the kinetics of particle growth on the surface of the IL.

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AFM and XPS characterization of TiO_2, Nb_2O_5, ZrO_2, and $Ti_xNb_yZr_zO_w$ thin films deposited by magnetron sputtering on Si(111)

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Titanium, due to its interesting properties such as high mechanical strength, excellent thermal stability, good corrosion resistance in extreme conditions, is a biocompatible metal commonly used in medical implants. Ti-6Al-4V is one of the main biomaterial alloys employed as implants, but the release of Al and V ions is associated to health problems and adverse tissue reactions. A new class of Ti alloys employs Zr for solid-solution hardening and Nb as β *phase stabilizer. Metals such as Ti, Nb, and Zr, known as valve metals, usually have their surfaces covered by a thin oxide film spontaneously formed in air. This oxide film constitutes a barrier between the metal and the medium. In this work, films of Ti, Nb, Zr, and Ti-Nb-Zr oxides have been produced by magnetron sputtering under an atmosphere of argon and oxygen, and their surface morphologies and compositions were studied by means of atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Ti films were produce at two different* O_2 *concentrations (5 and 20%). For the smaller* O_2 *concentration, three doublets were fitted in the Ti 2p XP-spectrum which corresponded to metallic Ti (5%), TiO (9%), and* TiO_2 *(86%). For the higher* O_2 *concentration, the Ti 2p spectrum was fitted by only one component which was associated to* TiO_2*. The Nb and Zr films were produced using 20%* O_2*, and only* Nb_2O_5 *and* ZrO_2 *were identified by XPS.*

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Morphological and crystalline studies of PHBV nanocomposites prepared with different nanoparticles

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Morphological and crystalline studies of poly(hydroxybutyrate-co-hydroxyvalerate) PHBV nanocomposites were investigated using transmission electron microscopy (TEM), X-ray diffraction (XRD), small-angle X-ray scattering (SAXS), and differential scanning calorimetry (DSC). In this work, two different nanoparticles, organically modified montmorillonite (OMMT) Cloisite 30B and unmodified tubular like clay halloysite (HNT), were incorporated in the PHBV matrix. The nanocomposites with 1, 3 and 5 wt% of nanoparticles were obtained by melt processing in a twin screw extruder using two different processing conditions (low and high shear intensity). From TEM and XRD results images, it was possible to observe that the number of aggregates increased with the nanoparticle concentration. Furthermore, the nanocomposites prepared in high shear conditions presented a better distribution of nanoparticles in the PHBV matrix. In these cases, the morphological structures were a combination of few tactoids and partially exfoliated structure. The values of the lamellar long period, measured by SAXS, were similar for both systems. However, when processed at high shear intensity and containing higher amounts of nanoparticles, the results evidenced the formation of a second ordered structure, as shown by the change in the scattering peaks, mainly in the case of the PHBV/OMMT nanocomposites. The crystallization behavior, analyzed by DSC, indicated a lower nucleation density and lower crystallinity with the addition of nanoparticles. Furthermore, the presence of OMMT platelets led to the formation of double melting peaks, which can be related to the formation of crystalline phases having different sizes and/or ordering.

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Control of crystalline structure of NWs III-V by varying a single parameter: the precursor flow

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Semiconductor nanowires (NWs) have gained a lot of attention over the past decade due to their unique geometry and properties. Different techniques of growth have reported that semiconductor NWs can present as crystalline structure either wurtzite (WZ), zincblend (ZB) or a mix of both structures WZ and ZB in alternating segments. Most studies of NWs associated SFs formation to the supersaturation level in the NP which depends on growth conditions. In this work, we investigated InP NW shape and length by a JEOL 6330 field emission scanning electron microscopy (SEM), operating at 5kV in the secondary electron mode. The crystal structure and composition were studied using high resolution transmission electron microscopy (HRTEM) and Energy Dispersive Spectroscopy (EDS), respectively, with a JEOL 3010 URP 1.7 operated at 300 kV and a JEOL 2100 ARP operated at 200 kV, both equipped with a MSC 794 slow scan CCD camera. All equipments are available at the Electron Microscopy Laboratory/LNLS. Varying the TMI flow, used as precursor of growth by VLS method, large growth rates (about 10 times larger than those usually found in planar growth for the same TMI supply at optimum growth conditions) can be obtained by chemical beam epitaxy (CBE) technique. For samples grown under low flow, tapered NWs and almost perfect WZ structures are observed. For the maximum TMI flow condition, diameter variations and large SF density along the NW length are present. EDS measurements carried out at the metallic nanoparticles have shown no difference in ex-situ In atomic concentration for NWs from both samples, cooled down under similar conditions. The SF formation is attributed to continuous changes in contact angle between metal and semiconductor during growth which is related to the different routes of In incorporation at the junction of the three phases (vapor-liquid-solid or the triple phase line, TPL). Thus, TPL fluctuations due to kinetic roughening are indicated as the origin for several features of InP NWs. Our results also show an important technological aspect since InP NWs with different morphologies and lateral roughness were achieved by controlling a single growth parameter such as TMI flow. ***

