

## Solid Solutions and Thermal Transformations in Nanosized $\text{LaPO}_4\text{-YPO}_4\text{-H}_2\text{O}$ and $\text{LaPO}_4\text{-LuPO}_4\text{-H}_2\text{O}$ Systems

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### Abstract

Nanosized powders of orthophosphates in the  $\text{LaPO}_4\text{-YPO}_4\text{-H}_2\text{O}$  and  $\text{LaPO}_4\text{-LuPO}_4\text{-H}_2\text{O}$  systems are synthesized to increase the mutual solubility of  $\text{LaPO}_4\cdot n\text{H}_2\text{O}$ ,  $\text{YPO}_4\cdot n\text{H}_2\text{O}$  and  $\text{LuPO}_4\cdot n\text{H}_2\text{O}$  initial components and to investigate physicochemical properties of nanosized solid solutions and their mixtures. The temperature dependence of nanoparticle size is investigated in the 200–1100 °C temperature range. Formation of limited hexagonal, monoclinic or tetragonal solid solutions is revealed, and the limits of their concentration and thermal stability are determined. In the  $\text{LaPO}_4\text{-YPO}_4\text{-H}_2\text{O}$  system a series of limited hexagonal  $\text{LaPO}_4\cdot n\text{H}_2\text{O}$ -based solid solutions is observed up to 500–600 °C within the  $0 \leq x \leq 0.5$  concentration range; a monoclinic  $\text{LaPO}_4$ -based form is observed up to at least 1000 °C within the  $0 \leq x \leq 0.7$  concentration range. Melting temperatures of  $\text{La}_{1-x}\text{Y}_x\text{PO}_4$  samples are found to be in the 2010–1960 °C temperature range. In the  $\text{LaPO}_4\text{-LuPO}_4\text{-H}_2\text{O}$  system corresponding hexagonal solid solutions are observed within the  $0 \leq x \leq 0.4$  concentration range; isomorphic capacity of the monoclinic form at 1100 °C is between 20–25 mol%. Solubility of  $\text{LaPO}_4$  in tetragonal  $\text{YPO}_4$  or  $\text{LuPO}_4$  in all cases is less than 10 mol%. The specific surface area of  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4\cdot n\text{H}_2\text{O}$  powders is in the range of 46.7–90.3 m<sup>2</sup>/g depending on  $x$ .

**Keywords:**  $\text{LaPO}_4\text{-YPO}_4\text{-H}_2\text{O}$  and  $\text{LaPO}_4\text{-LuPO}_4\text{-H}_2\text{O}$  systems, nanopowders, thermal behavior

### 1. Introduction

Rare earths orthophosphates are attracting considerable interest from researchers because of their unique properties and are now widely investigated. They are considered prospective catalysts for the oxidative dehydrogenation of ethylbenzene<sup>1</sup>, iso-butane to iso-butene<sup>2,3</sup>, as scintillators, laser hosts, and thermophosphors<sup>4,5,6</sup>. In addition, ceramics based on rare earth orthophosphates exhibit promising properties owing to their machinability<sup>7,8,9</sup> and high thermal and radiation stability and could be considered as matrices for radioactive waste immobilization (radioactive rare earth elements or trivalent actinides)<sup>10,11,12,13</sup>. Efficiency of such ceramic matrices is based on high isomorphic capacity in relation to immobilized elements. The main requirements for a ceramic matrix are formation of stable compositions with immobilized elements and high isomorphic capacity. In this connection the influence of nanoscale on mutual solubility of rare earths orthophosphates and other properties appears to be dramatic.

Rare earth orthophosphate nanopowders obtained with the sol-gel technique (precipitation from water solution) were used within the framework of preparation and in-

vestigation of properties of the ceramics.  $\text{LaPO}_4\text{-LuPO}_4\text{-H}_2\text{O}$  and  $\text{LaPO}_4\text{-YPO}_4\text{-H}_2\text{O}$  were chosen as modeling systems, where components belong to different structural groups (hexagonal  $\text{LaPO}_4\cdot n\text{H}_2\text{O}$  or monoclinic  $\text{LaPO}_4$  and tetragonal  $\text{YPO}_4\cdot n\text{H}_2\text{O}$  and  $\text{LuPO}_4\cdot n\text{H}_2\text{O}$  or  $\text{YPO}_4$  and  $\text{LuPO}_4$ )<sup>14</sup>.

Rare earth orthophosphate nanoparticles have often been synthesized by means of various modifications of sol-gel method. Analysis of the data presented in<sup>15,16,17,18</sup> has demonstrated that hydrated orthophosphates of rare-earth elements (REE) and their solid solutions are formed at stoichiometric ratio of interacting components ( $\text{Ln}(\text{NO}_3)_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$  or  $\text{H}_3\text{PO}_4$ ) in an aqueous solution in the form of stable colloids that coagulate at pH  $\approx$  7.

The hydrated REE orthophosphates (La to Dy), which crystallize in a hexagonal system upon precipitation contain 0.5–3 moles of  $\text{H}_2\text{O}$  per formula unit. These compounds are the analogues of rhabdophane, they lose water molecules on being heated up to 450–600 °C and then transform into monazite-type monoclinic form<sup>11,15,17,18,19,20</sup>. The dehydration of other REE orthophosphates (Ho-Lu, Y, Sc) takes place in the 150–450 °C temperature range with the complete removal of water. According to the data presented in<sup>15,16,21</sup>, the

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dehydration does not bring about structural transformations, i.e. the compounds retain the xenotime structure.

