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journal homepage: www.elsevier.com/locate/matresbuPreparation and investigation of Dy³⁺-doped Ca₉LiGd_{2/3}(PO₄)₇ single-phase full-color phosphorShihua Liu^a, Simei Liu^a, Jingjing Wang^a, Pengfei Sun^a, Yifan Zhong^a, Jung Hyun Jeong^b, Bin Deng^{c,*}, Ruijin Yu^{a,*}^a College of Chemistry & Pharmacy, Northwest A&F University, Yangling, Shaanxi 712100, PR China^b Department of Physics, Pukyong National University, Busan 608-737, Republic of Korea^c College of Chemistry & Biology and Environmental Engineering, Xiangnan University, Chenzhou, Hunan 423043, PR China

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ABSTRACT

Novel single-phased white-light-emitting Ca₉LiGd_{2/3}(PO₄)₇:xDy³⁺ ($x = 0.02, 0.05, 0.10, 0.15, 0.20, 0.25, \text{ and } 0.30$) β -Ca₃(PO₄)₂-type phosphate phosphors were synthesized. The phase structure, luminescence, and thermal stability of the phosphors were characterized by X-ray powder diffraction analysis, photoluminescence excitation and emission spectra, thermal quenching, and decay curves. XRD analysis confirmed the phase formation of Ca₉LiGd_{2/3}(PO₄)₇:Dy³⁺ materials. Under the excitation of 352 nm, the emission of the Ca₉LiGd_{2/3}(PO₄)₇:0.20Dy³⁺ sample centered at blue (488 nm) and yellow (580 nm), which corresponded to ⁴F_{9/2}–⁶H_{15/2} transition and ⁴F_{9/2}–⁶H_{13/2} transition. The optimum dopant concentration of Dy³⁺ ions was around 20 mol%, and the critical transfer distance of Dy³⁺ was calculated as 18 Å. The thermal-quenching temperature was above 500 K for Ca₉LiGd_{2/3}(PO₄)₇:0.20Dy³⁺. The developed phosphor has a great potential as a single-component white-light-emitting phosphor for UV-light-emitting diodes.

1. Introduction

Phosphates are excellent matrices for rare earth ion-activated phosphors due to their easy synthesis, low cost, and chemical thermal stability [1–5]. Compounds with a β -Ca₃(PO₄)₂-type structure have recently attracted tremendous interest. β -Ca₃(PO₄)₂ (space group R3c, Z = 21) is isostructural with the natural mineral whitlockite. This special crystal structure permits the rich heterovalent substitution of Ca²⁺ by M⁺ (monovalent), R³⁺ (trivalent), and R⁴⁺ (quadrivalent) cations. Such substitutions based on the initial β -Ca₃(PO₄)₂ produce different compounds with nonlinear-optical, catalytic, ferroelectric, ion-conductive, and luminescent properties for many potential applications [6–9]. In 2011, Huang first investigated Eu³⁺-doped Ca₉LiGd_{2/3}(PO₄)₇ phosphors and found that it can be efficiently excited by near-UV light to realize an intense red luminescence (611 nm). The weak concentration quenching and crystallographic site-occupancy of Eu³⁺ ions in the host were investigated in detail [10]. In 2016, Zhang reported the color-tunable emission from blue-violet to red in Ca₉LiGd_{2/3}(PO₄)₇:Ce³⁺, Mn²⁺ systems [11]. The resonant energy transfer from Ce³⁺ to Mn²⁺ via a dipole-quadrupole mechanism has been confirmed. Dy³⁺ has recently received considerable attention in white-emitting

phosphors. Dy³⁺ with 4f⁹ configuration has abundant f-block energy levels and strong emission in the visible range [12]. Dy³⁺ generally exhibits two principal emissions: a blue (~488 nm) emission associated with ⁴F_{9/2} → ⁶H_{15/2} transition and a yellow (~580 nm) emission associated with ⁴F_{9/2} → ⁶H_{13/2} transition ($\Delta L = 2; \Delta J = 2$). We also found the feeble red emission (~665 nm) due to ⁴F_{9/2} → ⁶H_{11/2} transition [13–15]. The intensity ratio of ⁴F_{9/2} → ⁶H_{13/2} to ⁴F_{9/2} → ⁶H_{15/2} can be affected by the surrounding environment of Dy³⁺ because the yellow emission ($\Delta L = 2; \Delta J = 2$) is a hypersensitive transition. The doping of Dy³⁺ ions in single-phase white light-emitting phosphate phosphors has reported (Sr_{0.85}Mg_{0.14})₃(P_{0.8}Si_{0.2}O₄):Dy³⁺ [16], Ca₅Y₃Na₂(PO₄)₅(SiO₄)F₂:Dy³⁺ [17], Sr₃Y(PO₄)₃:Dy³⁺ [18], K₂Gd_(1-x)(PO₄)(WO₄):Dy³⁺ [19], Ca₉La(PO₄)₅(GeO₄)F₂ [20]. However, the photoluminescence (PL) properties of Dy³⁺-doped Ca₉LiGd_{2/3}(PO₄)₇ phosphors have yet to be characterized. In this paper, we report the white emitting phosphors under NUV excitation. The effects of Dy³⁺-doped concentration on luminescence properties are discussed. The decay lifetime, CIE, and thermal stability are also investigated. The white LED was obtained in the method by combining near-UV InGaN chip with the prepared phosphor.

