

Red, White and Blue Light Emission from Europium Doped Al₂O₃ Confined into a Silica Matrix

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Abstract

The main drawbacks of fluorescent activated lanthanide luminescent materials in practical optoelectronic applications are the high cost of raw material and the limitation of a specific color depending on the lanthanide ion. In this work, the synthesis of red, white and blue light emitting composite powders of Al₂O₃:Eu³⁺@SiO₂ were successfully synthesized by the hydrolysis and condensation reactions of TEOS as the raw precursor of silica matrix on the Al₂O₃:Eu³⁺ surface. With the aim to change the CIE coordinates different weight ratios of Al₂O₃:Eu³⁺/SiO₂ powders from 13Al/87Si to 5Al/95Si were prepared. Besides, various excitation wavelength from 280 to 340 nm was used in order to change the ratio intensity; I_{red}/I_{blue} , between the red emission coming from the ⁵D₀→⁷F₂ transition of Eu³⁺ ions and the blue band of silica matrix. Chemical evolution of the hydrolysis and condensation reaction of TEOS were conducted by FTIR spectroscopy. The results indicate that from 500°C a complete TEOS to SiO₂ transformation is carried out.

Keywords

Luminescent Lanthanide, Luminescence, White Emission, Aluminium Oxide

1. Introduction

It is well known that rare-earth elements such as erbium, terbium, europium, cerium, and ytterbium are the most important activator centers of luminescence [1] [2], and this has given great impetus to the study of a variety of luminescent materials using a host crystal lattice: oxides, sulfides, selenides, and titanates doped with rare-earth ions for a broad application, such as in lasers, ceramics,

sensors, lighting, displaying, and heat-resistant materials [3] [4] [5] [6] [7]. The most important reason for using rare-earth ions as activator centers in matrices is undoubtedly their narrow band of emission and absorption, which is due to $4f \rightarrow 4f$ electronic transitions [8]. Europium is the most studied lanthanide ion because of its ability to be incorporated into different host. The Eu^{3+} ions show a red emission centered at around 613 nm coming from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions giving one of the three fundamental colors (red, blue, and green) [9]. Concerning host materials, special attention is put on metal oxides due to their high physical and chemical stability and easy fabrication. The Al_2O_3 crystal is a material with a significant technological importance because of the large optical transparency from ultraviolet to near-infrared, and because of its excellent mechanical properties and good chemical stability [10] [11] [12].

However, despite their excellent optical properties of lanthanide ions, the main drawback of these materials in practical optoelectronic applications is the high cost of salts lanthanides. In this regard, the amorphous silica (SiO_2) is a cheap material which can be obtained easily by soft chemical methods, *i.e.* sol-gel [13] [14]. Many recent reports indicate that silica can be used to confine luminescent material such as lanthanide doped oxide materials in order to protect the luminescent component from the environment or as functional silica nanoparticles for biological application or even increase the emission intensity [15] [16] [17] [18]. Moreover, for obtaining white light emission is common to mix the three fundamental colors (blue, green and red), which results in using different lanthanide ion making the final cost increased too. Interestingly, the cheaper amorphous silica matrix when excited with UV light shows a broad blue emission centered at 440 nm [19]. Thus, combining the optical properties of $\text{Al}_2\text{O}_3:\text{Eu}^{3+}$ (red emission) and silica (blue emission) it is expected to have a different color emission from their raw emission.

In this work, $\text{Al}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles were successfully embedded within a silica matrix in order to reduce the high cost of raw precursor and obtain a near white color by exciting the composite powders at different wavelengths from 270 to 340 nm with the aim to change the ratio emission intensity between the red emission coming from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+} ions and the wide blue band of silica matrix, $I_{\text{red}}/I_{\text{blue}}$. By changing this ratio, red, magenta, near white and blue light emission is obtained when exciting at 270, 290, 310 and 340 nm.

2. Experimental

2.1. Synthesis of SiO_2 Sol

The precursors used to synthesize the silica matrix by the sol-gel method were tetraethyl orthosilicate ($(\text{Si}(\text{OC}_2\text{H}_5)_4$, 98%, TEOS), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.9% Fermont), hydrochloric acid (HCl 37.1 %, Fermont), and distilled water. For the synthesis, 22.4 mmol of TEOS was dissolved in ethanol; a solution of ethanol/TEOS with a molar ratio of 4:1 was prepared according to Klein's diagram [13]. Later, a solution of distilled water and hydrochloric acid was prepared and

kept stirring for 1 h. Finally, this last solution was added to the ethanol/TEOS solution and kept stirring for 21 h.

