

# Crystal structures of lanthanide and zirconium phosphates with general formula $Ln_{0.33}Zr_2(PO_4)_3$ , where $Ln = Ce, Eu, Yb$

D.M. Bykov<sup>b</sup>, E.R. Gobechiya<sup>a</sup>, Yu.K. Kabalov<sup>a</sup>, A.I. Orlova<sup>b,\*</sup>, S.V. Tomilin<sup>c</sup>

<sup>a</sup>Geological Department, Moscow State University, Moscow 119992, Russia

<sup>b</sup>Chemical Department, Nizhny Novgorod State University, Nizhny Novgorod 603950, Russia

<sup>c</sup>Waste Immobilization Laboratory, Chemical and Technological Department, Research Institute of Atomic Reactors, Dimitrovgrad – 10, Ulyanovsk region 433510, Russia

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## Abstract

Crystal structures of synthetic phosphates  $Ce_{0.33}Zr_2(PO_4)_3$ ,  $Eu_{0.33}Zr_2(PO_4)_3$  and  $Yb_{0.33}Zr_2(PO_4)_3$  have been refined by Rietveld method using powder diffraction data. Unit cell parameters:  $a = 8.7419$  (4),  $c = 23.128$  (2) Å;  $a = 8.7659$  (1),  $c = 22.822$  (1) Å;  $a = 8.8078$  (4),  $c = 22.485$  (3) Å, respectively;  $Z = 6$ . Values of final  $R$ -factors in isotropic approximation:  $R_{wp} = 4.00$ ,  $R_p = 3.33$ ,  $R_{wp} = 4.12\%$ , respectively. New space group  $P\bar{3}c$  has been established for the compounds with general formula  $Ln_{0.33}Zr_2(PO_4)_3$ , where  $Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu$  and  $Y$ . It has been confirmed that the synthetic phosphates with general formula  $Ln_{0.33}Zr_2(PO_4)_3$  belong to the NZP (sodium zirconium phosphate) structure type.

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**Keywords:** Lanthanides; Framework phosphates; NZP; Crystal structure; Refinement; Rietveld method

## 1. Introduction

Lanthanide and zirconium phosphates with general formula  $Ln_{0.33}Zr_2(PO_4)_3$  are studied as representatives of the framework phosphates family  $M_x[T_2(PO_4)_3]^{n-}$ , where  $0 \leq x \leq 4$ , T-cations in various oxidation states,  $n$ -framework charge. Many of them crystallize in the structure type of  $NaZr_2(PO_4)_3$  (NZP) [1]. Compounds with  $[Zr_2(PO_4)_3]^{1-}$  framework are studied the most extensively. Its charge may be compensated by different cations, varying in oxidation state from 1+ to 4+. When compensating by  $M^{3+}$  cations, the series of compounds with general formula  $M_{0.33}Zr_2(PO_4)_3$  is formed.

Known phosphates with lanthanum and lanthanides  $Ln_{0.33}Zr_2(PO_4)_3$  appear to be perspective objects in developing ceramic materials with ultralow thermal expansion [2,3]. Additionally, they also gain an interest as potential solid electrolytes with mobile multivalent ions

[4–8]. Among series of compounds  $M_{0.33}[T_2(PO_4)_3]$ , zirconium phosphates with yttrium [5], bismuth [9], iron [10] and some titanium compounds with lanthanum [11] and europium [12] are also studied.

For the compounds with general formula  $Ln_{0.33}Zr_2(PO_4)_3$ , where  $Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Er, Tm, Yb$ , the  $R\bar{3}c$  space group has been ascertained [2]. Among phosphates of the NZP family such lattice symmetry is also known for the double phosphate of lanthanum and titanium  $La_{0.33}Ti_2(PO_4)_3$  [11] and the zirconium compounds with divalent cations  $M_{0.5}Zr_2(PO_4)_3$ ,  $M^{II} = Ca, Sr, Cd, Ba, Pb$  [13]. The conclusion that symmetry reduces in  $Ln_{0.33}Zr_2(PO_4)_3$  compounds from  $R\bar{3}c$ , typical for  $NaZr_2(PO_4)_3$ , to  $R\bar{3}$  resulted from analysis of powder X-ray diffractograms. This examination revealed the presence of two lines on the patterns, which were not indexed within the  $R\bar{3}c$  space group and corresponded to interplanar spacings of 7.56 and 5.70 Å [2]. No structural data have been reported in [2] for the studied compounds. On account of this an attempt was made to refine crystal structures of the phosphates we synthesized of general

\*Corresponding author. Fax: +78312345056.

