Crystal structure of new phosphates $Ca_{9-x}Pb_xEu(PO_4)_7$ from Rietveld refinement

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New phosphates $Ca_{9-x}Pb_xEu(PO_4)_7$ were obtained by solid state reaction techniques at 1213–1253 K in air atmosphere and were found to be isotypic with whitlockite-type β-$Ca_3(PO_4)_2$. The unit cell parameters were determinate using Le Bail decomposition. Rietveld method structural refining showed that Eu^{3+} ions are located statistically with calcium in *M*1, *M*2, and *M*3 sites, whereas Pb^{2+}-ions are preferentially located in the *M*3. Examination of optical second harmonic generation evidences nonlinear optical activity and confirms polar space group *R*3*c*. © *2015 International Centre for Diffraction Data*. [doi:10.1017/S0885715615000068]

Key words: whitlockite, polar structure, nonlinear optical activity, phase transition Rietveld refinement

I. INTRODUCTION

The phosphates with whitlockite-type structure crystallize in trigonal symmetry (Dickens *et al.*, 1974). The whitlockite-type (β-TCP) structure is built of isolated PO_4 tetrahedra, which connect the MO_n polyhedra into a three-dimensional framework via common vertices. The crystal structure encloses five crystallographic sites different in size and oxygen coordination (*M*1, *M*2, *M*3, *M*4, and *M*5) (Yashima *et al.*, 2003). The *M*1, *M*2, and *M*3 sites have eight-fold oxygen coordination. The *M*5 is the smallest and site has octahedral coordination. The surrounding of *M*4 and *M*6 sites are $M4O_{15}$ and $M6O_{13}$, respectively. The structural studies show that ions with radii ~1–1.6 Å, for example, cations of alkali metals and lead (Shannon, 1976; Sandstrom and Bostrom, 2006; Deyneko *et al.*, 2013), can occupy this (*M*4) site.

In connection with the substitution scheme $(3Ca^{2+}) \rightarrow (2Ln^{3+} + \square)$ supplementary vacancies are generated and located in *M*4 site. The non-centrosymmetric structure leads to ferroelectric properties and observing phase transitions. Besides, phosphates with whitlockite-type structure demonstrate multifunctional properties, such as ferroelectric (Lazoryak *et al.*, 2004), antiferroelectric (Stefanovich *et al.*, 2004) luminescence (Benhamou *et al.*, 2009), termoluminescence (Bessiere *et al.*, 2012), and ion conduction (Lazoryak *et al.*, 2003). The distribution of REE was studied in phosphates $Ca_9Ln(PO_4)_7$ (Bessiere *et al.*, 2012). Measure of occupancy of *M*1, *M*2, *M*3, and *M*5 sites by RE^{3+} depends on ionic radius. In case of Eu^{3+} only three sites *M*1, *M*2, and *M*3 can be occupied by Eu^{3+}. It was confirmed by Mossbauer (Lazoryak *et al.*, 1990) results and luminescence spectroscopy (Lazoryak *et al.*, 1989). The incorporation of high polarizable ion, such as Pb^{2+} or Bi^{3+} leads to noticeable changes of ferroelectric (Deyneko *et al.*, 2013) and luminescence (Yonglei *et al.*, 2014; Zhang *et al.*, 2014) properties.

Therefore, in this paper, a detailed study of the structural and nonlinear optical properties of $Ca_{9-x}Pb_xEu(PO_4)_7$ ($0 \leq x \leq 1$) phosphors is reported.

II. EXPERIMENTAL

A. Sample preparation

The new phosphates $Ca_{9-x}Pb_xEu(PO_4)_7$ were synthesized by solid state reaction from stoichiometric amounts of Eu_2O_3, $CaCO_3$, $CaHPO_4{\cdot}2H_2O$, and PbO at 1223–1273 K for 120 h. The mixture was heated progressively with intermittent grinding at 473 K (12 h), 773 K (12 h), 973 K (12 h), 1173 K (24 h), and 1253, 1233, 1213 K (24 h) (for $x = 0.2$, 0.5 and 1, respectively) in air atmosphere.

B. Powder diffraction data collection and reduction

The room temperature powder X-ray diffraction patterns of the $Ca_{9-x}Pb_xEu(PO_4)_7$ were recorded on Bruker Smart X2S. The main details of the data collection are given in Table I. To determine the lattice parameters, Le Bail decomposition (Le Bail *et al.*, 1988) was applied. The Rietveld refinement of the structure was performed using the JANA2006 software (Dusek *et al.*, 2001; Petrícek *et al.*, 2014).

The second harmonic generation (SHG) response of powder samples was measured with a Q-switched YAG:Nd laser at $\lambda_\omega = 1064$ nm in the reflection mode. The experimental set-up is described elsewhere (Kurts and Perry, 1968). The intensities of the SHG signal ($I_{2\omega}$) from the sample and that from a reference sample (polycrystalline α-SiO_2 with 3–5 μm particles size) were registered.

The powders were checked for centrosymmetry by SHG tests, which were performed with a laser system using fine powders as described elsewhere. The SHG signal was excited by the 1.064-μm line of a Minilite Q-switched pulsed Nd:YAG laser. The second harmonic intensity was measured as a function of temperature at a wavelength of 0.532 μm in reflection geometry using both powder and ceramic samples.

