Synthesis and Thermal Behavior of Nanopowders in LaPO$_4$-YPO$_4$(-H$_2$O), LaPO$_4$-LuPO$_4$(-H$_2$O) and YPO$_4$-ScPO$_4$(-H$_2$O) Systems for Ceramic Matrices

Abstract

Nanosized powders in the LaPO$_4$-YPO$_4$(-H$_2$O), LaPO$_4$-LuPO$_4$(-H$_2$O) and YPO$_4$-ScPO$_4$(-H$_2$O) systems have been synthesized to increase the mutual solubility of initial components and to prepare effective ceramic matrices by sintering them. Ceramic matrices were characterized by high isomorphic capacity, thermal and chemical resistance.

Keywords: Sol-gel; Ln’’$_x$PO$_4$nH$_2$O nanopowders; Ceramic matrices; Thermal; Chemical stability

Introduction

In many previous works, the monazite-type lanthanum orthophosphate (LaPO$_4$) and xenotime one (YPO$_4$) has been suggested as matrices for radioactive waste immobilization (radioactive rare earth elements or trivalent actinides) and sensors [1-8]. Nanopowder-based ceramics designed for immobilizing purpose should possess high chemical resistance and isomorphic capacity, high durability and thermal stability. It is supposed to use ceramics obtained by sintering nanopowders with general formula Ln’’$_x$PO$_4$nH$_2$O synthesized by sol-gel technique with inverse precipitation and further dehydrated upon high heating rate to retain nanoscale. From this point of view the aim of this study was to investigate peculiarities of formation of nanopowders in the systems where components belong to the same or different structural groups, to determine their isomorphic capacity, to study thermal behavior, and thereby to develop physical and chemical approaches to prepare ceramic samples (matrices) based on them. In this case the second component plays a role of immobilized ion (isotope).

The hydrated La orthophosphate crystallizes in hexagonal rhabdophane-type system upon precipitation and contain 0.5-3 moles of H$_2$O per formula unit. At temperature higher than 600 °C nanosized crystals loose water molecules and transform into monoclinic monazite-type form [9]. Yttrium, lutetium and scandium orthophosphates, hydrated and dehydrated, crystallizes in tetragonal xenotime-type form [9,10]. In this instance it was expected formation of limited solid solutions in the LaPO$_4$-YPO$_4$(-H$_2$O) and LaPO$_4$-LuPO$_4$(-H$_2$O) systems [9] and unlimited solid solutions in the YPO$_4$-ScPO$_4$(-H$_2$O) system [10].

Hydrated rare earth orthophosphate nanopowders were synthesized using sol-gel method at stoichiometric ratio of interacting components Ln(NO$_3$)$_3$ and NH$_4$H$_2$PO$_4$ in an aqueous solution in the form of stable colloids that coagulate at pH ≈ 7 [9-11]. The use of reverse precipitation as it was shown allows improving further physico-mechanical properties of ceramic samples (matrices) obtained by sintering of nanopowders preliminary calcined to remove water from crystalline lattice [10,11].

Experimental

The initial reagents for rare earth orthophosphate systems were REE$_3$O$_9$ (special-purity grade, 99.999%), mono substituted ammonium phosphate (special-purity grade, 99.5%), nitric acid (special-purity grade, 70%), aqua ammonia (special-purity grade, 25%), and distilled water. Synthesis of Ln’’$_x$PO$_4$nH$_2$O nanopowders was performed by sol-gel technique according the reactions described [11].