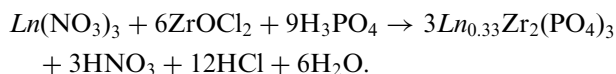
E-mail address: [oai@uic.nnov.ru](mailto:oai@uic.nnov.ru) (A.I. Orlova).

formula  $Ln_{0.33}Zr_2(PO_4)_3$  in order to obtain values of unit cell constants and interatomic distances. However, during our work we revealed and specially examined some additional reflections, which appeared at the XRD patterns of all the compounds under study but for La and were indexed within neither  $R\bar{3}c$  nor  $R\bar{3}$  space groups. For reason given, possible reduction of symmetry in such type of phosphates has been assumed to occur. Results of the experiment performed are given in the present paper.

## 2. Experimental

Synthesis of phosphates  $Ln_{0.33}Zr_2(PO_4)_3$ , where  $Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu$  and  $Y$  has been carried out using precipitation procedure. Solutions of reagent-grade lanthanum, lanthanides and yttrium nitrates (or corresponding metal oxides), zirconium oxychloride  $ZrOCl_2 \cdot 8H_2O$  and ortho-phosphoric acid solutions have been taken as starting reagents. Concentrations of the prepared solutions were determined by means of gravimetric analysis (gravimetric compound— $ZrO_2$ ) in case of zirconium oxychloride, and titration by the EDTA solution in the presence of Xylenol Orange as an indicator in case of lanthanides nitrates solutions [14].

Solutions of lanthanide nitrate (or weighed amount of its oxide powder preliminarily dissolved in a diluted nitric acid) and zirconium oxychloride were initially mixed together and then stoichiometric amount of phosphoric acid was added gradually dropwise to the obtained solution under continuous stirring within 15–20 min, followed by thermal treatment at 80, 600 and 800 °C. Duration of heating amounted to 24 h at each stage. Heating was alternated with intermediate careful grinding in an agate mortar. Chemical reaction during the synthesis proceeded according to the following scheme:



The samples obtained were finely crystalline white or slightly colored powders. They were pressed into pellets, additionally sintered at 800 °C for as long as 3 h and subsequently used for the XRD measurements. Diamond powder was used as an internal standard in order to verify precisely positions of peaks. A little amount of powder was deposited at the surface of each pellet prior to measurement.

X-ray phase analysis of the synthesized compounds has been performed using DRON 3 M X-ray diffractometer,  $\lambda CuK\alpha$ , Ni-filter, at room temperature over the angular range 7–80°  $2\theta$  with a step of 0.02 and a count time of 3 s/step.

Powder patterns of the samples with general formula  $Ln_{0.33}Zr_2(PO_4)_3$ , where  $Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu$  and  $Y$ , have been indexed assuming the  $R\bar{3}$  space group, structure type of  $NaZr_2(PO_4)_3$  [1] (Fig. 1).

