

Raman and infrared spectroscopy of monazite-type ceramics used for nuclear waste conditioning



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ABSTRACT

Raman and infrared spectroscopic investigations were performed on synthetic lanthanide orthophosphates ($LnPO_4$) within this study. Seven monoclinic monazite-type phosphates ($Ln = La-Gd$) were synthesised via precipitation route in aqueous solution at room temperature. Linear correlation between Raman band positions and the effective cationic radii of the Ln^{3+} was observed. New infrared spectroscopic data confirmed the expected steady increase of the $LnPO_4$ wavenumbers regarding the Ln atomic number.

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1. Introduction

Monazite ($LnPO_4$) is an accessory mineral in crystalline rocks like granites, gneisses, and pegmatites and is one of the most important ore minerals for rare earth elements. Beside trivalent lanthanides (Ln) such as Ce, La, Nd and Sm, monazite contains significant amounts of the tetravalent actinides Th and U (up to 27 wt% of ThO_2 and UO_2 (Ewing et al., 1995)). Monazites with high geological ages of about 3 Ga exist (Rasmussen et al., 2007; Montel et al., 1996). Although they can be very old, these minerals are rarely found in the metamict state (Boatner et al., 1988; Montel, 2011), despite relative high Th and U amounts. This reveals their strong resistance against ionising irradiation and their good chemical durability (Lumpkin, 2006; Schlenz et al., 2013; Weber et al., 2009; Meldrum et al., 1997).

Therefore, in the past, several investigations have been made to characterise monazite-type phases as a potential waste matrix for the conditioning of minor actinides and plutonium (Boatner et al., 1988; Tabuteau et al., 1988; Ewing and Wang, 2002; Dacheux et al., 2004; Ewing, 2007; Yudinsev et al., 2007; Oelkers and Montel, 2008; Clavier et al., 2011; Boatner, 2002; Bregiroux et al., 2007; de Kerdaniel et al., 2007). These radionuclides have long half-lives and are responsible for the high radiotoxicity of spent nuclear fuel. The outstanding properties of natural analogues underline, that monazite-type ceramics may present a good

alternative to the widely used borosilicate glasses, especially regarding the long-term safety of a deep geological repository (Sales et al., 1983). Systematic investigations of the crystal structure as well as thermal, mechanical and chemical properties are fundamental to evaluate synthetic monazites for nuclear waste management applications.

This study focuses on the analyses of the short-range order of stable monoclinic $LnPO_4$ series using vibrational spectroscopic methods. Numerous published data from different analytical methods show linear behaviour between corresponding material properties of the lanthanide orthophosphates and the atomic numbers or the ionic radii of the lanthanide cations (Ni et al., 1995; Aldred, 1984; Kizilyalli and Welch, 1976; Pepin and Vance, 1981; Begun et al., 1981; Silva et al., 2006). Many infrared spectra have been recorded so far, but only scarce data can be found for the systematic examination of the entire $LnPO_4$ -range ($Ln = La-Gd$) and no clear IR band shifts are observed. In the present work ($La-Gd$) PO_4 samples were synthesised by precipitation route and analysed with powder X-ray diffraction (XRD), Raman and infrared (IR) spectroscopy. This study can serve as a base for investigations on actinide-bearing monazite-type ceramics as the results can be related to that of phases like monazite-cheralite ($LnPO_4-Ca_{0.5}Th_{0.5}PO_4$) solid solutions (Podor, 1995; Terra et al., 2008).

Lanthanide orthophosphates ($LnPO_4$) occur in different modifications: 1) the before mentioned monazite ($Ln = La-Gd$), 2) xenotime ($Ln = Tb-Lu$), and different hydrated forms ($LnPO_4 \cdot x H_2O$) such as 3) rhabdophane ($x = 0.5-1$, $Ln = La-Dy$), 4) an orthorhombic phase ($x = 1.5$, $Ln = Dy$), and 5) weinschenkite ($x = 2$, $Ln = Gd-Yb$), respectively. Monazites crystallise in the monoclinic

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space group $P 2_1/n$ with $Z = 4$. The coordination of the Ln^{3+} -cations with nine oxygen atoms can be described as a “pentagonal interpenetrating tetrahedral polyhedron” in an idealised way (Mullica et al., 1984). The coordination of the Ln^{3+} is irregular with nine different Ln -O distances and also the PO_4 tetrahedra are slightly distorted, which result in a high flexibility of the structure (Lumpkin, 2006; Clavier et al., 2011; Beall and Boatner, 1981; Dacheux et al., 2013). Trivalent actinides show similar cationic radii and chemical behaviour compared to the lanthanides. For both a contraction of their radii with increasing atomic number exist. These trivalent actinides can easily be incorporated in the monazite’s crystal structure. Furthermore, the before mentioned flexibility of the structure allows the incorporation of tetravalent actinides via coupled substitutions $2 Ln^{3+} \rightleftharpoons An^{4+} + Ca^{2+}$ and/or $Ln^{3+} + P^{5+} \rightleftharpoons An^{4+} + Si^{4+}$ (with $An =$ actinides). The crystal structure of the hydrated $LnPO_4$ (rhabdophane) is determined as hexagonal ($P 6_222$) in most cases ($Z = 3$). However, especially spectroscopic studies suggest the similar trigonal crystal structure $P 3_121$ ($Z = 3$) because of the existence or absence of specific IR bands (see discussion mentioned below). The two different crystal structures of rhabdophane (database: ICSD #31563) and monazite (ICSD #79748), respectively are displayed in Fig. 1. Rhabdophane can be transformed into monazite or xenotime at high temperatures (Jonasson and Vance, 1986).

