

PHOTOLUMINESCENCE STUDY OF Eu³⁺ DOPED LITHIUM LANTHANUM BORATE PHOSPHOR

Eakgapon Kaewnuam^{a,*}, Sasithorn Saikaew^b, Nuanthip Wantana^{c,d}, Jakrapong Kaewkhao^{c,d}

^a*Physics Program, Faculty of Science and Technology, Muban Chombueng Rajabhat University, Ratchaburi, 70150, Thailand*

^b*Center for Science and Applied Science, Faculty of Science and Technology, Muban Chombueng Rajabhat University, Ratchaburi, 70150, Thailand*

^c*Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom, 73000, Thailand*

^d*Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom, 73000, Thailand*

Received 27 December 2016; Revised 20 March 2017; Accepted 5 April 2017

ABSTRACT

Phosphor compound, lithium lanthanum borate doped with Eu³⁺ (Eu₂O₃ 0.10 – 10.00 mol%) were prepared by a solid state reaction to study the structure and photoluminescence properties. X-ray diffraction indicated phase of the Li₃La₂(BO₃)₃ host structure appearing in all samples. Absorption spectra show that compound absorbs more photons with increasing of Eu₂O₃ concentration. Emission and excitation spectra exhibit the strongest emission at 613 nm wavelength with 394 nm excitation. The optimum concentration of Eu₂O₃ for this compound is 2.50 mol% which possess the highest intensity of emission via photo excitation. Color of emission was determined as the reddish orange by CIE 1931 chromaticity system. Lithium lanthanum borate doped with Eu³⁺ phosphor performs the interesting properties to be developed for using as the reddish orange-emitting material in screen and lamp.

KEYWORDS: *Lithium borate phosphor; Europium; Photoluminescence*

* Corresponding authors; e-mail: Eakgapon_9@hotmail.com

INTRODUCTION

Phosphor materials, luminescence powder, have been used in the important applications such as medical imaging, display, light source, light emitting diode and detector. Especially, lithium rare-earth (Gd, Y, Lu) borate doped with lanthanide ion (Ln³⁺) have been widely studied and developed [1-4] because of their low-temperature synthesis and high anisotropic crystalline structure of host material [5]. The interesting applications of these compound are neutron imaging and neutron detector due to a high thermal-neutron capture cross section of lithium, boron and gadolinium (Gd) [6]. Therefore, lithium gadolinium (Gd) borate compound such as Li₆Gd(BO₃)₃ was early researched but it shows some disadvantages. Gd element releases gamma ray when it captures neutron and this compound is high sensitive with gamma ray background from the neutron source [6]. This problem can be moderated by changing

Gd in compound to be others rare-earth element. Lithium yttrium (Y)/lutetium (Lu) borate then were presented. Lanthanum (La) is one of the rare-earth element group which also have a wide energy band gap close to Gd and Lu [7]. Furthermore, the lower atomic mass of La than Gd and Lu can reduce a compound sensitivity with gamma ray background from neutron source. However, Ln³⁺ doped lithium lanthanum borate has still not been comprehensively studied. In addition to neutron detector, this chemical also need to be more investigated about a potential to use in the other applications such as imaging, display and light source. For Ln³⁺ that have a role as luminescence center in the phosphor material, an europium ion (Eu³⁺) is very attractive. The intra 4f-4f transition of Eu³⁺ can generate the strong emission of visible light with red color and long decay time in the various phosphor [3, 8–10]. Therefore, Eu³⁺ should be doped in lithium lanthanum borate phosphor to study the

luminescence properties and analyze its application potential.

In this work, Eu^{3+} doped lithium lanthanum borate phosphor were synthesized to study the structure, optical and luminescence properties. Influence of Eu^{3+} concentration on the phosphor properties was also investigated to find the optimum condition of phosphor for using in luminescence application.

MATERIALS AND METHODS

Sample preparation

Phosphor samples were prepared by a solid state reaction. The high purity chemicals such as Li_2CO_3 , La_2O_3 , H_3BO_3 and Eu_2O_3 were mixed thoroughly via the appropriate stoichiometric amounts in agate mortar. The Eu_2O_3 concentration was varied between 0.10 – 10.00 mol%. The batches of sample were put in the alumina crucible and then sintered in an electrical furnace with temperature of 600 °C for 6 hr. Finally, phosphors were left to be cool to room temperature in the furnace.