2.2. Synthesis of $\text{Al}_2\text{O}_3:\text{Eu}^{3+}$ NPs@ SiO_2 Composites

The $\text{Al}_2\text{O}_3:\text{Eu}^{3+}$ powders were weighed and added to the silica solution previously synthesized in such a way that the following weight ratios for $\text{Al}_2\text{O}_3:\text{Eu}^{3+}/\text{SiO}_2$ were obtained: 13/87, 11/89, 9/91, 7/93 and 5/95. Subsequently, the mixture was placed under magnetically agitation at 60°C until a partial hydrolysis and condensation reaction of the SiO_2 sol to SiO_2 powders with a white appearance. With the aim to determinate the complete reaction transformation of SiO_2 and eliminate organic matter which is present in the xolegel silica powders, various annealing treatments at 200°C , 300°C , 500°C and 700°C for 1 h were conducted.

2.3. Characterization

In order to evaluate the chemical evolution, Fourier Transform Infrared spectroscopy (FTIR) measurements were performed on a Perkin Elmer 2000 spectrometer, using the KBr pellet method. For all measurements, the spectra were recorded from 4000 to 400 cm^{-1} . The emission and excitation spectra of the samples were recorded on a F-7000 fluorescence spectrophotometer, using a 450 W xenon lamp. The CIE coordinates for each sample were computed from the respective light emission spectra using a MATLAB code. The final uncertainty in the emission and excitation spectra was 16.8 a.u. of intensity (y axis) and 0.18 nm of wavelength (on the x axis), with a confidence level of 95%.

3. Results and Discussion

3.1. Chemical and Morphological Analyses

Figure 1 shows the FTIR spectra of the $\text{Al}_2\text{O}_3:\text{Eu}^{3+}/\text{SiO}_2$ composite powders obtained by the sol-gel method and annealed from 60°C to 700°C for 1 h. Despite the different silica concentration of each of the synthesized sample, the same bond vibrations related to TEOS and their decomposition to silica powders can be found. The bands in the $3000 - 3600\text{ cm}^{-1}$ range correspond to the stretching vibrations of the hydroxyl groups (νOH), due to the presence of water in the sample, and the band around 1634 cm^{-1} corresponds to the OH deformation vibrations (δOH) [20], the intensity of these bands is decreased as the temperature increases, which is related to the complete removal of chemically absorbed water. The absorption bands centered at 960 cm^{-1} are associated with silanol groups (SiOH), and the band centered at 585 cm^{-1} can be assigned to ethoxy groups ($\text{Si}(\text{OC}_2\text{H}_5)$); both are products of the hydrolysis of TEOS [13], at the same time, a condensation reaction between SiOH and the ethoxy groups (SiOC_2H_5) is carried out, and siloxane groups (Si-O-Si) is formed, which is reflected at 1080 cm^{-1} in the symmetry stretching of SiO_4 tetrahedra, at 798 and 450 cm^{-1} [21]. As expected, as temperature increases, the bands related to

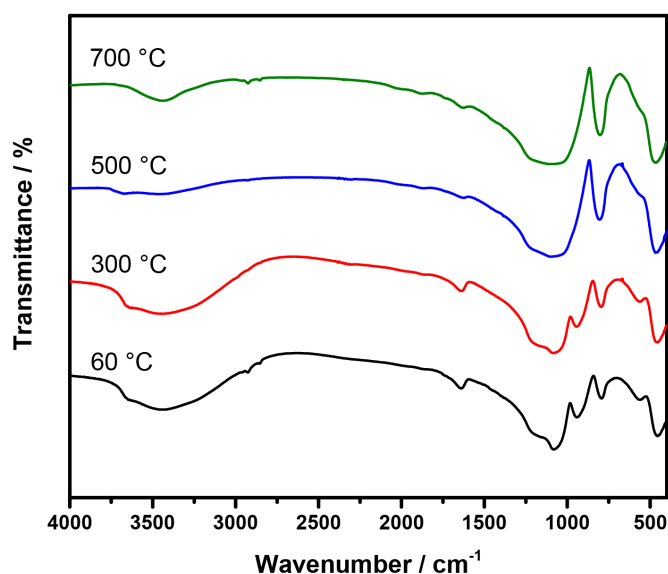


Figure 1. FTIR spectra of sample $5\text{Al}_2\text{O}_3:\text{Eu}^{3+}@95\% \text{SiO}_2$ annealed at a temperature range of 60°C to 700°C .

