

Contents lists available at ScienceDirect

Journal of Luminescence



journal homepage: http://www.elsevier.com/locate/jlumin

The crystal site engineering and turning of cross-relaxation in green-emitting β -Ca₃(PO₄)₂-related phosphors

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ABSTRACT

Series of Tb^{3+} -doped phosphates $Ca_{9-x}Zn_xTb(PO_4)_7$ and $Ca_{9-x}Zn_xLa_{0.99}(PO_4)_7$:0.01 Tb^{3+} with β -Ca₃(PO_4)₂-type structure were synthesized using a standard high temperature route. The luminescence properties of these compounds were determined by the photoluminescence emission (PL), the excitation (PLE) spectra and lifetime measurements. A green-emitting LED device was fabricated using the most effective one. No concentration quenching was detected in the whole region of solid solutions. Upon $Ca^{2+} \rightarrow Zn^{2+}$ substitution the crystal structure transformation from the polar to centrosymmetric. The ways of control the PL spectra and cross-relaxation process were determined. In both solid solutions a "green" magneto-dipole ${}^5D_4 \rightarrow {}^7F_5$ transition is predominant. The integral intensity increases in 3 times in the most effective $Ca_8ZnTb(PO_4)_7$ phosphor. The measured quantum yields (QY) reached 31%. Thus, a target substitution of Ca^{2+} by Zn^{2+} is a new path for crystal site engineering and allows to obtain an efficient green luminescence of Tb^{3+} ions in the β -Ca₃(PO₄)₂-type hosts.

1. Introduction

Solid state light sources, including white light emitting diodes (WLEDs), are one of the most developing area of researching fields. Nowadays, there are several approaches of the producing of the candidates for WLED application, such as Quantum Dots (QD) [1,2], organic phosphors and inorganic lanthanide-doped hosts [3-5]. The searching for new suitable compounds and modern components for the light industry is one of the major challenges, due to one important requirement - a high color rendering index (CRI) and suitable color coordinates. There are two main compounds for the WLED technology with high-quality lighting (i) the most general and commercially available is the YAG phosphor mixed with silicone gel and (ii) the InGaNblue chip [6]. However, the CRI of the YAG phosphor is low, which could be increased by the mixing of a red phosphor with green. Nevertheless, the green phosphor exhibits a low efficiency and entails high costs. Another way is to combine a near ultra violet (n-UV) chip with red, green, and blue phosphors, it also needs an improvement of a green phosphor.

A searching for the host structure is a key to find out the best combination for the most efficient green phosphor. Phosphates with the whitlockite-type structure [7] (or β -Ca₃(PO₄)₂-type structure) are excellent candidates for the backlight displays due to their high luminescence, narrow emission wavelength, and suitable correlated color

temperature (CCT). Moreover, modern trends of the research include a crystal site engineering [8] as well as a tuning of the photoluminescence spectra [9,10]. In the β -Ca₃(PO₄)₂-type compounds additional ions can be implemented into the host structure to stimulate purposeful cationic distributions. It was shown, that the Zn²⁺-doped host could be perspective for the improvement of luminescent properties of emitting lanthanide ions [11–14]. Tb³⁺ ions can be used as a green emitting phosphor and an effective energy transfer ion for Dy³⁺ [15], Mn²⁺ [16], Ce³⁺, Eu³⁺ [10,17] ions. It is well known [18,19], that Tb³⁺ ion generates a blue emission due to the ⁵D₄ \rightarrow ⁷F_J transition at low concentration and green emission due to the ⁵D₄ \rightarrow ⁷F_J transition at high concentration. So, a turning of the crystal structure is a way to find out the main principles and criteria to obtain new types of the green phosphors.

In the present work, we report the crystal site engineering and features of the luminescent properties as well as a possibility of tuning of the Tb^{3+} ions spectra in the $Ca_3(PO_4)_2$ -type host.