Measurements

All obtained powders were investigated the crystalline structure by using the x-ray diffractometer (XRD-6001, Shimadzu) with $\text{CuK}\alpha$ radiation (wavelength 0.154 nm). Absorption spectra of samples were studied by UV-VIS-NIR spectrophotometer (Shimadzu, UV-3600). Emission and excitation spectra were monitored by using a fluorescence spectrophotometer (Cary Eclipse) with xenon lamp as a light source. Color of photoluminescence was evaluated by using the Commission of International de L'Eclairage (CIE) 1931 chromaticity system.

RESULTS AND DISCUSSION

X-ray diffraction

Results of x-ray diffraction (XRD) are shown in Fig. 1. The $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ with monoclinic structure (JCPD 00-054-1117) was formed dominantly in all samples mixing with few orthorhombic structure of LaBO_3 (JCPD 00-012-0762). Samples doped with Eu_2O_3 in low concentration such as 0.10 and 2.50 mol% perform a good formation of $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ without Eu-composite structure. Adding Eu_2O_3 higher than 2.50 mol% results to the perturbation in crystal structure which can be indicated from fluctuation of XRD pattern. Most of pattern are degraded with increasing of Eu_2O_3 content from 5.00 to 10.00 mol% but some regions marking

with α and β symbol are promoted. Rising of α represents the Eu_2O_3 cubic structure (JCPD 00-034-0392) extending in compound. While, β region is possibly the evidence of some other Eu or Eu-oxide configuration in the structure but cannot be definitely determined with database.

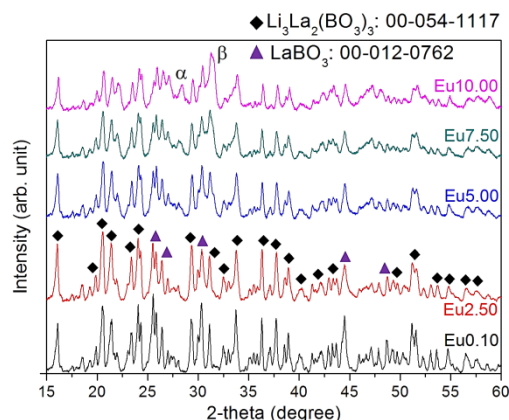


Fig. 1 X-ray diffraction result of Eu^{3+} lithium lanthanum borate phosphor.

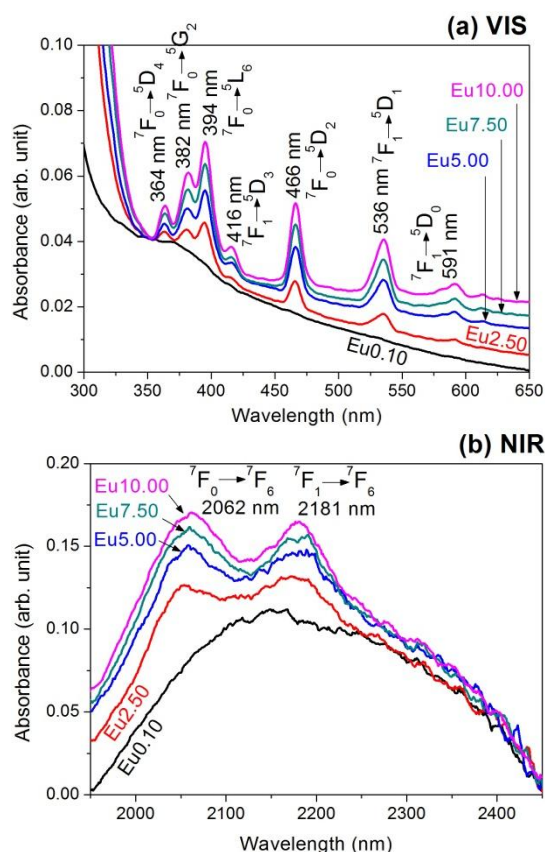


Fig. 2 Absorption spectra of $\text{Li}_3\text{La}_2(\text{BO}_3)_3:\text{Eu}^{3+}$ phosphor in VIS (a) and NIR (b) region.

