Research Article

Rare Earth Doped Lanthanum Calcium Borate Polycrystalline Red Phosphors

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Received 19 March 2014; Accepted 15 July 2014; Published 5 August 2014

Academic Editor: Somchai Thongtem

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Single-phased Sm^{3+} doped lanthanum calcium borate ($\text{Sm}_x\text{La}_{2-x}\text{CaB}_{10}\text{O}_{19}$, SLCB, $x = 0.06$) polycrystalline red phosphor was prepared by solid-state reaction method. The phosphor has two main excitation peaks located at 398.5 nm and 469.0 nm, which are nicely in accordance with the emitting wavelengths of commercial near-UV and blue light emitting diode chips. Under the excitation of 398.0 nm, the dominant red emission of Sm^{3+} in SLCB phosphor is centered at 598.0 nm corresponding to the transition of $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$. The Eu^{3+} fluorescence in the red spectral region is applied as a spectroscopic probe to reveal the local site symmetry in the host lattice and, hence, Judd-Ofelt parameters Ω_t ($t = 2, 4$) of Eu^{3+} in the phosphor matrix are derived to be 3.62×10^{-20} and $1.97 \times 10^{-20} \text{ cm}^2$, indicating a high asymmetrical and strong covalent environment around rare earth luminescence centers. Herein, the red phosphors are promising good candidates employed in white light emitting diodes (LEDs) illumination.

1. Introduction

White light emitting diodes (LEDs) are considered as the next generation solid-state lighting systems because of their excellent properties such as high efficiency, low power consumption, long lifetime, and lower toxicity [1–6]. The LED based solid-state lighting techniques have gained great achievements since the white LEDs became commercially available by Nichia Chemical Co. in 1997 [7–9]. There are three ways to produce white LEDs: (i) combining a blue LED with a yellow phosphor, for example, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, (ii) mixing red, green, and blue emissions from three LEDs, and (iii) exciting red/green/blue tricolor phosphors with a near-UV LED (370–410 nm). The third is a flexible and convenient way to obtain high quality white LEDs due to the following advantages, generated white color by phosphors, that is, high tolerance to UV chips' color variation and excellent color rendering index [10]. The main tricolor phosphors for near-UV InGaN-based LEDs are still under developing just as $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ for blue, $\text{ZnS}:\text{Cu}^+/\text{Al}^{3+}$ for green, and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ for red [11–13]. Among them, the red phosphor has received much attention due to the

fact that it can improve color rendering index; therefore it is meaningful to develop numerous red phosphors with higher efficiency to improve the performance of white LEDs [13–17].

During the past decades, rare earth ions doped in various host materials have been widely studied due to their characteristic luminescence properties. Among the rare earth ions, Sm^{3+} , Eu^{3+} , Tb^{3+} , and Dy^{3+} are important activator ions for producing visible light [18–25]. Sm^{3+} activated luminescent materials have received much attention at present [26, 27]. They show bright emissions in orange and red regions attributed to the transitions from the excited state $^4\text{G}_{5/2}$ to the ground state $^6\text{H}_{5/2}$ and the other state $^6\text{H}_j$ ($J = 7/2, 9/2$, and $11/2$), which can be used in high density optical storage, temperature sensors, under sea communication, various fluorescent devices, color display, and visible solid-state lasers [2, 28–30]. Luminescence of Eu^{3+} is especially useful to probe the local structure of luminescent centers in a host lattice because of its simple energy level structure, great sensitivity to ligand field, and similar lanthanide chemical properties to the other rare earth ions [31–33].

Growing interest recently has been focused on luminescence of trivalent rare earth ions in phosphates, tungstates, borates, molybdates, and aluminates, among which rare earth doped borates are especially attractive because of their wide UV transparency, exceptional optical damage thresholds, excellent chemical and thermal stability, and high luminescence efficiency [34–42]. Hence, a borate phosphor which efficiently emits red fluorescence under the UV and blue light excitation is of great significance to be synthesized for practical applications. The compound $\text{La}_2\text{CaB}_{10}\text{O}_{19}$ (LCB) is chemically stable and nonhygroscopic, which belongs to the monoclinic system with the space group of C2 and the lattice parameters $a = 1.1043 \text{ nm}$, $b = 0.6563 \text{ nm}$, $c = 0.9129 \text{ nm}$, $\alpha = \gamma = 90^\circ$, and $\beta = 91.47^\circ$ [43, 44]. The effect of Sm^{3+} doping in LCB host is seductive to be developed as a red phosphor for solid-state LED lighting.

Herein, Sm^{3+} activated lanthanum calcium borate phosphor ($\text{Sm}_x\text{La}_{2-x}\text{CaB}_{10}\text{O}_{19}$, SLCB) was prepared by the solid-state reaction technique, and an attempt was made to investigate its luminescence characteristics. Eu^{3+} was adopted as a probe in ELCB ($\text{Eu}_x\text{La}_{2-x}\text{CaB}_{10}\text{O}_{19}$, ELCB) phosphor through the calculation of J -O parameters to reflect the local microenvironment around the rare earth ions in the compounds. The bright red fluorescence obtained from SLCB phosphor suggests that the as-prepared phosphor is a promising red luminescent material for white LEDs.