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Synchrotron radiation techniques applied to the study of Ge_x Si_{1-x} nanoparticles embedded in silica

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Nanoparticles have been attracting great attention since it has been realized that the reduction of dimensionality offers an alternative pathway to manipulate and control materials properties, besides the more traditional control over chemical composition. To explore the potentialities of nanoparticles, a throughout understanding of the influence of preparation conditions on their final chemical and structural properties is required. However, this step can be hampered by the own nature of nanoparticles, making structural characterization a challenging task. Due to their reduced dimensionality, well-established techniques developed for crystallography might not be directly applicable. In compound nanoparticles, the problem of structural determination is even more complicated, requiring chemically selective structural determination. In this sense, the usual approach to nanostructure characterization involves a combination of several techniques, covering structure, morphology and chemical composition.

In this contribution, we highlight the importance and utility of synchrotron radiation-based techniques such as XAFS, GISAXS and anomalous XRD in the characterization of nanostructures. Such suite of techniques yields information on several length scales, covering structure, morphology and chemical composition. To our purposes, the system of choice are Si_x Ge_{1-x} nanoparticles embedded in silica thin films. This system presents several of the challenges that a materials scientist would face in the characterization of nanostructures: an initially unknown composition, polydispersity, strain and stress and mixed amorphous and crystalline populations, to mention just a few. Although the results presented herein illustrate the potentiality of such a combination of synchrotron techniques in the analysis of only one materials system, we think that our procedures are general enough to be directly applied to other nanostructured materials.

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Interpretation of SAXS and TEM data for analyses of the mesophase structures in hybrids silica-P(N-iPAAm)

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Hybrid functional nanosystems based on silica-P(N-iPAAm) have attracted much attention for control of molecular transport, including drug release, because self regulated delivery allows for drug release when it is needed (1). In this work, we study hybrids systems consisting of the P(N-iPAAm) and two kinds of mesoporous silica materials: SBA-15 and SBA-16. These mesoporous materials possess different structural characteristics. SBA-15 is composed of SiO2 channels arranged in the hexagonal array (1) and SBA-16 is an example of ordered mesoporous silica with cubic symmetry and cage-like pores (1). Although these materials are not crystalline, they diffract due to periodic voids in the amorphous framework. SAXS analysis was used and the results are compared with the TEM observations. In particular, five peaks were observed on the pattern for sample [SBA-15/P(N-iPAAm)] which can be indexed as (100), (110), (200), (210) and (300). For [SBA-16/P(N-iPAAm)] three peaks were observed which can be indexed as (110), (200) and (211). It should be noted that the (100) interplanar spacing, d100, multiplied by 1.155 provides the hexagonal unit-cell parameter, a0, which is equal to the distance between the centers of adjacent pores in the structure, and the (110) interplanar spacing, d110 multiplied by 1.414 provides the cubic unit-cell parameter. Therefore, the value found to the hexagonal unit-cell parameter and the cubic unit-cell parameter were 11.06nm and 15.6nm, respectively. These values were also estimated from TEM images and compared with SAXS results. Measurements of the center-to-center pore distance of two adjacent pores were realized in distinct regions. The average value calculated for a0 was (10.5 0.4) nm for [SBA-15/P(N-iPAAm)] and (15.2 0.7) for [SBA-16/P(N-iPAAm)]. The analysis showed a good agreement with SAXS results. Thus, TEM investigation gives consistent evidence that the ordered structure is preserved in the approach proposed to obtain hybrids systems.

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Ab-Initio study of structure, electronic properties and surface formation energies of tetragonal ZrO$_2$

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To determine the internal structure (cristalline core size) and nanoparticle surface relaxations , this work shows the simulations results of ZrO$_2$ compound in its tetragonal phase by means of the ab-initio DFT-pseudopotentials based SIESTA code. The electronic and structural properties of nanoparticles up to 2.4 nm, in two morphologically distinct types: quasi-spherical and faceted are studied. In the relaxed nanoparticles we have found that the surface termination inuences the degree of internal disorder (amorphization). From the study of the distribution of interatomic distances between Zr-O and Zr-Zr nearest neighbors and next nearest neighbors atoms, we obtain the lattice parameters of nanoparticles, and possible phase transition by size and shape from the tetragonal phase, to disordered cubic. The formation energy of the nanoparticle is also determined and used to determine the lowest energy conguration and its dependence with shape and size. Correlation of the nanoparticle structure with XANES experiments developed at the D06-DXAS line of LNLS Sincrotron, are done.

