Luminescence, structure and antiferroelectric-type phase transition in Ca$_8$ZnEu(PO$_4$)$_7$

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A R T I C L E   I N F O

Keywords:
Phosphates
Luminescence
Antiferroelectric
Crystal structure
Synchrotron radiation

A B S T R A C T

Photoluminescence excitation and emission spectra of new phosphate Ca$_8$ZnEu(PO$_4$)$_7$ have been investigated. The influence of the composition on the luminescence intensity has been shown. The substitution of Zn$^{2+}$ for Ca$^{2+}$ in Ca$_9$Eu(PO$_4$)$_7$ with the formation of Ca$_8$ZnEu(PO$_4$)$_7$ leads to the increased emission intensity $^5D_0 \rightarrow ^7F_2$ by about 1.5 times and to decreased number of bands from three to one in the range of $^5D_0 \rightarrow ^7F_2$ transition. Conditions of preparation do not influence the luminescent properties and distribution of Eu$^{3+}$ cations in the structure. DSC, SHG data and dielectric spectroscopy reveal that Ca$_8$ZnEu(PO$_4$)$_7$ belongs to antiferroelectrics ($T_c = 836$ K). The first-order antiferroelectric/paraelectric transformations are accompanied by a changing symmetry (R3c to R3m). The structure of Ca$_8$ZnEu(PO$_4$)$_7$ (sp. gr. R3c) was refined by the Rietveld method. The Zn$^{2+}$ cations occupy the M5 site. The Eu$^{3+}$ and Ca$^{2+}$ ions are located in the M1 and M3 sites of $\beta$-Ca$_9$(PO$_4$)$_7$-type structure.

1. Introduction

Light emitting diodes (LEDs) have received a lot of attention as promising solid-state light sources because of the efficient and direct conversion of electricity into light. Phosphor-converted WLEDs can be made by using blue/green/red tricolor phosphors excited by near-ultraviolet (UV) (360–410 nm) InGaN-based LEDs, and are competitive for applications that require a high quality of light (high color-rendering index, high color reproducibility, etc.). LEDs have high reliability, long lifetime, low energy consumption, and environment friendly characteristics [1,2]. However, LEDs also have disadvantages such as low emission intensity [3].

$\beta$-Ca$_9$(PO$_4$)$_7$ (β-TCP) [4] - related compounds Ca$_9$R(PO$_4$)$_7$ [5–10], Ca$_9$MeR(PO$_4$)$_7$ [11–17] and Sr$_9$R(PO$_4$)$_7$ [18–21] (R = Ln, Y, Bi, Sc; Me = Mg, Zn) are proposed as materials for light emitting diodes [11,12,17,19,21], especially for red emitting phosphors [3,7,8,12]. Moreover, the cation substitutions in the β-TCP-type framework allow to obtain multi-functional materials with the combination of properties such as high nonlinear optical activity, anti- [13,22] and ferroelectricity [23], large ionic conductivity [24–26] and high luminescence intensity [27,28].

Ca$_9$R(PO$_4$)$_7$ compounds are crystalized in trigonal syngony (sp. gr. R3c) without the center of symmetry [29]. In these compounds R$^{3+}$ cations together with Ca$^{2+}$ occupy three (M1, M2 and M3; R = La–Gd) or four (M1, M2, M3 and M5; R = Tb–Lu) sites [30] in polyhedra of the β-TCP-type structure. In Ca$_9$R(PO$_4$)$_7$:Eu$^{3+}$ cations of Eu$^{3+}$ always occupy M1, M2 and M3 sites, for example, in Ca$_9$Eu(PO$_4$)$_7$ [6,27,31,32], Ca$_9$Lu(PO$_4$)$_7$:Eu$^{3+}$ [33], Ca$_9$Al(PO$_4$)$_7$:Eu$^{3+}$ [9,33] and Ca$_9$Eu(VO$_4$)$_7$ [8]. In luminescent spectra of these phases three emission bands are observed in the range of $^5D_0 \rightarrow ^7F_2$ transition. The substitution of calcium for magnesium in the M5 position of non-centrosymmetric Ca$_9$R(PO$_4$)$_7$ is accompanied by the formation of centrosymmetric Ca$_9$MeR(PO$_4$)$_7$ (Me = Mg, Zn, Cd) [13,22]. PXRD patterns of centro- and non-centrosymmetric compounds are little distinguishable [34]. During the transition from non-centrosymmetric to centrosymmetric structure only a few weak bands disappear at PXRD patterns [34]. Since PXRD patterns of Ca$_9$R(PO$_4$)$_7$ and Ca$_9$MeR(PO$_4$)$_7$ are distinguished just a little, Ca$_9$MeR(PO$_4$)$_7$ compounds are considered to be non-centrosymmetric [3,11,12,14–17,35,36] and luminescent spectra are interpreted as an assumption that R$^{3+}$ cations are located in three positions of the β-TCP-type structure and not in one or two positions which is the case [13].
Thus, the true knowledge of the structure and a number of positions for $R^{3+}$ cations of the compounds of Ca$_8$M$_R$(PO$_4$)$_7$ is of great importance for correct interpreting of luminescent spectra of perspective materials for light emitting diodes.