The proper pH ≈ 7 for complete precipitation was reached by NH$_4$OH addition. The precipitates were kept in the mother liquor for 24 h, washed after that by decantation, filtered off, and air-dried at 110 °C for 24 h [9,11]. For X-ray powder diffraction analysis DRON-3 diffractometer (Russia) was used. Recording parameters were as follows: Ni-filtered CuK$_\alpha$ radiation, 38 kV, time constant 1, scanning speed 1 degree per minute. The thermal behavior of the samples was studied by means of stepwise heating of powders compacted into tablets under a pressure of 8–10 MPa within the temperature range of 850–1700 °C with further analysis by XRD or differential scanning calorimetry (DSC) and thermal gravimetry (TG).
The DSC/TG measurements were conducted in STA 449C (NETZSCH) calorimeter; sample mass was about 30 mg; heating rate was 20 °C/min. Preliminary calcined at 850 °C for 2 h nanopowders were compacted into tablets under a pressure of 8-10 MPa and then stepwise heated in air at 1000, 1200, 1600 and 1700 °C to obtain ceramic samples (matrices). Vickers microhardness measurement of ceramic samples (matrices) was performed under the loading of 20 g (2 N) using a PMT 3 microhardness meter (Russia) equipped with Microanalysis Microhardness software package developed at JSC LOMO (Russia). Scanning electron microscopy (SEM) was used for powders observations (Tescan Vega 3, Czech Republic).

For leaching experiments, the powders were compacted into cubes with a volume of 1 cm³ under a pressure of 8–10 MPa, after which they were stepwise calcined at 1000 (24 h), 1200 (24 h), and 1600°C (1 h). Ceramic cubes were placed into plastic containers and poured with 50 mL of contact solution (distilled water or 10% HNO₃ aqueous solution). The test temperature was 25±3 °C; a contact solution was changed within 1, 3, 7, 10 and 14 days. The La³⁺ and Y³⁺ concentrations in the solution upon leaching were determined by inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS test was performed at A.P. Karpinsky Russian Geological Research Institute (St.-Petersburg).

Results and discussion

Ln′ₐLn''ₐPO₄₋nH₂O (Ln’ = La, Y; Ln″ = Y, Sc; x = 0.0–1.0) nanopowders were synthesized by technique described above. According to results of electron microscopy analysis, the powders consist of large agglomerates of nanoscaled particles (Figure 1).

The XRD powder patterns of the Ln′ₐLn''ₐPO₄₋nH₂O systems and unlimited solid solutions for the YPO₄·ScPO₄·H₂O system. Substitutional solid solutions based on hexagonal LaPO₄·nH₂O extended to x = 0.6 for Y³⁺ and Lu³⁺ (Figure 1-5). Solid solutions based on tetragonal form were observed within narrower concentration range (Figure 2,3,6-9). Due to very broad reflexes precise determent of reflexes belonging to tetragonal solid solutions were difficult.

Unlimited tetragonal solid solutions formed in the YPO₄·ScPO₄·H₂O system in the whole concentration range (Figure 4). According to the DSC/TG results (Figure 5-7), Ln′ₐLn''ₐPO₄·nH₂O samples loose water in temperature range 50–600 °C and then were stable until at least 1000 °C.

A series of exothermic effects observed at temperatures higher than 600 °C (single and double) and not accompanied by the mass loss could be referred in our opinion to intensive crystallization of high dispersion powders containing tetragonal almost amorphous phase (Figure 5, curves 3–6; Figure 6, curves 1–10). Isomorphous capacity of dehydrated monoclinic LaPO₄ herewith appeared to be less then 80 mol% of YPO₄ (Figure 5, curve 3). Before sintering, Ln′ₐLn''ₐPO₄·nH₂O powders were calcined at temperature not higher then 850 °C (1 or 2 h) to keep high dispersion of dehydrated samples [12,13]. These anhydrous Ln′ₐLn''ₐPO₄ powders were then pressed into tablets and stepwise heated up to 1600-1700 °C to obtain ceramic samples (matrices).

Fracture surfaces of La₁₋ₓYₓPO₄ ceramic samples (matrices) calcined at different temperatures are presented in Figure 7. Here well created roundish grains which size does not exceed 2-3 μ are...
observed. Determined open porosity of ceramic samples is low and is in the range of 0.1-0.2% [12].

Figure 2: XRD patterns of initial La$_{1-x}$Y$_x$PO$_4$·$n$H$_2$O powders (reverse precipitation), for $x$: 0.0 (1), 0.1 (2), 0.3 (3), 0.5 (4), 0.7 (5), 0.8 (6), 0.9 (7), 0.95 (8), 1 (9), and the bar graphs represent the XRD patterns of LaPO$_4$·0.5H$_2$O and YPO$_4$·3H$_2$O of ICDD-PDF.