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A thermodynamic approach to predict dopant atoms segregation on nanocrystals

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The development of novel nanostructured devices requires reliable modeling procedures for the description of materials features at the atomic scale. Among the most significant challenges in this field is the prediction of nanocrystals morphology and growth behavior as function of synthesis parameters from first principles. This work describes a novel model for the evaluation of dopant segregation on faceted nanocrystals from the ab initio calculated surface energy values1 as function of dopant content for different crystalline planes. Starting from an arbitrary nanocrystal geometrical configuration, an iterative calculation procedure for incremental dopant contents is performed to verify the most likely dopant segregation state as a function of the nanocrystal overall composition. The selection rule applied at each iteration step was the minimization of the Wulff parameter deviation for each crystalline plane. The Wulff parameter for a given crystalline plane is equal to its surface energy density divided by its respective facet distance. The expected dopant segregation patterns for two geometrical configurations were compared to semi-empirical characterization results from Sb-doped (4.5%atom, 13.9%atom) SnO_2 *nanocrystals obtained by a nonaqueous synthesis route2. The comparison between the measured and the calculated dopant atoms distributions on the nanocrystals facets are in a good agreement, with a mean deviation value below 5%. The successful description of the dopant atoms segregation by this model indicates that first principles calculations can be used to predict nanocrystals features at thermodynamic equilibrium configurations, which is a feasible approximation for a number of experimental systems. In addition, the use of Wulff parameter deviation as the main selection rule points out that the real nanocrystalline systems tend to use dopant diffusion for the minimization of the overall surface energy as the growth processes take place.*

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Síntese de nanopartículas caroço@casca Ag@SnO_2

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Quando em escala nanométrica, os sistemas químicos integrados podem apresentar propriedades físicas e químicas drasticamente diferentes do seu sólido estendido[1]*. A síntese de nanopartículas caroço@casca (NCC), vem se destacando nos últimos anos, devido apresentarem propriedades diferenciadas em decorrência da ação sinergística entre os componentes. Nesse trabalho, foram preparadas NCC Ag@*SnO_2 *pela redução de* Ag^+ *em solução (*$AgNO_3$ *em N,N-dimetilformamida-DMF)*[2] *combinada com a hidrólise e condensação do terc-butóxido de estanho (método sol-gel), em uma única etapa reacional. No estudo feito por UV-Vis, observou-se um aumento de intensidade da banda plásmon (propriedade ótica das NPs de Ag), atribuído ao aumento da população de NPs e um deslocamento para região de menor energia (red shift) em relação ao espectro de NPs de Ag em suspensão em DMF, que pode estar relacionado à transferência de carga da casca de* SnO_2 *para o núcleo metálico ou ainda ao aumento do índice de refração em torno das NPs de prata. Os difratogramas de raios X confirmaram a presença de Ag metálica e* SnO_2 *cristalino no sistema Ag@*SnO_2*. Pelas imagens de microscopia eletrônica de transmissão, observou-se uma população de NPs, predominantemente esferoidais, formadas por sistemas contendo um núcleo de prata recoberto totalmente por uma casca de* SnO_2 *de espessura irregular. As NCC apresentam tamanho médio de 20 nm, sendo o caroço de prata de aproximadamente 7 nm de diâmetro e a casca de* SnO_2 *de cerca de 13 nm de espessura. A metodologia proposta na preparação das NCC Ag@*SnO_2*, em uma única etapa, mostrou-se viável. A transferência de carga fotoinduzida aponta para a possibilidade de aplicação desse sistema em reações fotocatalíticas e células fotovoltaicas.*

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Superficial aspects of Hydroxyapatite: HRTEM evidence and theoretical modeling

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The focus of this paper is to present a theoretical and experimental study of the ultrastructural properties of a synthetic hydroxyapatite (HAP). HAP is the simplest chemical and structural model that describes the mineral phase of bones and teeth. HAP samples were prepared by wet chemical method at physiological temperature (37 °C). The ultrastructural characterization of the samples was performed using a high-resolution transmission electron microscope (HRTEM JEM-3010 URP) with a LaB_6 *thermo-ionic electron gun and 1.7 of point-to-point of resolution. The experimental study was complemented with X-ray diffraction (XRD) measurements, using synchrotron radiation, and Fourier transform infrared spectroscopy (FTIR). The results showed the precipitation of one crystalline phase, chemically and structurally similar to the inorganic phase of bone. Based on high-resolution images interpretations, from focal series reconstruction technique (with spherical aberration correction), was made a theoretical study of the HAP surface, using the Density Functional Theory by testing two models; one with a hydrated layer and the other dry.*

Acknowledgements: The electron microscopy work has been performed with the JEM-3010 URP microscope of the LME and x-ray diffraction measurements were taken at the LNLS, Campinas, Brazil. Theoretical calculations were performed using the facilities of the Chemistry Department at Northwestern University, IL, USA. FTIR analyzes were performed at the CBPF, Rio de Janeiro, Brazil.

Estudo do efeito do cério em nanocatalisadores de platina aplicados à reação de deslocamento gás-água.

