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Studies on thermal and mechanical properties of monazite-type ceramics for the conditioning of minor actinides

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ABSTRACT

Lanthanum and europium phosphates with various La/Eu ratios were synthesised using the wet-chemical microwave-assisted hydrothermal method. The thermal behaviour of the (La, Eu)PO_4 powders was investigated by thermogravimetric analysis coupled with differential scanning calorimetry (TG-DSC) and X-ray diffraction (XRD). Pelletisation of the phosphates was performed using uniaxial hot pressing at a sintering temperature of 1350 °C. The sintering density for all five compositions reached 98% of the theoretical density. According to XRD data, single-phase solid solutions were obtained in all cases. The physical properties of these pellets were studied. The mechanical properties (microhardness and fracture toughness) of the pellets were observed to be linearly dependent on the europium content.

1. Introduction

The disposal of high-level radioactive waste is one of the most pressing challenges of the 21st century. With respect to long-term safety aspects of geological disposal, actinide elements are of particular concern due to their long half-lives and high radiotoxicity (Baetsle and De Raedt, 1997; Westlen, 2007).

Ceramic waste forms for the immobilisation of actinides have been investigated extensively over the last few decades because they appear to have certain advantages over other waste forms (incl. borosilicate glasses and spent fuel) for the disposal of specific waste streams (Lumpkin, 2006; Weber et al., 2009; Clavier et al., 2011; Schlenz et al., 2013; Boatner, 2002; Dacheux et al., 2013).

Monazite ceramics ($LnPO_4$, Ln = La − Gd) are promising materials for potential nuclear waste forms. They can be used to condition minor actinides, such as Am and Cm, due to properties such as high loading, high chemical stability and irradiation resistance (Lumpkin, 2006; Weber et al., 2009; Clavier et al., 2011; Schlenz et al., 2013; Boatner, 2002; Dacheux et al., 2013). Monazites are also attractive from a geochemical point of view because they are the most abundant lanthanide phosphates present observed in natural samples (Förster, 1998; Cuney and Mathieu, 2000). In addition, they can contain significant amounts of natural radioelements, such as Th and U, for several hundred millions of years without suffering amorphisation due to radiation damages (Cuney and Mathieu, 2000; Boatner, 2002; Montel et al., 1996). However, systematic investigations on mixed solid solution series are scarce in the literature.

This work focuses on the thermal and mechanical properties of lanthanum phosphates, $La_{(1-)}Eu_xPO_4$ (x = 0.0, 0.2, 0.5, 0.8, 1.0), with monazite structure and the partial or full exchange of lanthanum with europium − an inactive surrogate for the minor actinides. Physical properties such as microhardness and fracture toughness are important for the characterisation of the quality of compact materials and they help to describe and to understand crack formation caused by swelling processes due to He evolution during α-decay.

2. Materials and methods

Powders of nominal composition $La_{(1-x)}Eu_xPO_4$ (x = 0.0, 0.2, 0.5, 0.8, 1.0) were synthesised via a microwave-assisted hydrothermal method, described by Meyssamy et al. (1999). As starting materials, $La(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar), $Eu(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar), NaOH (GPR RECTAPUR) and $(NH_4)_2HPO_4$ (Merck) of analytical grade were used. Fig. 1 shows the flow sheet for the process of powder synthesis with subsequent pelletisation.

The first synthesis step was the precipitation of rare earth element (REE) hydroxides according to Reaction {1}. Certain amounts of the REE metal salts depending on the envisaged composition were dissolved in deionised water. As a precipitation reagent, 1 M NaOH was used. The hydroxides were transformed into mixed REE phosphates using diammonium hydrogen phosphate and hydrothermal conditions. The final pH was adjusted to

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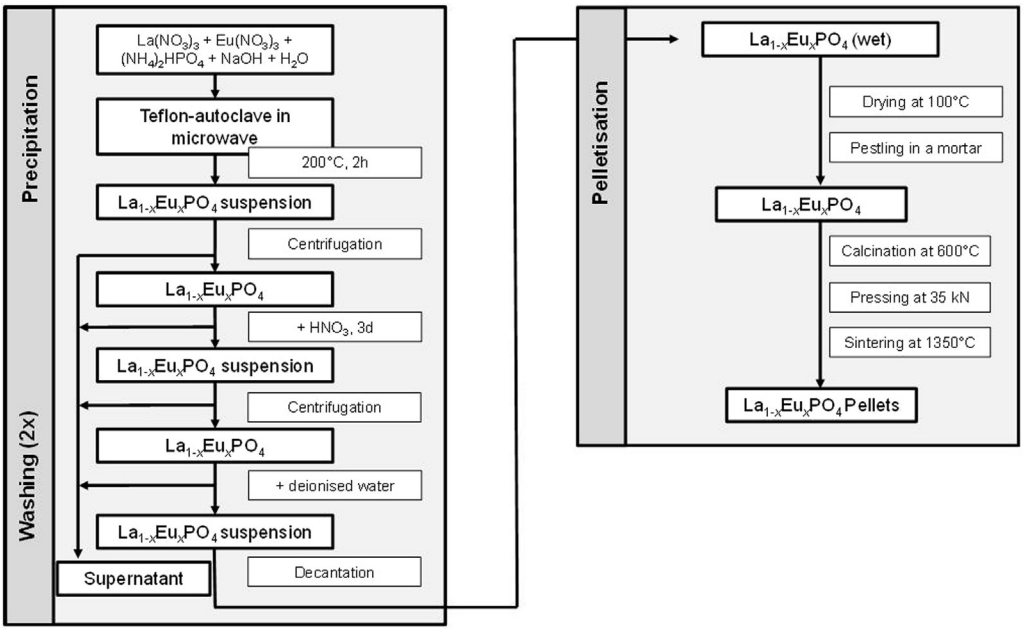