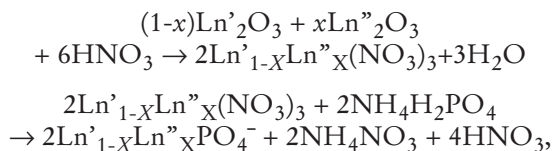
According to our previous investigation<sup>22</sup>, mutual solubility of RE orthophosphates belonging to different structural groups, whose particles have the micron size, is insignificant and makes up 2–3 mol% from each side (for instance, in the  $\text{LaPO}_4\text{--YbPO}_4$  system the limited solid solutions have the following compositions -  $\text{La}_{0.98}\text{Yb}_{0.02}\text{PO}_4$  (monoclinic) and  $\text{La}_{0.03}\text{Yb}_{0.97}\text{PO}_4$  (tetragonal)). In the  $\text{LaPO}_4\text{--YPO}_4$  system, according to<sup>23</sup>, solubility of tetragonal  $\text{YPO}_4$  in monoclinic  $\text{LaPO}_4$  at 1200 °C ranges up to 20 mol%. Tetragonal solid solution concentration range is not more than several mol%. Hexagonal  $\text{La}_{0.3}\text{Y}_{0.7}\text{PO}_4 \cdot n\text{H}_2\text{O}$  solid solution, and a series of monoclinic  $\text{La}_{1-x}\text{Y}_x\text{PO}_4$  solid solutions obtained by calcination of initial hexagonal compositions were investigated in<sup>18,24</sup>. According to this research, heat treatment at 950 °C caused the decomposition of hexagonal  $\text{La}_{0.3}\text{Y}_{0.7}\text{PO}_4 \cdot n\text{H}_2\text{O}$  solid solution into a monoclinic  $\text{La}_{1-x}\text{Y}_x\text{PO}_4$  solid solution and tetragonal  $\text{YPO}_4$ . The solid solubility of Y in  $\text{LaPO}_4$  in the 1000–1600 °C temperature range increases from ~12 at. % at 1000 °C to ~42 at. % at 1600 °C<sup>18</sup>.

The purpose of this work is to increase the mutual solubility of initial components in the case of nanosized  $\text{LaPO}_4\text{--YPO}_4\text{--H}_2\text{O}$  and  $\text{LaPO}_4\text{--LuPO}_4\text{--H}_2\text{O}$  systems and to investigate physicochemical properties of nanosized solid solutions and their mixtures.

## II. Experimental

The initial reagents for lanthanum-yttrium and lanthanum-lutetium orthophosphates were  $\text{La}_2\text{O}_3$  (LaO-D OST 48–194–81, 99.999 %),  $\text{Y}_2\text{O}_3$  (ItO-Lyum OST 48–4–191–72, 99.999 %), and  $\text{Lu}_2\text{O}_3$  (LyuO-D OST 48–207–81, 99.999 %), monosubstituted ammonium phosphate (special-purity grade, 99.5 %), nitric acid (special-purity grade, 70 %), aqua ammonia (special-purity grade, 25 %), and distilled water.

Synthesis of  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  and  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  nanoparticles was performed with a conventional technique according to following reaction:



where  $\text{Ln}' = \text{La}$ ;  $\text{Ln}'' = \text{Y, Lu}$ .

Proper pH  $\approx 7$  for complete precipitation was reached with  $\text{NH}_4\text{OH}$  addition. The precipitates were kept in the mother liquor for 24 h, then washed by means of decantation, filtered off, and dried at 110 °C in air for 24 h<sup>16,17,25</sup>.

For x-ray powder diffraction analysis a Siemens D-500HS x-ray diffractometer (Germany) and DRON-3 diffractometer (Russia) were used. The recording parameters were the following: Ni-filtered  $\text{CuK}_\alpha$  radiation, 38 kV, time constant 1, scanning speed 1 degree per minute.

Nanoparticle size was determined from the broadening of the diffraction peaks according to Scherrer's formula and with the use of transmission electron microscopy (EM-125 electron microscope, Russia,  $U_{\text{acc}} = 75$  kV).

Temperature dependence of nanoparticle size was determined in the temperature range of 200–1100 °C with isothermal exposure for 1 h.

The specific surface area of powder samples was measured with a Nova 1200e instrument (Quantachrome, USA) using nitrogen (99.9999 %) as adsorbing gas. All calculations were performed using the NovaWIN (Quantachrome, USA) 11 software. Degassing procedure was performed at 300 °C for 10 h.

The thermal behavior of the samples was studied by means of stepwise heating of powders compacted into tablets under 8–10 MPa pressure in the 200–1000 °C temperature range with further analysis with XRD or differential scanning calorimetry (DSC) and thermal gravimetry (TG).

The DSC/TG measurements were conducted in a STA 449C (Netzsch) calorimeter; sample mass was about 30 mg; heating rate was 10 °C/min. The onset of the thermal effect was determined from the intersection of the tangents to the base line of the DSC curve and to the branch of the thermal peak.

The melting temperatures of the samples of the  $\text{LaPO}_4\text{--YPO}_4$  system were determined using visual polythermal analysis (VPA) in Galakhov's modified microfurnace<sup>26,27,28</sup>. The working temperature range in the microfurnace was 900–2300 °C. Temperature measurement accuracy was about  $\pm(10-15)$  K. The measurements were conducted in an inert atmosphere (argon) at a total pressure in the system of about 0.5 MPa. To avoid active interaction between a specimen and a holder, the latter was produced from iridium.

