



Synthesis and dissolution kinetics of zirconia based ceramics



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ABSTRACT

In this study, an ideal $\text{Nd}_2\text{Zr}_2\text{O}_7$ pyrochlore and a defect fluorite ceramic were synthesised by coprecipitation, pressing and sintering. Detailed investigations by electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) and powder X-ray diffraction (XRD) were used for the characterisation of the powders. In particular both powders were found to be single phase ceramics.

All batch and dynamic dissolution experiments were conducted in $C(\text{HCl}) = 0.1 \text{ M}$ at 90°C to compare the two types of Nd-zirconia structures and the experimental approaches. A good agreement between batch and dynamic dissolution experiments was observed for the pyrochlore with a Nd-based final dissolution rate in the range between 0.84×10^{-5} and $1.95 \times 10^{-5} \text{ g m}^{-2} \text{ d}^{-1}$. The dynamic experiments indicate a strongly incongruent preferential release of Nd from the pyrochlore ceramic at the beginning of the experiment and a close to congruent dissolution at the end of the experiment.

The dissolution behaviour of defect fluorite in dynamic experiments is observed to be very similar to the pyrochlore. An incongruent dissolution during the early stages is followed by a congruent steady state. The defect fluorite steady state dissolution rate is lower than the one determined for pyrochlore.

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1. Introduction

Plutonium and the minor actinides (MA = Am, Cm, Np) are the main contributors to the long-term radiotoxicity of spent nuclear fuel. Ceramic waste forms can be fabricated tailor-made for specific waste streams in order to improve the long-term safety compared to glass or the direct disposal of spent nuclear fuel. The major requirements for ceramic waste forms are a high chemical and thermal stability, high waste loading, chemical flexibility and high radiation resistance (Lumpkin, 2006). As a structural group, the pyrochlores $\text{A}_2\text{B}_2\text{O}_7$ meet most of these criteria. However there are differences especially regarding the radiation resistance, which strongly depends on the type of cation on the B position (Ewing, 2011). Some pyrochlore types e.g. the TiO_2 based pyrochlores become amorphous as a consequence of radiation damage, whereas ZrO_2 based pyrochlores undergo a phase transition to the defect fluorite crystal structure (Sickafus et al., 2007).

The pyrochlore crystal structure is chemically very flexible. Lanthanide (Ln) pyrochlore solid solutions with actinides (An) have been synthesised, resulting in $(\text{Ln},\text{An})_2\text{B}_2\text{O}_7$ pyrochlores (Nästren et al., 2009; Holliday et al., 2013). In addition to the ideal $\text{Ln}_2\text{B}_2\text{O}_7$ pyrochlore, a wide range of chemical compositions with the

pyrochlore structure or the defect fluorite structure exist due to variations of the A and B (= Zr) cation ratio (Fabrichnaya et al., 2011). Depending on the Nd/Zr ratio, the defect fluorite structure is formed as the pyrochlore solid solution becomes unstable (Ewing, 2011). The pyrochlore structure transforms to the defect fluorite structure by disordering of anion and cation sites. Little is known about the consequences of this structural transition regarding properties such as the dissolution behaviour.

In the present work, powders with pyrochlore and defect fluorite structure were synthesised and characterised in detail. Moreover, we present new experimental data for the dissolution kinetics of $\text{Nd}_2\text{O}_3\text{--ZrO}_2$ ceramics from static and dynamic experiments. Nd was included as a surrogate for the trivalent actinides.

2. Materials and methods

Two powder samples – one pyrochlore (33.3 mol% Nd_2O_3) and one defect fluorite (12.9 mol% Nd_2O_3) were synthesised, characterised and used for dissolution experiments.

2.1. Powder preparation for dissolution experiments

The coprecipitation synthesis route was carried out according to Chen et al. (2009). Aqueous solutions with a concentration of 0.1 M of the starting materials $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% purity, Alfa Aesar) were prepared. All solution concentrations were

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checked by inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo Scientific iCAP6500) measurements due to the hygroscopic nature of the starting salts. Batches of 6 mmol of the desired composition were prepared in order to obtain about 2.5 g of pyrochlore and defect fluorite compositions, respectively. The desired proportions of both metal salt solutions were mixed and the hydroxides were quantitatively precipitated by concentrated NH_4OH or by inserting gaseous NH_3 . Afterwards, the precipitate was washed thoroughly until the washing water was free of chloride and nitrate. After drying, the powders were calcined for 2 h at 600 °C and ground. For the pellet formation 2.5 g of the powders were subjected to a cold press (50 kN). The obtained pellets were sintered in a hot uniaxial press (HP W 5, FCT Systeme GmbH) at 1450 °C and 3.9 kN in inert gas atmosphere. In order to adjust the oxygen deficit the pellets were resintered for 5 h at 1600 °C in air. Afterwards, well defined powders for the dissolution experiments were prepared by crushing and wet sieving into the fraction of 100–180 μm . About 1 g of the desired powder fraction was obtained from a 2.5 g pellet.

The crystal structure of the powders was analysed using powder X-ray diffraction (Bruker D4 Endeavor with a θ - 2θ -geometry). The samples were prepared on a plastic slit sample holder and measured in the 2θ region between 10 and 90°. The phases were identified using the MATCH! software (version 1.11f) from Crystal Impact and the PDF-2 database from ICDD. The specific surface area was then determined by N_2 -BET. The morphology and chemical composition were analysed using a FEI Quanta 200 FEG scanning electron microscope (SEM) equipped with a Genesis energy dispersive X-ray (EDX) system. The SEM measurements were carried out in a low-vacuum mode at 0.4–0.6 mbar (7–20 kV).