Fig. 1. Flow sheet for the process of $La_{(1-x)}Eu_xPO_4$-powder synthesis with subsequent pelletisation.

pH = 10.5 by adding drops of 4 M NaOH solution, and the resulting mixture was poured into Teflon autoclaves and treated in the microwave (MLS GmbH) at 200 °C for 2 h (vapour pressure over water $P \approx 11$ bar), according to Reaction {2}.

Reaction {1}: $(1-x)\ La(NO_3)_3 + x\ Eu(NO_3)_3 + 3\ NaOH \rightarrow (1-x)\ La(OH)_3 + x\ Eu(OH)_3 + 3\ NaNO_3$

Reaction {2}: $(1-x)\ La(OH)_3 + x\ Eu(OH)_3 + (NH_4)_2HPO_4 \rightarrow La_{(1-x)}Eu_xPO_4 + 2\ NH_4OH + H_2O$

The precipitate was centrifuged (10,000 rpm, 10 min), and transferred to a beaker with HNO_3 ($C = 0.1$ M). The pH was adjusted to pH = 1 by adding 1 M HNO_3 solution. The suspension was mixed with a magnetic stirrer for 3 days at room temperature to dissolve possible unreacted lanthanum and/or europium hydroxide.

The precipitate was centrifuged again and transferred to a beaker containing 100 mL of deionised water, and the suspension was stirred for 30 min. The washing step was repeated three to five times until the supernatant was free of nitrate ions (NO_3^- test strips).

Since the powder often still contains small amounts of impurities, a calcination step was necessary. After washing, the powders were dried in an oven at 100 °C for 12 h. The dried powders were ground in an agate mortar to increase the surface area, thereby facilitating the decomposition and diffusion of impurities. The milled powders were calcined for 2 h at 600 °C. Then, the powders were finely ground in a mortar. Green powders obtained after calcination were pelletised in a cold uniaxial press with 35 kN, and finally uniaxially hot pressed. The maximum compacting pressure for hot pressing was 50 MPa, and the sintering temperature was 1350 °C. The hot-pressing process was carried out in nitrogen atmosphere because graphite pressing tools were used.

2.1. Characterisation

Thermogravimetric analysis (TG) coupled with differential scanning calorimetry (DSC) was performed using the thermoanalyser Netzsch STA 449C Jupiter in the temperature range 100–1150 °C with a heating rate of 10 °C min^{-1}.

Qualitative phase analysis was carried out by X-ray diffraction (XRD) using the diffractometer D4 Endeavor Bruker AXS GmbH with a θ–2θ geometry, operating at 50 kV and 30 mA with a CuK_α radiation ($\lambda = 1.5418$ Å) in the range $2\theta = 10$–130°. The analysis of the diffractograms was performed using the software "Match" (version 1.10) from Crystal Impact.

The lattice parameters were determined using the program Topas version 4.2 from Bruker AXS GmbH. The unit cell volume V was calculated from the lattice parameters.

2.2. Mechanical properties

Microhardness was studied with a Vickers diamond indenter (Anton Paar MHT 10). The investigated pellets were thoroughly polished with diamond paste ($d = 1$ μm). The polishing process was controlled with an optical microscope. Then, the pellets were thermally etched at 1000 °C for 2 h. The thoroughly polished and thermally etched surface was indented with a loading force of 0.5–3.5 N to determine the optimal loading force. The full indentation load was applied for 10 s. For each indenting force, ten measurements were performed. Based on these measurements, values were determined for the average microhardness, fracture toughness and their experimental dispersions.

Microhardness (H_V, GPa) was calculated using the following formula (Munz and Fett, 1999):

$$H_V = 18.544 \cdot \frac{F}{d_c^2} \quad (1)$$

where F (N) is the applied load, d_c (μm) is the average length of the diagonal of the Vickers indenter.

The fracture toughness K_{1c} (MPa $m^{1/2}$) was determined using the Anstis equation as recommended by Munz and Fett (1999):

$$K_{1c} = 0.032 H_v \cdot \left(\frac{d_c}{2}\right)^{0.5} \cdot \left(\frac{E}{H_V}\right)^{0.5} \cdot \left(\frac{2c_L}{d_c}\right)^{-1.5} \quad (2)$$

where c_l (μm) is the average length of the cracks and E (GPa) is the Young's modulus. The Young's modulus of $LaPO_4$ and $EuPO_4$ was