

## Conditioning of Minor Actinides in Monazite-type Ceramics

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**Abstract** – Monazite-type ceramics are promising candidates for the conditioning of minor actinides. Monazite ( $\text{LaPO}_4$ ) was prepared by hydrothermal synthesis and its hydrated form ( $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$ ) was synthesised by co-precipitation. The first characterisation results, structural and morphological combined with thermal behaviour and physical properties, are presented.

### A. INTRODUCTION

Plutonium and the minor actinides (MA) neptunium, americium and curium are mainly responsible for the long-term radiotoxicity of the high active waste (HAW) generated during nuclear power operation. If these long-lived radionuclides are removed from the HAW by partitioning and converted by neutron fission (transmutation) into shorter-lived or stable elements, the remaining waste loses most of its long-term radiotoxicity. Thus, partitioning and transmutation (P&T) are considered as attractive options for reducing the burden on geological disposals. As an alternative, these separated MAs can also be conditioned (P&C strategy) in specifically adapted ceramics to ensure their safe final disposal over long periods of time.

At the moment, spent fuel elements are foreseen either for direct disposal in deep repositories, while the highly reactive liquid waste produced during reprocessing must be conditioned industrially using a vitrification process before final disposal. Although the widely used borosilicate glasses meet most of the specifications for a mixture of radionuclides comprising up to 40 elements, ceramic matrices appear to be even more suitable in terms of the solubility of certain radionuclides (e.g. separated americium) and resistance to leaching and radiation. The development of new materials based on tailor-made highly specific ceramics with extremely stable behaviour would make it possible to improve the final storage of long-lived high-level radiotoxic waste.

Because of the increasing need for the immobilization of large quantities of HLW, there is, however, a strong motivation to reconsider many of the alternative types of wasteform and to identify new candidate materials, such as alternative glass compositions, glass-ceramic materials, and ceramics. These materials should be able to condition specific fission products or minor actinides after their partitioning. The research on crystalline ceramic waste forms as hosts for selected actinides (Am, Cm, Np and Pu) and mobile fission products (I, Cs), is done on different components: synroc, perovskite, zirconolite, zircon, zirconates, pyrochlore and monazite, among others ceramics [1; 2].

Owing to their good properties, e.g. irradiation resistance and chemical durability, monazite-type ceramics have been chosen in this study as promising host matrices for the conditioning of tri- and tetravalent actinides [3].

$REPO_4$  ceramics are named after their natural mineral analogue: monazite for  $RE = \text{La to Gd}$  (monoclinic structure) and xenotime for  $RE = \text{Tb to Lu and Y}$  (tetragonal structure).

To avoid radioactive dust formation, synthesis routes like conventional solid state reaction are not advisable. Thus wet chemical routes such as hydrothermal synthesis and precipitation were chosen within our recent research. Structural and morphological results applying XRD and SEM are presented here combined with thermal behaviour and physical properties.

### B. MONAZITE AND RHABDOPHANE

Wet-chemical methods were applied in this work for the preparation of  $\text{LaPO}_4$  and  $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$ . Monazite samples were prepared by hydrothermal synthesis. This fabrication process partly followed that described by Meyssamy [4]. Rhabdophane ( $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$ ) powders were synthesised by

precipitation from lanthanum–citrate chelate solution (La–Cit) and phosphoric acid. This process was partially adapted from the route described by Boakye et al. [5].

After the synthesis, the thermal behaviour of the dried powders was investigated from room temperature up to 1000°C by thermogravimetry (TG) coupled with differential scanning calorimetry analysis (DSC) in air atmosphere with a heating rate of 10 K/min. Figure 1 shows the comparison of the TG-DSC measurements for monazite ( $\text{LaPO}_4$ ) and rhabdophane ( $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$ , at pH=5 after washing). The mass loss of the monazite sample is about 4% while the one of the rhabdophane is about 10% after a thermal treatment up to 1000°C. This difference is partly caused by the residual crystal water contained in the rhabdophane structure.

For both powders a broad endothermic peak is observed between 100 and 200°C, which can be explained by the elimination of adsorbed gas and residual water. For the rhabdophane powder, an additional endothermic peak at ~270°C is observed which is linked to the elimination of the 0.5 mol of the crystal water.