This paper describes new whitlockite-type phosphate Ca$_8$ZnEu(PO$_4$)$_7$ which was synthesized by the high temperature solid state method. Its luminescent properties and high-temperature phase transitions have been studied and the Zn$^{2+}$ for Ca$^{2+}$ replacement influence on luminescent properties in Ca$_9$Eu(PO$_4$)$_7$ has been revealed.

2. Experimental

2.1. Synthesis

Ca$_8$ZnEu(PO$_4$)$_7$ was synthesized by the solid-state method from stoichiometric mixtures of CaHPO$_4$·2H$_2$O (99.9%), CaCO$_3$ (99.9%), ZnO (99.99%) and Eu$_2$O$_3$ (99.9%) at 1273 K for 100 h in air with several intermediate grindings followed by slow cooling to room temperature ($T_R$) (Sample I). The X-ray diffraction (XRD) pattern of the prepared compound was checked by using JCPDS PDF-2 Data Base and it was found that it did not contain reflections of the initial phases.

For the comparison of luminescent properties Ca$_8$Eu(PO$_4$)$_7$ was synthesized by the solid-state method from stoichiometric mixtures of CaHPO$_4$·2H$_2$O (99.9%), CaCO$_3$ (99.9%), and Eu$_2$O$_3$ (99.9%) at 1273 K for 100 h in air with several intermediate grindings followed by slow cooling to $T_R$.

For determination of preparation condition influence on distribution of Eu$^{3+}$ ions in structure position, Ca$_8$ZnEu(PO$_4$)$_7$ was annealed and cooled under different conditions. One part of the sample was heated at 773 K for 6 h and cooled slowly to the room temperature (Sample II) while the second part was heated at 923 K for 6 h and quenched to liquid nitrogen (Sample III).

The cation composition of Ca$_8$ZnEu(PO$_4$)$_7$ was determined by energy-dispersive X-ray spectroscopy (EDXs) using a Tescan VEGA3 scanning electron microscope equipped with an EDX spectrometer (Oxford Instruments).

Powder X-ray diffraction (PXRD) patterns were collected on a Thermo ARL XTRA powder diffractometer (Bragg–Brentano geometry, Peltier-cooled CCD detector, CuK$_\alpha$ radiation, $\lambda = 1.5418$ Å). XRD data were collected at $T_R$ in 2θ range between 5’ to 75’ with a step interval of 0.02’.

Synchrotron PXRD data for samples prepared under different annealing and cooling conditions were measured with a large Debye-Scherrer camera at the BL15SU beamline of SPring-8. The intensity data were collected in 2θ range from 1’ to 62’ with step 0.003’. The incident beam was monochromatized at $\lambda = 0.65297$ Å. The samples were packed into Lindemann glass capillaries with inner diameter of 0.1 mm, that were rotated during the measurement. The absorption coefficients were also measured. Rietveld analysis [37] was performed using JANA2006 programme package [38].

The second harmonic generation (SHG) signal was measured with a Q-switched YAG:Nd laser at $\lambda_w = 1064$ nm in the reflection mode. The experimental set-up and arrangement have been described in [39].

Differential scanning calorimetry (DSC) measurements were performed on a NETZSCH DSC 204 F1 calorimeter in the temperature range from 303 to 873 K with heating rate 10 K·min$^{-1}$ in nitrogen flow of 40 ml/min.

