



## The luminescence characteristics of Eu<sup>3+</sup>-doped lithium-gadolinium borate glasses

Kitipun Boonin<sup>1,2,\*</sup>, Warawut Sa-ardsin<sup>1</sup>, Jakrapong Kaewkhao<sup>1,2</sup>

<sup>1</sup>Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom, 73000, Thailand

<sup>2</sup>Center of Excellence in Glass Technology and Materials Science, Nakhon Pathom Rajabhat University, Nakhon Pathom, 73000, Thailand

\* Corresponding Author: [kboonin@hotmail.com](mailto:kboonin@hotmail.com)

Received: 24 June 2015; Revised: 1 September 2015; Accepted: 18 December 2015; Available online: 20 April 2016

Paper selected from Sakon Nakhon Rajabhat University - International Conference 2015 (SNRU-IC 2015)

DOI: 10.14456/snrujst.2016.16

### Abstract

Eu-doped lithium-gadolinium borate glasses with the formula  $[60\text{Li}_2\text{O}:10\text{Gd}_2\text{O}_3:(30-x)\text{B}_2\text{O}_3:x\text{Eu}_2\text{O}_3]$  (LGBO:Eu<sup>3+</sup>) were fabricated using melt quenching technique. The 5 glass samples with different concentrations of Eu<sub>2</sub>O<sub>3</sub> were prepared under atmospheric pressure. The samples were investigated on their properties: density, molar volume, absorption spectra and photoluminescence. The trend of density swings at the first 2 concentrations and then tends to decrease with the increment of the concentrations. The molar volume trend is in the opposite way to that of the density. It is obvious that there are 2 peaks for near infrared wavelengths and other 2 peaks for the visible range which show the Eu<sup>3+</sup> in the glass structure. The higher concentration of the dopant, the higher peaks of intensity. The excitation spectra show 6 peaks representing the energy transitions from the ground state <sup>7</sup>F<sub>0</sub> to different excited states. The emission spectra were measured with 395 nm light from Xenon compact arc lamps. The spectra trends to increase with increasing concentration of the dopant.

**Keywords:** Glass, Eu doped, Luminescence glass

©2016 Sakon Nakhon Rajabhat University reserved

### 1. Introduction

White light emitting diodes (LEDs) are the optical devices which are extensively used in many applications. There are many techniques used in the production of this type of diodes. The interesting option for this application is rare-earth-doped glasses. Some properties of the glass systems such as absorption and luminescence properties can be applied to this application. There are some evidences that borate glasses are good hosts for rare-earth ions [1].

Several researches studied on  $\text{Eu}^{3+}$  ion utilized the simplicity of its energy level structure with non-degenerate ground ( ${}^7\text{F}_0$ ) and excited ( ${}^5\text{D}_0$ ) states [2-7]. White light can be produced using the conventional technique by exciting multiple phosphors to generate white combined light. Unfortunately, this method depends on different sources, therefore it is not stable. Some materials can be excited by ultraviolet light and consequently the white light can be emitted directly, therefore this kind of materials can be used in the application. Eu-doped glasses are materials of choice for this application.

The present work studies on the densities, molar volume, absorption, photoluminescence of the Eu-doped lithium-gadolinium borate glasses with the formula  $[\text{60Li}_2\text{O}:10\text{Gd}_2\text{O}_3:(30-x)\text{B}_2\text{O}_3:x\text{Eu}_2\text{O}_3]$  (LGBO:Eu $^{3+}$ ).

## 2. Materials and Methods

The  $\text{Eu}^{3+}$ : LGBO glasses of chemical composition range of (in mol %)  $60\text{Li}_2\text{O}: 10\text{Gd}_2\text{O}_3: (30-x)\text{B}_2\text{O}_3: x\text{Eu}_2\text{O}_3$  (where  $x = 0.05, 0.1, 0.5, 1.0$  and  $1.5$  mol %) were prepared by conventional melt quenching technique. All glass samples of 15 g batch compositions of homogeneous powders were melted at  $1,000\text{ }^\circ\text{C}$  in alumina crucibles for about 3 hours in an electrical furnace. They were quenched at room temperature under an air atmosphere on a couple stainless steel and annealed at  $300\text{ }^\circ\text{C}$  for 3 hours to remove thermal strains [8]. The polished glass samples were cut into  $1.0 \times 1.5 \times 0.3\text{ cm}^3$  shape for optical measurements. Densities ( $\rho$ ) of glasses were measured by using the Archimedes method using a digital balance (4-digit sensitive microbalance A&D, HR-200) and then molar volumes were calculated. UV-VIS-NIR spectrophotometer (UV-3600 Shimadzu) was used to measure the absorption spectra ranged from 400 to 2500 nm. Emission and excitation spectra were measured using Cary Eclipse Fluorescence Spectrophotometer with 395 nm excited radiation from a Xenon compact arc lamps.