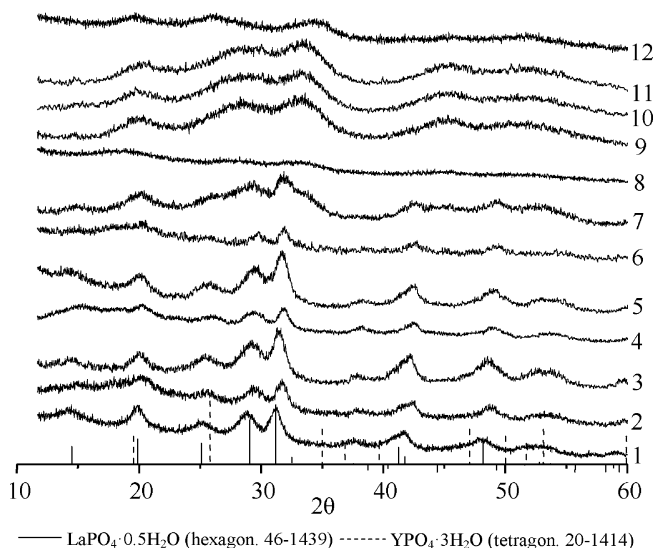
## III. Results and Discussion

$\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  ( $x = 0.0, 0.1, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.75, 0.8, 0.85, 0.9, 0.95$  and  $1.0$ ) and  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  ( $x = 0.0, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.75, 0.8, 0.9$  and  $1.0$ ) nanopowders were synthesized with the technique described above.

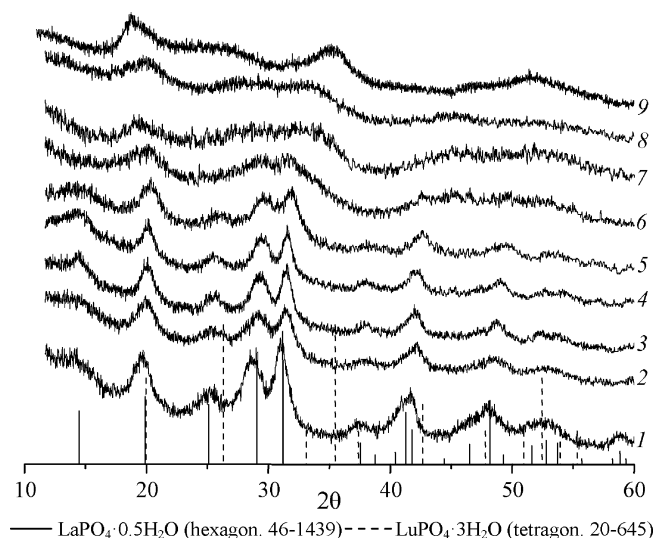
The XRD patterns of the  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  and  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples thus obtained are shown in Figs. 1 and 2. They indicate that the powders are nanoscaled, and at temperature of synthesis (room temperature) limited solid solutions are formed.

Substitutional solid solutions based on hexagonal  $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$  extend to concentration of  $\text{Y}^{3+}$  approximately of  $x = 0.5(0.7)$  (Fig. 1, 1–5(7)), and solid solutions based on tetragonal  $\text{YPO}_4 \cdot n\text{H}_2\text{O}$  are observed in a narrow concentration range (Fig. 1, 9–12). Unfortunately, nanoparticle size of specimens in the  $0.4 \leq x \leq 1.0$  concentration range is so small that x-ray patterns do not allow precise determination of reflexes belonging to these or those solid solutions.

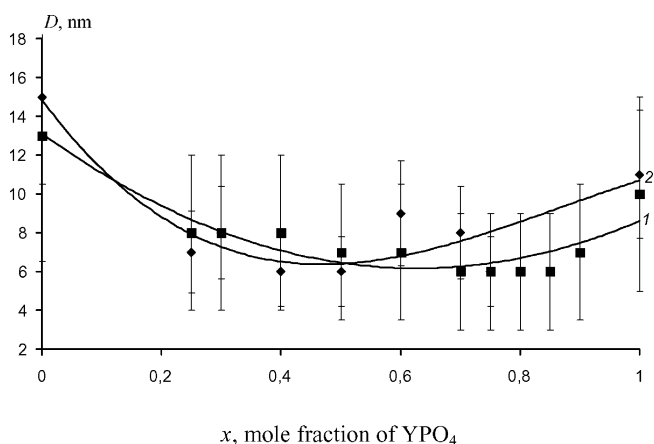
X-ray patterns of  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples shown in Fig. 2 allow assumption of an extension of hexagonal solid solutions approximately to  $x = 0.5-0.6$  (Fig. 2, 1–6). Solubility of  $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$  in  $\text{LuPO}_4 \cdot n\text{H}_2\text{O}$  at room temperature is difficult to assess owing to very broad reflexes with low intensity (Fig. 2, 7–9).



**Fig. 1:** XRD patterns of initial  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples,  $x$ : 0.0 (1), 0.25 (2), 0.3 (3), 0.4 (4), 0.5 (5), 0.6 (6), 0.7 (7), 0.75 (8), 0.8 (9), 0.85 (10), 0.9 (11), 1.0 (12), and the bar graphs represent the XRD patterns of  $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$  and  $\text{YPO}_4 \cdot 3\text{H}_2\text{O}$  of ICDD-PDF.