2. Experiments

SLCB phosphor was synthesized by a solid-state reaction route at high temperature using the following chemical reaction:

Here, the x value of SLCB sample is the molar replacement of La^{3+} by Sm^{3+} , which is adopted to be 0.06 to maintain the brightness of phosphors and avoid the fluorescence quenching because of high concentration doping. Reagents La_2O_3 (99.99%), CaCO_3 (99.99%), H_3BO_3 (99.9%), and Sm_2O_3 (99.99%) were used as raw materials. They were weighed according to the stoichiometric proportion, except for H_3BO_3 with an excess of 6.5 wt% to compensate for the volatilization of B_2O_3 at high temperature. After being ground and mixed thoroughly in an agate mortar, the mixture was placed into an electric furnace and preheated at 500°C for 10 h. Being cooled and ground again, the mixture was sintered at 930°C for 24 h twice with the intermediate grinding.

The crystallographic structure of SLCB powders was characterized by X-ray powder diffraction analysis using a D/Max-3B X-ray diffractometer with 40 kV, 20 mA. The excitation and emission spectra were recorded on a Jobin Yvon FluoroLog-3 spectrophotometer with a R928 photomultiplier tube (PMT) detector, and a commercial CW Xe-lamp was used as pump source. A JSM-6460LV scanning electron microscopy was used for the observation of particle morphology. The photographs of the samples were taken by a Sony $\alpha 200$ digital camera. ELCB phosphor was prepared by

the same way except that Eu_2O_3 was used instead of Sm_2O_3 and the measurements were carried out at the same condition as SLCB phosphor.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis. To check the phase purity and the structure of the sample, the powder X-ray diffraction (XRD) measurement for the sample was carried out. Figure 1 presents a comparison between the experimental result for SLCB phosphor and JCPDS card 54-0033 ($\text{La}_2\text{CaB}_{10}\text{O}_{19}$). The observed peaks are in good agreement with the JCPDS data indicating that the main phase of the prepared phosphor is LCB. Because of lanthanide contraction, rare earth ions have similar radius, coordination environment, and physical-chemical properties. When La^{3+} in the lattice is replaced by Sm^{3+} , the crystal structure does not change dramatically. The doped product crystallizes as monoclinic structure with a space group of C2 and lattice parameters values $a = 1.1028 \text{ nm}$, $b = 0.6556 \text{ nm}$, $c = 0.9114 \text{ nm}$, and $\beta = 91.431^\circ$, which is almost consistent with pure LCB phase [44, 45]. These results show that the Sm^{3+} has been incorporated into LCB lattices successfully and the small amount of Sm^{3+} ions has negligible effect on the basic crystal structure of LCB. The same result was verified in ELCB phosphor.

3.2. Photoluminescence Characteristics of SLCB Phosphor.

The excitation spectrum of SLCB phosphor monitored at 598.0 nm consists of several bands peaking at 245.0, 340.0, 358.0, 370.0, 398.5, 412.5, and 469.0 nm as depicted in Figure 2. The broadband around 245.0 nm is due to the charge transfer (CT) band of $\text{Sm}^{3+}-\text{O}^{2-}$ [45, 46]. The other excitation peaks at 340.0, 358.0, 370.0, 398.5, 412.5, and 469.0 nm have been assigned to the 4f-4f inner shell transitions of Sm^{3+} [47–49]. The efficient excited wavelength range of Sm^{3+} in SLCB phosphor covers the whole long-wavelength UV, purple, blue, and bluish-green spectral regions. This suggests that the effective excitation range matches the output wavelengths of InGaN-based LED chips well; thus the phosphors have potential application in the solid-state LED lighting.

Figure 3 is the emission spectrum of SLCB phosphor excited by 398.0 nm. The characteristic emissions of SLCB phosphor consist of five emission bands, which are attributed to the transitions from $^4\text{G}_{5/2}$ state to $^6\text{H}_J$ ($J = 5/2, 7/2, 9/2, 11/2$, and $13/2$) states of Sm^{3+} . Among these, the strongest emission peak located at 598.0 nm originates from the typical transition $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ and the other peaks at 562.0, 646.5, 706.0, and 735.0 nm are attributed to the transitions of $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$, and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{13/2}$, respectively [50–54]. Among these emission peaks, the transition emission $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (598.0 nm, orangish red) with $\Delta J = \pm 1$ is a magnetic dipole (MD) allowed one, but it is also electric dipole (ED) dominated one and the other transition $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ (646.5 nm, red) is purely an ED one. The MD transition does not appreciably depend on the chemical surroundings of the luminescent center and its symmetry; however, the ED

FIGURE 1: X-ray diffraction patterns of SLCB phosphor and the referenced LCB (JCPDS number 54-0033).

transition belongs to hypersensitive transitions. Generally, the intensity ratio of ED to MD transitions has been used to evaluate the symmetry of the local environment of the trivalent 4f ions. The greater the intensity of the ED transition, the more the asymmetry nature [55]. In this work, the emission due to $^4G_{5/2} \rightarrow ^6H_{9/2}$ (ED) transition of Sm^{3+} is more intense than $^4G_{5/2} \rightarrow ^6H_{5/2}$, specifying the asymmetric nature of host matrix. And the three main emission peaks of SLCB phosphor always split just similarly to the reports of $LiBaBO_3:Sm^{3+}$ [56], $Gd_2MoO_6:Sm^{3+}$ [57], and $GdVO_4:Sm^{3+}$ [58]. Those splits result from the crystal field effects, and the split extents are related to the structure characteristic of the crystal field.