(SiOH) and $\text{Si}(\text{OC}_2\text{H}_5)$ at 960 and 585 cm^{-1} disappear in the spectra at 500 and 700°C . This phenomenon can be attributed to the complete hydrolysis of ethoxy groups ($\text{Si}(\text{OC}_2\text{H}_5)$) to silanol groups and from silanol to siloxane groups.

3.2. Photoluminescence Characterization of $\text{Al}_2\text{O}_3:\text{Eu}^{3+}@ \text{SiO}_2$ Composites

The luminescent properties of $\text{Al}_2\text{O}_3:\text{Eu}^{3+}@ \text{SiO}_2$ composite powders were evaluated. At first, the light emission properties of the composites were analyzed as a function of the weight quantity as depicted in **Figure 2**. The samples were excited at a wavelength of 280 nm . The main emission peak at 613 nm can be ascribed to the transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, and the emissions at 577 , 592 and 650 nm correspond to the transitions ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ respectively [22]. From the spectra, it is observed that the bare $\text{Al}_2\text{O}_3:\text{Eu}^{3+}$ sample show the maximal emission intensity. When silica is incorporated to the alumina powders to form the composite powders, the emission decreases in half for all the samples: Al/Si equal to 13/87, 11/89, 9/91, 7/93 and 5/95. Thus, even with a higher concentration of 95 w% the emission intensity is kept. Besides, with the addition of silica, a broad band centered at 440 nm appears but the intensity emission is poor because the samples were excited at 280 nm . Besides, with the addition of silica, a broad band centered at 440 nm appears but the intensity emission is poor because the adequate excitation for Al_2O_3 is at 350 nm . It is an excellent approach to reduce the cost and obtain a bigger quantity of luminescent material.

On the other hand, by varying the excitation wavelength from 270 to 340 nm , the intensity emission of the composite powders of the sample 5/95 is highly affected (**Figure 3**). For instance, when the sample is excited at 270 nm the intensity at 610 nm is the more intense, but as the wavelength increases to 290 to 310 and

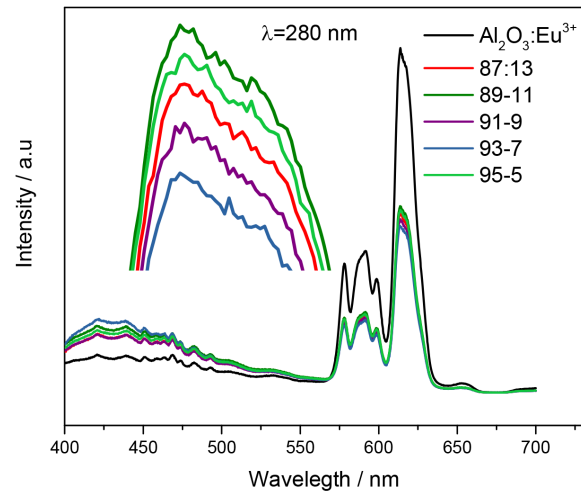


Figure 2. Emission spectra of $\text{Al}_2\text{O}_3:\text{Eu}^{3+}@\text{SiO}_2$ as function of SiO_2 concentration.