## 3. Results and Discussion

### *Density and molar volume*

As shown in Fig. 1, the trend of density swings at the first 2 concentrations because of preparation of chemicals need to calculate mole%, first. After that convert to wt% to get weight of chemical composition. Weight results of  $\text{Gd}_2\text{O}_3$  will be reduced when  $\text{Eu}_2\text{O}_3$  content increased that affects the uncertainty of density trends and then trends to decrease with the increasing of  $\text{Eu}_2\text{O}_3$  concentrations. The molar volume trend is in the opposite way to that of the density. The increases of the molar volume result the increases of the inter-atomic spacing of the glass network. It can be predicted that the  $\text{Eu}_2\text{O}_3$  acts as network modifier and produces more non-bridging oxygen (NBOs) in glass matrices [9-10].

### *Absorption spectrum and energy levels*

The absorption spectra of the LGBO glasses doped with  $\text{Eu}^{3+}$  in VIS regions (400-500 nm) and NIR regions (1700-2500 nm) are shown in Fig. 2 and Fig. 3 respectively. The absorption bands of  $\text{Eu}^{3+}$  represent the transitions from the ground state  ${}^7\text{F}_0$  to various excited states. The absorption spectra shown four bands in all regions can be separated as two regions. Fig. 2 shows two bands due to  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$  (392 nm) and  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  (464 nm) transitions in

the VIS regions. NIR regions shows two intense bands due to  ${}^7F_0 \rightarrow {}^7F_6$  (2095 nm) and  ${}^7F_1 \rightarrow {}^7F_6$  (2205 nm) transitions in the NIR regions. It is well known that, except for  $\text{Eu}^{3+}$  ion, all the other trivalent RE<sup>3+</sup> ions possess single populated ground state.

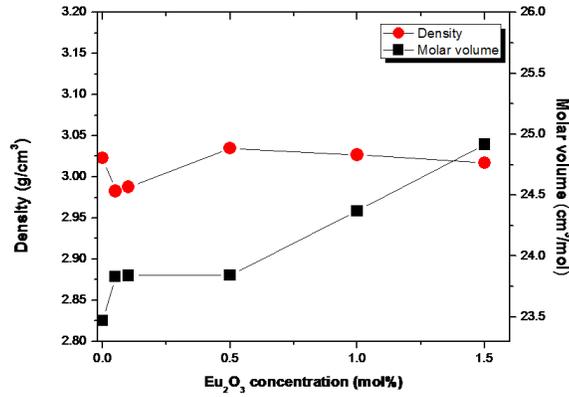


Fig. 1 Densities and molar volumes for different concentration of  $\text{Eu}_2\text{O}_3$