3.3. Intensity Parameters of the Spectroscopic Probe Eu^{3+} in ELCB Phosphor. Figure 4 presents the emission spectrum of ELCB phosphor excited at 391.0 nm in the wavelength of 560–720 nm. There are several typical emission bands around 560–720 nm assigned to the $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) transitions of Eu^{3+} [59–63], of which the red emission band at 617 nm is the most intense one due to the electric dipole transition $^5D_0 \rightarrow ^7F_2$.

Luminescence of Eu^{3+} is especially useful to probe the local symmetry and bonding characteristics of luminescent

FIGURE 2: Excitation spectrum of SLCB phosphor ($\lambda_{em} = 598.0$ nm).

FIGURE 3: Emission spectrum of SLCB phosphor ($\lambda_{ex} = 398.0$ nm). Inset of (a): fluorescence from SLCB phosphor under 365.0 nm radiation. Inset of (b): SLCB phosphor under natural light.

FIGURE 4: Emission spectrum of ELCB phosphor ($\lambda_{ex} = 391.0$ nm). Inserted photo: fluorescence from ELCB phosphor under 365.0 nm excitation.

FIGURE 5: SEM images of as-prepared SLCB (a) and ELCB (b).

centers in a host lattice on account of its unsplit 7F_0 ground state and relatively simple energy level scheme. The symmetry of the crystal site in which Eu^{3+} is located can be determined by the intensity ratio between ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_1$ transition emissions in ELCB [64–67]. Here, the ratio is 1.9076 in ELCB phosphor from Figure 4, indicating that ${}^5D_0 \rightarrow {}^7F_2$ electric dipole transition is dominated and Eu^{3+} is in an inversion asymmetrical site.

Moreover, in order to further identify the asymmetry of Eu^{3+} in ELCB phosphor, the intensity parameters are calculated. Generally, J - O intensity parameters are derived from absorption spectra; however, in consideration of the special energy level structure of Eu^{3+} , they should be calculated from the emission spectra because the recorded absorption peaks are not enough to get accurate results [68–70]. The transitions of Eu^{3+} from 5D_0 to 7F_J ($J = 2, 4$, and 6) are electronic dipole allowed ones and hypersensitive to the local environment around Eu^{3+} . The spontaneous emission probability A_{ed} from $|\psi J\rangle$ to $|\psi' J'\rangle$ is given by the following expression:

$$A_{\text{ed}} = \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} \times \sum_{t=2,4,6} \Omega_t \langle \psi J \| U^{(t)} \| \psi' J' \rangle^2, \quad (2)$$

where e is the electron charge, ν is the emission peak wavenumber, h is the Planck constant, n is the refractive index, $2J+1$ is the degeneracy of the excited state, and $\langle \psi J \| U^{(t)} \| \psi' J' \rangle^2$ is the square of the reduced matrix elements of the tensor operator, which connects the initial state $|\psi J\rangle$ with the final state $|\psi' J'\rangle$ and is considered to be independent of host matrix. The ${}^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} is magnetic-dipole allowed one and insensitive to the host matrix. The spontaneous emission probability of it (A_{md}) is given by

$$A_{\text{md}} = \frac{64\pi^4 \nu^3}{3h(2J+1)} n^3 S_{\text{md}}, \quad (3)$$

where the magnetic dipole line strength S_{md} is constant and independent of the matrix, so the value of A_{md} can be

estimated by the value of fluoride glass ($A'_{\text{md}} = 60.3 \text{ s}^{-1}$). The relationship is

$$A_{\text{md}} = \left(\frac{n}{n'} \right)^3 A'_{\text{md}}, \quad (4)$$

where n ($= 1.679$) and n' ($= 1.522$) are the refractive indices of ELCB crystal [71] and fluoride glass [72], respectively.

Based on the calculated A_{rad} , the selection rules, and the characteristic of transition intensities of Eu^{3+} , each of the $\langle \psi J \| U^{(t)} \| \psi' J' \rangle^2$ parameters decides the intensities of transitions because the remaining two are zero. Thus, the Ω_t can be estimated from the intensity ratios of ${}^5D_0 \rightarrow {}^7F_{2,4}$ transitions to ${}^5D_0 \rightarrow {}^7F_1$ transition as

$$\frac{\int I(\nu) d\nu}{\int I_{\text{md}}(\nu) d\nu} = \frac{A_J}{A_{\text{md}}} = \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9A_{\text{md}}} \Omega_t \langle \psi J \| U^{(t)} \| \psi' J' \rangle^2. \quad (5)$$

The calculated Ω_t ($t = 2$ and 4) values of Eu^{3+} in ELCB phosphor are 3.62×10^{-20} and $1.97 \times 10^{-20} \text{ cm}^2$, respectively. This result confirms a high inversion asymmetric and strong covalent environment of Eu^{3+} in the phosphor. The value of Ω_6 cannot be given since the ${}^5D_0 \rightarrow {}^7F_6$ emission is unable to be experimentally detected in this work.