The electrical conductivity, dielectric permittivity $\varepsilon$ and dielectric loss tangent $\tan \delta$ in air were measured by the double-contact method in the frequency range of 1-10$^7$ Hz at 300–1270 K (heating rate of 5 K·min$^{-1}$), with the help of precision voltmeter Solartron 7081 and frequency response analyzer Solartron 1260. Ceramic pellets (1.5 mm-thick and 5–6 mm in diameter) were prepared by pressing and sintering at 1473 K for 12 h. Pt paste was put on flat surfaces of the pellets and then they were heated at 1023 K for 4 h to produce platinum electrodes.

Photoluminescence emission (PL) and photoluminescence excitation (PLE) spectra were recorded on a Lot-Oriel MS-257 spectrophotograph with a Marconi CCD detector and 150 W xenon lamp as an excitation source at room temperature. Photoluminescence spectrum was measured under the same condition at $T_R$.

3. Results and discussion

3.1. Element compositions

Energy dispersion X-ray spectroscopy (EDXs) data are performed at 30 points of the sample I. The cation ratios were found to be as Eu:Zn:Ca = 1.00 ± 0.02:0.95 ± 0.02:7.92 ± 0.05. This experimental composition is close to the theorectical cation ratios and reveals a homogeneous element distribution in the sample. The oxygen and phosphorus content has not been quantified by EDX.

3.2. SHG, DSC and dielectric measurements

A very weak SHG response ($I_{SHG}/I_{2\theta(SiO_2)} < 0.1$) detected for Ca$_8$ZnEu(PO$_4$)$_7$ strongly suggests a centrosymmetric crystal structure. A similar very weak SHG response was detected for other zine (R = La, Nd, Gd, Yb) [22] and magnesium (R = La – Lu) [13,22] containing phosphates.

A fragment of heating/cooling DSC curves for Ca$_8$ZnEu(PO$_4$)$_7$ are shown in Fig. 1. The heating/cooling DSC curves indicate the presence of only one peak at the temperature of 836 and 826 K, respectively. The peak of the heating DSC versus T curve indicates an endothermic first-order phase transition. The presence of the minimum/maximum from 810 to 840 K on the cooling/heating DSC curve exhibits that first-order phase transitions are reversible.

Temperature dependencies of dielectric permittivity ($\varepsilon$) and dielectric loss tangent (tanδ) at different frequencies of Ca$_8$ZnEu(PO$_4$)$_7$ (sample I) are given in Figs. 2 and 3. Dielectric penetrability of Ca$_8$ZnEu(PO$_4$)$_7$ is increasing with the increasing temperature. As shown in Fig. 2, all $\varepsilon$(T) curves demonstrate characteristic $\lambda$-like maxima in the temperature range from 820 to 850 K. The temperature position of this anomaly on the $\varepsilon$(T) curves does not depend on the frequency (Fig. 2a), however, it is heating/cooling temperature-dependent. The phase transition temperature $T_c$ during heating/cooling comes to 848 K and 826 K, correspondingly. $\lambda$-like maximum can characterize ferroelectric as well as antiferroelectric phase transition. However, the absence of anomaly on the tanδ versus T curves at the temperature of 500–1000 K (Fig. 3) points to antiferroelectric character of the phase transition. For the first time, antiferroelectric phase transition for the $\beta$-Ca$_8$(PO$_4$)$_7$-type compounds was found and structurally characterized in Sr$_3$In(PO$_4$)$_7$ [40]. Later similar phase transitions were revealed in a series Ca$_8$-M$_x$R (PO$_4$)$_7$ ($x = 1$, 1.5; $M = Mg$, Zn, Cd, $R = Ln$, Y) [22], and Ca$_8$MgEu(PO$_4$)$_7$ [13].

The absence of SHG response and the presence of an antiferroelectric phase transition suggest that the crystal structures of Ca$_8$ZnEu

![Fig. 1. Heating and cooling DSC curves for Ca$_8$ZnEu(PO$_4$)$_7$. Heating/cooling rate is 10 K·min$^{-1}$.](image-url)
The electric conductivity of Ca$_8$ZnEu(PO$_4$)$_7$ is increasing:

(a) in a frequency range from 50 kHz to 1 MHz on heating; b) at 1 MHz frequency on heating (1) and cooling (2).

The temperature dependence of the conductivity of Ca$_8$ZnEu(PO$_4$)$_7$ is the same as characteristic for phosphates and vanadates of Ca$_9$R(EO$_4$)$_7$ (E = P, V) [23,24,41] and is resulting from mobility of calcium cations [25,26].