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A reação de deslocamento gás-água é uma reação chave na produção de hidrogênio [1]. Para que o mecanismo dessa reação pudesse ser compreendido, uma vez que a literatura mostra que ele ocorre em rotas bifuncionais com participação tanto do metal quanto do suporte, nanocatalisadores de Pt foram preparados [2] empregando-se três suportes distintos contendo Ce nos quais o teor de Ce e o método de preparação foram variados. Esses materiais foram caracterizados e os resultados de XPS mostraram que as espécies presentes na superfície dependem do método de preparação e do teor de Ce. Esses parâmetros também influenciam o estado de oxidação do Ce durante a reação o que foi investigado através de medidas de XANES in situ. Medidas na borda da Pt também foram realizadas para que pudéssemos observar seu comportamento em condições de reação sendo que esta apresentou-se completamente reduzida porém desempenhando um papel importante para a atividade catalítica uma vez que em sua ausência o catalisador não apresenta atividade. Logo, neste trabalho destacamos que as espécies de Ce presentes na superfície do catalisador e no bulk em condições de reação são influenciadas pelo método de preparação e teor de Ce dos catalisadores e além disso, a atividade catalítica para a reação WGS pode estar associada ao efeito de redução do Ce promovido pela Pt. [1] I.B. Whittington, J.C. Jiang, L.D. Trimm, Catal. Today 26 (1995) 4144. [2] D. M. Meira, R.U. Ribeiro, J.M.C Bueno e D. Zanchet, Anais CICAT-Chile (2010) 200.

Acknowledgements: CNPQ; FAPESP (07/57723-3); LNLS pela utilização das instalações.

A New Insight into Copper-Based Catalysts: Microwave-Assisted Morphosynthesis, *In Situ* ***Reduction Studies and Ethanol Dehydrogenation Reaction***

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Cu-based catalysts have shown activities for a variety of reactions, such as water-gas shift reaction, ethanol dehydrogenation and others. Different intermediates in oxidative states of Cu can be present both in reduction and reactive environment, and particularities between them could make a difference in its catalytic properties. The aim of this work was investigate CuO with different morphologies obtained by a singular microwave-assisted hydrothermal method and correlated them with catalytic properties to ethanol dehydrogenation. Using time-resolved in situ XANES measurements at the Cu K-edge during TPR experiments the degree of reduction was monitored. Semi-quantitative estimation of the different chemical forms of copper (i.e., Cu (II), Cu (I), and/or Cu(0) were obtained. The results suggest intrinsic particularities of CuO by its different morphologies at activate state in the kinetics of reduction.

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Atomic ordering dependence on growth method in Ge:Si(001) islands: Influence of surface kinetic and thermodynamic interdiffusion mechanisms

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Interdiffusion in self-assembled Ge:Si(001) islands has been explained by models based on either thermodynamic and/or surface kinetic considerations. In order to analyze the relevance of bulk and surface diffusion on the final composition state, we performed a set of controlled x-ray diffraction experiments to study both composition and atomic ordering in Ge/Si(001) islands grown by different methods. Surface diffusion strongly enhances the overall interdiffusion during island growth by solid source molecular beam epitaxy while chemical-vapor-deposited islands are closer to thermodynamic model systems. The growth conditions play a crucial role on the appearance of atomic ordering. In particular, a remarkable correlation between atomic ordering and surface diffusion kinetics is found. Finally, the energies in volved on the growth of Ge islands in pre-patterned Si substrates are discussed, providing insights on the surface energies involved in the self-positioning process.

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Estudo da ordem de longo alcance e propriedades termodinâmicas de multicamadas de ácidos fosfônicos pela técnica de difração de raios-x dispersiva em energia

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Medidas de difração de raios-X foram realizadas em multicamadas auto-organizadas de ácidos fosfônicos OPA e OcPA. Esses dois sistemas apresentam ordenamento lamelar de longo alcance quando depositados em substratos planos como silício, GaAs e mica, por exemplo. Periodicidades distintas são observadas nos padrões de difração, apontando para o fato que diferentes formas de empacotamentos podem ser encontradas. Para estudar o comportamento termodinâmico do sistema, a temperatura foi variada a fim de observar modificações estruturais no empilhamento das multicamadas. Medidas de difração convencional permitiram introduzir modelos de empilhamento demonstrando modificações na estrutura de empilhamento em função da temperatura. Utilizando difração de raio-x dispersiva em energia que permite realizar medidas em curto intervalo de tempo mas com menor resolução analisamos a fração volumétrica presente na amostra para cada tipo de ordenamento em vários intervalos de temperatura. O padrão de ordenamento das moléculas no plano do substrato foi também investigado realizando-se medidas em geometria de transmissão de raios-x (SAXS/WAXS). Os resultados mostram uma transição entre empacotamento planar hexagonal para baixas temperaturas e empacotamento cúbico para temperaturas acima de 75 ^{o}C. A correlação entre a transição estrutural planar e as transições lamelares estão sob investigação e serão discutidas nesse trabalho.