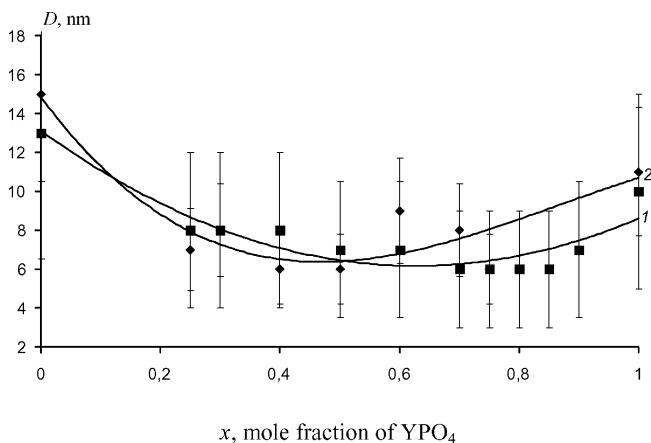


**Fig. 2:** XRD patterns of initial  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples,  $x$ : 0.0 (1), 0.25 (2), 0.3 (3), 0.4 (4), 0.5 (5), 0.6 (6), 0.7 (7), 0.75 (8), 1.0 (9), and the bar graphs represent the XRD patterns of  $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$  and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

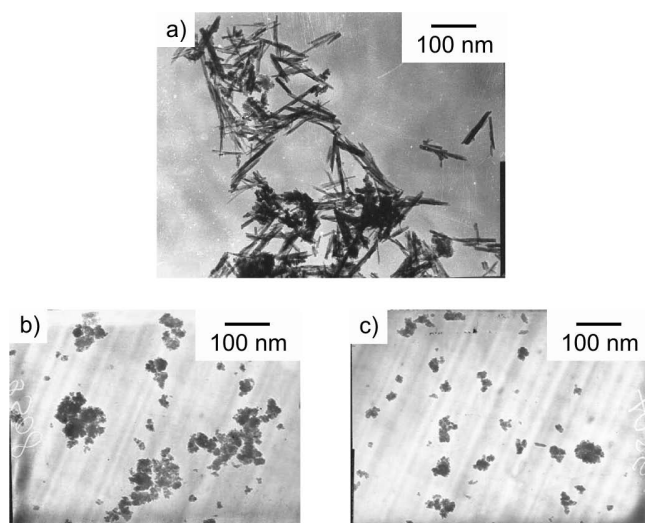


**Fig. 3:** Dependence of nanoparticle size ( $D$ ) of initial  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples on  $x$  according to (1) X-ray powder diffraction and (2) electron microscopy.

The data obtained from x-ray powder diffraction (Figs. 3, 4, curve 1) and transmission electron microscopy (Figs. 3, 4, curve 2) indicate the nanoscale  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  and  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  particles. In addition, according to electron microscopy, the samples under investigation consist of nanoparticles in the form of rods ( $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ ) or thin plates ( $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  and  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ), and of a great amount of sufficiently large agglomerates (Fig. 5).



**Fig. 4:** Dependence of nanoparticle size ( $D$ ) of initial  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples on  $x$  according to (1) X-ray powder diffraction and (2) electron microscopy.



**Fig. 5:** Micrographs of nanocrystals: (a)  $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ , (b)  $\text{La}_{0.75}\text{Y}_{0.25}\text{PO}_4 \cdot n\text{H}_2\text{O}$  and  $\text{La}_{0.75}\text{Lu}_{0.25}\text{PO}_4 \cdot n\text{H}_2\text{O}$  (c) prepared at room temperature.

When heated, hexagonal  $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$  and its solid solutions in 500–600 °C temperature range transform into monoclinic form (Figs. 6, 7) stable until at least 1000–1100 °C (Figs. 8, 9). Isomorphous capacity of monoclinic  $\text{LaPO}_4$  therefore appeared to be 70 mol% of  $\text{YPO}_4$ , and not more than 25 mol% of  $\text{LuPO}_4$ . Solubility of  $\text{LaPO}_4$  in tetragonal  $\text{YPO}_4$  and  $\text{LuPO}_4$  is obviously less than 10 mol%.

The lattice parameters determined at room temperature (PDWin program) from the broadening of the diffraction peaks according to the Scherrer formula for monoclinic

$\text{La}_{1-x}\text{Y}_x\text{PO}_4$  series calcined at 1000 °C (1 h) are presented in <sup>29</sup>. The concentration dependence of unit cell parameters confirms, in our opinion, 70 mol% isomorphous capacity of monoclinic  $\text{LaPO}_4$  at 1000 °C in respect of  $\text{YPO}_4$ .

The concentration dependence of monoclinic  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4$  unit cell parameters apparently shows the monoclinic  $\text{LaPO}_4$  isomorphous capacity at about 20 mol% (Fig. 10). This is in agreement with  $\text{Y}^{3+}$  and  $\text{Lu}^{3+}$  ionic radii for coordination number 8 (0.116 and 0.112 nm respectively).

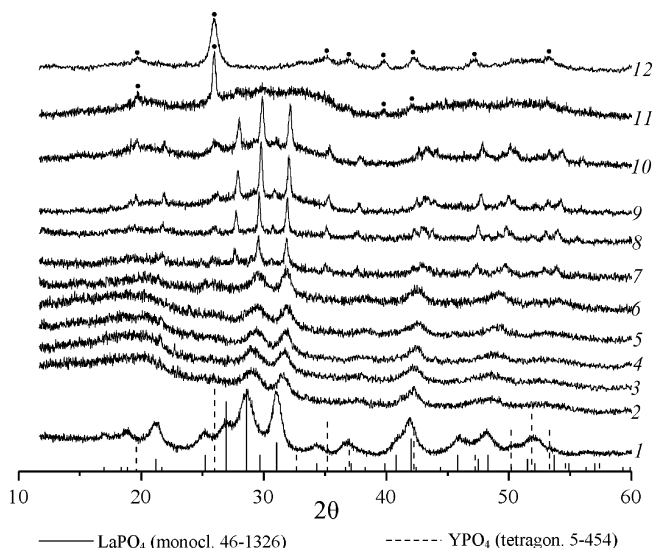


Fig. 6: XRD patterns of  $\text{La}_{1-x}\text{Y}_x\text{PO}_4$  samples after heating at 600 °C for 1 h,  $x$ : 0.0 (1), 0.25 (2), 0.3 (3), 0.4 (4), 0.5 (5), 0.6 (6), 0.7 (7), 0.75 (8), 0.8 (9), 0.85 (10), 0.9 (11), 1.0 (12), and the bar graphs represent the XRD patterns of  $\text{LaPO}_4$  and  $\text{YPO}_4$  of ICDD-PDF – tetragonal phase.