3.3. X-ray diffraction study

PXRD patterns of Ca$_8$ZnEu(PO$_4$)$_7$ samples are similar to other β-TCP-type Ca$_8$MgR(PO$_4$)$_7$ (R = La, Pr, Nd, Sm, Lu, and Y) compounds [13]. The absence of any impurity reflections on PXRD patterns shows that Eu$^{3+}$ and Zn$^{2+}$ cations were completely incorporated into the β-TCP-type host framework.

The β-TCP-type structure (sp. gr. R3c, Z = 21) consists of isolated AO$_4$ tetrahedra that connect the CaO$_3$ polyhedra into a 3D framework via common vertices [4]. Ca$^{2+}$ cations occupy five M1–M5 positions, where M1–M3 (18-fold) and M5 (6-fold) positions are fully occupied while M4 (6-fold) and M6 (6-fold) sites are half-occupied and vacant, respectively. Phosphorus atoms fully occupy three P1–P3 positions. The changing of symmetry from R3c to R3c leads to equivalency of the M1 and M2 sites, P2O$_4$ and P3O$_4$ tetrahedra. The M5 site is disposed at the center of symmetry. The P1 and M3 positions in the R3c space group are located near the positions with the site symmetry 18d (1/2, 0, 0) and 6a (0, 0, 1/4), respectively. The structure refinement in such model result in high values of atomic displacement parameters ($U_{iso}$) for Ca$^{2+}$ and P1 ions. For this reason, P1 ions were displaced from the 6a special position to a half-occupied special position 12c and the M3 positions with the site symmetry 18d to a half-occupied position with site symmetry 36f. The O1 and O2 atoms are located in 12c and 36f sites, respectively with half-occupied position. Previously similar structure refinement was carried out for Ca$_8$MgR(PO$_4$)$_7$ [13] and β-Ca$_8$In(PO$_4$)$_7$ [42].

The fractional atomic coordinates for Ca$_8$MgEu(PO$_4$)$_7$ (sp. gr. R3c) [13] were used as the starting model for refinements of synchrotron PXRD patterns of Ca$_8$ZnEu(PO$_4$)$_7$ samples prepared under two different annealing and cooling conditions (sample II and III). Zn$^{2+}$ ions were placed in the M5 position. The Eu$^{3+}$ and Ca$^{2+}$ ions were located in the M1 and M3 sites. Despite the fact that the M2 position is absent in the R3c structure, we keep the same position notations as in the β-TCP-type structure. At the first stage, the f curves for Ca$^{2+}$ (M1, M3 sites) and Zn$^{2+}$ (M5 site) were used, and all the parameters of the chosen model were refined. The analysis of the occupancies has demonstrated that the Eu$^{3+}$ cations are distributed between the M1 and M3 sites in the structure. The occupancy of the M5 position by Zn$^{2+}$ is close to unity. At the second stage, the distribution of the Eu$^{3+}$

Fig. 2. (a) Temperature dependences of dielectric constant ($\varepsilon$) for Ca$_8$ZnEu(PO$_4$)$_7$; (a) in a frequency range from 50 kHz to 1 MHz on heating; b) at 1 MHz frequency on heating (1) and cooling (2).

Fig. 3. Temperature dependencies of dielectric loss tangent, tanδ(T) for Ca$_8$ZnEu(PO$_4$)$_7$.

Fig. 4. Electric conductivity of Ca$_8$ZnEu(PO$_4$)$_7$ at 50 kHz: heating (1), cooling (2).
cations over the M1 and M3 positions in the Ca8ZnEu(PO4)7 structures was refined considering their multiplicities (M1 = nCa2++(1−n)Eu3+ and M3 = nCa2++(0.5−n)Eu3+).

After the structure refinement a good agreement between the calculated and the experimental synchrotron PXRD patterns was observed at insignificant values of the reliability factors Rall and Rp. As an example, Fig. 5 displays portion of the observed, calculated, and difference synchrotron PXRD patterns of Ca8ZnEu(PO4)7 samples. Other numerical characteristics illustrating the quality of the structure refinements are presented in Table 1. The fractional atomic coordinates, isotropic atomic displacement parameters and cation occupancies are listed in Table S1 of the Supporting information. The main relevant interatomic distances are listed in Table S2 of the Supporting information.