2. Experimental section

2.1. Materials and sample preparation

 $Ca_{9-x}Zn_{x}Tb(PO_{4})_{7}$ and $Ca_{9-x}Zn_{x}La_{0.99}(PO_{4})_{7}$:0.01 Tb^{3+} solid

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https://doi.org/10.1016/j.jlumin.2020.117196

Received 26 November 2019; Received in revised form 2 March 2020; Accepted 4 March 2020 Available online 12 March 2020 0022-2313/© 2020 Elsevier B.V. All rights reserved. solutions were synthesized by a solid-state method from stoichiometric mixtures of CaHPO₄·2H₂O (99.9%), CaCO₃ (99.9%), ZnO (99.99%), La₂O₃ (99.9%) and Tb₄O₇ (99.9%) at 1273 K for 50 h in air with several intermediate grindings followed by slow cooling to room temperature. The powder X-ray diffraction (PXRD) patterns of the prepared compounds were checked using JCPDS PDF-2 Database and they did not indicate any reflections of the initial or intermediate phases.

2.2. Characterization

The PXRD patterns were collected on a Thermo ARL X'TRA powder diffractometer (Bragg–Brentano geometry, Peltier-cooled CCD detector, CuK α radiation, $\lambda = 1.5418$ Å). The data were collected at room temperature in the 2 θ range between 5° and 65° with a step interval of 0.02°. The Le Bail method [20] was applied to determine the lattice cell parameters using the JANA2006 software [21]. Illustrations were created with JANA2006 and DIAMOND [22].

The second harmonic generation (SHG) signal was measured with a *Q*-switched YAG:Nd laser at $\lambda_{\omega} = 1064$ nm in the reflection mode. The experimental set-up and arrangement have been described previously [5].

Differential scanning calorimetry (DSC) measurements were performed on a thermal analyzer SDT Q600 V8.1 Build 99 (TA Instruments) with a Pt/Rh thermocouple in the temperature range from 303 to 1073 K with heating/cooling rate of 5 K/min.

To measure the dielectric permittivity (ε) and loss tangent (tan δ), we used samples in the form of pellets (~1 mm in thickness and ~5 mm in diameter). They were pelletized at 200 kgf/cm² and then heated at 1273 K for 4 h. A Pt paste was put on flat surfaces of the pellets and then they were heated to 923 K to produce metal electrodes. Temperature dependences of ε and tan δ in interval 300–1070 K were registered with computer-controlled *ac*-bridges R5083 and E7-12 at electric-field frequencies between 1 kHz and 1 MHz.

Photoluminescence emission (PL) and excitation (PLE) spectra, as well as decay curves, were recorded on an Agilent Cary Eclipse fluorescence spectrometer with a 75 kW xenon light source (pulse length $\tau = 2 \mu$ s, pulse frequency $\nu = 80$ Hz, wavelength resolution 0.5 nm; PMT Hamamatsu R928). The powder was placed in a Cu cell ($0 \ 20 \text{ mm} \times 10 \text{ mm}$) with a light-reflecting coating. Photoluminescence spectra of all samples were measured under the same conditions. All measurements were performed at room temperature and corrected for the sensitivity of the spectrometer.

The quantum yields were measured on an Edinburgh Instruments FS5 spectrofluorometer equipped with a 450 W Ozone-Free Xenon Lamp. All measurements were performed at room temperature and corrected for the sensitivity of the spectrometer. To obtain the correct results of calculating the quantum yield of luminescence, 30 scanning cycles were performed in the signal accumulation mode for each sample.

3. Results

3.1. Crystal structure

The powder XRD patterns of $Ca_{9-x}Zn_xTb(PO_4)_7$ solid solution are shown in Fig. 1. A considerable shift to higher 20 angles could be explained by an isomorphic substitution of Ca^{2+} by Zn^{2+} with smaller ionic radii [23] resulted in a reduction of the unit cell.

The calculations of the unit cell parameters (*a* and *c*) and volume (*V*) (Table S2) shows a non-monotonic behaviour with an abrupt decreasing together with the increasing of Zn^{2+} concentration (Table S1, Fig. S1). A sharp recession at the range 0.5 < x < 0.6 can be explained by the crystal structure transformation from polar to centrosymmetric (Fig. 2, Table S1).