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2. Experimental

Dysprosium-doped $\text{Ca}_9\text{LiGd}_{2(1-x)/3}\text{Dy}_{2x/3}(\text{PO}_4)_7$ (CLGP:Dy³⁺) ($x = 0.01\text{--}0.15$) were prepared via solid-state reaction. High-purity CaCO_3 (> 99%), Li_2CO_3 (99.99%), Gd_2O_3 (99.99%), $\text{NH}_4\text{H}_2\text{PO}_4$ (99.9%), and Dy_2O_3 (99.99%) from Sigma–Aldrich were weighed per the following balanced equation. Samples were ground together in an agate mortar, heated to 650 °C for 3 h, and finally heated to 1150 °C for 5 h by several intermediate grindings. X-ray powder diffraction (XRD) was performed with D2 PHASER (Bruker) with Cu K α radiation ($\lambda = 0.15405$ nm, with 40 kV and 40 mA). Composition analysis was carried out using field emission scanning electron microscopy (SEM, JEOL JSM-6490F). Photoluminescence spectra were obtained with a Hitachi F-4600 spectrophotometer. A 150 W Xenon lamp with light was used as an excitation source. Thermal quenching was also investigated via temperature-dependent photoluminescence intensity from 300 K to 480 K. Lifetime measurements of the samples were obtained on an Edinburgh FLS 920 spectrometer.

3. Results and discussion

The $\text{Ca}_3(\text{PO}_4)_2$ crystal structure is rhombohedral, with space group R3c. The cell can accommodate five distinct Ca²⁺ sites (namely Ca1–Ca5) with coordination number at 6, 7, 8, and various Ca–O distances [21,22]. The $\beta\text{-Ca}_3(\text{PO}_4)_2$ structure can allow the iso- and heterovalent substitutions of Ca²⁺ by M⁺ (monovalent), R³⁺ (trivalent), and R⁴⁺ (tetravalent) cations. $\text{Ca}_9\text{LiGd}_{2/3}(\text{PO}_4)_7$ can be obtained with $1.5\text{Ca}^{2+} + \square = \text{Li}^+ + 2/3\text{Gd}^{3+}$ replacement in the $\beta\text{-Ca}_3(\text{PO}_4)_2[\text{Ca}_{10.5}(\text{PO}_4)_7]$ structure. Fig. 1(b) shows the whitlockite structure of $\text{Ca}_9\text{LiGd}_{2/3}(\text{PO}_4)_7$ viewed along the *a* axis [23]. Ca(1), Ca(2), and Ca(3) occupy general positions (18b) while Gd is located at 6a sites on the threefold rotation axis. Ca(1), Ca(2), Ca(3), and Ca(5) are coordinated with seven, eight, eight, and six oxygen atoms, respectively. Therefore, this crystal structure of $\text{Ca}_9\text{LiGd}_{2/3}(\text{PO}_4)_7$ consists of a 3D packing of $[\text{PO}_4]$, Ca(1)O₇, Ca(2)O₈, Ca(3)O₈, and Ca(5)(Gd)O₆ polyhedra through corner- and edge-sharing. The Ca(2)O₈ and P(2)O₄ groups are linked by a sharing corner. The Ca(1)O₇ and P(3)O₄ groups are also linked by a sharing corner. Ca(3)O₈ is linked with the Ca(1)O₇ and Ca(2)O₈ groups by sharing edges [21,24].

XRD patterns indicate that all the synthesized CLGP: $x\text{Dy}^{3+}$ ($x = 0.02, 0.05, 0.10, 0.15, 0.20, 0.25$, and 0.30) samples are single phase (shown in Fig. 2), which agrees well with the standard data $\text{Ca}_9\text{LiGd}_{2/3}(\text{PO}_4)_7$ of phase (JCPDS 48-1194). The lattice constants of CLGP: 0.20Dy^{3+} are calculated to be $a = b = 10.4128$ Å, $c = 37.2714$, and $V = 3499.81$ Å³, which are consistent with the literature [25]. Thus, the Dy³⁺ ions possibly occupy the Gd³⁺ ions in the host lattice.