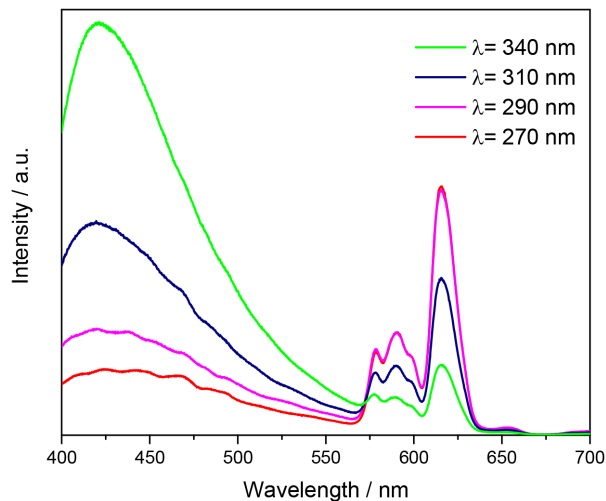


Figure 3. Emission spectra of $\text{Al}_2\text{O}_3:\text{Eu}^{3+}@\text{SiO}_2$ powder excited at different wavelengths.

340 nm, this transition is highly reduced. Nevertheless, as wavelength increases, the silica shows a broader and a higher emission intensity. Thus, it is possible that controlling the intensity ratio between the blue from silica and red from $\text{Al}_2\text{O}_3:\text{Eu}^{3+}$, the emission color changes from red to magenta to white to blue as wavelength increases from 280 to 340 nm.

Figure 3 shows the emission intensity of sample 5:95 excited at 280, 310 and 340 nm. When the composite powders are excited at 270 nm, the europium transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ (where $J = 0, 1, 2, 3$) are more intense and a low intense broadband covering the blue region is observed. However, when the sample is excited at 310 nm the blue emission centered at 440 nm is increased but the red emission is reduced. The same tendency is shown when the sample is excited at 340 nm.

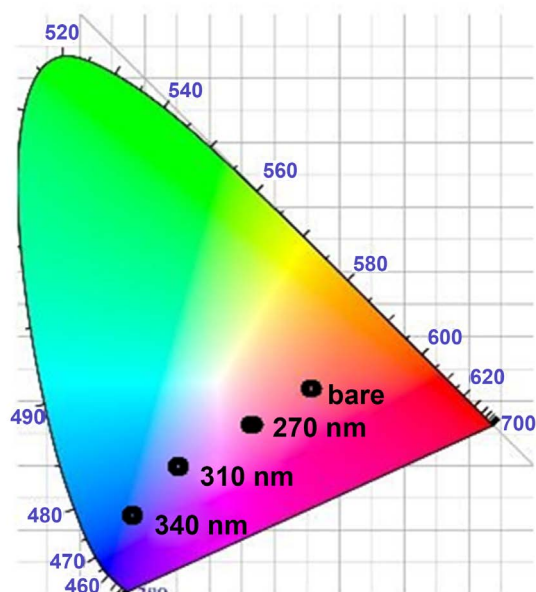


Figure 4. CIE diagram of Al₂O₃:Eu³⁺@SiO₂ by varying wavelength excitation.

Table 1. Optical properties of the composites excited at various wavelengths.

λ_{exc}	x	y	color	I_{blue}/I_{red}
270	0.38	0.27	Near white	0.4
310	0.29	0.22	Cyan	1.3
340	0.19	0.13	Blue	5.7

Figure 4 shows the CIE coordinates of sample 5:95 excited at 270, 310 and 340 nm, in addition, the pure Al₂O₃:Eu³⁺ CIE coordinates are put as a comparison. For pure Al₂O₃:Eu³⁺ powders, a red emission is obtained because of the main ⁵D₀→⁷F₂ transitions from Eu³⁺. By exciting the composite powders at 270 nm, the intensity ratio, $I_{blue}/I_{red} = 0.4$ and the emission is a white near color with CIE coordinates about $x = 0.34$, $y = 0.27$. The europium transition is more intense than the broad band centered at 440 nm covering the blue region. However, when the sample is excited at 310 and 340 nm the blue emission centered at 440 nm is highly increased, giving $I_{blue}/I_{red} = 5.7$ with an excitation of 340 nm.

The **Table 1** shows the optical properties of the composite powders. As can be seen, different color emission can be obtained as a function of wavelength. For the bare Al₂O₃:Eu³⁺ sample, the transition ⁵D₀→⁷F₂ gives a strong band at 613 nm (red emission) while increasing the wavelength excitation to 310 and 340 the emission intensity decreases.