Fig. 1. (a) Powder XRD patterns for $Ca_{9-x}Zn_xTb(PO_4)_7$ solid solution; (b) magnified XRD data of h k l (0 2 10).

3.2. DSC data

Phase transitions (PT) were detected by DSC measurements (Fig. 3). During the heating, solid solutions demonstrate an endothermic effect. A diffusing of the thermal effects can be associated with a non-uniform distribution of Ln^{3+} cations over the cation sites in the host structure.

3.3. SHG study

The obtained results of SHG study are listed in Table 1. Weak signal responses ($I_{2\omega}/I_{2\omega}$ (SiO₂)) were detected for all the samples and declined up to zero with *x*. Previously [24], the influence of Zn^{2+} cation substitution on the ferroelectric properties was studied. The reducing of the ferroelectric activity of the synthesized phosphates suggests a formation of a centrosymmetric crystal structure. The path of such transition is $R3c \rightarrow R\overline{3}c.\overline{33}$.



Fig. 2. The general view of the compounds characterized by polar (Ca₉Tb (PO_4)₇) and non-polar (Ca₈ZnTb(PO_4)₇) structures.



Fig. 3. DSC curves of $Ca_{9-x}Zn_xLa_{0.99}(PO_4)_7$:0.01 Tb³⁺ (a) and $Ca_{9-x}Zn_xTb$ (PO₄)₇ (b) solid solutions on a heating rate. The heating rate was 5 deg per min.

	SHG response, $I_{2\omega}/I_{2\omega}(SiO_2)$		
x	Ca _{9-x} Zn _x La _{0.99} (PO ₄) ₇ :0.01 Tb ³⁺	x	$Ca_{9-x}Zn_xTb(PO_4)_7$
0	0.81	0	0.20
0.2	0.75	0.25	0.18
0.5	0.60	0.5	0.13
0.6	0.42	0.8	0.09
0.7	0.38	1.0	0
0.8	0.12		
0.9	0.02		
1.0	0		

3.4. Dielectric measurements

The temperature correlations of the dielectric permittivity (ε) and dielectric loss tangent (tan δ) for Ca_{9-x}Zn_xTb(PO₄)₇ solid solution are shown in Fig. 4. On the heating curves $\varepsilon(T)$ the characteristic frequency independent maxima at 660–680 K were observed. The temperature of the maximum of the dielectric permittivity approximately coincides with the effects in the DTA curves and temperatures of disappearance of the SHG signal upon heating. The tan δ of the samples had a different behaviour (Fig. 4): in the Ca₈₋₅Zn₀₋₅Tb(PO₄)₇ compound the maxima was observed preceding $\varepsilon(T)$ maxima while the Ca₈ZnTb(PO₄)₇ compound had no anomalies. The DSC, SHG and dielectric data confirm the assumption that members of the solid solution are characterized by different space groups.



Fig. 4. The temperature dependence of $\varepsilon(T)$ (a) and dielectric loss tangent tan^{δ} for the Ca_{8.5}Zn_{0.5}Tb(PO₄)₇ (1) and Ca₈ZnTb(PO₄)₇ (2) compounds.

3.5. Photoluminescence properties

3.5.1. Photoluminescence properties of $Ca_{9-x}Zn_xLa_{0.99}(PO_4)_7$:0.01 Tb^{3+} solid solution

The PLE spectra are shown in Fig. 5. Several sharp lines can be assigned to the transition from the 7F_6 ground state to the $^5L_{10,}$ 5G_6 (378 nm), 5D_3 (369 nm), 5G_5 (357 nm), 5L_9 (351 nm), $^5L_{7,8}$ (341 nm), 5D_1 (326 nm), 5H_7 (319 nm), and 5H_6 (303 nm) states. The transitions located below 300 nm were attributed to $4f^75\,d^1$ levels of Tb^{3+} ion [19].

The PL spectra controlled at $\lambda_{exc} = 369$ nm provide the distinctive characteristic of the ${}^{5}D_{3} \rightarrow {}^{7}F_{J}$ and ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 3-6) optical transitions of Tb³⁺ ion (Fig. 6). The locations of these transition are given in Table 2. Among these characteristic peaks, the emission of the ${}^{5}D_{4} - {}^{7}F_{5}$ transition at 544 nm is predominant and predicted by large values of the reduced matrix elements at J = 5 as well as by the Judd–Ofelt theory [25].