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TABLE I. Crystallographic data and details in the data collection and refinement parameters for the $Ca_{9-x}Pb_xEu(PO_4)_7$.

$Ca_{8.5}Pb_{0.5}Eu(PO_4)_7$
Space group: $R3c$ [$Z = 6$, $a = 10.470\ 15(4)$ Å, $b = 10.470\ 15(4)$ Å, $c = 37.4873\ (2)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, and $V = 3558.94(3)$ Å^3
Experimental data
Temperature, 298 K; angular range, $4.003° \le 2\theta \le 99.992°$; step scan increment ($2\theta$), 0.01°
Conventional Rietveld R-factors, $R_{WP} = 3.1\%$; $R_P = 2.1\%$; $R_E = 1.1\%$; $\chi^2 = 2.88$
$Ca_8PbEu(PO_4)_7$
Space group: $R3c$ [$Z = 6$, $a = 10.489\ 94(9)$ Å, $b = 10.489\ 94(9)$ Å, $c = 37.5571\ (3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, and $V = 3579.06(5)$ Å^3
Experimental data
Temperature, 298 K; angular range, $4.003° \le 2\theta \le 99.992°$; step scan increment ($2\theta$), 0.01°
Conventional Rietveld R-factors, $R_{WP} = 3.8\%$; $R_P = 2.5\%$; $R_E = 1.1\%$; $\chi^2 = 3.40$

The optical nonlinearity of the materials was evaluated from the second-harmonic signal intensity $I_{2\omega}$ relative to that of a α-quartz reference powder with a particle size in the range 3–5 μm.

III. RESULTS AND DISCUSSION

The experimental powder diffraction pattern is shown in Figure 1. Structural parameters are given in Table I.

The unit cell parameters for $Ca_{9-x}Pb_xEu(PO_4)_7$ are listed in Table I. All solid solution crystallizes in polar space group $R3c$, $Z = 6$. Initially, the structure refined by the Rietveld method was carried out starting from data (Benhamou *et al.*, 2009). Further, the population of the cation positions was refined. The JANA2006 program was ran using the pseudo-Voigt profile function to refined atomic coordinates and distances. The Ca/Eu splitting was not used in structure refinement.

At first, it was determined, that $M5$ site is fully occupied by Ca^{2+} ions. After that the occupancy of $M1$–$M3$ sites with Ca^{2+}, Eu^{3+}, and Pb^{2+} ions was found.

After the last refinement, there was a good agreement between the observed and calculated patterns. According to the

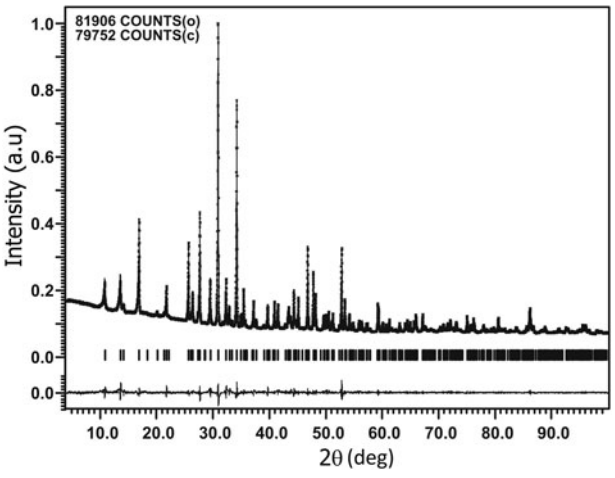


Figure 1. Rietveld plot for $Ca_8PbEu(PO_4)_7$ observed (crosses), calculated (solid) and angular positions of possible Bragg reflections (bars). Lower plot: (I_c–I_o) difference curve.

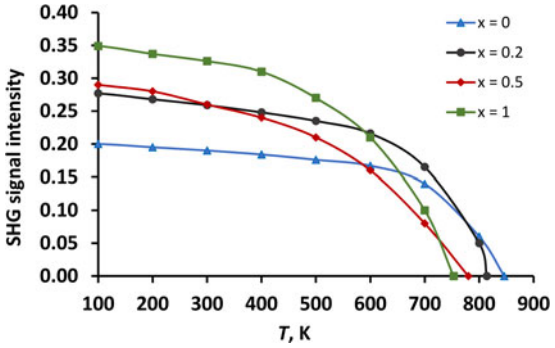


Figure 2. (Color online) Temperature dependence of SHG intensity for $Ca_{9-x}Pb_xEu(PO_4)_7$.

obtained data, Eu^{3+} ions preferentially occupy $M1$, $M2$, and $M3$ sites with calcium, contradicting previously published Mössbauer results (Lazoryak *et al.*, 1990). $M5$ site fully occupied by Ca^{2+}. Pb^{2+} ions primarily enters into the $M3$ site and only then shares positions $M1$, $M2$ with calcium or Eu^{3+} ions. SHG tests evidenced higher nonlinear optical activity of Pb^{2+}-containing compositions in comparison with $Ca_9Eu(PO_4)_7$, and it also reveals ferroelectric type phase transitions to centrosymmetric group $R3c \rightarrow R\text{–}3c$ between 750 and 850 K (Figure 2).

Structural mechanisms and dielectric features of phase transitions are strongly influenced by the exact distributions of guest atoms over the positions.

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SUPPLEMENTARY MATERIALS AND METHODS

The supplementary material for this article can be found at http://www.journals.cambridge.org/PDJ

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