Absorption spectra

The Absorption spectra of all $\text{Li}_3\text{La}_2(\text{BO}_3)_3:\text{Eu}^{3+}$ phosphors are shown in Fig. 2 (a)

and 2 (b). Powders absorb photon in the visible light region (VIS) with 364, 382, 394, 416, 466, 536 and 591 nm and in the near infrared (NIR) region with 2062 and 2181 nm. These absorption bands are the result of Eu^{3+} energy transition from ${}^7\text{F}_0$ and ${}^7\text{F}_1$ ground state to upper state such as ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_1 \rightarrow {}^5\text{D}_3$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$, ${}^7\text{F}_1 \rightarrow {}^5\text{D}_1$, ${}^7\text{F}_1 \rightarrow {}^5\text{D}_0$, ${}^7\text{F}_0 \rightarrow {}^5\text{F}_6$ and ${}^7\text{F}_1 \rightarrow {}^7\text{F}_6$, respectively [11,12]. All band sharpness increases with increasing of Eu_2O_3 concentration that indicates the more photo-absorption ability with higher Eu^{3+} amount in the powder. Photon with wavelength 394 nm (${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$) and 2062 nm (${}^7\text{F}_0 \rightarrow {}^5\text{F}_6$) were maximum absorbed in VIS and NIR region, respectively. The ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition is hypersensitive with a ligand positioning-arrangement around Eu^{3+} . Asymmetric environment of Eu^{3+} make this transition/absorption band to be strong [11].

Emission and excitation spectra

The most absorbed photon in VIS region, light with 394 nm wavelength, was used to excite all $\text{Li}_3\text{La}_2(\text{BO}_3)_3:\text{Eu}^{3+}$ phosphors to investigate the emission spectra as show in Fig. 3 (a). Four emission bands centered at 590, 613, 650 and 700 nm wavelength relates to the Eu^{3+} energy transition, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$, respectively [11,12]. The strongest emission belongs to the light with 613 nm. This emission intensity increases with increasing of Eu^{3+} concentration from 0.10 to 2.50 mol% after that it decreases by a concentration quenching effect, the emitting photon re-absorption by near neighbor ion. The optimum concentration of Eu_2O_3 for $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ phosphor for the light excitation is therefore 2.50 mol%. From very sharp band of emission spectra at 590 and 613 nm, the light signal emitted from this phosphor is so strong and has good resolution. $\text{Li}_3\text{La}_2(\text{BO}_3)_3:\text{Eu}^{3+}$ phosphor, therefore, perform an interesting potential for detecting and imaging application. Comparison between the magnetic dipole (MD) ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition and the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ induced electric dipole (ED) transition indicates that ED is stronger than MD for all samples. ED is hypersensitive transition which shows the high strength for asymmetric environment of Eu^{3+} , while MD is not. Therefore, it can be said that Eu^{3+} was surround by the asymmetric particle arrangement in monoclinic structure of the main $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ host. To confirm and find another excitation wavelengths for the strongest emission of 613 nm, the excitation spectra were then monitored as show in Fig 3 (b). It is realized that 613 nm emission of this phosphor can be occurred by the photo excitation with 362, 382,

394 (best excitation), 415, 465 and 535 nm corresponding to Eu^{3+} transition, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_1 \rightarrow {}^5\text{D}_3$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ and ${}^7\text{F}_1 \rightarrow {}^5\text{D}_1$, respectively [11,12]. Eu^{3+} energy transition process of the emission and excitation spectra are discussed in Fig. 4. Start from Eu^{3+} were excited and changed the energy level from ground state, ${}^7\text{F}_0$ or ${}^7\text{F}_1$, up to various initial excited states. Non-radiative relaxation (NR) process then decay the Eu^{3+} energy states down to the same ${}^5\text{D}_0$ stable excited state for all excitation. This NR decay didn't emit photon but it releases energy as the thermal phonon. After that, emission of Eu^{3+} occurred by energy transition from the ${}^5\text{D}_0$ stable excited state.