The relative band intensities due to the ${}^{5}D_{3} \rightarrow {}^{7}F_{J}$ (J = 3-6) (blue) and ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (green) transitions were also changed in accordance with Zn^{2+} concentration. The ratio of the integrated emission intensity of the ${}^{5}D_{3} \rightarrow {}^{7}F_{J}$ (J = 3-6) to the ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ transitions is referred as a green-toblue luminescence intensity ratio – I_{G}/I_{B} [26]. The calculated I_{G}/I_{B} values for Tb³⁺ are helpful to understand the crystal environment of dopant. The decreasing of I_{G}/I_{B} ratio is usually observed due to increased



Fig. 5. The PLE spectra of $Ca_{9-x}Zn_xLa_{0.99}(PO_4)_7$:0.01 Tb³⁺ ($\lambda_{em} = 544$ nm).



Fig. 6. The PL spectra of $Ca_{9-x}Zn_{x}La_{0.99}(PO_{4})_{7}{:}0.01~\text{Tb}^{3+}~(\lambda_{em}=369~\text{nm}).$

Table 2

The location of transitions on PL spectra of $Ca_{9_x}Zn_xLa_{0.99}(PO_4)_7{:}0.01~Tb^{3+}$ and $Ca_{9_x}Zn_xTb(PO_4)_7$ solid solutions.

Transition	$Ca_{9-x}Zn_xLa_{0.99}(PO_4)_7:0.01 \text{ Tb}^{3+}$	$Ca_{9-x}Zn_xTb(PO_4)_7$
${}^{5}D_{3} - {}^{7}F_{6}$	382 nm	-
${}^{5}D_{3} - {}^{7}F_{5}$	413 nm	-
${}^{5}D_{3} - {}^{7}F_{4}$	436 nm	-
${}^{5}D_{3} - {}^{7}F_{3}$	456 nm	-
${}^{5}D_{3} - {}^{7}F_{2}$	472 nm	-
${}^{5}D_{4} - {}^{7}F_{6}$	489 nm	490 nm
${}^{5}D_{4} - {}^{7}F_{5}$	544 nm	543 nm
${}^{5}D_{4} - {}^{7}F_{4}$	586 nm	587 nm
${}^{5}D_{4} - {}^{7}F_{3}$	621 nm	621 nm

activator activator interactions and the presence of the cross-relaxation processes [27].

3.5.2. Photoluminescence properties of $Ca_{9-x}Zn_xTb(PO_4)_7$ solid solution The PLE and PL spectra of $Ca_{9-x}Zn_xTb(PO_4)_7$ solid solution are shown



Fig. 7. The PLE and PL spectra of $\rm Ca_{8.5}Zn_{0.5}Tb(PO_4)_7$ phosphate. The inset shows portion of PL spectra.

in Fig. 7 and Fig. S2. The PLE spectra are similar to above mentioned Ca_{9-x}Zn_xLa_{0.99}(PO₄)₇:0.01 Tb³⁺ ones and consist of typical transitions of Tb³⁺ ion. The main difference (Fig. 7 inset) is the absence of bands attributed to the ${}^{5}D_{3}{}^{-7}F_{J}$ transitions located at 400–475 nm, while the main luminescence band is associated to the ${}^{5}D_{4}{}^{-7}F_{5}$ transition.

Fig. 8 provides the fluorescence decay curves and lifetimes of Tb³⁺ ion in Ca_{9-x}Zn_xLa(PO₄)₇:Tb³⁺ system. The probability of radiative transitions from the ⁵D₄ and ⁵D₃ levels in Ca₈ZnTb(PO₄)₇ (CZTb) and Ca₈ZnLa_{0.99}(PO₄)₇:0.01 Tb³⁺ (CZLaTb) differs very slightly (Fig. 9). The data on the lifetimes τ in the excitation state ⁵D₄ were successfully fitted by single exponential function approximation (determination factors R^2 for fitting quality assessment are presented in Table 3).