In Ca9Eu(PO4)7 structure Eu3+ cations occupy 18-fold M1, M2 and M3 positions with the ratio Eu1:Eu2:Eu3 = 0.159:0.107:0.068 [30]. There are 4.8 cations ((0.159 + 0.107)×18) and 1.2 cations (0.068×18) Eu3+ in M1+M2 and M3 sites, respectively. In Ca8ZnEu(PO4)7 structure Eu3+ cations occupy 36-fold M1 and M3 positions with the ratio of Eu1:Eu3 = (0.0479 (II) and 0.051 (III)):0.0479 (II) and 0.051 (III)). The ratio of Eu3+ ions in these sites is: M1 = (0.115×36 (II) and 0.118×36 (III)) = 4.1−4.3 cations and M3 = (0.0479×36 (II) and 0.051×36 (III)) = 1.7−1.8 cations. The similar content of Eu3+ ions in M1 = 4.3 and M3 = 1.7 [13] sites is observed in Ca8MgEu(PO4)7. Thus, the redistribution of Eu3+ cations in the structure sites is observed during Zn2+ (or Mg2+) substitution by Ca2+.

3.4. Luminescent properties

PLE and PL spectra of Ca8ZnEu(PO4)7 samples at TR are given in Figs. 6 and 7, respectively. The PLE spectrum includes a broad band in the region from 240 to 310 nm, that attributed to the O2−–Eu3+ charge transfer state band (CTB) from the completely filled 2p orbital of O2− to the partially filled 4f orbital of Eu3+ [12,32]. The peaks in the

Table 1

| Crystallographic data for Ca8ZnEu(PO4)7 samples annealed and cooled under different conditions (SG R3̅c, Z = 6, T = 293 K). |
| Sample preparation | Sample II | Sample III |
| Sample preparation | at 773 K followed by slow cooling to Tg | at 923 K followed by quenching to liquid N2 |
| Lattice parameters: a, Å | 10.36900(9) | 10.37044(8) |
| c, Å | 37.1217(5) | 37.1272(3) |
| Unit cell volume, Å³ | 3456.46(6) | 3457.94(5) |
| Calculated density, g/cm³ | 3.47(1) | 3.47(1) |
| Data Collection | Diffractometer | BL15XU beamline of SPring-8 |
| Radiation/ Wavelength (λ, Å) | Synchrotron / 0.65297 | |
| Absorption coefficient, μ (mm⁻¹) | 4.846 | 4.843 |
| F(000) | 3492 | 3492 |
| 2θ range (°) | 3.077-39.612 | 3.512-46.862 |
| Step scan (2θ) | 0.003 | |
| Number of points | 12178 | 261970 |
| Refinement | Rietveld | |
| Background function | Legendre polynomials, 18 terms | |
| No. of reflections (All/observed) | 454/454 | 739/739 |
| No. of refined parameters/ refined atomic parameters | 60/35 | 60/35 |
| R and Rp (%) for Bragg reflections | 5.57/5.57 and 3.85/3.85/3.80/ | 5.02/5.02 and 4.37/0.80/ |
| R and Rp (%) for Bragg reflections | 5.57/5.57 and 3.85/3.85/3.80/ | 5.02/5.02 and 4.37/0.80/ |
| Goodness of fit (ChiQ) | 0.74/−0.85 | 0.99/−1.18 |
| Selected crystal structure data | 1.280(4) | 1.294(3) |
| 1.280(4) | 1.294(3) |
| Selected crystal structure data | 0.626(2) | 0.6216(2) |
| Selected crystal structure data | 0.626(2) | 0.6216(2) |

Fig. 5. Observed, calculated and difference (from below) synchrotron PXRD patterns for Ca8ZnEu(PO4)7 samples II (a) and III (b). Tick marks denote the peak positions of possible Bragg reflections.

Fig. 6. PLE spectra (λex = 395 nm) of Ca8ZnEu(PO4)7 (sample I) refined at room temperature.
region from 350 to 500 nm correspond to the intraconfigurational 4f–4f transitions of Eu3+. The most intense Eu3+ 4f–4f excitations can be attributed to the 5D0 → 7F j transitions, as in other phosphates with β-TCP-type structure [6,12,16,20,25].

PL spectra of Ca8ZnEu(PO4)7 samples are shown in Fig. 7. PL spectra in the range of 570–715 nm exhibit the red emitting of Eu3+, caused by 5D0 → 7Fj (j = 0–4) transitions. The maximum luminescence intensity is observed for electric dipole transition 5D0 → 7F2 (∼ 612 nm), which indicates the absence of the center of symmetry of the Eu3+ position [43,44]. The 5D0 → 7F2 emission intensity of Ca8ZnEu(PO4)7 is about 1.5 times higher than that of Ca9Eu(PO4)7.