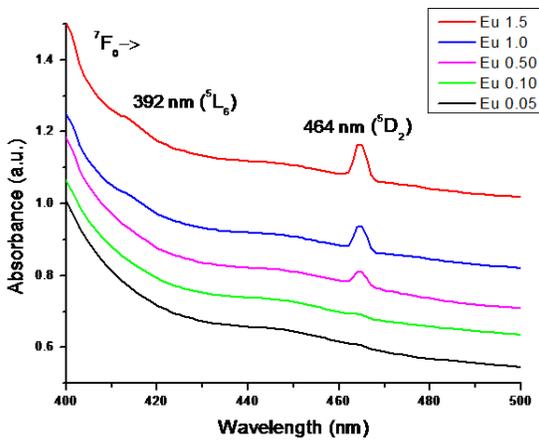


Fig. 2 The absorbance spectra for LGBO:  $\text{Eu}^{3+}$  glasses in VIS range

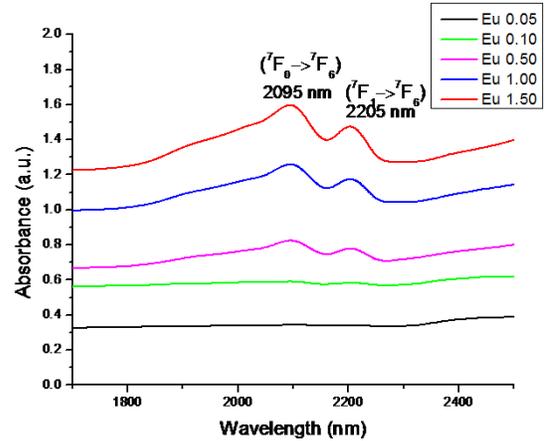


Fig.3 The absorbance spectra for LGBO:  $\text{Eu}^{3+}$  glasses in NIR range

*Excitation and emission spectra*

In Fig. 4, six obvious peaks in excitation spectra represent the transition from the ground state  ${}^7F_0$  to the excited states:  ${}^5D_4$  (363nm),  ${}^5L_7$  (383nm),  ${}^5L_6$  (395nm),  ${}^5D_3$  (414nm),  ${}^5D_1$  (465nm) and  ${}^7F_1$  to  ${}^5D_1$  (533nm) of  $\text{Eu}^{3+}$  but the  ${}^7F_0$  to  ${}^5D_1$  (485nm) was not observed. The excitation spectrum exhibited the transitions originating not only from the ground state ( ${}^7F_0$ ), but also from the first excited state ( ${}^7F_1$ ) to  ${}^5D_1$ . As shown in Fig. 4, the  ${}^7F_0$  to  ${}^5L_6$  transition is most intense compared to other transitions.

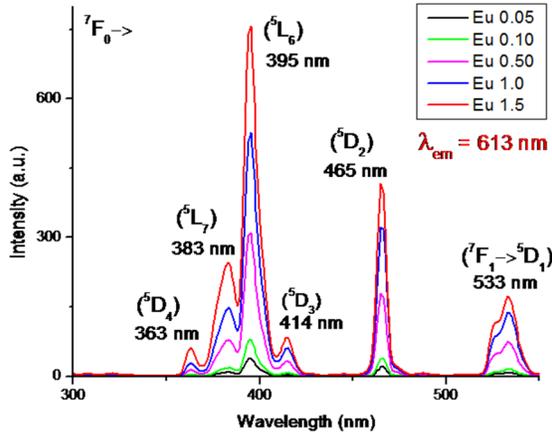


Fig.4 The excitation spectra for LGBO glasses doped with different mol% of  $\text{Eu}^{3+}$

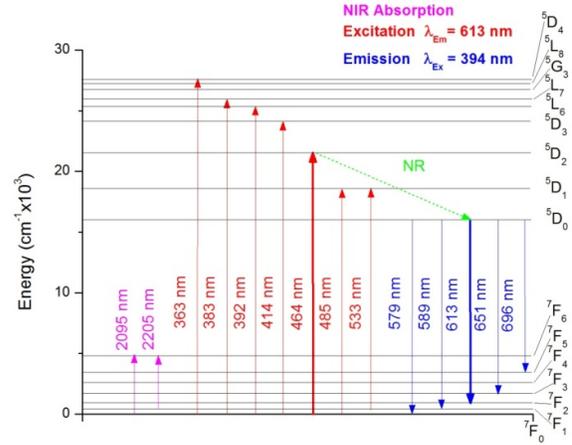


Fig. 5 The Energy level diagram for the transitions of  $\text{Eu}^{3+}$ -doped glasses

When  $\text{Eu}^{3+}$  ions are excited to any energy level above  ${}^5\text{D}_0$  level, the non-radiative decay will transit down to  ${}^5\text{D}_0$  level as shown in the energy level diagram in Fig. 5. The emission spectra were measured with 395 nm light from Xenon compact arc lamps. The Fig. 6 shows emission spectra of  $\text{Eu}^{3+}$ : LGBO glasses. All the spectra occurred four emission bands corresponding to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  (591 nm; orange),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (614 nm; red),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$  (652 nm; deep-red) and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  (701 nm; deep-red) transitions [11-12]. All spectra were increased with increasing concentration of the dopant. The  ${}^5\text{D}_0$  to  ${}^7\text{F}_2$  transition shows the strongest peak compared to other transitions.