4. Conclusion

Europium doped alumina powders embedded in a silica matrix with different weight ratios from 13Al/87Si to 5Al/95Si were successfully obtained by the sol-gel

method. The emission intensity for all samples synthesized was kept similar, proving it is possible to use very high concentration of inert SiO₂ matrix without loss the optical properties of Al₂O₃:Eu³⁺. The composite powders exhibited luminescent properties in the red, white and blue region of the visible spectra. In the case of near white emission, the computed CIE coordinates were ($x = 0.38$, $y = 0.27$) which was a function of the intensity ratio, $I_{\text{blue}}/I_{\text{red}} = 0.4$. Finally, by FTIR spectroscopy, it is determined that the complete transformation of TEOS molecules to amorphous SiO₂ is reached at 500°C.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Bünzli, J.C.G. (2016) Light Conversion: Lanthanide-Containing Systems. In: *Reference Module in Materials Science and Materials Engineering*, Elsevier, Amsterdam. <https://doi.org/10.1016/B978-0-12-803581-8.01855-5>
- [2] Romero, V.H., De la Rosa, E., Salas, P. and Velázquez-Salazar, J.J. (2012) Strong Blue and White Photoluminescence Emission of BaZrO₃ Undoped and Lanthanide Doped Phosphor for Light Emitting Diodes Application. *Journal of Solid State Chemistry*, **196**, 243-248. <https://doi.org/10.1016/j.jssc.2012.06.026>
- [3] Wolfbeis, O.S. (2015) An Overview of Nanoparticles Commonly Used in Fluorescent Bioimaging. *Chemical Society Reviews*, **44**, 4743-4768. <https://doi.org/10.1039/C4CS00392F>
- [4] Li, Z., Zhang, Y., La, H., Zhu, R., El-Banna, G., Wei, Y. and Han, G. (2015) Upconverting NIR Photons for Bioimaging. *Nanomaterials*, **5**, 2148-2168. <https://doi.org/10.3390/nano5042148>
- [5] Sivakumar, S., Diamante, P.R. and van Veggel, F.C.J.M. (2006) Silica-Coated Ln³⁺-Doped LaF₃ Nanoparticles as Robust Down- and Upconverting Biolabels. *Chemistry—A European Journal*, **12**, 5878-5884. <https://doi.org/10.1002/chem.200600224>
- [6] Li, C., Quan, Z., Yang, J., Yang, P. and Lin, J. (2007) Highly Uniform and Monodisperse β -NaYF₄:Ln³⁺ (Ln = Eu, Tb, Yb/Er, and Yb/Tm) Hexagonal Microprism Crystals: Hydrothermal Synthesis and Luminescent Properties. *Inorganic Chemistry*, **46**, 6329-6337. <https://doi.org/10.1021/ic070335i>
- [7] Gao, Y., Fan, M., Fang, Q. and Yang, F. (2014) Uniform Lu₂O₃ Hollow Microspheres: Template-Directed Synthesis and Bright White Up-Conversion Luminescence Properties. *New Journal of Chemistry*, **38**, 146-154. <https://doi.org/10.1039/C3NJ00913K>
- [8] Liu, Y., Luo, W., Zhu, H. and Chen, X. (2011) Optical Spectroscopy of Lanthanides Doped in Wide Band-Gap Semiconductor Nanocrystals. *Journal of Luminescence*, **131**, 415-422. <https://doi.org/10.1016/j.jlumin.2010.07.018>