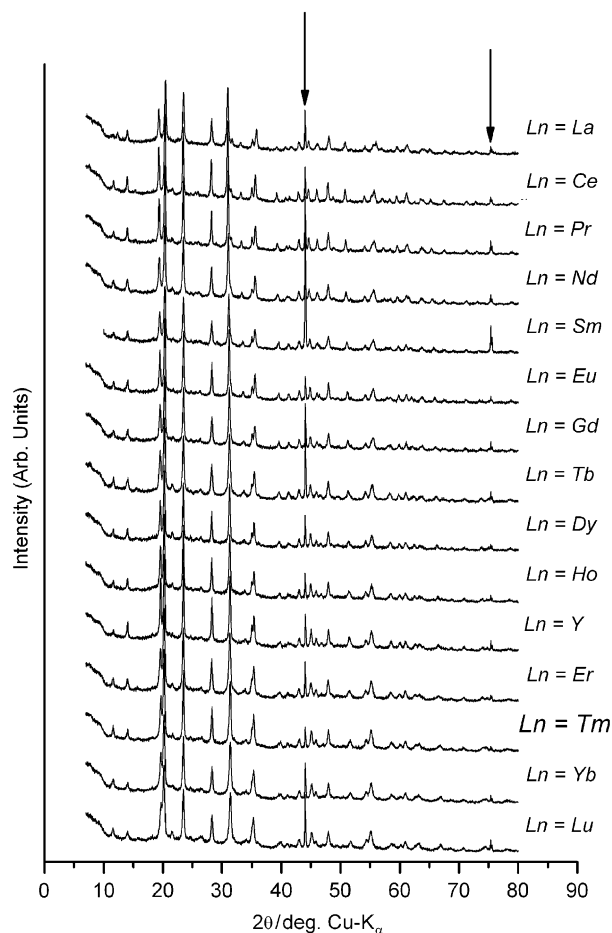


Fig. 1. X-ray diffraction patterns of the compositions  $Ln_{0.33}Zr_2(PO_4)_3$ , where  $Ln = La, Ce-Lu$  and  $Y$ , prepared at 800 °C. Arrows indicate peak positions of diamond standard.

X-ray diffraction patterns of the powder samples  $Ce_{0.33}Zr_2(PO_4)_3$ ,  $Eu_{0.33}Zr_2(PO_4)_3$ ,  $Yb_{0.33}Zr_2(PO_4)_3$ , chosen for the structural refinement, have been obtained at ADP-2 diffractometer,  $\lambda CuK\alpha$ , Ni-filter,  $15^\circ < 2\theta < 110^\circ$ ,  $2\theta$  step was  $0.02^\circ$ , and a counting time was 10 s/point. XRD patterns processing has been carried out using WYRIET program, version 3.3 [15]. Peaks profiles approximation was performed according to Pearson VII function at  $6F_{WHM}$  (region was confined by six values of width ( $W$ ) at half height  $H$  of a maximum). Asymmetry correction refined at  $2\theta < 60^\circ$ . Ion scattering curves have been used in the calculations for all elements.

Atomic coordinates for  $Cd_{0.5}Zr_2(PO_4)_3$ ,  $R\bar{3}$  space group, were used as a starting model [13]. However, already at the initial stage of refinement it became evident that some reflexes are present at the diffraction patterns of the investigated compounds (Table 1, Fig. 2(A)), being not indexed within the  $R\bar{3}$  space group. The presence of additional reflexes revealed either a secondary phase in the sample or possible reduction of symmetry to the space group, where these reflexes would meet rules of systematic extinctions. The additional reflexes have

Table 1

Experimental  $2\theta$  values, interplanar spacings and intensities of the reflections, being not indexed within the  $R\bar{3}$  space group for the powder diffraction pattern of  $\text{Eu}_{0.33}\text{Zr}_2(\text{PO}_4)_3$

No.	$2\theta$ (deg)	$d$ (Å)	$I$	$hkl^a$
1	15.481	5.719	5	004
2	21.666	4.099	9	112
3	25.571	3.480	5	114
4	26.146	3.406	6	016
				106
5	49.323	1.846	1	0112
				1012

<sup>a</sup>Indices of the X-ray reflections within the  $P\bar{3}c$  space group.

been examined in order to see if they belong to possible secondary phases which could stem from synthetic procedure. The following possible phases have been checked:  $\text{LaPO}_4$  (PDF# 75-881, 73-0188),  $\text{Zr}_2\text{P}_2\text{O}_9$  (PDF# 70-0888),  $\text{ZrP}_2\text{O}_7$  (PDF# 73-2297),  $\text{La}_2\text{O}_3$  (PDF# 83-1355),  $\text{ZrO}_2$  (PDF# 83-0944) [16]. This search failed to yield beneficial effect. Furthermore, it should be noted that additional peaks were reproduced for all lanthanide phosphates and appeared at diffraction patterns of the compounds, obtained at different times, by different authors and in different laboratories of the world, their location and relative intensity did not depend on reagents' prehistory. As long as additional lines appeared at all powder XRD patterns of the compounds with general formula  $\text{Ln}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ , where  $\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$  and  $\text{Y}$  and additional phases were not found, a thorough analysis has been undertaken, which revealed that these reflexes belong to investigated phases. In this connection a decision has been made to reduce the space group from  $R\bar{3}$  to  $P\bar{3}$ , i.e., to re-count atomic coordinates, excluding  $R$ -translation, and to refine crystal structures of the investigated compounds in a new space group. A pattern obtained consequently demonstrates an excessive increase of number of reflexes at the theoretical XRD pattern (Fig. 2(B)), which also does not correspond to the experimental data, despite the satisfactory reliability factors values:  $R_{\text{wp}} = 4.57\%$ ,  $S = 1.57$  (for  $\text{Eu}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ ). The best convergence of the experimental and theoretical patterns is observed when structures of the investigated compounds are refined assuming the  $P\bar{3}c$  space group (Fig. 2(C)). In this case, recalculation of the atomic coordinates was carried out with addition of symmetry plane  $c$ .