The broad exothermic peak between 600 and 800°C belongs to the phase transformation from hexagonal to monoclinic (from rhabdophane to monazite) structure. Naturally, this peak does not appear on the monazite plot (magenta plot).

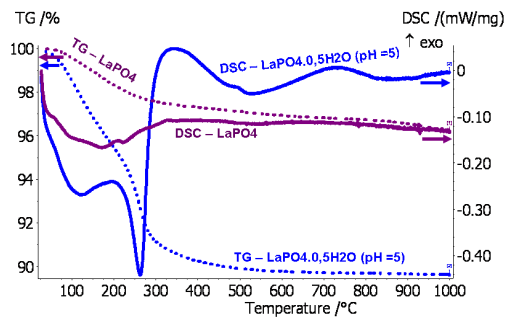


Figure 1 : TG-DSC measurements of monazite and rhabdophane (washed until pH=5) powders.

Figure 2 shows the X-ray diffraction patterns of the dried monazite (left) and rhabdophane (right) powders. The XRD result of the monazite ( $\text{LaPO}_4$ ) sample confirms that the phase is pure. After calcination of the rhabdophane powder at 1000°C, XRD results show the similitude of the monazite (light blue) and the calcined rhabdophane (dark blue). The hexagonal to monoclinic phase transformation occurs. The FWHM (full width at half maximum) decreased for the 1000°C-calcined rhabdophane due to beginning of the material recrystallization. The diffractogram of rhabdophane powder also confirms the purity of this phase just after the precipitation.

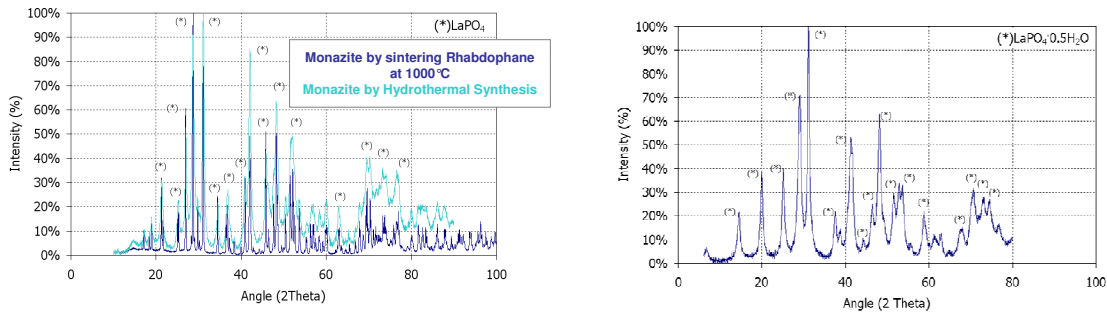
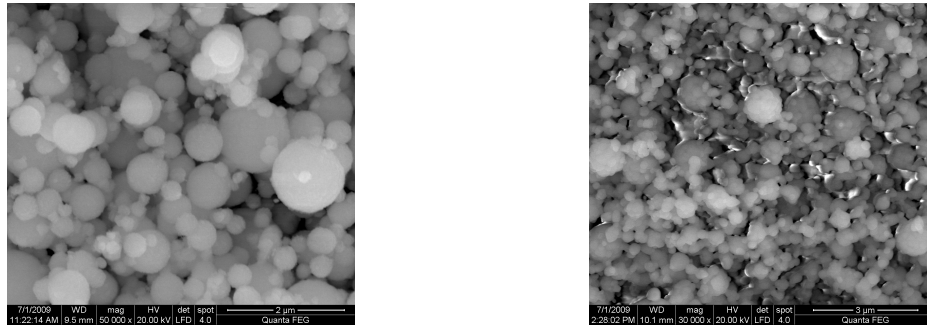


Figure 2: XRD patterns of monazite obtained after hydrothermal synthesis and by calcination of rhabdophane (left). XRD of rhabdophane for comparison (right).