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Synchrotron XRD and HRTEM of Heterostructured TiO_2-WO_3 Nanoparticles

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Recently, much attention has been given to the synthesis of nanostructured inorganic materials with hierarchical morphologies for application in catalysis, microeletronic devices and sensors [1,2]. TiO_2 *and* WO_3*, are promising materials and have been the subjects of many studies in order to undertand their physical and chemical properties [2,3]. Heterostructured nanoparticles were synthesized in porous Vycor glass (PVG) by means of impregnation of PVG pieces with oxide precursors. For* TiO_2 *and for* WO_3*, titanium (IV) di-(propoxy)-di-(2-ethylhexanoate) and* $[W_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(OH_2)_3][W_3(\mu_3\text{-}O)_2(\mu\text{-}CH_3CO_2)_6(CH_3CO_2)_3]_2$ *were used, respectively. After impregnation, the PVG was submitted to thermal treatment for 8 h under air at 750 C (for* TiO_2 *precursor) and 600 C (for* WO_3 *precursor). The HRTEM images were obtained from the JEOL JEM3010 microscope (300 kV, 1.7 point resolution) at the LNLS. XRD data were collected at the D10B-XPD beamline of the LNLS. The synchrotron XRD and HRTEM results indicate the nanoparticles of* TiO_2 *and* WO_3 *are dispersed in the PVG pores, are crystalline and sphere-like. The nanoparticle sizes after 3, 5 and 7 impregnation decomposition cycle are 3.4, 4.3 and 5.1 nm for* TiO_2 *and 2.9, 4.6 and 5.7 nm for* WO_3*, respectively. HRTEM images of* $PVG/5TiO_2$-$7WO_3$ *reveals that the nanoparticles are crystalline and nearly spherical. The reason for not observing the nanoparticles core-shell hierarchy by HRTEM is most probably due the low lattice mismatch of the core and shell interfaces and also due to the small shell thickness. However, Raman spectroscopy analysis (data not shown) supplies important information regarding the formation of heterostructure between* TiO_2 *and* WO_3 *[3].*

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Estudo da fase austenita expandida formada em amostras AISI 316L nitretadas a plasma através de difração com fonte radiação síncrotron.

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Dentre os materiais metálicos usados como biomateriais em implantes, temos o aços inoxidáveis ASTM F138 e AISI 316L cujas propriedades importantes neste contexto são maior dureza, resistência ao desgaste e à corrosão. O uso da nitretação a plasma no tratamento desses materiais, em temperaturas até 400 °C, produz uma camada nitretada que consiste de uma fase γ_N*, ao lado de nitretos de Ferro. A fase* γ_N*, resultado da difusão de Nitrogênio na matriz, apresenta boas propriedades mecânicas, tribológicas e de resistência à corrosão, que dependem da quantidade difundida, e vem sendo apontada como a principal fase responsável pela melhoria dessas propriedades. Uma das características que esta fase apresenta é de linhas largas de difração, o que dificulta a análise dos difratogramas obtidos com radiação convencional, uma vez que a maioria dos nitretos formados apresenta ângulos de difração bastante próximos, ficando mascarados. Há quase 2 décadas que a natureza cristalográfica desta fase vem merecendo atenção, resultando em diferentes descrições, o que dificulta ainda mais uma análise mais refinada de sua estrutura cristalina. Poucos estudos utilizaram a radiação síncrotron, sendo que o trabalho mais recente* (1) *mostrou que picos até reflexão* {622} *foram observados, o que permitiu testar dez possíveis estruturas. No presente trabalho foi utilizado o refinamento pelo método de Le Bail, de dados de difração com fonte síncrotron, na análise de amostras nitretadas do aço inoxidável AISI 316L, cuja camada nitretada variou de 1 até 9 micra e apresentou a formação da fase* γ_N*.*

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Estudo por XANES in-situ *com resolução espacial de catalisadores de cobalto suportados aplicados à reforma autotérmica do etanol*