3.5.3. Color coordinates

The CIE 1931 chromaticity coordinates [28] have been used for the detailed determination of the color characteristics of the synthesized phosphors. The coordinates (x, y, z) can be calculated using the following formula [29] (Table S4):

$$x = \frac{X}{X + Y + Z}; y = \frac{Y}{X + Y + Z}; z = \frac{X}{X + Y + Z};$$

where
$$X = \int_{\lambda inf}^{\lambda sup} S(\lambda) \overline{x}(\lambda) d(\lambda); Y = \int_{\lambda inf}^{\lambda sup} S(\lambda) \overline{y}(\lambda) d(\lambda); Z = \int_{\lambda inf}^{\lambda sup} S(\lambda) \overline{z}(\lambda) d(\lambda);$$

 $S(\lambda)$ is the intensity at wavelength λ , nm, x; y; z – the 1931CIE color



Fig. 8. The room-temperature decay curves of the Tb^{3+} emission ($\lambda_{em} = 544$ nm, $\lambda_{exc} = 370$ nm) in the $Ca_{9-x}Zn_xLa_{0.99}(PO_4)_7$:0.01 Tb^{3+} .



Fig. 9. Photoluminescence decay curves of samples $Ca_8ZnTb(PO_4)_7$ and $Ca_8ZnLa_{0.99}(PO_4)_7$:0.01 Tb³⁺ at $\lambda_{exc} = 222$ nm and 370 nm.

Table 3 Lifetimes of the components from 5D_4 state for $Ca_8ZnTb(PO_4)_7$ and $Ca_8ZnLa_{0.99}(PO_4)_7$:0.01 Tb $^{3+}$.

Sample	$\lambda_{\text{exc}},\text{nm}$	$\lambda_{em}\text{, }nm$	Lifetime, ms	R^2
Ca ₈ ZnTb(PO ₄) ₇	222	490	2.0798	0.99982
		544	2.0688	0.99996
		621	2.0596	0.99816
Ca ₈ ZnLa _{0.99} (PO ₄) ₇ :0.01 Tb ³⁺	222	490	2.5619	0.98688
		544	2.7304	0.9777
		621	2.7326	0.97679
Ca ₈ ZnTb(PO ₄) ₇	370	490	2.0606	0.99996
		544	2.0583	0.99997
		621	2.0672	0.99992
Ca ₈ ZnLa _{0.99} (PO ₄) ₇ :0.01 Tb ³⁺	370	490	2.5560	0.9869
		544	2.6805	0.97817
		621	2.6951	0.97849

coordinates for wavelength λ , nm.

Fig. 10 shows the shifting of the CIE coordinates from green (0.288; 0.486) in CZLaTb to yellow-green (0.316; 0.592) in CZTb due to a cross-relaxation process and the depressing of blue transitions.

The synthesized phosphors could produce a green emission in the visible spectrum *via* Tb^{3+} doping. To evaluate the potential application of *as*-prepared phosphors in WLEDs the device was fabricated by depositing the CZLaTb powder on 366 nm UV chip. This composition was chosen due to the most suitable CIE coordinates and the highest

emitting intensity (Fig. 10 (b)), which shows a bright green emission.

4. Discussion

The *as*-prepared new phosphates have a β -Ca₃(PO₄)₂-type structure. The X-ray study shows the existence of solid solutions in range 0 < x < 1. The phase transitions were detected by DSC (Fig. 3), SHG (Table 1) and dielectric measurements (Fig. 4) and reveal transformation to hightemperature $R\overline{3}m$ sp. gr. The analysis of crystal structure shows that in the similar phosphates Ca₉Tb(PO₄)₇ and Ca₉La(PO₄)₇ there are different distributions of Ln among the crystallographic sites. The structure refinement of the Ca₉La(PO₄)₇ compound reveals that the M1-M5 sites are predominantly occupied by Ca^{2+} and La^{3+} ions. The $Ca_{9-x}Zn_xLa$ $(PO_4)_7$:Tb³⁺ contains only doping concentration of emitting Tb³⁺ ion, which is diffused among M1 and M3, as well, as M5 sites. Due to lower ionic radii r (Tb³⁺) < r (La³⁺) it became possible to occupy *M*5 site by Tb^{3+} , in opposite to La^{3+} ions, which are only located at *M*1 and *M*3 sites. Such distribution is confirmed by the smaller unit cell parameters of the $Ca_9Tb(PO_4)_7$ in comparison with the $Ca_9La(PO_4)_7$. Similarly, the occupation of the M5 position by zinc cations effects on the unit cell parameters (Fig. S1).