Figure 5 presents the SEM pictures of the as-prepared SLCB and ELCB phosphors. The two samples have similar morphology and particle size distribution. Also, they have good dispersion and relatively narrow size distribution with the average size of about $0.5\sim 6 \mu\text{m}$. However, the particles have no regular and uniform shape, and some of them are agglomerated. The main reasons are that the primary nanocrystals with high energy would assemble to minimize the surface energy and they would be sintered in the heat treatment process.

4. Conclusion

A red emitting phosphor SLCB ($\text{Sm}_x\text{La}_{2-x}\text{CaB}_{10}\text{O}_{19}$) was prepared by solid-state reaction method in the air. XRD analysis indicates that the crystal belongs to a monoclinic system with unit cell parameters $a = 1.1028\text{ nm}$, $b = 0.6556\text{ nm}$, $c = 0.9114\text{ nm}$, and $\beta = 91.431^\circ$. The excitation spectrum shows that the phosphor can be efficiently excited by the commercial near-UV and blue light emitting diodes. Under the excitation of 398.0 nm, the phosphor presented red luminescence with efficient emissions at 562.0, 598.0, 646.5, 706.0, and 735.0 nm, corresponding to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$ ($J = 5/2, 7/2, 9/2, 11/2$, and $13/2$) transitions, respectively. Eu^{3+} is used as a spectroscopic probe for the microstructure of ELCB ($\text{Eu}_x\text{La}_{2-x}\text{CaB}_{10}\text{O}_{19}$) phosphor and, thus, Judd-Ofelt parameters Ω_t ($t = 2, 4$) of Eu^{3+} in ELCB phosphor are derived to be 3.62×10^{-20} and $1.97 \times 10^{-20}\text{ cm}^2$, indicating a high asymmetrical and covalent environment around rare earth luminescence centers in the host lattice. The red fluorescence suggests that the two phosphors are potential candidates for light emitting diode applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant no. 61275057) and the Undergraduate Training Programs for Innovation and Entrepreneurship of Dalian Polytechnic University (Grant no. 2013013).