Crystallographic characteristics, basic parameters of the experiments and structures refinement results for the compounds  $\text{Ce}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ ,  $\text{Eu}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ ,  $\text{Yb}_{0.33}\text{Zr}_2(\text{PO}_4)_3$  are given in Table 2. Final coordinates, thermal parameters of the atomic displacements in isotropic approximation and occupancies of basic atoms positions are presented in Table 3. Experimental and theoretical XRD patterns of the

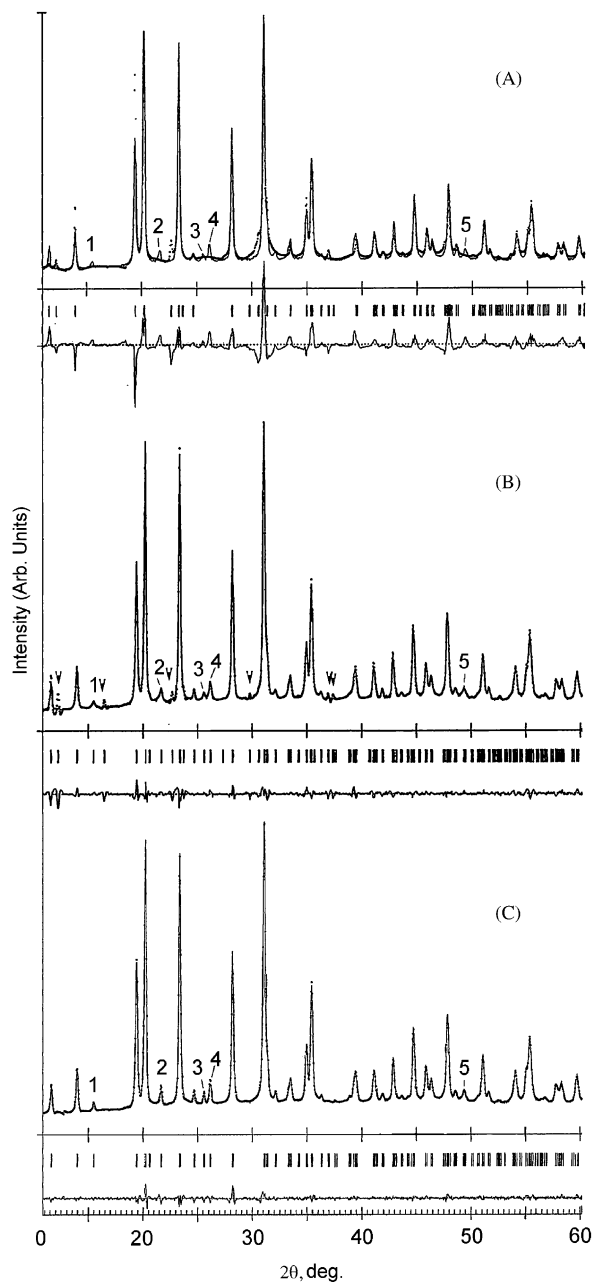


Fig. 2. Fragments of experimental (—) and theoretical (.....) profiles of the compound  $\text{Eu}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ , space groups (A)  $R\bar{3}$ , (B)  $P\bar{3}$  (additional reflexes at the theoretical pattern are marked with ticks), (C)  $P\bar{3}c$ . Vertical markers—position of reflexes of theoretical XRD patterns; curve at the bottom of each pattern—differential curve of intensities of experimental and theoretical profiles; numbered are the reflexes being not indexed within the  $R\bar{3}$  space group.

investigated phosphates are shown in Fig. 3(A)–(C). A fragment of the structure is presented in Fig. 4(A)–(C).