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A reação de reforma a vapor do etanol ocorre via decomposição e pirólise, ou seja, o etanol é primeiramente adsorvido à superfície catalítica, sofre desidrogenação seguido de quebra da ligação C-C, resultando em dois radicais (CO e CH_x*) sobre a superfície do catalisador. A formação de C* é favorecida em catalisadores de Co e, por isso, pode ocorrer acumulo de C* sobre a superfície [1,2]. Assim, um grande desafio é desenvolver catalisadores a base de Co que apresentem atividade equilibrada entre as diferentes etapas de formação e oxidação de C*. Resultados obtidos por nosso grupo na linha DXAS do LNLS na borda K do Co utilizando um reator tubular possibilitaram observar que, em atmosfera de* H_2*, os catalisadores de Co passam por um processo de redução em duas etapas:* Co_3O_4 *-* CoO *-* Co^0*. Em atmosfera de reforma autotérmica, o catalisador é re-oxidado a CoO em temperaturas menores que 673 K, mas volta a reduzir em temperaturas superiores a 673 K devido à formação de* H_2*. Recentemente, foi conduzido um experimento na linha DXAS que teve como objetivo verificar a absorção de raios-X com resolução espacial in-situ de uma amostra de Co suportada em céria e alumina. A amostra foi distribuída homogeneamente ao longo de 1 cm de um reator capilar de quartzo (1 mm de diâmetro interno) e o feixe de luz foi posicionado na direção normal à parede do reator. Os experimentos demonstraram que, a 773 K, na entrada do leito catalítico, a amostra encontra-se completamente oxidada. Entretanto, existe uma redução gradativa no decorrer do leito. Provavelmente, o metal ativo é oxidado pelo oxigênio da alimentação até sua depleção. Após o consumo total de oxigênio, a quantidade de hidrogênio produzido é determinada pelo equilíbrio termodinâmico entre as reações de reforma a vapor e water-gas shift. Outro fato observado foi a formação de* $CoAl_2O_4$ *após algum tempo de reação, o que reduziu a seletividade a* H_2 *e a conversão de etanol.* $CoAl_2O_4$ *é provavelmente formado pela migração de átomos de Co na estrutura da alumina quando este se encontra no estado de oxidação +2. No entanto, uma vez formado,* $CoAl_2O_4$ *não pode ser novamente reduzido a* Co^0*, o que leva à queda da atividade catalítica. Resumindo, foi determinado que o estado de oxidação do Co é fortemente dependente da temperatura e da composição da mistura reacional. [1] R.U. Ribeiro et al. Appl. Catal. B-Environ. 91 (2009) 670-678. [2] Liberatori et al. Appl. Catal. A-Gen. 327 (2007) 197-204.*

Acknowledgements:

XANES, XPS and FT-IR investigations of Cu/ZrO$_2$ catalyst for ethanol dehydrogenation.

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Copper-based catalysts were found to be excellent catalysts for ethanol dehydrogenation (ethyl acetate/acetaldehyde). At reduction and reactive environment different Cu species can be present. In this work Cu/ZrO$_2$ was studied both by TPR-H$_2$ and under ethanol environment. Time-resolved in situ XANES was carried out and semi-quantitative estimation of the Cu species was obtained. XPS provided the chemical state of Cu at catalyst surface, and FT-IR, a complementary study to this Cu species as well as adsorption/desorption properties of ZrO$_2$ by it CO interaction. These results suggest that a combination of Cu(0)/Cu(I) at the ZrO$_2$ surface seems to be essential to highly activity and selectivity for this reaction.

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Grazing-emission X-Ray Fluorescence (GE-XRF) Method for Interfacial Diffusion Studies on Multi-Layered Thin Films

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Surface characterization techniques often need spatial resolution in order to be able to analyze their properties in different points. This is actually an intrinsic limitation of the grazing-incidence (GI) excitation condition in which the collected information normally comes from a large area of the sample surface.

The grazing-emission (GE) experiments provide the same information as (GI) experiments, according to the optical reciprocity theorem but, since in this case the excitation is normal to the sample surface, the combination of GE-XRF and synchrotron x-ray microprobe permits surface-sensitive analysis with spatial resolution.

In this work we have been exploiting the depth profiling capability of the GE-XRF technique, close to the critical angle, to study the interfacial diffusion of a Cr/Au/Cr system at a specific location on the surface. For this purpose, Cr and Au thin films with thicknesses of $40nm$ *and* $20nm$ *respectively were sputtered onto a silicon substrate so as to create a patterns of layered thin films. Measurements were performed on samples as deposited, as well as on those thermally treated to* 200^oC *and* 400^oC *in order to induce interfacial diffusion. The results show a clearly change in the GE-XRF curve for samples treated to* 400^oC*.Moreover, the theoretical model used to simulate the experimental data indicates that diffusion effect must be also considered for the non-thermally treated samples.*

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Thermal stability of PbTe nanocrystals embedded in silica glass

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The thermal stability of PbTe nanocrystals embedded in a silica glass thin film on Si (100) was investigated by grazing-incidence small-angle x-ray scattering (GISAXS). PbTe was deposited using pulsed laser deposition (PLD) and the silica glass by plasma-enhanced chemical vapour deposition (PECVD) techniques. The analysis of the GISAXS intensity of the as-prepared sample shows that the radius distribution of PbTe nanocrystals can be well described by a lognormal function with an average radius equal to 1,0 nm and a size dispersion of 28 %. The silica glass film containing the PbTe nanocrystals was annealed during 1h at several different temperatures in the range between 400 and 600 ^{o}C. After each isothermal treatment the GISAXS intensity of the sample was measured. From the analysis of the GISAXS intensity the radius distribution function of the PbTe nanocrystals as a function of temperature was determined. The results show an increasing trend in the nanocrystals average size in the 400-500 ^{o}C range followed by a reduction of this parameter for higher annealing temperatures. This behavior is consistent with a dissolution mechanism in which the concentration of solute atoms in the matrix is lower than the equilibrium concentration. In the initial stage of thermal treatment the smaller particles dissolve faster, shifting the average radius to larger values. With an additional annealing at higher temperatures the whole set of clusters has their radius significantly smaller leading to a decrease in the nanocrystals average radius.