2.2. Dissolution experiments

Experimental setups following a batch and a dynamic approach were used to determine dissolution rates of pyrochlore and defect fluorite powders. All dissolution experiments were carried out in $\text{C}(\text{HCl}) = 0.1 \text{ M}$ at 90 °C.

The experimental setup of the batch experiment with ideal pyrochlore was adapted from Oelkers and Poitrasson (2002). In a first stage of the experiment, the powder was pre-leached for 28 days in a perfluoroalkoxy polymer (PFA) bottle ($V = 30 \text{ mL}$) by adding 25 mL of leachant to 200 mg of pyrochlore powder. The temperature was kept at 90 °C using a shaking oil bath. The powder was washed with water, dried and afterwards used for the final batch dissolution experiment. The solid/liquid ratio of 8 g L^{-1} was identical to the pre-leaching. Regularly, an aliquot of 500 μL was sampled. In order to avoid fines that may be present due to the powder preparation, or particles that may have been removed during sampling, the solution was filtered with an USY-1 ultrafilter (10,000 Da, Advantec). Afterwards, the Nd-concentration was determined by inductively coupled plasma mass spectrometry (ICP-MS). Measurements were performed with an ICP-MS ELAN 6100 DRC (PerkinElmer SCISX) instrument.

The experimental setup of the dynamic dissolution experiments was adapted from Neeway et al. (2011). About 900 mg of the prepared powder were placed in a PFA flow-through reactor (Saville, 50 mL) and 45 mL of the leachant were added. A peristaltic pump continuously exchanged the solution within the reactor. Due to the high density and the coarse grain size used within the experiments, no filters were needed in the setup to keep the ceramic powder inside the flow-through reactor. The flow rate was adjusted to 0.15 mL min^{-1} . The effluent was collected in order to monitor the flow rate by mass balance. Samples of the outflow solution were taken regularly for chemical analyses of Nd and Zr. In order to avoid any possible colloids or fines, ultrafilters (10,000 Da, Advantec)

were used. The filter was saturated with Zr using 6 mL of the effluent which were discarded before the final filtration took place. The Nd- and Zr-concentrations were analysed by ICP-MS measurements.

3. Results

3.1. Sample characterisation

The crystal structure of the powders was confirmed via powder X-ray diffraction. The typical X-ray diffraction pattern for the cubic defect fluorite structure is shown for the 12.9 mol% Nd_2O_3 powder in Fig. 1a. Only the characteristic reflexes for the defect fluorite phase are present. The diffraction pattern of the 33.3 mol% Nd_2O_3 sample (see Fig. 1b) shows additionally the superstructure reflexes marked with asterisks. The superstructure reflexes are present due to the higher ordering within the pyrochlore crystal structure compared to the defect fluorite structure.

SEM observations indicate the formation of mainly intergranular pores during the synthesis of the defect fluorite and pyrochlore ceramics (Fig. 2). This is confirmed by the specific surface area which is 0.4 $\text{m}^2 \text{g}^{-1}$ for the pyrochlore and 1.0 $\text{m}^2 \text{g}^{-1}$ for the defect fluorite, respectively, and in both cases high compared to the geometric surface area of the rather coarse grains.

3.2. Dissolution kinetics of pyrochlore and defect fluorite

Normalised dissolution rates R from batch experiments were determined from a linear fit of the Nd-concentration versus time (see Fig. 3a) according to:

$$R(\text{Nd}) = \frac{dC(\text{Nd})}{dt} \cdot \frac{V}{x(\text{Nd}) \cdot S \cdot m} \quad (1)$$

where $C(\text{Nd})$ refers to the concentration of Nd in the dissolution medium at the time t , V is the volume of the dissolution agent, $x(\text{Nd})$ the molar fraction of Nd within the pyrochlore, S the specific surface area of the ceramic powder and m the mass of the ceramic powder (Claparede et al., 2011).

The initial and final batch dissolution rates of the pyrochlore were determined from the pre-leaching experiment as well as from the initial (day 1–14) and final stages (after day 14) of the batch dissolution experiment. The Nd-based pyrochlore dissolution rate decreased from the pre-leaching experiment ($4 \times 10^{-5} \text{ g m}^{-2} \text{ d}^{-1}$)

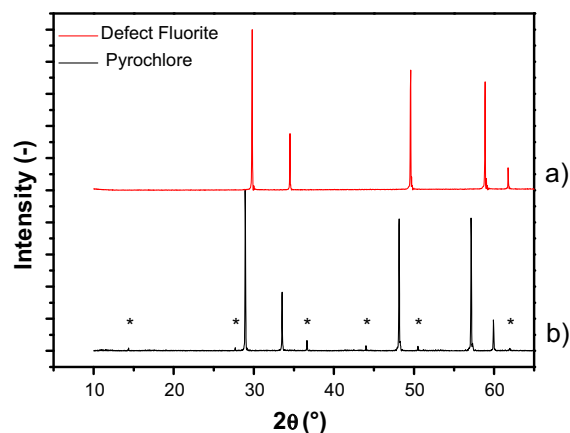


Fig. 1. (a) Diffraction patterns of the defect fluorite (12.9 mol% Nd_2O_3) and (b) pyrochlore (33.3 mol% Nd_2O_3) samples synthesised within this study. The superstructure reflexes of the pyrochlore crystal structure are marked with asterisks.

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