### 3. Results and discussion

Unit cell parameters calculated in the series of compounds from La to Lu change regularly (Fig. 5(A)–(C)). Thus, with increasing an atomic number of lanthanide a

Table 2

Crystallographic characteristics, basic parameters of the experiments and results of structures refinement of the phosphates  $Ce_{0.33}Zr_2(PO_4)_3$ ,  $Eu_{0.33}Zr_2(PO_4)_3$ ,  $Yb_{0.33}Zr_2(PO_4)_3$  by Rietveld method

Characteristic	$Ce_{0.33}Zr_2(PO_4)_3$	$Eu_{0.33}Zr_2(PO_4)_3$	$Yb_{0.33}Zr_2(PO_4)_3$
$a$ (Å)	8.7419(4)	8.7659(1)	8.8078(4)
$c$ (Å)	23.128(2)	22.822(1)	22.485(3)
$V$ (Å <sup>3</sup> )	1530.69(2)	1518.68(1)	1510.60(1)
Space group	$P\bar{3}c$	$P\bar{3}c$	$P\bar{3}c$
$2\theta$ -range (deg)	10.50–109.98	10.50–109.98	10.50–109.98
Number of reflections	1351	1336	1330
General number of points	4975	4975	4975
Number of parameters refined	55	55	55
$R_{wp}$ (%)	4.00	3.33	4.12
$R_p$ (%)	3.11	2.60	3.20
$R_B$ (%)	2.20	2.60	2.10
$R_F$ (%)	1.15	1.61	1.69
$R_{exp}$ (%)	3.09	2.90	2.78
$S$	1.29	1.15	0.95

tendency is observed for  $c$ -parameter to decrease, which is due to the lanthanide contraction phenomenon, at the same time an increasing of  $a$ -parameter and decreasing of  $V$  occurs. Unit cell parameters of lanthanum zirconium phosphate drift from the general trend for other lanthanide and zirconium phosphates. Presumably, owing to the bigger size of  $La^{3+}$  ion in comparison with other rare earth elements, it behaves differently in the structure, i.e., a process of disordering of La ions along the interstitial cavities starts, thus finding a reflection in values of unit cell parameters and shape of IR spectra of the corresponding phosphate [17].

The base of the structures  $Ce_{0.33}Zr_2(PO_4)_3$ ,  $Eu_{0.33}Zr_2(PO_4)_3$ ,  $Yb_{0.33}Zr_2(PO_4)_3$  is formed of three-dimensional mixed framework, built up in such a way, that each  $[ZrO_6]$ -octahedron is bound up with six  $[PO_4]$ -tetrahedrons by corner-sharing (Fig. 4). Range of interatomic distances in coordination polyhedra is close to the ordinary one for the phosphates with frameworks  $[Zr_2(PO_4)_3]_{\infty}^-$ : for the structure  $Ce_{0.33}Zr_2(PO_4)_3$ : Zr–O 2.04 (1)–2.22 (2), P–O 1.46 (2)–1.60 (2) Å;  $Eu_{0.33}Zr_2(PO_4)_3$ : Zr–O 2.03 (3)–2.17 (2), P–O 1.49 (3)–1.55 (4) Å;  $Yb_{0.33}Zr_2(PO_4)_3$ : Zr–O 2.02 (3)–2.16 (2), P–O 1.48 (4)–1.56 (4) Å.

Interstitial cavities of the octahedral shape, are for 1/3 occupied by atoms of Ce (Ce–O = 2.70 (2) Å × 6), Eu (Eu–O = 2.60 (3) Å × 6), Yb (Yb–O = 2.56 Å × 6) in structures of the phosphates  $Ce_{0.33}Zr_2(PO_4)_3$ ,  $Eu_{0.33}Zr_2(PO_4)_3$ ,  $Yb_{0.33}Zr_2(PO_4)_3$ , respectively.

Thus, in the investigated compounds, crystallizing in the NZP structure type, the symmetry reduces to the  $P\bar{3}c$  space group. Obviously, this conclusion is valid for the whole series of the phosphates concerned save for La phosphate in accordance with complete similarity of their XRD patterns (Fig. 1). This conclusion is also confirmed by the

Table 3

Final coordinates, thermal parameters of atomic displacements in isotropic approximation and occupancies ( $q$ ) of basic atoms positions in the structures of phosphates  $Ce_{0.33}Zr_2(PO_4)_3$ ,  $Eu_{0.33}Zr_2(PO_4)_3$ ,  $Yb_{0.33}Zr_2(PO_4)_3$