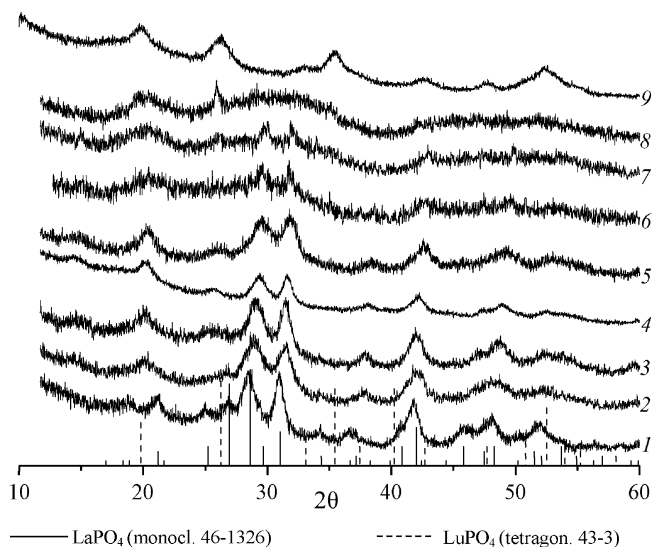


Fig. 7: XRD patterns of  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4$  samples after heating at 600 °C for 1 h,  $x$ : 0.0 (1), 0.25 (2), 0.3 (3), 0.4 (4), 0.5 (5), 0.6 (6), 0.7 (7), 0.75 (8), 1.0 (9), and the bar graphs represent the XRD patterns of  $\text{LaPO}_4$  and  $\text{LuPO}_4$  of ICDD-PDF.

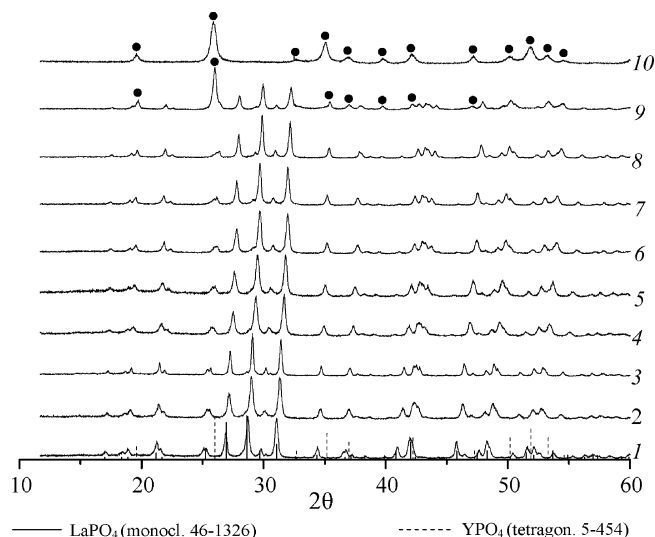


Fig. 8: XRD patterns of  $\text{La}_{1-x}\text{Y}_x\text{PO}_4$  samples after heating at 1000 °C for 1 h,  $x$ : 0.0 (1), 0.25 (2), 0.3 (3), 0.5 (4), 0.6 (5), 0.7 (6), 0.8 (7), 0.85 (8), 0.9 (9), 1.0 (10), and the bar graphs represent the XRD patterns of  $\text{LaPO}_4$  and  $\text{YPO}_4$  of ICDD-PDF – tetragonal phase.

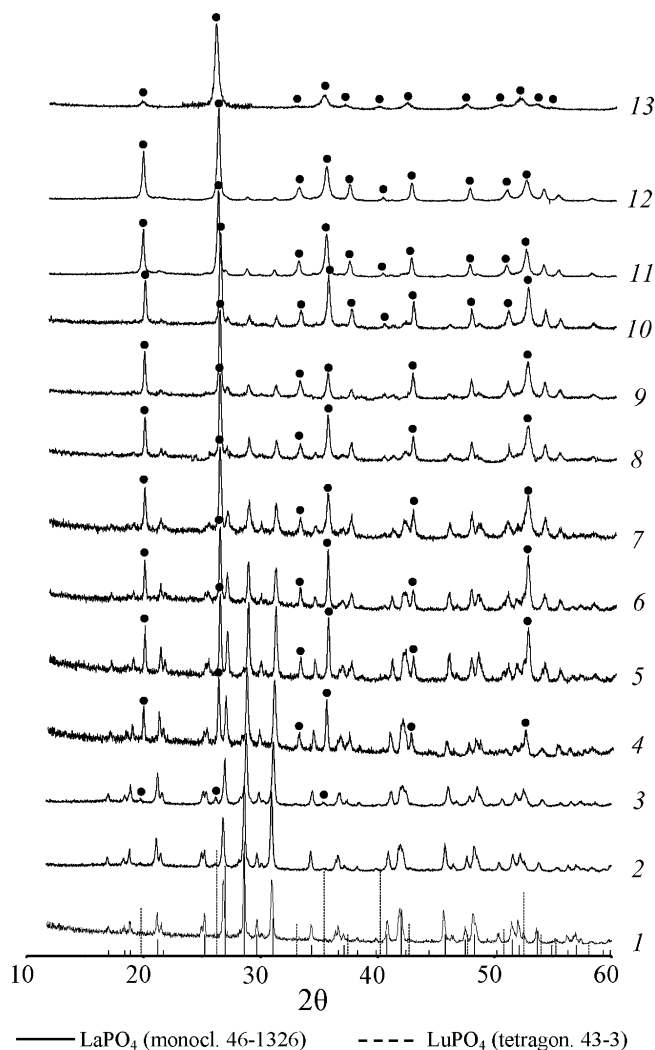


Fig. 9: XRD patterns of  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4$  samples after heating at 1100 °C for 1 h,  $x$ : 0.0 (1), 0.1 (2), 0.2 (3), 0.25 (4), 0.3 (5), 0.4 (6), 0.5 (7), 0.6 (8), 0.7 (9), 0.75 (10), 0.8 (11), 0.9 (12), 1.0 (13), and the bar graphs represent the XRD patterns of  $\text{LaPO}_4$  and  $\text{LuPO}_4$  of ICDD-PDF – tetragonal phase (main lines).