References

- [1] F. Yang, Z. P. Yang, Q. M. Yu, Y. F. Liu, X. Li, and F. C. Lu, "Sm³⁺-doped Ba₃Bi(PO₄)₃ orange reddish emitting phosphor," *Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy*, vol. 105, pp. 626–631, 2013.
- [2] D. Kang, H. S. Yoo, S. H. Jung, H. Kim, and D. Y. Jeon, "Synthesis and photoluminescence properties of a novel red-emitting Na₂Y₂Ti₃O₁₀:Eu³⁺, Sm³⁺ phosphor for white-light-emitting diodes," *Journal of Physical Chemistry C*, vol. 115, no. 49, pp. 24334–24340, 2011.
- [3] Y. H. Won, H. S. Jang, K. W. Cho, Y. S. Song, D. Y. Jeon, and H. K. Kwon, "Effect of phosphor geometry on the luminous efficiency of high-power white light-emitting diodes with excellent color rendering property," *Optics Letters*, vol. 34, no. 1, pp. 1–3, 2009.
- [4] Z. Cui, R. Ye, D. Deng et al., "Eu²⁺/Sm³⁺ ions co-doped white light luminescence SrSiO₃ glass-ceramics phosphor for White LED," *Journal of Alloys and Compounds*, vol. 509, no. 8, pp. 3553–3558, 2011.
- [5] Y. H. Song, G. Jia, M. Yang, Y. J. Huang, H. P. You, and H. J. Zhang, "Sr₃Al₂O₅Cl₂:Ce³⁺, Eu²⁺: a potential tunable yellow-to-white-emitting phosphor for ultraviolet light emitting diodes," *Applied Physics Letters*, vol. 49, Article ID 091902, 2009.
- [6] H. Yamamoto, "White LED phosphors: the next step," in *Optical Components and Materials VII*, Proceedings of SPIE, 2010.
- [7] M. K. Jung, W. J. Park, and D. H. Yoon, "Photoluminescence characteristics of red phosphor Eu³⁺, Sm³⁺ co-doped Y₂O₃ for white light emitting diodes," *Sensors and Actuators B: Chemical*, vol. 126, no. 1, pp. 328–331, 2007.
- [8] S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, "High-power InGa_N single-quantum-well-structure blue and violet light-emitting diodes," *Applied Physics Letters*, vol. 67, p. 1868, 1995.
- [9] H. J. Qian, J. Y. Zhang, and L. Q. Yin, "Crystal structure and optical properties of white light-emitting Y₂WO₆:Sm³⁺ phosphor with excellent color rendering," *RSC Advances*, vol. 3, no. 23, pp. 9029–9034, 2013.
- [10] M. M. Haque, H. I. Lee, and D. K. Kim, "Luminescent properties of Eu³⁺-activated molybdate-based novel red-emitting phosphors for LEDs," *Journal of Alloys and Compounds*, vol. 481, pp. 792–796, 2009.
- [11] I. Pekgozlu, S. Cakar, and J. Lumin, "Photoluminescence properties of Li₆CaB₃O_{8.5}: M³⁺ (M³⁺: Dy and Sm)," *Journal of Luminescence*, vol. 132, no. 9, pp. 2312–2317, 2012.
- [12] H. Yu, D. Deng, D. Zhou et al., "Ba₂Ca(PO₄)₂:Eu²⁺ emission-tunable phosphor for solid-state lighting: luminescent properties and application as white light emitting diodes," *Journal of Materials Chemistry C*, vol. 1, no. 35, pp. 5577–5582, 2013.
- [13] S. Neeraj, N. Kijima, and A. K. Cheetham, "Novel red phosphors for solid-state lighting: the system NaM(WO₄)_{2-x}(MoO₄)_x:Eu³⁺ (M, Gd, Y, Bi)," *Chemical Physics Letters*, vol. 387, pp. 2–6, 2004.
- [14] G. R. Dillip, S. J. Dhoble, L. Manoj, C. Madhukar Reddy, and B. Deva Prasad Raju, "A potential red emitting K₄Ca(PO₄)₂:Eu³⁺ phosphor for white light emitting diodes," *Journal of Luminescence*, vol. 132, no. 11, pp. 3072–3076, 2012.
- [15] C. B. Azevedo, É. A. De Souza, E. H. De Faria et al., "Optical properties of Eu-doped hybrid materials prepared from dimethyl and methyl alkoxides precursors," *Journal of Luminescence*, vol. 134, pp. 551–557, 2013.
- [16] Y. G. Su, L. P. Li, and G. S. Li, "Synthesis and optimum luminescence of CaWO₄-based red phosphors with codoping of Eu³⁺ and Na⁺," *Chemistry of Materials*, vol. 20, no. 19, pp. 6060–6067, 2008.
- [17] R. J. Wiglus, T. Grzyb, A. Lukowiak, A. Bednarkiewicz, S. Lis, and W. Strek, "Tuning luminescence properties of Eu³⁺ doped CaAl₂O₄ nanophosphores with Na⁺ co-doping," *Journal of Luminescence*, vol. 133, pp. 102–109, 2013.
- [18] N. S. Hussain, G. Hungerford, R. El-Mallawany et al., "Absorption and emission analysis of RE³⁺ (Sm³⁺ and Dy³⁺): Lithium boro tellurite glasses," *Journal of Nanoscience and Nanotechnology*, vol. 9, no. 6, pp. 3672–3677, 2009.
- [19] M. D. Que, Z. P. Ci, Y. H. Wang, G. Zhu, Y. R. Shi, and S. Y. Xin, "Synthesis and luminescent properties of Ca₂La₈(GeO₄)₆O₂:RE³⁺ (RE³⁺=Eu³⁺, Tb³⁺, Dy³⁺, Sm³⁺, Tm³⁺) phosphors," *Journal of Luminescence*, vol. 144, pp. 64–68, 2013.
- [20] A. Tang, D. F. Zhang, and L. Yang, "Photoluminescence characterization of a novel red-emitting phosphor In₂(MoO₄)₃:Eu³⁺ for white light emitting diodes," *Journal of Luminescence*, vol. 132, no. 6, pp. 1489–1492, 2012.
- [21] S. A. Naidu, S. Boudin, U. V. Varadaraju, and B. Raveau, "Eu³⁺ and Tb³⁺ emission in molybdenophosphate Na₂Y(MoO₄)(PO₄)," *Journal of the Electrochemical Society*, vol. 159, no. 4, pp. J122–J126, 2012.
- [22] X. L. Dong, J. H. Zhang, X. Zhang, Z. D. Hao, and S. Z. Lv, "Synthesis and photoluminescence properties of Eu²⁺