	$Ce_{0.33}Zr_2(PO_4)_3$	$Eu_{0.33}Zr_2(PO_4)_3$	$Yb_{0.33}Zr_2(PO_4)_3$
Ln	$x$	0	0
Ln	$y$	0	0
Ln	$z$	0	0
Ln	$B_{iso}$	2.8(3)	2.7(3)
Ln	$q$	0.166(3)	0.164(4)
Zr(1)	$x$	0	0
Zr(1)	$y$	0	0
Zr(1)	$z$	0.1499(2)	0.1476(3)
Zr(1)	$B_{iso}$	0.2(3)	0.3(5)
Zr(1)	$q$	0.334(5)	0.335(8)
Zr(2)	$x$	0.6667	0.6667
Zr(2)	$y$	0.3333	0.3333
Zr(2)	$z$	0.4747(4)	0.4745(7)
Zr(2)	$B_{iso}$	0.3(4)	0.5(6)
Zr(2)	$q$	0.334(8)	0.33(1)
Zr(3)	$x$	0.3333	0.3333
Zr(3)	$y$	0.6667	0.6667
Zr(3)	$z$	0.8137(4)	0.8130(7)
Zr(3)	$B_{iso}$	0.2(3)	0.1(6)
Zr(3)	$q$	0.334(5)	0.333(9)
P(1)	$x$	0.290(2)	0.293(4)
P(1)	$y$	0	0
P(1)	$z$	0.25	0.25
P(1)	$B_{iso}$	0.7(8)	1(2)
P(1)	$q$	0.50(3)	0.50(4)
P(2)	$x$	0.959(1)	0.958(2)
P(2)	$y$	0.339(2)	0.338(3)
P(2)	$z$	0.577(2)	0.580(2)
P(2)	$B_{iso}$	0.7(4)	0.9(5)
P(2)	$q$	1.00(3)	1.00(5)
O(1)	$x$	0.169(3)	0.183(6)
O(1)	$y$	−0.061(3)	−0.025(7)
O(1)	$z$	0.200(1)	0.197(1)
O(1)	$B_{iso}$	1.1(5)	0.9(7)
O(2)	$x$	0.839(4)	0.843(6)
O(2)	$y$	0.303(4)	0.310(6)
O(2)	$z$	0.527(1)	0.527(2)
O(2)	$B_{iso}$	0.7(5)	0.6(9)
O(3)	$x$	0.511(4)	0.519(6)
O(3)	$y$	0.637(5)	0.657(8)
O(3)	$z$	0.865(1)	0.863(2)
O(3)	$B_{iso}$	0.7(5)	0.8(8)
O(4)	$x$	0.214(3)	0.206(4)
O(4)	$y$	0.176(4)	0.171(5)
O(4)	$z$	0.090(1)	0.087(2)
O(4)	$B_{iso}$	0.7(5)	0.6(5)
O(5)	$x$	0.858(4)	0.859(5)
O(5)	$y$	0.493(4)	0.499(5)
O(5)	$z$	0.415(1)	0.419(3)
O(5)	$B_{iso}$	0.8(5)	0.7(7)
O(6)	$x$	0.526(3)	0.525(5)
O(6)	$y$	0.837(4)	0.834(6)
O(6)	$z$	0.753(2)	0.752(2)
O(6)	$B_{iso}$	0.7(5)	0.7(7)

results of IR spectroscopy study of the synthetic phosphates with general formula  $Ln_{0.33}Zr_2(PO_4)_3$ , where  $Ln = La, Ce-Lu$  and  $Y$  [17].