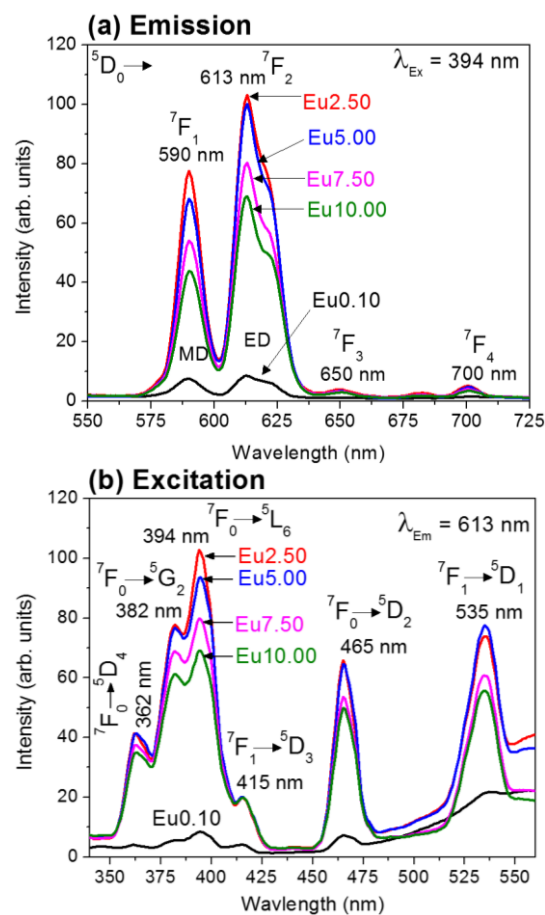


Fig. 3 Emission (a) and excitation (b) spectra of $\text{Li}_3\text{La}_2(\text{BO}_3)_3:\text{Eu}^{3+}$ phosphor.

CIE 1931 chromaticity

Emission spectrum with 394 nm excitation wavelength of 2.50 mol% doped phosphor was used to analyze the color of emission by CIE 1931 chromaticity system as show in Fig.5. Calculated color coordinate (x, y) is (0.63, 0.37) which locates at a blue star symbol

- [5] B. Ardiçoğlu, G. Özbayoğlu, Z. Özdemir, A. Yılmaz, Production and identification of rare-earth doped lithium triborate, *J. Alloys Compd.* 418 (2006) 77–79.
- [6] C.W.E. van Eijk, Inorganic scintillators for thermal neutron detection, *Radiat. Meas.* 38 (2004) 337 – 342.
- [7] W.C. Martin, R. Zalubas, L. Hagan, Atomic energy Levels-The Rare-Earth Element, National Bureau of Standards, Washington, D.C., USA, 1978, pp. 27–45.
- [8] Y.Ch. Li, Y.H. Chang, Y.F. Lin, Y.S. Chang, Y.J. Lin, Synthesis and luminescent properties of Ln³⁺ (Eu³⁺, Sm³⁺, Dy³⁺)-doped lanthanum aluminum germanate LaAlGe₂O₇ phosphors, *J. Alloy. Compd.* 439 (2007) 367–375.
- [9] Z. Liang, F. Mo, X. Zhang, L. Zhou, Luminescence of the LiMgBO₃:Eu³⁺, Bi³⁺ phosphor, *J. Lumin.* 151 (2014) 47–51.
- [10] Y. Kang, Ch. Liu, X. Kuang, J. Mi, H. Liang, Q. Su, Synthesis and luminescence properties of the lithium-containing lanthanum-oxycarbonate-like borates, *J. Solid State Chem.* 194 (2012) 225–232.
- [11] N. Vijaya and C.K. Jayasankar, Structural and spectroscopic properties of Eu³⁺-doped zinc fluorophosphate glasses, *J. Mol. Struct.* 1036 (2012) 42–50.
- [12] C.R. Kesavulu, K. Kiran Kumar, N. Vijaya, Ki-Soo Lim, C.K. Jayasankar, Thermal vibrational and optical properties of Eu³⁺-doped lead fluorophosphate glasses for red laser applications, *Mater. Chem. Phys.* 141 (2013) 903–911.
- [13] S. Gage, D. Evans, M.W. Hodapp, H. Sorensen, *Optoelectronics Applications Manual*, McGraw Hill, New York, 1979.