- doped $\text{Sr}_9\text{Sc}(\text{PO}_4)_7$ phosphors for white light-emitting diodes," *Ceramics International*, vol. 40, no. 4, pp. 5421–5423, 2014.
- [23] P. Abdul Azeem, M. Kalidasan, R. R. Reddy, and K. Ramagopal, "Spectroscopic investigations on Tb³⁺ doped lead fluoroborate glasses," *Optics Communications*, vol. 285, no. 18, pp. 3787–3791, 2012.
- [24] E. Cavalli, P. Boutinaud, R. Mahiou, M. Bettinelli, and P. Dorenbos, "Luminescence dynamics in Tb³⁺-doped CaWO_4 and CaMoO_4 crystals," *Inorganic Chemistry*, vol. 49, no. 11, pp. 4916–4921, 2010.
- [25] A. Boukhris, M. Hidouri, B. Glorieux, and M. Ben Amara, "Correlation between structure and photoluminescence of the europium doped glaserite-type phosphate $\text{Na}_2\text{SrMg}(\text{PO}_4)_2$," *Materials Chemistry and Physics*, vol. 137, no. 1, pp. 26–33, 2012.
- [26] Y. Zhang, C. H. Lu, L. Y. Sun, Z. Z. Xu, and Y. R. Ni, "Influence of Sm_2O_3 on the crystallization and luminescence properties of borocaluminosilicate glasses," *Materials Research Bulletin*, vol. 44, pp. 179–183, 2009.
- [27] M. Sobczyk, P. Starynowicz, R. Lisiecki, and W. Ryba-Romanowski, "Synthesis, optical spectra and radiative properties of $\text{Sm}_2\text{O}_3\text{:PbO:P}_2\text{O}_5$ glass materials," *Optical Materials*, vol. 30, no. 10, pp. 1571–1575, 2008.
- [28] V. Venkatramu, P. Babu, C. K. Jayasankar, T. Tröster, W. Sievers, and G. Wortmann, "Optical spectroscopy of Sm^{3+} ions in phosphate and fluorophosphate glasses," *Optical Materials*, vol. 29, no. 11, pp. 1429–1439, 2007.
- [29] S. Nishiura, S. Tanabe, K. Fujioka, and Y. Fujimoto, "Properties of transparent Ce:YAG ceramic phosphors for white LED," *Optical Materials*, vol. 33, no. 5, pp. 688–691, 2011.
- [30] X. M. Zhang and H. J. Seo, "Luminescence properties of novel Sm^{3+} , Dy^{3+} doped LaMoBO_6 phosphors," *Journal of Alloys and Compounds*, vol. 509, pp. 2007–2010, 2011.
- [31] A. M. Pires, M. F. Santos, M. R. Davolos, and E. B. Stucchi, "The effect of Eu^{3+} ion doping concentration in Gd_2O_3 fine spherical particles," *Journal of Alloys and Compounds*, vol. 344, no. 1–2, pp. 276–279, 2002.
- [32] K. Driesen, V. K. Tikhomirov, and C. Gorller-Walrand, " Eu^{3+} as a probe for rare-earth dopant site structure in nano-glass-ceramics," *Journal of Applied Physics*, vol. 102, Article ID 024312, 2007.
- [33] C. H. Yan, L. D. Sun, C. S. Liao et al., " Eu^{3+} ion as fluorescent probe for detecting the surface effect in nanocrystals," *Applied Physics Letters*, vol. 82, no. 26, pp. 3511–3513, 2003.
- [34] R. Stefani, A. D. Maia, E. E. S. Teotonio, M. A. F. Monteiro, M. C. F. C. Felinto, and H. F. Brito, "Photoluminescent behavior of $\text{SrB}_4\text{O}_7\text{:RE}^{2+}$ ($\text{RE}=\text{Sm}$ and Eu) prepared by Pechini, combustion and ceramic methods," *Journal of Solid State Chemistry*, vol. 179, no. 4, pp. 1086–1092, 2006.
- [35] Y. Won, H. Jang, W. Im, D. Jeon, and J. Lee, "Red-emitting $\text{LiLa}_2\text{O}_2\text{BO}_3\text{:Sm}^{3+}$, Eu^{3+} phosphor for near-ultraviolet light-emitting diodes-based solid-state lighting," *Journal of The Electrochemical Society*, vol. 155, no. 9, pp. J226–J229, 2008.
- [36] M. Ayvaci, A. Ege, and N. Can, "Radioluminescence of $\text{SrAl}_2\text{O}_4\text{:Ln}^{3+}$ ($\text{Ln} = \text{Eu}$, Sm , Dy) phosphor ceramic," *Optical Materials*, vol. 34, no. 1, pp. 138–142, 2011.
- [37] Y. M. Yang, Z. Y. Ren, Y. C. Tao, Y. M. Cui, and H. Yang, " Eu^{3+} emission in $\text{SrAl}_2\text{B}_2\text{O}_7$ based phosphors," *Current Applied Physics*, vol. 9, pp. 618–621, 2009.
- [38] D. Tu, Y. J. Liang, R. Liu, Z. Cheng, F. Yang, and W. L. Yang, "Photoluminescent properties of $\text{LiSr}_x\text{Ba}_{1-x}\text{PO}_4\text{:RE}^{3+}$ ($\text{RE} = \text{Sm}^{3+}$, Eu^{3+}) f–f transition phosphors," *Journal of Alloys and Compounds*, vol. 509, no. 18, pp. 5596–5599, 2011.