The above-mentioned crystal structure features also effect on spectroscopic properties of synthesized solid solutions. Both systems undergo symmetry changes from polar structure to centro-symmetric one at $x \sim 0.5$, and contain two-phase area. Apparently, this area consists of a mixture of phases characterized by R3c and R3c sp. gr. Previously [30],





Fig. 10. The CIE coordinates of $Ca_8ZnTb(PO_4)_7$ and $Ca_8ZnLa_{0.99}(PO_4)_7$:0.01 Tb^{3+} (a). The fabricated LED device from $Ca_8ZnLa_{0.99}(PO_4)_7$:0.01 Tb^{3+} powder and 366 nm UV chip (b).

such transition was shown in the relative hosts by Eu^{3+} luminescence. This rearrangement was reflected on the calculated parameters of the spectra. The transition, detected based on the DSC data at high temperature, has an antiferroelectric nature and was described previously [30].

 Zn^{2+} ion substitutes Ca^{2+} in the *M*5 site. Thus, when concentration of Tb^{3+} is relatively low the activator-activator $Tb^{3+}-Tb^{3+}$ interactions are negligibly small, and it is possible to observe the enhanced blue luminescence corresponding to the ${}^{5}D_{3} \rightarrow {}^{7}F_{J}$ (J = 2-5) transitions of Tb^{3+} (Fig. 6). There is no concentration quenching in both solid solutions,

however, there is an increasing of the integral intensity (Fig. 11). The integral intensity increases in 1.5 and 3 times in the Ca_{9-x}Zn_xLa(PO₄)₇: Tb³⁺ and Ca_{9-x}Zn_xTb(PO₄)₇, respectively, after complete transformation of the structure to a centrosymmetric state. The luminescence intensity of the CZTb is higher than in CZLaTb upon excitation of both phosphors through f-f transitions $^{7}F_{6} \rightarrow ^{5}L_{10}$ (370 nm) and $^{7}F_{6} \rightarrow ^{5}D_{3} + ^{5}G_{6}$ (378 nm). Also, the emission efficiency of samples upon excitation through allowed f-d transitions in order higher than the efficiency of emission through parity forbidden f-f transitions. Fig. 12 shows the excitation spectra of the studied compounds in the region of f-d transitions (200 ÷ 250 nm).

The most intense component f-d excitation band is spin-allowed transition $^7F_6 \rightarrow ^7S_3\Gamma_{d1}$ [31]. For YPO₄:Tb^{3+} [31] the A1 band (224.3 nm) corresponding to this transition was indicated as the most intense. In the *as*-prepared samples the highest absorption intensity peak corresponding to 222 nm (Fig. 12). Despite the fact that transitions to the 9S_4 level are spin-forbidden, an intense band in the range 200–210 nm with a peak at 204 nm, which can be attributed to the $^7F_6 \rightarrow ^9S_4\Gamma_{d3}$ transition, can be observed in the PLE spectra (Fig. 12). The intensity of photon absorption for the studied samples in the f-f transitions region (250 \div 500 nm) is significantly lower than that for f-d transitions (Fig. 5). The ratio of the integral excitation intensities in the region of f-d absorption bands to f-f bands ($I_{\rm f-d}/I_{\rm f-f}$) are presented in Table 4.