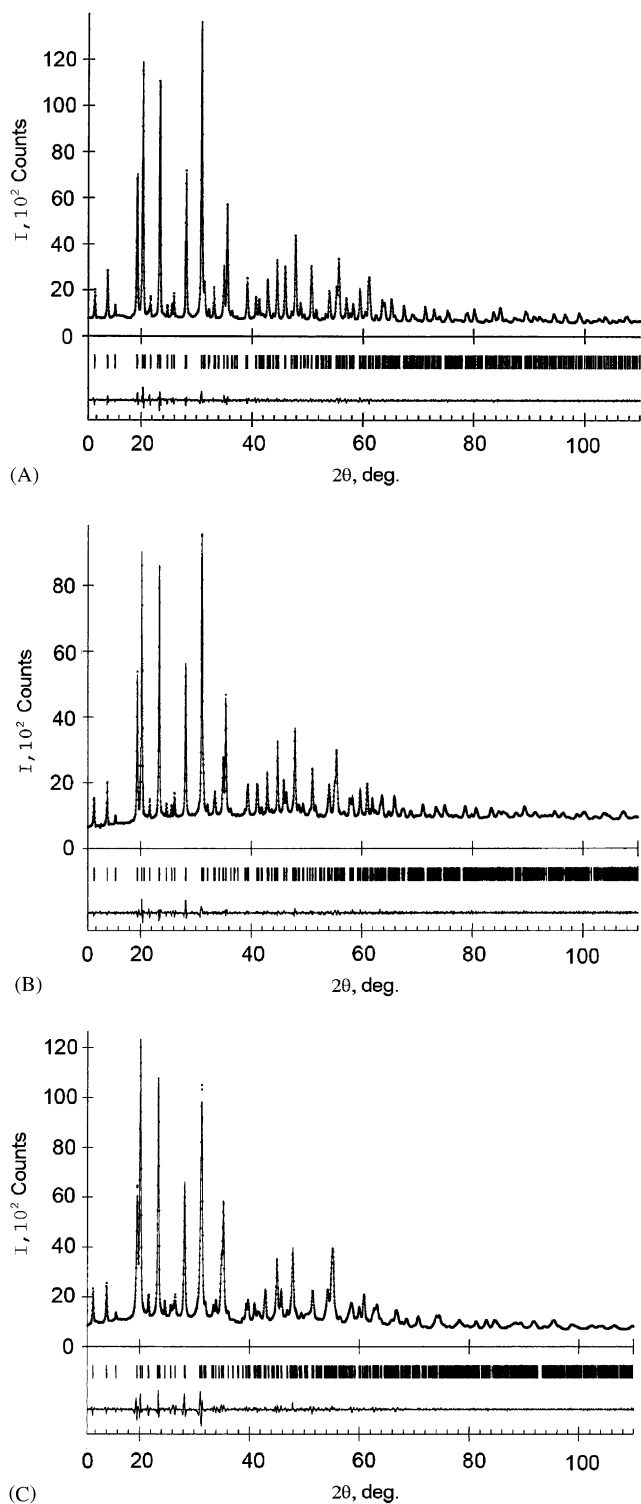


Fig. 3. Experimental (—) and theoretical ( . . . ) XRD patterns of the compounds: (A)  $\text{Ce}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ ; (B)  $\text{Eu}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ ; (C)  $\text{Yb}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ , space group  $P\bar{3}c$ . Vertical markers—position of reflexes of theoretical XRD pattern; curve at the bottom of the pattern—differential curve of intensities of experimental and theoretical profiles.

On the whole, generalizing the results obtained in the present work and the data known from literature on the trigonal phosphates of the NZP

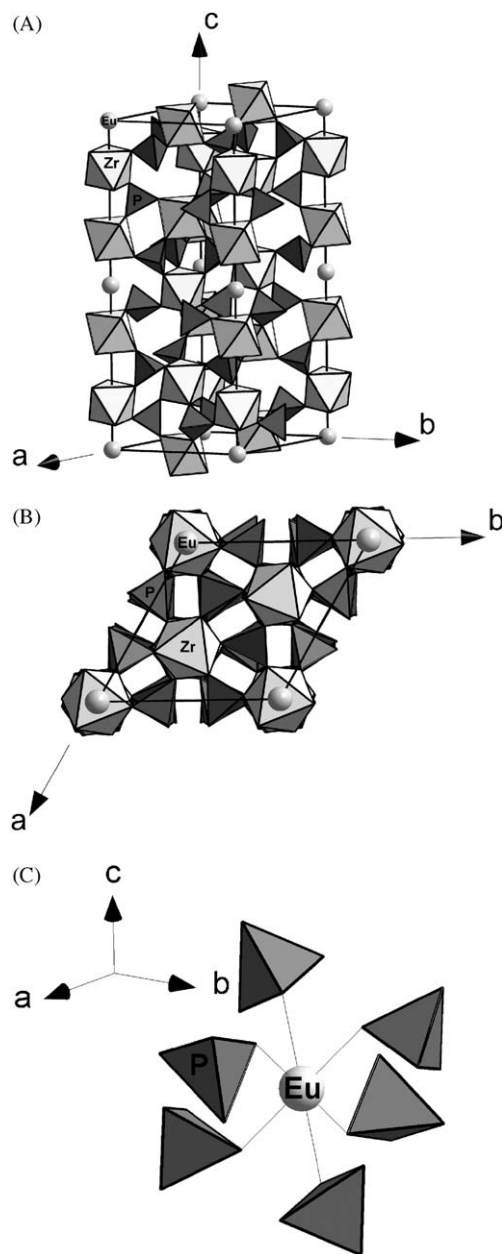


Fig. 4. (A) Fragment of structure of synthetic phosphate  $\text{Eu}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ ; (B) projection of structure of synthetic phosphate  $\text{Eu}_{0.33}\text{Zr}_2(\text{PO}_4)_3$  onto the (110) plane; (C) coordination of Eu atom.