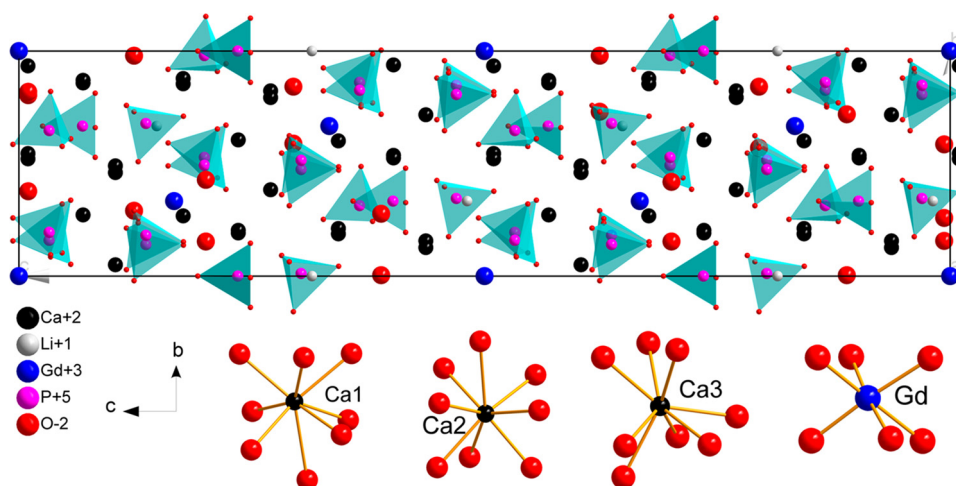


Fig. 1. Crystal structure of $\text{Ca}_9\text{LiGd}_{2/3}(\text{PO}_4)_7$ viewed along the *a* axis and coordination polyhedra groups.

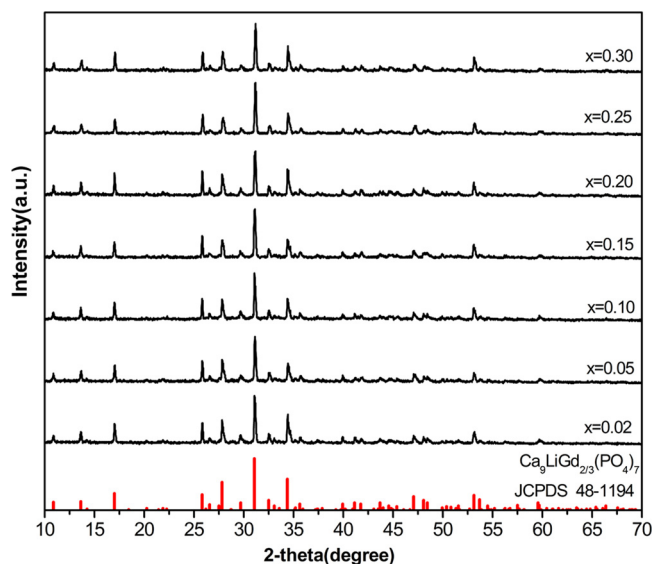


Fig. 2. XRD patterns of all CLGP: $x\text{Dy}^{3+}$ ($x = 0.02, 0.05, 0.10, 0.15, 0.20, 0.25$, and 0.30) samples.

This finding might be due to the similar ionic radii and identical valence of Dy³⁺ ($r = 0.912$ Å, CN = 6) and Gd³⁺ (1.053 Å, CN = 8; 0.938 Å, CN = 6) [26].

Fig. 3 exhibits the SEM morphology of two representative CLGP:Dy³⁺ samples. Many irregularly shaped particles are distributed non-uniformly into sizes around 10 μm due to the high-temperature annealing process. They are morphologically similar to the reported results in $\text{Ca}_9\text{ZnLi}(\text{PO}_4)_7\text{:Eu}^{3+}$ [27] and $\text{Ca}_9\text{LiGd}_{2/3}(\text{PO}_4)_7\text{:Ce}^{3+}, \text{Mn}^{2+}$ [11]. Thus, the phosphor could basically meet the commercial fabrication demand for white light-emitting diodes.

Fig. 4 shows the excitation spectra of CLGP: 0.20Dy^{3+} phosphor when recorded at 580 nm. Commonly, the absorption of the host lattice (PO_4^{3-} groups) is around 170 nm located at the vacuum UV region. Huang et al. [10] also found the charge transfer band (CTB) of Eu–O at 265 nm (4.67 eV) in Eu³⁺-doped CLGP phosphor. Dorenbos [28] proposed that the CTB energy of Dy³⁺ always appears 2.04 eV higher than that of Eu³⁺ in the same host compound. The CTB of Dy³⁺ is estimated to be around 185 nm. Therefore, the phosphate host absorption and CTB band from O²⁻ → Dy³⁺ ions could not be detected in the present condition. The sharp excitation is located at 275 nm, indicating that energy transfer from Gd³⁺ to Dy³⁺ ions may occur [29]. Meanwhile, the phosphor sample has an effective energy absorption mainly in the

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