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Redução* in-situ *de nanopartículas de Pt e Ni suportadas em zeólitas HUSY e HBEA

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A reação de isomerização é emprega catalisadores bifuncionais, os quais combinam as funções hidrogenante/desidrogenante de um sítio metálico com um sítio ácido (zeólitas) para melhorar a octanagem da gasolina. A caracterização e determinação das suas propriedades específicas é interessante para atividade catalítica, conversã e seletividade destes catalisadores [1]. Neste trabalho foram preparados catalisadores monometálicos do tipo HBEA e HUSY (100% de Pt e 100% de Ni), além de catalisadores bimetálicos também do tipo HBEA e HUSY em diversas combinações de porcentagens destes dois metais. Diversos trabalhos presentes na literatura utilizam a técnica de XAS para a caracterizaçção destes tipos catalisadores, com o objetivo principal de investigar as propriedades eletronicas e a composição das nanopartículas suportadas [2-3]. Neste trabalho foram realizados estudos de redução à temperatura programada (25 - 400 a 10 C/min) acompanhados de mediçções por espectroscopia de raios-X (XAS) in-situ. Os catalisadores foram avaliados na região próxima à borda de absorção (XANES) nas bordas L_{III} da Pt e K do Ni. A técnica permitiu obter informações do perfil da temperatura de redução dos metais Pt e Ni por meio da variaçção da intensidade da energia absorvida (linha branca). Através das informações contidas nos espectros de XANES normalizados destes catalisadores foi possível concluir que para nanopartículas de Pt o processo de reduccão acontece na faixa de temperatura 200 - 400. Utilizando a mesma faixa de temperatura, a redução das nanopartículas de Ni foi parcial. Através da avaliação dos catalisadores bimetálicos na borda K do Ni, foi possível observar redução completa das nanopartículas de Ni a temperatura entorno de 400. Estes resultados permitiram concluir que a inserção de nanopartículas de Pt em catalisadores contendo Ni, auxiliam na redução deste metal.Referencias: [1] LIMA et al. Microp. Mesop. Mater. 124, 236 (2009); [2] YOSHIOKA et al. Appl. Catalysis. 355, 20 (2009); [3] MATTOS et al. Stud. Surf. Sci. and Catal., 130B, 1103 (2000).

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Avaliação da cinética de redução de nanopartículas de Pt e Ni suportadas em zeólita HBEA.

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Atualmente a reação de isomerização de n-alcanos como alternativa à substituição de compostos cancerígenos utilizados pela indústria petroquímica para o aumento da octanagem de combustíveis. Este tipo de reação utiliza catalisadores bifuncionais que contêm um metal sobre um suporte com propriedades ácidas (zeólitas). Recentemente estudos têm sido realizados sobre a aplicação na isomerização do n-alcanos, de catalisadores bimetálicos Pt/Ni suportados em zeólita BEA. Estes estudos tem procurado relacionar o processo de ativação destes catalisadores com suas respectivas atividades catalítica [1-2]. Na literatura, trabalhos utilizam a técnica de caracterização XAS para obter informações químicas, eletrônicas e estruturais deste tipo de catalisadores [2-3]. O objetivo deste trabalho foi estudar o perfil de redução de nanopartículas de Pt e Ni suportadas em zeólita HBEA. Neste trabalho foram realizados experimentos de redução à temperatura programada (25 - 800 a 10 C/min) acompanhados de medições in-situ por espectroscopia de raios-X dispersivo (DXAS). Os catalisadores foram avaliados na região próxima à borda de absorção (XANES), L_{III} *da Pt e K do Ni. A técnica permitiu obter informações da cinética do perfil da temperatura de redução dos metais Pt e Ni por meio da variação da intensidade da linha branca. Através das informações contidas nos espectros de XANES normalizados destes catalisadores foi possível concluir que para nanopartículas de Pt o processo de redução acontece na faixa de temperatura 145 - 400C. Para as nanopartículas de Ni o processo de redução acontece entre as temperaturas de 550 - 750C. Através da avaliação dos catalisadores bimetálicos na borda K do Ni, foi possível observar redução completa das nanopartículas de Ni a temperatura entorno de 450 C. Estes resultados permitiram concluir que a inserção de nanopartículas de Pt em catalisadores contendo Ni, auxiliam na redução deste metal. Referencias: [1] LIMA et al. Microp. Mesop. Mater. 124, 236 (2009); [2] YOSHIOKA et al. Appl. Catalysis. 355, 20 (2009); [3] MATTOS et al. Stud. Surf. Sci. and Catal., 130B, 1103 (2000).*