family with general formula  $M_x[\text{T}_2(\text{PO}_4)_3]$ ,  $x = 1, 0.5, 0.33$  it might be concluded that symmetry reduction may occur in two ways:

1.  $R\bar{3}c \rightarrow R\bar{3}$  (transition from  $M^I\text{Zr}_2(\text{PO}_4)_3$  to  $M^{II}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  with layered (by 1/2) occupation of the interstitial positions by divalent ions of alkaline-earth elements and Cd and loss of  $c$ -planes;
2.  $R\bar{3}c \rightarrow P\bar{3}c$  (transition from  $M^I\text{Zr}_2(\text{PO}_4)_3$  to  $M^{III}_{0.33}\text{Zr}_2(\text{PO}_4)_3$  with occupation of 1/3 of the interstitial positions by trivalent ions of lanthanides and yttrium and loss of  $R$  translations.

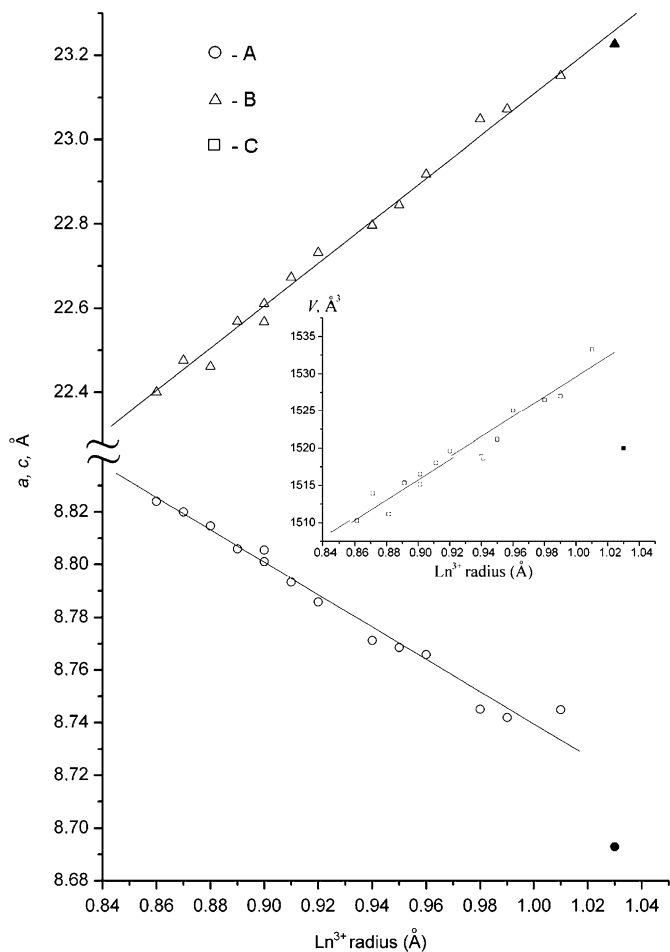


Fig. 5. Unit cell parameters versus  $Ln^{3+}$  ionic radius for the phosphates  $Ln_{0.33}Zr_2(PO_4)_3$ : (A)  $a$ -parameter; (B)  $c$ -parameter; (C) volume ( $V$ );  $Ln = La$  (● ▲ ■), Ce–Lu and Y (○ △ □).

#### 4. Conclusions

Phosphates with general formula  $Ln_{0.33}Zr_2(PO_4)_3$ , where  $Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu$  and  $Y$  have been synthesized using precipitation method. They were characterized by powder X-ray diffraction analysis. Rietveld refinement has been carried out for the selected representatives of the row, namely  $Ce_{0.33}Zr_2(PO_4)_3$ ,  $Eu_{0.33}Zr_2(PO_4)_3$ ,  $Yb_{0.33}Zr_2(PO_4)_3$ , which revealed symmetry reduction in this type of phosphates.

Atomic coordinates, thermal parameters of atomic displacements and occupancies of basic atoms positions have been obtained. The new space group  $P\bar{3}c$  has been established for the whole series of compounds  $Ln_{0.33}Zr_2(PO_4)_3$  with  $Ln = Ce-Lu$  and  $Y$ .

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