The asymmetry of the Eu3+ environment in the polyhedra of the structure can be rated by magnitude of I(5D0 → 7F2)/I(5D0 → 7F1) ratio [45]. The values of ratio for Ca8ZnEu(PO4)7 samples prepared under different conditions (5.45–5.47) is more than Ca8MgEu(PO4)7, (4.24–4.27) [13], but less than Ca9MgEu(PO4)7. Eu3+ (7) [46]. According to the data given above, the Eu3+ polyhedron in Ca8ZnEu(PO4)7 and Ca8MgEu(PO4)7 is more distorted in compounds with zinc.

Insets in Fig. 7 show parts of PL spectra of Eu3+ in the range of 5D0 → 7F0 transition for Ca8ZnEu(PO4)7 prepared under different conditions (I–III). The 5D0 → 7F0 transition is forbidden for electric and magnetic dipole interactions and for this reason, its intensity is very low or not observed at all. For cations Eu3+ with C3 symmetry such transition can appears. The 5D0 → 7F0 transition generally is observed in β-TCP-type structure compounds [6–8,13,16,27,28,31–33]. The number of bands in 5D0 → 7F0 transition area corresponds to the number of Eu3+ sites in the structure with C3 symmetry.

Earlier, the relationship between distributions of Eu3+ cations in the sites of Ca9Eu(PO4)7 structure and location of the bands in PL spectrum in the region of 5D0 → 7F0 transition had been established [6]. The energy positions of 5D0 → 7F0 bands for non-equivalent Eu3+ centers were related to the mean length of Eu-O bonds, 5D0 → 7F0/5D0 → 7F1 intensity ratio and lifetimes of the 5D0 → 7F0 emission. The 5D0 → 7F0 transition shifted toward shorter wavelengths (higher energy) and the emission lifetime decreased with increasing Eu-O distances and distortion of the Eu3+ oxygen environment [47]. Three bands at 578.5, 579.5 and 580.1 nm which observed for the 5D0 → 7F0 transition in Ca9Eu(PO4)7 PL spectrum are corresponding to Eu3+ cations in M3, M1 and M2 positions of the β-TCP-type structure, respectively [6,31]. Eu3+ cations occupy 18-fold M3–M3 positions with the ratio Eu1: Eu2:Eu3 = 0.159:0.107:0.068 [6]. The determined occupancies of M1 + M2 and M3 by Eu3+ cations in the structure of Ca8ZnEu(PO4)7 are 4.8 atoms ((0.159 + 0.107)×18) and 1.2 atoms (0.068×18), respectively (Fig. 8).

On the PL spectra of Ca8ZnEu(PO4)7 and Ca8MgEu(PO4)7 [13] only one peak was detected for the 5D0 → 7F0 transition (Fig. 7). The position and the linewidth of the 5D0 → 7F0 band do not change practically with changing of the annealing and cooling conditions (∼ 579 nm). The substitution of Zn2+ for Ca2+ in Ca9Eu(PO4)7 with the Ca8ZnEu(PO4)7 formation leads to a significant increase of the amount of Eu3+ in the M3 position (1.8–1.7 atoms; 36-fold) and to a decrease of the occupancy of M1 (36-fold) by Eu3+ (4.1–4.3 atoms) (Fig. 8). The average M–O bond lengths in the M1O8 polyhedra are practically unchanged (d C-M1-O = 2.46–2.47 Å) while the distortion of the M1O8 polyhedra decreases with the substitution of Zn2+ / Mg2+ for Ca2+. The difference between the shortest and longest distances changes from 0.62 Å (Ca) [6] to 0.33 Å (Zn) and 0.365 Å (Mg) [13]. The increasing amount of Eu3+ in the M3 position for Ca8ZnEu(PO4)7 structure in comparison with Ca9Eu(PO4)7 leads to an increase of the average M3–O bond lengths from 2.54 Å [6] to 2.56–2.58 Å in Ca8ZnEu(PO4)7 and the distortion of the M3O8 polyhedra. The difference between the shortest and longest dM3O8 distances changes from 0.67 Å [6] to 0.80 Å (Fig. 9).

Fig. 8. The distribution of ions on M1, M2 and M3 sites in Ca8MeEu(PO4)7 (Me = Mg2+ [13], Zn2+ and Ca2+ [6]) structures.

