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The effect of the synthesis route of monazite precursors on the microstructure of sintered pellets

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ABSTRACT

The influence of synthesis route on morphology of $La_{0.5}Eu_{0.5}PO_4$ monazite precursor and the microstructure of pellets after sintering have been investigated. $La_{0.5}Eu_{0.5}PO_4$ precursor materials were synthesised by hydrothermal precipitation in acidic (pH 1) and basic (pH 10.5) media as well as by co-precipitation in acidic media (pH 1) forming needle-like, spherical and rice-shaped particles, respectively. A phase transition from rhabdophane to monazite was observed only for the hydrothermally precipitated precursors at 600–800 °C by TG-DSC. After conventional sintering, all $La_{0.5}Eu_{0.5}PO_4$ powders were found to be single-phase solid solutions with a monazite structure by PXRD and Raman measurements. From microscopic (SEM) and density investigations, it was ascertained that the synthesis route significantly influences the morphology of the precursor material and the microstructure of the sintered pellets. The needle-like materials seem to be the most promising precursor for nuclear waste application since pellets with a density of ~92.5% TD and intragranular closed porosity are formed during sintering which can serve as cavities to compensate He built up and therefore avoid swelling and crack formation during long-term storage in a repository.

1. Introduction

Phosphate-based ceramics ($LnPO_4$, Ln = La – Gd) with a monazite structure are considered as promising nuclear waste forms for the conditioning of trivalent actinides such as Am(III), Cm(III) and Pu(III). The incorporation of these elements on lattice sites of the monazite structure allows high loading rates and offers certain advantages over other waste forms (incl. borosilicate glasses and spent fuel) in terms of long-term stability including chemical durability and irradiation resistance (Dacheux et al., 2013; Lumpkin, 2006; Schlenz et al., 2013; Weber et al., 2009).

These outstanding properties of the monazite materials are proven by natural analogues. From a natural point of view, monazite is known to be a metamorphic mineral, i.e. which is formed from the alteration of other phases (such as apatites or pelitic rocks) by hydrothermal fluids (Wing et al., 2003; Kohn and Malloy, 2004; Harlov et al., 2005). Monazite is the most abundant lanthanide phosphate found in natural samples (Cuney and Mathieu, 2000; Förster, 1998). It appears in granites, gneisses and pegmatites (Boatner, 2002) as well as in alluvial deposits and beach sands.

Natural monazite minerals can contain up to 27 wt% natural radioelements, such as tetravalent Th and U and trivalent ^{228}Ac as a daughter product from the ^{232}Th series, for several hundred millions of years without suffering from amorphisation due to radiation damages (Boatner, 2002; Cuney and Mathieu, 2000).

Besides radiation tolerance the outstanding chemical resistance of natural monazites demonstrates the long-term stability of these materials. For instance, recent studies on natural monazites which have been exposed to weathering since several hundred millions of years show significant modifications due to mechanical abrasion but not due to chemical alteration (Montel et al., 2011).

Synthetic monazites have been investigated extensively in recent decades with a focus on their structure, dissolution behaviour and response to ionising radiation (Brandt et al., 2014; Clavier et al., 2011; Ewing et al., 1995; Heuser et al., 2014; Nasdala et al., 2010; Ni et al., 1995; Oelkers and Poitrasson, 2002). Chemical durability is one of the most important properties for the long-term

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stability of a ceramic waste form since immobilised radionuclides may be dissolved out of the waste matrix and migrate into the geo- and biosphere if the waste matrix comes into contact with groundwater. Migration can occur in the aqueous phase or for strongly sorbing radionuclides associated on mobile solid colloids or nanoparticles (Kretzschmar and Schäfer, 2005; Schäfer et al., 2012). The dissolution behaviour of ceramic materials depends on several parameters, such as composition, homogeneity, crystallinity, and microstructure of the waste matrix, the pH, temperature, ion strength as well as the composition of the aqueous environment (Claparede et al., 2011; Horlait et al., 2012; Szenknect et al., 2012). As instance, recent results from geochemical modelling calculations using modelling tool Geochemist's Workbench® indicate that trace components such as fluorine may affect the aqueous *Ln*-speciation scheme and *Ln*-solubility distinctively (Deissmann et al., 2015). However, the impact of the synthesis route on the microstructure and hence on the dissolution behaviour of the ceramic waste form is often neglected.

The present work focuses on the effect of the synthesis route on morphology of $La_{0.5}Eu_{0.5}PO_4$ monazite precursors and on the microstructure of sintered pellets, where europium serves as a non-radioactive surrogate for trivalent actinides.

2. Materials and methods

2.1. Synthesis

Lanthanum-europium phosphates were synthesised by three various synthesis methods in order to obtain powders with different particle morphologies. As starting materials, $La(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar), $Eu(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar), NH_4OH (GPR RECTAPUR), HNO_3 (Merck), and H_3PO_4 (Merck) of analytical grade were used without additional purification.