- [9] Irfanullah, M., Sharma, D.K., Chulliyil, R., Layek, A., De, S. and Chowdhury, A. (2017) Heterogeneity in Optical Properties of near White-Light Emissive Europium Complex Species Revealed by Spectroscopy of Single Nanoaggregates. *Chemical Physics Letters*, **667**, 247-253. <https://doi.org/10.1016/j.cplett.2016.10.065>
- [10] Nogami, M. and Abe, Y. (1996) Properties of Sol—Gel-Derived Al₂O₃-SiO₂ Glasses Using Eu³⁺ Ion Fluorescence Spectra. *Journal of Non-Crystalline Solids*, **197**, 73-78. [https://doi.org/10.1016/0022-3093\(95\)00621-4](https://doi.org/10.1016/0022-3093(95)00621-4)
- [11] Nogami, M., Kawaguchi, T. and Yasumori, A. (2001) Spectral Hole Burning of Eu³⁺-Doped Al₂O₃-SiO₂ Glass Prepared by Melt Quenching. *Optics Communications*, **193**, 237-244. [https://doi.org/10.1016/S0030-4018\(01\)01228-7](https://doi.org/10.1016/S0030-4018(01)01228-7)
- [12] Nogami, M., Nagakura, T. and Hayakawa, T. (2000) Site-Dependent Fluorescence and Hole-Burning Spectra of Eu³⁺-Doped Al₂O₃-SiO₂ Glasses. *Journal of Luminescence*, **86**, 117-123. [https://doi.org/10.1016/S0022-2313\(99\)00601-8](https://doi.org/10.1016/S0022-2313(99)00601-8)
- [13] Klein, L.C. (1985) Sol-Gel Processing of Silicates. *Annual Review of Materials Science*, **15**, 227-248. <https://doi.org/10.1146/annurev.ms.15.080185.001303>
- [14] Stöber, W., Fink, A. and Bohn, E. (1968) Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range. *Journal of Colloid and Interface Science*, **26**, 62-69. [https://doi.org/10.1016/0021-9797\(68\)90272-5](https://doi.org/10.1016/0021-9797(68)90272-5)
- [15] Zhai, J., Tao, X., Pu, Y., Zeng, X.-F. and Chen, J.-F. (2010) Core/Shell Structured ZnO/SiO₂ Nanoparticles: Preparation, Characterization and Photocatalytic Property. *Applied Surface Science*, **257**, 393-397. <https://doi.org/10.1016/j.apsusc.2010.06.091>
- [16] Panigrahi, S., Bera, A. and Basak, D. (2011) Ordered Dispersion of ZnO Quantum Dots in SiO₂ Matrix and Its Strong Emission Properties. *Journal of Colloid and Interface Science*, **353**, 30-38. <https://doi.org/10.1016/j.jcis.2010.09.055>
- [17] Wang, X., Zhou, S. and Wu, L. (2013) Facile Encapsulation of SiO₂ on ZnO Quantum Dots and Its Application in Waterborne UV-Shielding Polymer Coatings. *Journal of Materials Chemistry C*, **1**, 7547-7553. <https://doi.org/10.1039/c3tc31479k>
- [18] Raevskaya, A.E., Panasiuk, Y.V., Stroyuk, O.L., Kuchmiy, S.Y., Dzhagan, V.M., Millekhin, A.G., Yeryukov, N.A., Sveshnikova, L.A., Rodyakina, E.E., Plyusnin, V.F. and Zahn, D.R.T. (2014) Spectral and Luminescent Properties of ZnO-SiO₂ Core-Shell Nanoparticles with Size-Selected ZnO Cores. *RSC Advances*, **4**, 63393-63401. <https://doi.org/10.1039/C4RA07959K>
- [19] Reyes Miranda, J., García Murillo, A., Carrillo Romo, F.J., Oliva Uc, J., Flores Sandoval, C.A., Morales Ramírez, A.J., Velumani, S., de la Rosa Cruz, E. and Garibay Febles, V. (2014) Synthesis and Optical Properties of BaTiO₃:Eu³⁺@SiO₂ Glass Ceramic Nano Particles. *Journal of Sol-Gel Science and Technology*, **72**, 435-442. <https://doi.org/10.1007/s10971-014-3480-8>
- [20] Socrates, G. (2001) Infrared and Raman Characteristics Group Frequencies. John Wiley & Sons, Hoboken.
- [21] Catauro, M., Dell'Era, A. and Vecchio Cipriotti, S. (2016) Synthesis, Structural, Spectroscopic and Thermoanalytical Study of Sol-Gel Derived SiO₂-CaO-P₂O₅ Gel and Ceramic Materials. *Thermochimica Acta*, **625**, 20-27. <https://doi.org/10.1016/j.tca.2015.12.004>
- [22] Mariscal, A., Quesada, A., Camps, I., Palomares, F.J., Fernández, J.F. and Serna, R. (2016) Tuning Eu³⁺ Emission in Europium Sesquioxide Films by Changing the Crystalline Phase. *Applied Surface Science*, **374**, 71-76. <https://doi.org/10.1016/j.apsusc.2015.09.183>