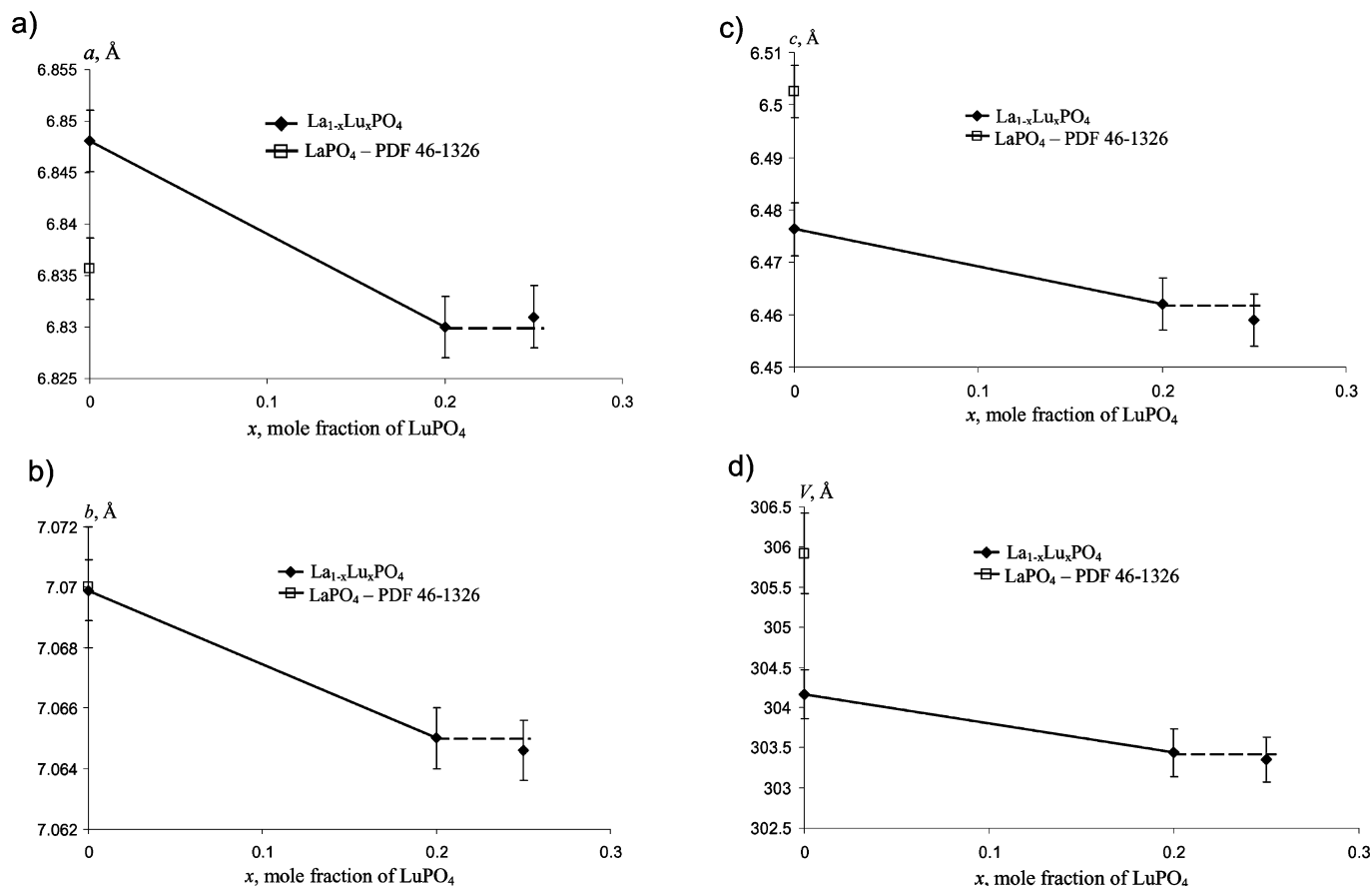


Fig. 10: Unit cell parameters of a monoclinic  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4$  series of samples calcined at 1000 °C (1 h): (a) – parameter  $a$ , Å; (b) – parameter  $b$ , Å; (c) – parameter  $c$ , Å; (d) – volume  $V$ , Å<sup>3</sup>.

Fig. 11 presents the DSC/TG curves of the  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples at various yttrium concentrations ( $x$ ). If these curves are compared with the curves given in <sup>17</sup> for the  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  series, we can say that they illustrate the existence of two types of solid solutions with very similar thermal behavior for each type (endothermic effects observed in the range of 90–400 °C and the considerable weight loss of the samples is associated with water removal <sup>17, 19, 20, 21, 22, 24, 25, 30</sup>).

Weak exothermic effects with onset in the range of 425–485 °C observed for the samples with  $\text{Lu}^{3+}$  content up to  $x = 0.5$ – $0.6$  can be referred to monotropic hexagonal-monoclinic phase transformation according to <sup>17, 19</sup> and Fig. 7. A  $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$  sample usually does not reveal this effect <sup>31</sup>.