Figure 3: XRD patterns of initial La$_{1-x}$Lu$_x$PO$_4$·$n$H$_2$O powders (direct precipitation), for $x$: 0.0 (1), 0.25 (2), 0.3 (3), 0.4 (4), 0.5 (5), 0.6 (6), 0.7 (7), 0.75 (8), 1.0 (9), and the bar graphs represent the XRD patterns of LaPO$_4$·0.5H$_2$O and LuPO$_4$·3H$_2$O of ICDD-PDF.

Figure 4: XRD patterns of initial Y$_{1-x}$Sc$_x$PO$_4$·$n$H$_2$O powders (reverse precipitation), for $x$: 0.0 (1), 0.1 (2), 0.2 (3), 0.3 (4), 0.4 (5), 0.5 (6), 0.6 (7), 0.7 (8), 0.8 (9), 0.9 (10), 1.0 (11), and the bar graphs represent the XRD pattern of YPO$_4$·3H$_2$O of ICDD-PDF.

Figure 5: DSC curves for the La$_{1-x}$Y$_x$PO$_4$·$n$H$_2$O samples (reverse precipitation), for $x$: 0.0 (1), 0.3 (2), 0.8 (3), 0.9 (4), 0.95 (5), 1.0 (6), TG curve for La$_{1.2}$Y$_{0.8}$PO$_4$·$n$H$_2$O (7').

Figure 6: DSC curves for the Y$_{1-x}$Sc$_x$PO$_4$·$n$H$_2$O samples (reverse precipitation) for $x$: 0.0 (1), 0.2 (2), 0.3 (3), 0.4 (4), 0.5 (5), 0.6 (6), 0.7 (7), 0.8 (8), 0.9 (9), 1.0 (10). TG curve for ScPO$_4$·$n$H$_2$O (10').

According to calculated lattice parameters for monoclinic La$_{1-x}$Y$_x$PO$_4$ and La$_{1-x}$Lu$_x$PO$_4$ series calcined at 1000 °C, 24 h isomorphic capability was about 70 mol% for YPO$_4$ and 20-25 mol% for LuPO$_4$ [9,12]. It is worth to compare the values with isomorphic capacity of monoclinic LaPO$_4$ in respect of HoPO$_4$ (~30 mol%) [13] which is in a good accordance with ionic radii for coordination number 8 (Y$^{3+}$ 0.116; Ho$^{3+}$ 0.115; Lu$^{3+}$ 0.112 nm).

The microhardness values of Ln$^{3+}$PO$_4$ ceramic samples (matrices) calcined at different temperatures are given in Table 1. These values depend on the chemical composition, a ratio of components and heat treatment temperature. They are significantly higher than those obtained for individual La, Gd, Dy or Y phosphate ceramics (4.5-7.8 GPa) [14-18] or 7.2 GPa for phosphate glass ceramics, and 8.0–8.5 GPa for SYNROC [19].
This could be associated with very high dispersion of initial powders. Leaching experiments exhibit quite good resistance of Ln\(^{1–x}\)Ln\(^x\)PO\(_4\) matrices in a strongly acid HNO\(_3\) solution (pH 1–2) at room temperature (Figure 8 & 9). The results of leaching experiments for Ln\(^{1–x}\)Ln\(^x\)PO\(_4\) are close to [20] for GdPO\(_4\) in strongly HCl and HNO\(_3\) solutions (pH 1–2) corresponding to value of \(\sim 10^{-2}\) g L\(^{-1}\).