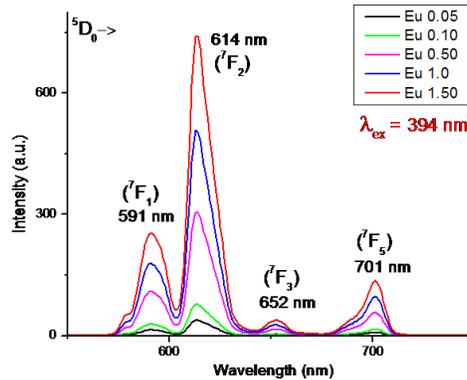


Fig.6 The emission spectra for LGBO glasses doped with different mol% of  $\text{Eu}^{3+}$

#### 4. Conclusion

$\text{Eu}$ -doped lithium-gadolinium borate glasses were prepared. The samples were investigated on their physical and optical properties. The trend of density swings at the first 2 concentrations and then trends to decrease with increasing of the concentrations. The molar volume trend is in the opposite way to that of the density. It is obvious that there are 2 peaks for near infrared wavelengths and other 2 peaks for the visible range which show the  $\text{Eu}^{3+}$  in the glass structure. The excitation spectra show 6 peaks representing the energy transitions from the

ground state  ${}^7F_0$  to different excited states and first excited state ( ${}^7F_1$ ) to  ${}^5D_1$ . The emission spectra trend to increase with increasing concentration of the dopant.

## 5. References

- [1] V. Venkatramu, P. Babu, C.K. Jayasankar, Fluorescence properties of  $\text{Eu}^{3+}$  ions doped borate and fluoroborate glasses containing lithium, zinc and lead. *Acta A.* 63 (2006) 276-281.
- [2] J.A. Capobianco, P. Proulx, N. Raspa, Optical spectroscopy and crystal field analysis of  $\text{Eu}^{3+}$  in calcium tartrate tetrahydrate, *Chem. Phys. Lett.* 189(2) (1989) 151-157.
- [3] S. Todoroki, S. Tanabe, K. Hirao, N. Soga, Phonon sideband spectra and local structure around  $\text{Eu}^{3+}$  ions in sodium silicate glasses, *J. Non-Cryst Solids.* 136(3) (1991) 213-218.
- [4] V. Lavin, V.D. Rodriguez, I.R. Martin, U.R. Rodriguez-Mendoza, Site selective study in  $\text{Eu}^{3+}$ -doped fluorozirconate glasses and glass-ceramics, *J. Lumin.* 72-74 (1997) 437-438.
- [5] R. Balda, J. Fernandez, J.L. Adam, M.A. Arriandiaga, Time-resolved fluorescence-line narrowing and energy transfer studies in a  $\text{Eu}^{3+}$ -doped fluorophosphate glass, *Phys. Rev. B.* 54 (1996) 12076-12086.
- [6] R. Balakrishnaiah, R. Vijaya, P. Babu, C.K. Jayasankar, M.L.P. Reddy, Characterization of  $\text{Eu}^{3+}$ -doped fluorophosphate glasses for red emission, *J. Non-Cryst Solids.* 353(13-15) (2007) 1397-1401.
- [7] P. Babu, C.K. Jayasankar, Optical spectroscopy of  $\text{Eu}^{3+}$  ions in lithium borate and lithium fluoroborate glasses, *Physica B.* 279(4) (2000) 262-281.
- [8] A. Thulasiramudu, S. Budduhudu, Optical characterization of  $\text{Cu}^{2+}$  ion-doped zinc lead borate glasses, *J. Quant. Spectrosc. Ra.* 97 (2006) 181–194.
- [9] A.K. Varshneya, *Fundamental of Inorganic Glasses*, Academic Press, San Diego, 1994.
- [10] Y. B. Saddeek, L.A.E. Latif, Effect of  $\text{TeO}_2$  on the elastic moduli of sodium borate glasses, *Physica B.* 348 (2004) 475-484.
- [11] J. Kaewkhao, K. Boonin, P. Yasaka, H.J. Kim, Optical and luminescence characteristics of Eu doped zinc bismuth borate (ZBB) glasses, *Mater. Res. Bull.* 71 (2015) 37-41.
- [12] J.L. Adam, V. Poncon, J. Lucas, G. Boulon, Site selection spectroscopy in  $\text{Eu}^{3+}$ -doped fluoro zirconate glass. *J. Non-Cryst Solids.* 91(2) (1987) 191-202.