2.1.1. Hydrothermal precipitation in basic conditions (HTS-10.5)

$La_{0.5}Eu_{0.5}PO_4$-powder was synthesised hydrothermally at pH 10.5 according to Meyssamy et al., 1999. The precursor material is prepared using a two-stage method that can be described as follows:

$$1)\ 0.5\ La(NO_3)_3 + 0.5\ Eu(NO_3)_3 + 3\ NH_4OH \rightarrow 0.5\ La(OH)_3 + 0.5\ Eu(OH)_3 + 3\ NH_4NO_3$$

$$2)\ 0.5\ La(OH)_3 + 0.5\ Eu(OH)_3 + (NH_4)_2HPO_4 \rightarrow La_{0.5}Eu_{0.5}PO_4 + 2\ NH_4OH + H_2O$$

In the first synthesis step, lanthanide hydroxides were precipitated from 0.5 M aqueous solution of nitrates using NH_4OH. The hydroxides were transformed into mixed lanthanide phosphates using $(NH_4)_2HPO_4$ and hydrothermal conditions. In this aim, the final pH was adjusted to 10.5 by adding drops of 25% NH_4OH solution, and the resulting mixture was poured into Teflon-lined steel autoclaves (Parr instruments) and treated at 200 °C for 2 h ($p \approx 35$ bar).

After centrifugation (10,000 rpm, 10 min), the powder was stirred at pH 1 (adjusted with 1 M HNO_3) for 3 days at room temperature in order to remove lanthanum/europium hydroxide by-products.

2.1.2. Hydrothermal precipitation in acidic conditions (HTS-1)

$La_{0.5}Eu_{0.5}PO_4$-powder was also obtained by hydrothermal precipitation at pH 1 according to Meyssamy et al., 1999.

$$0.5\ La(NO_3)_3 + 0.5\ Eu(NO_3)_3 + (NH_4)_2HPO_4 \rightarrow La_{0.5}Eu_{0.5}PO_4 + 2\ NH_4NO_3 + HNO_3$$

Mixed lanthanide phosphate was precipitated from 0.5 M aqueous lanthanide nitrate solution with aqueous $(NH_4)_2HPO_4$ solution. The resulting pH of the reaction mixture was 1. Subsequently the reaction mixture was treated hydrothermally in steel Teflon-lined autoclaves at 200 °C for 2 h ($p \approx 35$ bar).

2.1.3. Synthesis by co-precipitation from acidic solution (Prec-1)

$La_{0.5}Eu_{0.5}PO_4$ powder was finally synthesised by direct precipitation in excess concentrated H_3PO_4 at 140 °C according to Schatzmann et al., 2009. 0.5 M water solution of lanthanide nitrates was slowly dropped into the heated H_3PO_4.

$$0.5\ La(NO_3)_3 + 0.5\ Eu(NO_3)_3 + H_3PO_4 \rightarrow La_{0.5}Eu_{0.5}PO_4 + 3\ HNO_3$$

All pristine precipitates from both hydrothermal methods as well as from precipitation route were centrifuged and washed by suspending them in 100 mL deionised water for 30 min in order to remove nitrates coming from the starting materials prior to thermal treatment. The washing step was repeated three to five times until the supernatant was free of nitrate ions (NO_3^- test strips).

2.2. Calcination and sintering

After washing, the powders were dried in an oven at 100 °C for 12 h. They were then milled in agate mortar and fired for 2 h at 600 °C in order to remove residues of nitrates in the case of the two hydrothermal synthesis methods or for 2 h at 800 °C. The temperature was selected based on the TG-DSC measurements (see Section 3.1).

Ground raw powders obtained after calcination at 600 °C were pelletized in a cold uniaxial press at 250 MPa, and finally sintered in a high-temperature furnace at 1450 °C for 5 h (heating and cooling rate: 3 °C min^{-1}).

2.3. Characterisation

The phase transition from precursor to monazite was investigated by thermogravimetric analysis (TG) coupled with differential scanning calorimetry (DSC) using the thermo-analyser Netzsch STA 449C Jupiter in the temperature range 100–1150 °C with a heating rate of 10 °C min^{-1}.

The green density was determined geometrically. The density of sintered pellets was measured using Archimedes principle with water as the immersion liquid at ambient temperature and with a He pycnometer (Micromeritics ACCUPYC 1340) for the determination of bulk and closed porosity, respectively.

Scanning electron microscope (SEM) observations were conducted directly on pristine powdered samples and on sintered and thermally etched (1000 °C, 4 h) pellets without prior preparation, such as metallisation, using a FEI Quanta 200 environmental scanning electron microscope (ESEM) coupled with a gaseous secondary electron detector (GSED). The high voltage ranged between 15 kV and 30 kV, and the remaining gas pressure in the chamber was 50–300 Pa. These conditions were chosen to compensate charging effects on the surface of the ceramic materials during SEM imaging. The particle size of the pristine powders, as well as the grain size of the sintered pellets was analysed using ImageJ Software. The grain size is given for elongated particles and grains as width and length combination and for the isotropic grains as average grain diameter in case of the sintered HTS-10.5 pellets. The size of the spherical particles of the as synthesised HTS-10.5 powder was not determined more precisely since the average diameter is in the nano-range according to the ESEM micrographs and literature data (Meyssamy et al., 1999).

Powder X-ray diffraction (PXRD) patterns were obtained at RT

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