- [39] J. H. Hao, J. Gao, and M. Cocivera, "Tuning of the blue emission from europium-doped alkaline earth chloroborate thin films activated in air," *Applied Physics Letters*, vol. 82, no. 17, pp. 2778–2780, 2003.
- [40] A. E. Henkes and R. E. Schaak, "Synthesis of nanocrystalline REBO_3 ($\text{RE}=\text{Y}$, Nd , Sm , Eu , Gd , Ho) and $\text{YBO}_3\text{:Eu}$ using a borohydride-based solution precursor route," *Journal of Solid State Chemistry*, vol. 181, no. 12, pp. 3264–3268, 2008.
- [41] G. F. Ju, Y. H. Hu, H. Y. Wu et al., "A red-emitting heavy doped phosphor $\text{Li}_6\text{Y}(\text{BO}_3)_3\text{:Eu}^{3+}$ for white light-emitting diodes," *Optical Materials*, vol. 33, pp. 1297–1301, 2011.
- [42] J. Yang, C. M. Zhang, C. X. Li, Y. G. Yu, and J. Lin, "Energy transfer and tunable luminescence properties of Eu^{3+} in TbBO_3 microspheres via a facile hydrothermal process," *Inorganic Chemistry*, vol. 47, no. 16, pp. 7262–7270, 2008.
- [43] Y. C. Wu, J. G. Liu, P. Z. Fu et al., "A new lanthanum and calcium borate $\text{La}_2\text{CaB}_{10}\text{O}_{19}$," *Chemistry of Materials*, vol. 13, no. 3, pp. 753–755, 2001.
- [44] H. Lin, D. Hou, L. Li, Y. Tao, and H. Liang, "Luminescence and site occupancies of Eu^{3+} in $\text{La}_2\text{CaB}_{10}\text{O}_{19}$," *Dalton Transactions*, vol. 42, no. 36, pp. 12891–12897, 2013.
- [45] Y. Chen, J. Wang, C. M. Liu, X. J. Kuang, and Q. Su, "A host sensitized reddish-orange $\text{Gd}_2\text{MoO}_6\text{:Sm}^{3+}$ phosphor for light emitting diodes," *Applied Physics Letters*, vol. 98, Article ID 081917, 2011.
- [46] V. Kumar, A. K. Bedyal, S. S. Pitale, O. M. Ntwaeaborwa, and H. C. Swart, "Synthesis, spectral and surface investigation of $\text{NaSrBO}_3\text{:Sm}^{3+}$ phosphor for full color down conversion in LEDs," *Journal of Alloys and Compounds*, vol. 554, pp. 214–220, 2013.
- [47] Y. Zhou and B. Yan, " $\text{RE}_2(\text{MO}_4)_3\text{:Ln}^{3+}$ ($\text{RE} = \text{Y}$, La , Gd , Lu ; $\text{M} = \text{W}$, Mo ; $\text{Ln} = \text{Eu}$, Sm , Dy) microcrystals: controlled synthesis, microstructure and tunable luminescence," *CrystEngComm*, vol. 15, no. 28, pp. 5694–5702, 2013.
- [48] S. A. Yan, J. W. Wang, Y. S. Chang, W. S. Hwang, and Y. H. Chang, "Synthesis and luminescence properties of Ln^{3+} ($\text{Ln}^{3+} = \text{Er}^{3+}$, Sm^{3+})-doped barium lanthanum tungstate BaLa_2WO_7 phosphors," *Optical Materials*, vol. 34, no. 1, pp. 147–151, 2011.
- [49] Z. G. Xia and D. M. Chen, "Synthesis and luminescence properties of $\text{BaMoO}_4\text{:Sm}^{3+}$ phosphors," *Journal of the American Ceramic Society*, vol. 93, no. 5, pp. 1397–1401, 2010.
- [50] F. He, P. Yang, D. Wang et al., "Hydrothermal synthesis, dimension evolution and luminescence properties of tetragonal $\text{LaVO}_4\text{:Ln}$ ($\text{Ln} = \text{Eu}^{3+}$, Dy^{3+} , Sm^{3+}) nanocrystals," *Dalton Transactions*, vol. 40, no. 41, pp. 11023–11030, 2011.
- [51] G. S. R. Raju, J. Y. Park, H. C. Jung et al., "Excitation induced efficient luminescent properties of nanocrystalline $\text{Tb}^{3+}/\text{Sm}^{3+}\text{:Ca}_2\text{Gd}_8\text{Si}_6\text{O}_{26}$ phosphors," *Journal of Materials Chemistry*, vol. 21, no. 17, pp. 6136–6139, 2011.
- [52] X. Lin, X. S. Qiao, and X. P. Fan, "Synthesis and luminescence properties of a novel red $\text{SrMoO}_4\text{:Sm}^{3+}, \text{R}^{3+}$ phosphor," *Solid State Sciences*, vol. 13, no. 3, pp. 579–583, 2011.
- [53] Z. Yang, Z. Zhao, M. Que, and Y. Wang, "Photoluminescence and thermal stability of $\beta\text{-SiAlON:Re}$ ($\text{Re} = \text{Sm}$, Dy) phosphors," *Optical Materials*, vol. 35, no. 7, pp. 1348–1351, 2013.
- [54] M. Puchalska and E. Zych, "The effect of charge compensation by means of Na^+ ions on the luminescence behavior of Sm^{3+} -doped CaAl_4O_7 phosphor," *Journal of Luminescence*, vol. 132, no. 3, pp. 826–831, 2012.
- [55] G. Lakshminarayana, R. Yang, J. R. Qiu, M. G. Brik, G. A. Kumar, and I. V. Kityk, "White light emission from $\text{Sm}^{3+}/\text{Tb}^{3+}$