From the analysis of the presented in Table 4 data, it follows that the f-d band for the CZLaTb sample is more strongly split, and the population of the 4f level excited states is lower, than in CZTb. One explanation for the lower luminescence intensity of the CZLaTb sample compared to CZTb is the low rate of the nonradiative process ${}^{5}D_{3} \rightarrow {}^{5}D_{4}$, and intense lines related to transitions from the ${}^{5}D_{3}$ level are observed (Fig. 6).

For the rating of the Tb^{3+} luminescence efficiency the Quantum Yields (QY) were measured (Table 5). The data were matched in comparison with commercial $Y_2O_2S:Tb^{3+}$ phosphor.

The Y₂O₂S:Tb³⁺ standard has a high luminescence QY (74%) at λ_{exc} = 240 nm (Table 5), but it also has intense emission lines in the UV, violet, and blue regions, as well as for the CZLaT sample, and the result emission color is shifted to the blue area. The highest luminescence QY = 31% at λ_{exc} = 370 nm (commercial UV LEDs or UVA chips can be used as a source) has a CZTb sample. In addition, it is characterized by the greatest stability of the green emission. The QY of the synthesized systems shows the comparable values with previously studied phosphates [32,33].

Two factors lead to an increase in the emission intensity of phosphors during radiative relaxation from the 5D_4 level: an increase in the rate of energy transfer through cross-relaxation channels (CR) (${}^5D_3 \rightarrow {}^5D_4$) \rightarrow (${}^7F_6 \rightarrow {}^7F_1$) [34–39], and increase in the rate of multiphonon relaxation (MR). The CR process is stimulated by an increase in the Tb³⁺ concentration [35,38,39], i. e CZTb is characterized by a higher CR speed than CZLaTb. The increase of the material phonon energy [34] effects on in the MR speed. In addition, the CR rate increases with decreasing radius



Fig. 11. A comparison of the integral intensity in $Ca_{9-x}Zn_xTb(PO_4)_7$ and $Ca_{9-x}Zn_xLa(PO_4)_7$:Tb³⁺, x = 0 (1), x = 1 (2).



Fig. 12. The part of PLE spectra for $Ca_8ZnLa_{0.99}(PO_4)_7{:}0.01~Tb^{3+}$ (a) and $Ca_8ZnTb(PO_4)_7$ (b).

Table 4

The I_{f-d}/I_{f-f} ratio of Ca₈ZnTb(PO₄)₇ and Ca₈ZnLa_{0.99}(PO₄)₇:0.01 Tb³⁺.

Sample	Emission Wavelength, nm	$I_{\rm f-d}/I_{\rm f-f}$
Ca ₈ ZnTb(PO ₄) ₇	490	8.425
	544	8.504
	621	7.807
Ca ₈ ZnLa _{0.99} (PO ₄) ₇ :0.01 Tb ³⁺	490	27.030
	544	23.996
	621	50.366

Table 5

The Quantum Yields for the as-prepared samples and commercial phosphor.

Sample	QY% ($\lambda_{exc} = 240 \text{ nm}$)	QY% ($\lambda_{exc} = 370 \text{ nm}$)
Ca ₈ ZnTb(PO ₄) ₇	24	31
Ca9Tb(PO4)7	13	24
Ca ₈ ZnLa _{0.99} (PO ₄) ₇ :0.01 Tb ³⁺	8	3
Ca ₉ La _{0.99} (PO ₄) ₇ :0.01 Tb ³⁺	4	2
Y ₂ O ₂ S:Tb ³⁺	74	4

of the incorporated ion (r_{VIII} (Tb³⁺) < r_{VIII} (La³⁺)), vice versa the MR rate increases with increasing radius of the modifying ion.