In case of  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples, these weak exothermic effects based on monotropic hexagonal-monoclinic phase transformation are observed in the range of 420–480 °C up to  $x = 0.7$ – $0.75$ .

At higher temperatures exothermic effects appear on the DSC curves of both the  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  (Fig. 11) and  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  series of samples <sup>17, 25</sup> which are not accompanied by mass loss.

In particular, a  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  series shows exothermic effects in 613–690 °C temperature range. At  $\text{Y}^{3+}$  concentration of  $x = 0.6$ , a weak broadened effect appears at 690 °C. Then at  $\text{Y}^{3+}$  content of  $x = 0.7$ – $0.75$  double exothermic effects appear with onset at 616 and 678 °C, and 618 and 677 °C respectively. In the case of

$\text{YPO}_4 \cdot n\text{H}_2\text{O}$ , a weak broadened effect is observed at 613 °C.

A similar phenomenon takes place in the case of  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples <sup>17</sup>. In  $0.6 \leq x \leq 0.75$  concentration range of  $\text{Lu}^{3+}$  double exothermic effects appear, namely at 715 and 790 °C for  $x = 0.6$ , 725 and 795 °C for  $x = 0.7$ , 760 and 840 °C for  $x = 0.75$ . In the case of  $\text{LuPO}_4 \cdot n\text{H}_2\text{O}$  a weak broadened effect is observed at 570 °C.

The size effect of orthophosphates is noticeable in the general run of DSC curves, especially for the samples containing tetragonal phase <sup>16, 17, 25</sup>. Thus on DSC curves the onset of the exothermal effects is observed at 600–700 °C (Fig. 11, curves 6–9), and was not observed for micron-size particles of Ho, Tm, Er, Yb, Lu and Y orthophosphates <sup>21, 30, 32, 33, 34</sup> and considered to be associated with intensification of nanograin growth process (Figs. 12, 13).

Temperature dependences of the particle sizes  $D$  versus concentrations  $x$  for  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4(\cdot n\text{H}_2\text{O})$  samples clearly illustrate an existence of two types of solid solutions (monoclinic and tetragonal). In the case of  $\text{La}_{1-x}\text{Y}_x\text{PO}_4(\cdot n\text{H}_2\text{O})$  this is not so obvious, very likely due to a narrower concentration range for the coexistence of the two solid solutions (Figs. 12, 13).

Specific surfaces for  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4(\cdot n\text{H}_2\text{O})$  samples compared with literature data and melting temperatures of  $\text{La}_{1-x}\text{Y}_x\text{PO}_4$  samples are presented in Table 1 and Table 2, respectively.

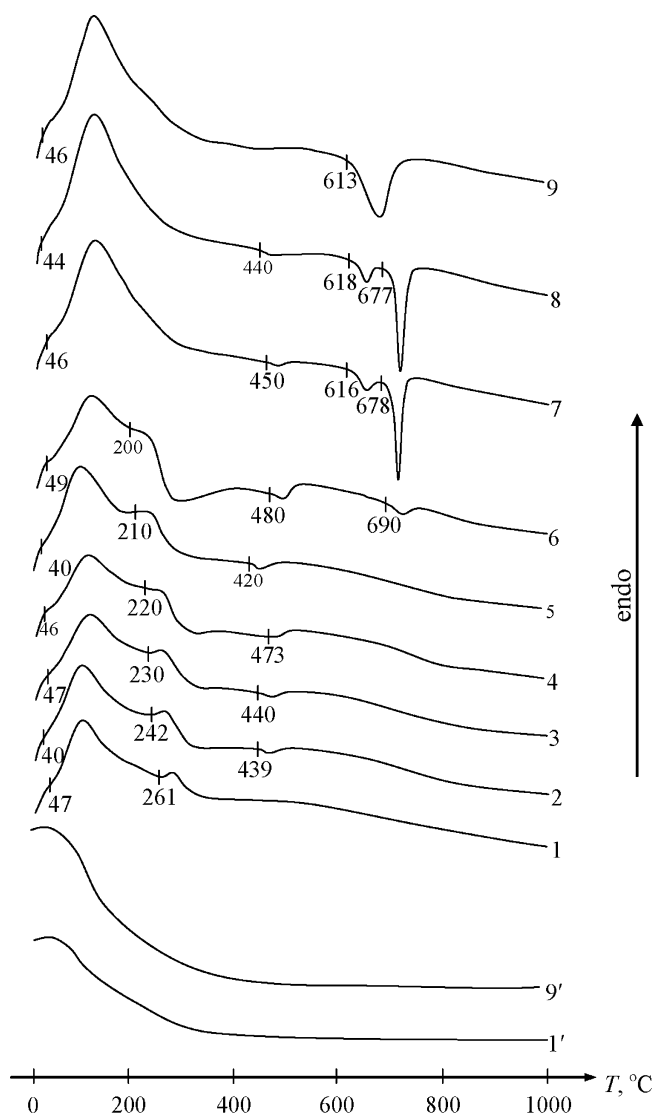


Fig. 11: DSC curves for the  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples at yttrium concentrations  $x$ : 0.0 (1), 0.25 (2), 0.3 (3), 0.4 (4), 0.5 (5), 0.6 (6), 0.7 (7), 0.75 (8), 1.0 (9). TG curves for  $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$  (1') and  $\text{YPO}_4 \cdot n\text{H}_2\text{O}$  (9') samples.