- codoped oxyfluoride aluminosilicate glasses under UV light excitation,” *Journal of Physics D: Applied Physics*, vol. 42, no. 1, Article ID 015414, 2009.
- [56] P. L. Li, Z. J. Wang, Z. P. Yang, Q. L. Guo, and X. Li, “Emission features of $\text{LiBaBO}_3\text{:Sm}^{3+}$ red phosphor for white LED,” *Materials Letters*, vol. 63, no. 9-10, pp. 751-753, 2009.
- [57] M. N. Huang, Y. Y. Ma, X. Y. Huang, S. Ye, and Q. Y. Zhang, “The luminescence properties of Bi^{3+} sensitized $\text{Gd}_2\text{MoO}_6\text{:RE}^{3+}$ ($\text{RE} = \text{Eu}$ or Sm) phosphors for solar spectral conversion,” *Spectrochimica Acta A*, vol. 115, pp. 767-771, 2013.
- [58] S. Tang, M. Huang, J. Wang, F. Yu, G. Shang, and J. Wu, “Hydrothermal synthesis and luminescence properties of $\text{GdVO}_4\text{:Ln}^{3+}$ ($\text{Ln} = \text{Eu}, \text{Sm}, \text{Dy}$) phosphors,” *Journal of Alloys and Compounds*, vol. 513, pp. 474-480, 2012.
- [59] N. Zhang, C. Guo, and H. Jing, “Photoluminescence and cathode-luminescence of Eu^{3+} -doped NaLnTiO_4 ($\text{Ln} = \text{Gd}$ and Y) phosphors,” *RSC Advances*, vol. 3, no. 20, pp. 7495-7502, 2013.
- [60] L. Q. An, J. Zhang, M. Liu, S. Chen, and S. W. Wang, “Preparation and photoluminescence of Sm^{3+} and Eu^{3+} doped Lu_2O_3 phosphor,” *Optical Materials*, vol. 30, no. 6, pp. 957-960, 2008.
- [61] S. C. Prashantha, B. N. Lakshminarasappa, and B. M. Nagabhushana, “Photoluminescence and thermoluminescence studies of $\text{Mg}_2\text{SiO}_4\text{:Eu}^{3+}$ nano phosphor,” *Journal of Alloys and Compounds*, vol. 509, no. 42, pp. 10185-10189, 2011.
- [62] L. Chen, G. T. Yang, J. Q. Liu, X. Shu, G. B. Zhang, and Y. Jiang, “Photoluminescence properties of and in host under vacuum ultraviolet/ultraviolet excitation,” *Journal of Applied Physics*, vol. 105, no. 1, Article ID 013513, 2009.
- [63] A. Dhahri, K. Horchani-Naifer, A. Benedetti, F. Enrichi, and M. Ferid, “Combustion synthesis and photoluminescence of Eu^{3+} doped LaAlO_3 nanophosphors,” *Optical Materials*, vol. 34, no. 11, pp. 1742-1746, 2012.
- [64] S. Mishra, R. Rajeswari, N. Vijayan et al., “Probing the structure, morphology and multifold blue absorption of a new red-emitting nanophosphor for LEDs,” *Journal of Materials Chemistry C*, vol. 1, no. 37, pp. 5849-5855, 2013.
- [65] W. A. Pisarski, J. Pisarska, G. Dominiak-Dzik, and W. Rybaromanski, “Transition metal (Cr^{3+}) and rare earth (Eu^{3+} , Dy^{3+}) ions used as a spectroscopic probe in compositional-dependent lead borate glasses,” *Journal of Alloys and Compounds*, vol. 484, no. 1-2, pp. 45-49, 2009.
- [66] L. A. Bueno, A. S. Gouveia-Neto, E. B. da Costa, Y. Messaddeq, and S. J. L. Ribeiro, “Structural and spectroscopic study of oxyfluoride glasses and glass-ceramics using europium ion as a structural probe,” *Journal of Physics Condensed Matter*, vol. 20, no. 14, Article ID 145201, 2008.
- [67] A. Ellens, F. Zwaschka, F. Kummer, A. Meijerink, M. Raukas, and K. Mishra, “ Sm^{2+} in BAM: fluorescent probe for the number of luminescing sites of Eu^{2+} in BAM,” *Journal of Luminescence*, vol. 93, no. 2, pp. 147-153, 2001.
- [68] J. Huang, J. Loriers, and P. Porcher, “Spectroscopic properties of some Eu^{3+} doped scheelite-related rare earth sesquimolybdates and sesquitungstates,” *Journal of Solid State Chemistry*, vol. 48, no. 3, pp. 333-345, 1983.
- [69] M. Karbowiak, A. Mech, A. Bednarkiewicz, and W. Stręk, “Synthesis and properties of solution-processed $\text{Eu}^{3+}\text{:BaY}_2\text{F}_8$,” *Journal of Luminescence*, vol. 114, no. 1, pp. 1-8, 2005.
- [70] Y. Tian, B. J. Chen, R. N. Hua et al., “Optical transition, electron-phonon coupling and fluorescent quenching of $\text{La}_2(\text{MoO}_4)_3\text{:Eu}^{3+}$ phosphor,” *Journal of Applied Physics*, vol. 109, Article ID 053511, 2011.
- [71] M. Dejneka, E. Snitzer, and R. E. Riman, “Blue, green and red fluorescence and energy transfer of Eu^{3+} in fluoride glasses,” *Journal of Luminescence*, vol. 65, no. 5, pp. 227-245, 1995.
- [72] R. Guo, Y. C. Wu, P. Z. Fu, and F. L. Jing, “Optical transition probabilities of Er^{3+} ions in $\text{La}_2\text{CaB}_{10}\text{O}_{19}$ crystal,” *Chemical Physics Letters*, vol. 416, no. 1-3, pp. 133-136, 2005.