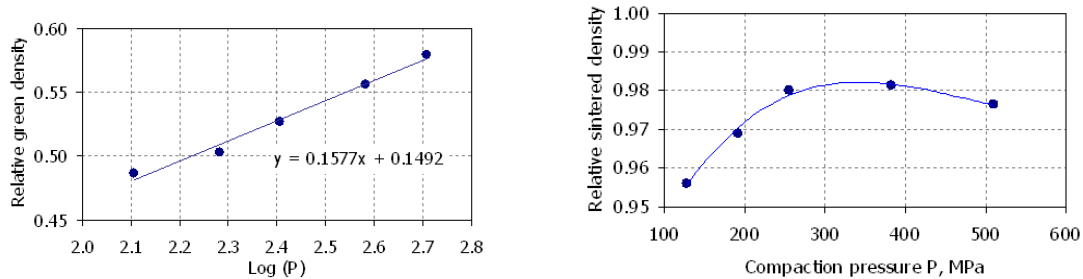
The morphology of the powder was studied with scanning electron microscopy (SEM) as shown in Figure 3. The rhabdophane particles were round and their diameter sizes is between 0.1 and 2 µm.

The rhabdophane particles consolidate together during a heating process at 1000°C. This is the beginning of the sintering process. The comparison between the left and the right photo in Figure 3 shows significantly the beginning of the densification.



**Figure 3: SEM images of LaPO<sub>4</sub>·0.5H<sub>2</sub>O sample (left) and of calcined (1000°C) LaPO<sub>4</sub>·0.5H<sub>2</sub>O sample (right).**

The investigated powders were compacted by cold uniaxial pressing, applying pressures between 130 and 510 MPa. The pellets were made by powder synthesised by hydrothermal synthesis. The relative green density and the relative sintered density both depend on the applied pressure (see Figure 4). The results of the relative green density in relation to the logarithm of the pressure show that the values form a linear function. This is typical behaviour for ceramic materials [6]. After the sintering at 1400°C, the relative sintered density of the pellets was determined by Archimedes method, i.e. by hydrostatic weighing in water (see Figure right). The value of the pressure related to the maximal density - optimal pressure - is between 250 and 400 MPa. The sintered density at this optimal pressure is above 98% of theoretical density.



**Figure 4: Compressibility curve for monazite powders (left) and relative sintered density of monazite pellets, as a function of compaction pressure (right).**

### C. CONCLUSION AND OUTLOOK

Monazite-type ceramics, as a promising candidate for the conditioning of minor actinides, were studied in this work. Monazite (LaPO<sub>4</sub>) and Rhabdophane (LaPO<sub>4</sub>·0.5H<sub>2</sub>O) powders were prepared by wet hydrothermal synthesis and by co-precipitation. The thermal analysis and XRD show that the monazite powders are already crystalline after synthesis and subsequent drying, whereas the Rhabdophane crystallizes at temperatures over 800°C to the monoclinic monazite structure. On the base of the synthesised monazite powder, pellets with a 98% of the theoretical density were prepared by cold pressing and sintering.

In order to simulate actinide integration into the lattice structure of the monazite-type matrix, lanthanide-doped monazite/xenotime matrices, La<sub>(1-x)</sub>Ln<sub>x</sub>PO<sub>4</sub> (Ln = Nd, Eu, Gd or Er, x = 0.10 to 1.00) have been synthesised, but have yet to be characterised. The full characterisation of the ceramic compounds is in progress and it is foreseen to study also the behaviour of immobilized actinides, such as americium and curium.

Primary focus of this work is the study of the thermodynamic properties of the solid matrices. Additionally the corrosion behaviour of synthetic ceramics will be investigated in detail on an atomic basis. To this end, the ceramics will be subjected to leach tests under conditions of relevance for final

repositories. The second essential parameter describing the stability of the host phases is the resistance to radiolysis. Radiation damage to the monazite type ceramics will be induced either by direct doping with radioactive nuclides or by means of ion bombardment.

## Aknowledgements

This work is supported by the Ministerium für Innovation, Wissenschaft, Forschung und Technologie des Landes (MIWFT) Nordrhein-Westfalen; AZ: 323-005-0911-0129.

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