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Silica@lysozyme composites: Preliminary results of ultrastructural organization and antimicrobial effectiveness

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Infections originated from cirurgical procedures are a persistent and serious health issue. The first step towards reducing these infections is inhibiting bacterial colonization on cirurgical devices [1]. Currently, antimicrobial methods have been applied involving either modification of the physiochemical properties of the device surface or application of coatings that resist cell adhesion [2]. These processes invariably increase the cost over the device production and, in the most of cases, are not really effective to inhibit colonization over time from a wide range of opportunistic microorganisms. Based on the antibacterial properties of lysozyme, we have synthesized silica@lysozyme composites in order to generate an ultrastructural organization which is able to retain the biological activity and functionality of the protein [3]. One of the main advantages of this method, when compared to the used ones, is the low cost of production. In addition, due to the tailorability of composites size, a wide range of applications can be envisaged such as the process of containers coating used to storage cirurgical devices. In the present work, we present a simple strategy for producing colloidal silica@lysozyme composites by means of a one-step entrapment sol-gel reaction self-catalysed by the protein. Through this process, it was possible to control the size of the composites while a high entrapment yield of lysozyme was seen. Scanning electron microscopy, nitrogen adsorption-desorption and small-angle X-ray scattering techniques were used to understand how lysozyme presence affects the composite structure as well as to reconstruct the multi-level organization of the particles. The antimicrobial effectiveness of silica@lysozyme composites has been tested against different types of microorganisms to demonstrate the retention of lysozyme antimicrobial properties when entrapped into the composite.

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Optical Properties of individual Quantum Discs in a Nanowire and their correlation to atomic resolved morphology

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The wave-like character of electrons can be exploited in a number of devices that rely on quantum effects, like laser or photodetectors. Quantum confinement for instance is the base of quantum dots, discs and wells which mimic atomic properties with tailored design. To probe optical properties in an actual device, we developed an optimized cathodoluminescence (CL) system installed in a VG HB-501 scanning transmission electron microscopy (STEM). This apparatus is capable of acquiring CL spectral imaging in parallel acquisition mode (a full spectrum for each pixel of the image) with an electron probe of about 1 nm and spectral sampling better than 1 nm (at 300 nm) with a relatively fast acquisition.

We have studied a photodetector based on Quantum Discs (QDiscs) and correlated the optical properties of the QDiscs with their morphology. The detector is composed of 2 bulk GaN wires between which a succession of 20 AlN and GaN layers were grown forming a series of QDiscs (see L. Rigutti et al. Nano Lett. 2010, 10, 2939). Dark Field STEM images can easily locate the QDiscs region between bulk GaN wires and resolve their structure. The optical properties of the bulk wire and that of the DQiscs were obtained by use of our custom made CL system. The emission of each QDisc was individually determined thanks to high spatial and spectral resolution and sampling of the spectrum images. Some of the QDiscs emit at higher energies than the strained GaN band-gap (at 3.5 eV). These emissions are due to Quantum confinement imposed on QDiscs. The morphology of the wire was explored a posteriori by atomically resolved HR-STEM performed on an aberration corrected Nion USTEM. With the exact thickness of each QDiscs, simulated optical propertied can be calculated and compared with experimental results. The relation between QDisc thickness and its emission properties will be discussed.

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Interdependent Chemical and Elastic Analysis of GexSi1-x:Si(001) islands using Finite Elements Simulation and Quantitative High Resolution Transmission Electron Microscopy

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Applications of nanostructured semiconductors in electronic and optoelectronic require a precise knowledge of the chemical and electronic properties. Moreover, a quantitative 3D analysis of the chemical and strain distributions on such nanostructures are major challenges. In a previous work [1], we demonstrated a new approach to infer the 3D chemical distribution on epitaxial GexSi1-x:Si(001) alloyed strained dome-shape islands, based on a quantitative high resolution transmission electron microscopy technique (QHRTEM). The chemical composition and strain state determine their size, stability, and physical properties of these islands [2]. Additionally, it was shown that the island composition is not only different from the nominally deposited material, but is also non-uniform as a result of the interdiffusion process. Here, we combined the 3D chemical distribution obtained from QHRTEM with finite element (FE) modeling in order to solve the island 3D strain/stress state [3]. The adequacy of the continuum approximation in predicting strain/stress state for such nanostructures (40nm12nm) was also verified. Therefore, the combined use of advanced characterization techniques as QHRTEM and FE modeling opens new opportunities for the complete understanding of strained alloyed nanostructures.

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Índice Remissivo