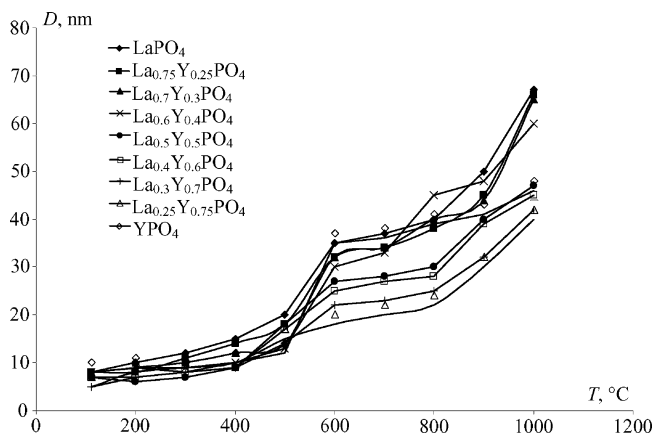


Fig. 12: Dependences of the average particle size  $D$  on the calcination temperature (1 h) for the  $\text{La}_{1-x}\text{Y}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples at various yttrium concentrations  $x$  (within experimental and estimating error of about 50 % for Scherrer's formula and about 30 % for electron microscopy).

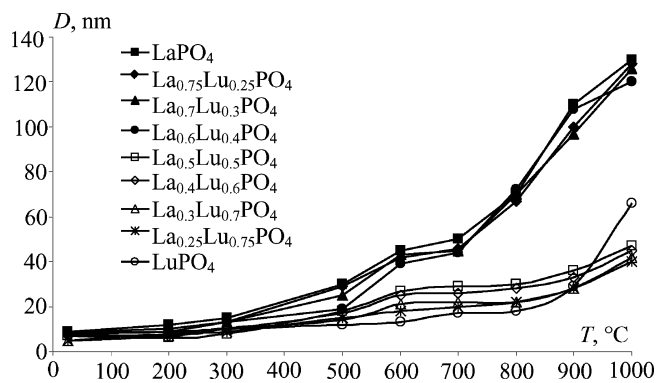


Fig. 13: Dependences of the average particle size  $D$  on the calcination temperature (1 h) for the  $\text{La}_{1-x}\text{Lu}_{0.25}\text{PO}_4 \cdot n\text{H}_2\text{O}$  samples at various lutetium concentrations  $x$  (within experimental and estimating error of about 50 % for Scherrer's formula and about 30 % for electron microscopy).

Table 1: Specific surface area of  $\text{La}_{1-x}\text{Lu}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$  powders determined with the multipoint BET method compared with literature data for  $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ .

Sample, $x$	Crystal structure	Specific surface area, $\text{m}^2/\text{g}$	Specific surface area, $\text{m}^2/\text{g}$ (from literature)
0.0	Hexagonal	62.0	55 – 97 <sup>34</sup> , 76 <sup>35</sup>
0.25	Hexagonal	90.3	–
0.3	Hexagonal	66.7	–
0.4	Hexagonal	64.6	–
0.5	Hexagonal	53.8	–
0.6	Hexagonal	46.7	–
0.7	Hexagonal	61.1	–
0.75	Hexagon. + tetragon.	63.5	–
1.0	Tetragonal	3.3	–

Table 2: Melting temperatures of  $\text{La}_{1-x}\text{Y}_x\text{PO}_4$  samples determined by using VPA in Galakhov's modified microfurnace (argon, total pressure in the system – 0.5 MPa)

Sample, $x$	Crystal structure	Melting temperature, ( $\pm$ (10 – 15 K))
0.0	Monoclinic	2050
0.25	Monoclinic	2010
0.3	Monoclinic	2040
0.4	Monoclinic	1987
0.5	Monoclinic	1984
0.6	Monoclinic	1993
0.7	Monoclinic	1985
0.75	Monocl. + tetragon.	1960
1.0	Tetragonal	1980



#### IV. Summary

The synthesized individual orthophosphates ( $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$ ) and their binary compositions in  $\text{LaPO}_4\text{-YPO}_4\text{-H}_2\text{O}$  and  $\text{LaPO}_4\text{-LuPO}_4\text{-H}_2\text{O}$  systems are nanodispersed, with an average grain size of 10–20 nm and high specific surface area of hexagonal samples.

Three types of solid solutions were found in the systems – hexagonal, monoclinic and tetragonal.

In the  $\text{LaPO}_4\text{-YPO}_4\text{(-H}_2\text{O)}$  system, a series of limited hexagonal solid solutions based on  $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$  is observed up to 500–600 °C within the  $0 \leq x \leq 0.5$  concentration range which transforms above this temperature into a monoclinic form based on  $\text{LaPO}_4$  and remains up to at least 1000 °C. The isomorphic capacity of monoclinic  $\text{LaPO}_4$  at 1000 °C is therefore about 70 mol%.

In the  $\text{LaPO}_4\text{-LuPO}_4\text{(-H}_2\text{O)}$  system, a series of limited hexagonal solid solutions based on  $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$  is observed up to the same temperatures (500–600 °C) within the  $0 \leq x \leq 0.4$  concentration range. Monoclinic form in this system remains up to 1100 °C, and its isomorphic capacity at this temperature is about 20 mol%.

Solubility of  $\text{LaPO}_4$  in tetragonal  $\text{YPO}_4$  or  $\text{LuPO}_4$  in all cases is less than 10 mol%.

Therefore, rare earths orthophosphate nanopowders are suitable for the preparation of ceramics for radioactive waste immobilization relating to actinide/rare-earth group occurring in high-level waste (HLW) because rare earths orthophosphates possess high chemical resistance and isomorphic capacity, as well as high thermal stability.

Melting temperatures of  $\text{La}_{1-x}\text{Y}_x\text{PO}_4$  samples were found to be in the 2010–1960 °C temperature range, which is high enough for the purpose of radioactive waste immobilization.

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