2. Materials and methods

2.1. Synthesis route

Rhabdophane-type phosphates ($LnPO_4 \cdot x H_2O$, $Ln = La-Gd$) were synthesised using a wet-chemical precipitation route at room temperature similar to (Boakye et al., 2008). Aqueous Ln -nitrate ($Ln = La, Pr-Gd$) solutions (Alfa Aesar, $\geq 99.9\%$ purity) were poured into citric acid and stirred for approximately 1 h in a first step. Subsequently, H_3PO_4 (Merck, EMSURE[®]) was added at a $Ln:P$ ratio of 1:5 with ongoing stirring. The pH was adjusted to approx. 10 with NH_3 solution (25%; Merck, EMSURE[®]) to precipitate the hydrated Ln -phosphates ($LnPO_4 \cdot x H_2O$, $x \sim 0.5$) quantitatively. The colours of the precipitates varied from white (La, Eu, Gd), light yellow (Sm) over green (Pr) to violet (Nd). For the preparation of $CePO_4$ a modified synthesis had to be chosen to prevent the oxidation of Ce^{3+} to Ce^{4+} . An aqueous $Ce(NO_3)_3 \cdot 6H_2O$ solution (Alfa Aesar, $\geq 99.5\%$ purity) was added drop-wise to a H_3PO_4 solution with stirring ($Ce:P = 1:1$) until a white precipitate was formed. All products were washed several times with distilled water to

eliminate traces of nitrate, afterwards they were dried at $90^\circ C$ over night and ground in an agate mortar. Small quantities of the as-prepared powder samples were used for IR measurements. For further investigations the powders were calcined at $600^\circ C$ for 5 h. These calcined powders were partly sintered at $1500^\circ C$ for 5 h for IR analyses and partly cold-pressed (~ 450 MPa) to green pellets, also sintered at $1500^\circ C$ for 5 h and polished afterwards to use them for XRD and Raman measurements.

2.2. Analytical methods

X-ray diffraction patterns were measured on polished sintered pellets with a Bruker D4 ENDEAVOR, equipped with a LynxEye detector using $Cu K\alpha$ (1.54 Å) radiation, tube voltage of 40 kV and current of 40 mA, respectively. The samples were rotated with 15 rpm during the measurement in the 2θ range of $10-100^\circ$. A step size of $0.01^\circ/2\theta$ with 1 s per step and a fixed divergence slit of 0.1° were used.

Raman spectra were recorded on sintered pellets in the range of $100-1200\text{ cm}^{-1}$ with a HORIBA Jobin Yvon LabRam HR set up with a focal length of 800 mm, equipped with a Peltier-cooled CCD-detector. For the measurements a He-Ne laser (wavelength 632.8 nm), a grating with 1800 grooves per millimetre and an Olympus 100 \times -objective were used. Hole and slit were set to 1000 and 100 μm , respectively. The exposition time was set to 15 s, with an accumulation of 2.

Infrared spectroscopic investigations were carried out in the wavenumber range of $400-4000\text{ cm}^{-1}$ using a Bruker AXS FT-IR spectrometer EQUINOX 55. Approximately 1 mg of the as-prepared as well as the sintered powder of each sample was mixed with 250 mg KBr and pressed to pellets for the measurements. Opus software (Bruker) was used for peak search.

3. Results and discussion

3.1. X-ray powder diffraction

X-ray powder diffraction was used for qualitative analyses of the sintered samples. All samples showed the desired monoclinic crystal structure of monazite-type $LnPO_4$ phases. The sole exception was the Gd-phosphate, where a small amount of tetragonal $GdPO_4$ (xenotime-type, $I 4_1/amd$) could be detected, although the monoclinic phase is the thermodynamically stable crystal structure. Nevertheless, xenotime-type orthophosphates might be formed during sintering, if the initial content of crystallisation water was

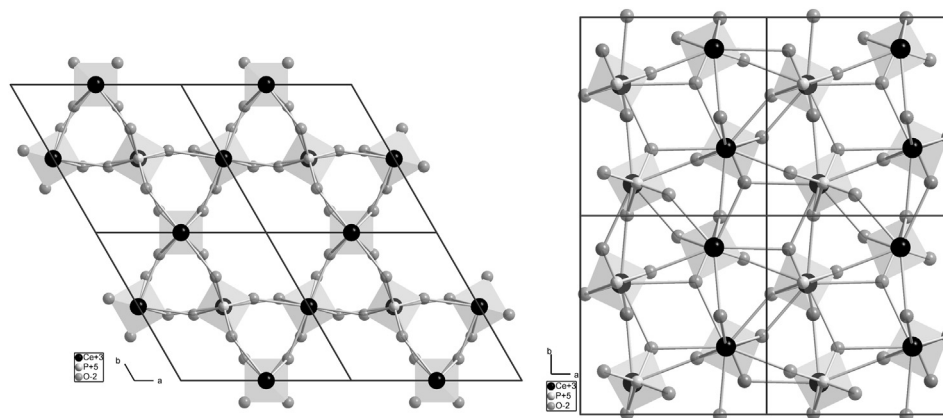


Fig. 1. Crystal structure of hexagonal Ce-rhabdophane-type orthophosphate, (ICSD #31563) on the left side and monoclinic Ce-monazite-type orthophosphate (ICSD: #79748) to the right, viewing directions parallel [001], grey shades of different ions: P^{5+} light grey, O^{2-} mid grey, and Ce^{3+} black, respectively.

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