### Table 1: Microhardness for La\(_{1–x}\)Y\(_x\)PO\(_4\) and Y\(_{1–x}\)Sc\(_x\)PO\(_4\) ceramic samples (matrices) after heat treatment.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Microhardness, GPa, ± 0.1</th>
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<tr>
<td></td>
<td>Heat Treatment Temperature, °C</td>
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<tr>
<td></td>
<td>1000 (24 h)</td>
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<tr>
<td>La(<em>{0.5})Y(</em>{0.5})PO(_4)</td>
<td>10.9</td>
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<tr>
<td>La(<em>{0.7})Y(</em>{0.3})PO(_4)</td>
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<tr>
<td>La(<em>{0.8})Y(</em>{0.2})PO(_4)</td>
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<tr>
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<tr>
<td>La(<em>{0.5})Y(</em>{0.5})PO(_4)</td>
<td>10.2</td>
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<td>La(<em>{0.7})Y(</em>{0.3})PO(_4)</td>
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<td>La(<em>{0.9})Y(</em>{0.1})PO(_4)</td>
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<tr>
<td>YPO(_4)</td>
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<tr>
<td>YPO(_4)</td>
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<td>Y(<em>{0.9})Sc(</em>{0.1})PO(_4)</td>
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<tr>
<td>ScPO(_4)</td>
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**Figure 7:** Fracture surface of La\(_{0.5}\)Y\(_{0.5}\)PO\(_4\) ceramic sample (matrix) calcined at 1000 °C for 24 h (a), 1200 °C for 24 h (b), NTEGRA atomic-force microscope; 1700 °C for 1 h (c), EM transmission electron microscope; black spots are remains of zylonite (celluloid) replica.

**Figure 8:** Ions concentration (C) in contact solutions (10% HNO\(_3\)) during leaching experiments: a) La\(^{3+}\) for La\(_{1–x}\)Y\(_x\)PO\(_4\) matrices; b) Y\(^{3+}\) for La\(_{1–x}\)Y\(_x\)PO\(_4\) matrices; c) Y\(^{3+}\) for Sc\(_{1–x}\)Y\(_x\)PO\(_4\) matrices.

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Leaching rate of both ions for La$_{1-x}$Y$_{PO_4}$ was within the range $10^{-3}$-$10^{-2}$ g/(cm$^2$ day) that is lower than the leaching rate in distilled water for La$^{3+}$ and Y$^{3+}$ ions ($10^{-5}$-$10^{-7}$ g/(cm$^2$ day)) [13] but compared with leaching rate of Y$^{3+}$ for Y$_{1-x}$Sc$_x$PO$_4$ ($10^{-5}$-$10^{-7}$ g/(cm$^2$ day)) presented in Figure 9. It is worth to note that for La$_{1-x}$Y$_{PO_4}$ matrices almost no falling of rate is observed. Usually at first the ceramic cube surface is intensively dissolved, and then rate decreases, being limited to diffusion. It looks like a uniform etching. In this case Y$_{1-x}$Sc$_x$PO$_4$ matrices are considered as a very steady system.

Summary

High dispersion La$_{1-x}$Y$_{PO_4}$·nH$_2$O and Y$_{1-x}$Sc$_x$PO$_4$·nH$_2$O powders were synthesized by sol-gel technique with reverse precipitation, and La$_{1-x}$Lu$_{PO_4}$·nH$_2$O powders with direct precipitation.

Ln$^{3+}$, Ln$^{4+}$PO$_4$ ceramic samples (matrices) obtained by sintering of preliminary dehydrated powders exhibited high isomorphic capacity in respect of the second components playing role of an immobilized ion (isotope), i.e. up to 70 mol% of YPO$_4$-20-25 mol% of LuPO$_4$, and complete mutual solubility in Y$_{1-x}$Sc$_x$PO$_4$ series.

Ln$^{3+}$, Ln$^{4+}$PO$_4$ ceramic samples (matrices) were stable up to 1600(1700) °C, and possessed high microhardness increased with increasing heat treatment temperature (up to 28 GPa). Leaching rate of both lanthanum and yttrium ions from La$_{1-x}$Y$_{PO_4}$ ceramic matrices was almost within the range $10^{-3}$-$10^{-2}$ g/(cm$^2$ day), and yttrium ions from Y$_{1-x}$Sc$_x$PO$_4$ ceramic matrices were lower (within the range $10^{-5}$-$10^{-3}$ g/(cm$^2$ day)). Therefore, rare earths orthophosphate ceramic matrices are suitable to immobilize radioactive waste relating to actinide/rare-earth group occurred in high level waste (HLW) because they possess high chemical resistance, isomorphic capacity, thermal stability and microhardness.

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References