The emission ascribed to the ${}^{5}D_{4}-{}^{7}F_{5}$ transition of Tb³⁺ is an electricdipole allowed transition, and hypersensitive to surroundings [25], so its intensity is strongly dependents on the Tb³⁺ environment. The ratio of integral intensities of ${}^{5}D_{4}-{}^{7}F_{5}/{}^{5}D_{4}-{}^{7}F_{6}$ transitions in Tb³⁺-containing compounds, referred as the "green-to-blue" (G/B) factor [26,27,40], also describe the asymmetry of the local environment around the optically active dopant. The calculated G/B factor increased with the increasing of Zn^{2+} concentration (Table S3). The increasing of the G/B factor corresponds to a higher local symmetry of the crystallographic sites, occupied by Tb^{3+} , as well, as a transition from polar structure (Ca₉Ln(PO₄)₇, R3c sp. gr.) to non-polar one (Ca₈ZnLn(PO₄)₇, R3c sp. gr.). The values of the G/B for synthesized phosphates reach 2.58 for Ca_{9-x}Zn_xTb(PO₄)₇ and 2.47 for Ca_{9-x}Zn_xLa_{0.99}(PO₄)₇:0.01Tb³⁺, respectively (Table S3).

From the measurements data the lifetime in the excited ${}^{5}D_{4}$ state for CZLaTb is higher than for CZTb (Fig. 9, Table 3). Taking into account that the probability of a radiative transition from an excited state is directly proportional to the lifetime in this state, it can be concluded that the luminescence intensity and QY upon doping the Ca₈ZnLa(PO₄)₇ matrix with Tb³⁺ ions should be higher in comparison to Ca₉₋₅Zn(PO₄)₇. However, the low Tb³⁺ activator concentration lead to the lower QY for the CZLaTb than for CZTb phosphors. Considering decay curves upon Zn²⁺ concentration the lifetimes is slightly rising from 2.03 ms in Ca₉La_{0.99}(PO₄)₇:0.01 Tb³⁺ to 2.68 ms in Ca₈ZnLa_{0.99}(PO₄)₇:0.01 Tb³⁺. The increasing of the luminescence intensity upon Zn²⁺ incorporation apparently is associated with rising of polyhedra distortion. Such effect was previously observed in Ref. [14].

5. Conclusions

In summary, two series of solid solutions were prepared and spectroscopic properties of Tb^{3+} ion in the β -Ca₃(PO₄)₂-type host were studied. The green-emitting LED device was fabricated. It was revealed by DSC and SHG tests that during the $Ca^{2+} \rightarrow Zn^{2+}$ substitution the crystal structure transforms from polar to centrosymmetric state at x \sim 0.5. Such transformation was reflected in anomalies of luminescent parameters of studied compounds. It was shown that the small concentration of Tb^{3+} in $Ca_{9-x}Zn_xLa_{0.99}(PO_4)_7$:0.01 Tb^{3+} demonstrates the absence of cross-relaxation and effectively emission from the ⁵D₃ level. In both solid solutions the "green" magneto-dipole ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition is predominant. There was no concentration quenching detected in the whole region of solid solutions. The integral intensity increases in 3 times in the most effective Ca_{9-x}Zn_xTb(PO₄)₇ phosphor. The CIE coordinates and CCT were calculated and confirm suitable characteristics. The changing of the G/B parameter is reflected on the CIE diagram by the shifting from yellow-green (Ca₈ZnLa_{0.99}(PO₄)₇:0.01 Tb³⁺) to green (Ca₈ZnTb(PO₄)₇) color. The measured QY reached 31%. Thus, the proposal substitution of Ca²⁺ in the β -Ca₃(PO₄)₂-type related hosts by Zn²⁺ is a pathway for obtaining the efficient green luminescence from Tb³⁺ ion.

Declaration of competing interest

The authors confirm that there are no conflicts to declare.

CRediT authorship contribution statement

Dina V. Deyneko: Data curation, Funding acquisition, Project administration, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. Vladimir A. Morozov: Methodology, Writing - review & editing. Andrey A. Vasin: Data curation, Investigation, Writing - review & editing. Sergey M. Aksenov: Formal analysis, Writing - original draft, Writing - review & editing. Yury Yu Dikhtyar: Investigation, Writing - review & editing. Sergey Yu Stefanovich: Formal analysis, Writing - review & editing, Validation. Bogdan I. Lazoryak: Formal analysis, Writing - review & editing, Validation.

Acknowledgements

This work was supported by Russian Science Foundation (Grant 19-

77-10013). The authors are grateful to I.D. Popov (Institute of Solid State Chemistry UB RAS) for additional PLE measurements.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jlumin.2020.117196.

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