Fig. 10 shows that the replacement of Zn2+ for Ca2+ in ferroelectric Ca9Eu(PO4)7 (R3c) is accompanied by the formation of antiferroelectric Ca8MgEu(PO4)7 (R3c) and vanishing of two bands in the range of 5D0 → 7F0 transition. In luminescent spectra of Ca8ZnEu(PO4)7 and Ca8MgEu(PO4)7 [13] only one band is observed at ∼ 579 nm in the range of 5D0 → 7F0 transition, which points to the presence of only one Eu3+ position in these compounds. According to the structural data in Ca8ZnEu(PO4)7 the Eu3+ cation occupies two positions M1 and M3. The M3
position is located near the center of symmetry and the transition of $^5D_0 \rightarrow ^7F_0$ is banned for Eu$^{3+}$ cation in this position. These results are completely in agreement with previously published data [6] on relationship between distributions of Eu$^{3+}$ cations in the sites of Ca$_9$Eu (PO$_4$)$_7$ structure and location of the bands of PL spectrum in the region of $^5D_0 \rightarrow ^7F_0$ transition. Thus, for antiferroelectrics (centrosymmetric phases with $\beta$-TCP-type structure) only one band is observed in the range of $^5D_0 \rightarrow ^7F_0$ transition.

4. Conclusions

Ca$_8$ZnEu(PO$_4$)$_7$ compounds with $\beta$-TCP-type structure were prepared by a standard solid-state method. The presence of the reversible antiferroelectric first-order phase transitions is revealed by differential scanning calorimetry and dielectric measurements. Structures of Ca$_8$ZnEu(PO$_4$)$_7$ samples prepared under the different conditions (II, III) were refined by Rietveld method in centrosymmetry space group $R\overline{3}c$. The distribution of Ca$^{2+}$ and Eu$^{3+}$ cations among the sites of the $\beta$-TCP-type structure was found. The refinement of the synchrotron PXRD data and luminescent properties for Ca$_8$ZnEu(PO$_4$)$_7$ samples prepared under different annealing and cooling conditions reveal that the preparation conditions practically do not affect the distribution of Ca$^{2+}$ and Eu$^{3+}$ cations among the structure positions and the linewidth of bands on PL spectra. The study of the luminescent properties demonstrates that all Ca$_8$ZnEu(PO$_4$)$_7$ phosphors emit intense red light dominated by the $^5D_0 \rightarrow ^7F_2$ transition at $\sim$612 nm. The substitution of Zn$^{2+}$ for Ca$^{2+}$ in Ca$_9$Eu(PO$_4$)$_7$ with the formation of Ca$_8$ZnEu(PO$_4$)$_7$ leads to increasing emission intensity of $^5D_0 \rightarrow ^7F_2$ by about 1.5 times, to decreased number of bands (from three to one) in the range of $^5D_0 \rightarrow ^7F_0$ and changing distribution of Eu$^{3+}$ cations between the crystal sites. It has been revealed that in centrosymmetric $\beta$-TCP-type phosphates there is only one luminescence band of Eu$^{3+}$ in the range of $^5D_0 \rightarrow ^7F_0$ transition unlike non-centrosymmetric phosphates, where three bands are present.

Acknowledgement

This research was supported by Russian Science Foundation (Grant 16-13-10340).

Appendix A. Supplementary data

Fractional atomic coordinates, site symmetry, isotropic displacement atomic parameters ($U_{iso}$) and site occupation for two Ca$_8$ZnEu(PO$_4$)$_7$ samples from synchrotron PXRD data (Table S1). Selected distances (Å) in two Ca$_8$ZnEu(PO$_4$)$_7$ samples from synchrotron PXRD data (Table S2).

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.materresbull.2018.03.052.

References


Fig. 9. The divergence of distances $d_{\text{Eu–O}}$ from mean $d_{\text{Eu–O}}$ in M3O$_9$ polyhedra in Ca$_9$MeEu(PO$_4$)$_7$ (Me = Mg$^{2+}$ [13], Zn$^{2+}$ and Ca$^{2+}$ [6]) structures.

Fig. 10. Location of Eu$^{3+}$ cations in centrosymmetric and non-centrosymmetric sites of $\beta$-TCP-type structure and location of luminescence bands of Eu$^{3+}$ in the range of $^5D_0 \rightarrow ^7F_0$ transition.


