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Synthesis-temperature effect on the luminescence under light and UV excitation of Eu^{3+} doped lithium lanthanum borate phosphor

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Abstract

Eu^{3+} doped lithium lanthanum borate phosphors were prepared by the solid-state reaction with different temperature in the range of 400 – 700 °C. Influence of preparing temperature on the phosphor structure and luminescence property were investigated. X-ray diffraction indicates the obvious structure of monoclinic $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ and orthorhombic LaBO_3 formed in powder. $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ was constructed better with increasing of the synthesis-temperature between 500 – 700 °C. For absorption spectra, phosphor can absorb more photons in visible light and near-infrared region with the synthesis temperature rising. Visible light with 394 nm and ultraviolet with 275 nm were used to monitor the emission spectra and the strongest emission at 613 nm wavelength was founded. Powders prepared at 600 and 700 °C performed the maximum intensity of emission when they were excited with mentioned ultraviolet and visible light, respectively. This difference corresponds to the variation of $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ and LaBO_3 structure via thermal synthesis. Phosphor in this work is suitable for using in the ultraviolet-light converter, display, light source and performs an interesting potential for neutron-imaging application.

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1. Introduction

The luminescence powder called “phosphor” has been used as the light generator in various photonic instrument such as fluorescence light bulb, light emitting diode (LED), display, imaging screen and detector. X-ray imaging is a popular technique used to look inside the human body for medical and some objects in industry. However, if that object consists of heavy metal, the X-ray penetration is reduced because of interaction with free electron and imaging will be unclear. Neutron imaging has been used to solve this problem and give a good detail inside the object with heavy metal. The screen or detector in neutron imaging system should be coated or contained with the phosphor that can capture neutron and transfer the neutron energy to be light signal. Lithium (Li), gadolinium (Gd) and boron (B) possess high capture cross-section for the thermal neutron [1]. But Gd element can release the gamma ray when it captures neutron and it is also high sensitive with gamma ray background from the neutron source [1]. Since lanthanum is one of the rare-earth element group like Gd and have same wide energy band gap [2], La was used instead of Gd combining with Li and B to synthesize the phosphor in our previous work [3]. Because of its characteristic luminescence with red color and long decay time by 4f-4f intra transition [4-7], Eu^{3+} was used to be doped as the luminescence activator of phosphor in that work and it performed a very sharp emission spectrum. Effect of Eu^{3+} concentration on its luminescence properties in the lithium lanthanum borate compound has been already determined but influence of the synthesis-temperature of phosphor on the light emitting still need to be clarified. The obviousness of this relation is advantage for choosing the best preparing condition of such phosphor to use in various photonic applications.

In this work, Eu^{3+} doped lithium lanthanum borate phosphors were prepared with different temperature to study and explain about the synthesis-temperature effect on the Eu^{3+} luminescence properties.

2. Experiment

2.1. Preparation

Phosphor powders were prepared by a solid-state reaction with different temperature. The high purity grade of Li_2CO_3 , La_2O_3 , H_3BO_3 and Eu_2O_3 chemicals were mixed thoroughly with stoichiometric amounts in an agate mortar. The mixing chemicals were taken into an alumina crucible and then sintered in an electrical furnace with temperature range of 400 - 700 °C for 6 hr. After that, phosphors were left to be cool to room temperature in the furnace.

2.2. Measurement

All obtained phosphors were studied the crystalline structure of inside component by the X-ray diffractometer (XRD-6001, Shimadzu) using $\text{CuK}\alpha$ radiation (wavelength 0.154 nm). Absorption spectra of samples were monitored by UV-VIS-NIR spectrophotometer (Shimadzu, UV-3600). Excitation and emission spectra were observed via a fluorescence spectrophotometer (Cary Eclipse) with xenon lamp as a light source.

3. Results and discussion

3.1. XRD

The XRD results of phosphors are shown in Fig.1. Phosphor prepared with 400 °C consists of orthorhombic $\text{Li}_4\text{B}_2\text{O}_5$ with JCPDs 00-018-0719 (yellow diamond), cubic Eu_2O_3 with JCPDs 00-034-0392 (green circle) and cubic LaB_6 with JCPDs 00-059-0332 (pink down-triangle). The dominant structure belongs to orthorhombic of $\text{Li}_4\text{B}_2\text{O}_5$ composition. $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ compound with monoclinic structure via JCPDs 00-054-1117 (red square) starts to formed in phosphor with 500 °C synthesis-temperature. However, orthorhombic LaBO_3 with JCPDs 00-012-0762 (blue up-triangle) also forms and it is the dominant structure at this temperature. Thermal energy at 600 °C make the atomic movement in phosphor structure which results to the structure enhancement and degradation of $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ and LaBO_3 , respectively. The formation level of both compound structure is became to be nearby, there is no

dominant structure at this condition. Finally, in the preparation with 700 °C, $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ structure is formed better than LaBO_3 structure. The monoclinic $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ becomes to be the dominant structure in phosphor. It can be said that $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ structure is improved with increasing of synthesis-temperature between 500 – 700 °C, while LaBO_3 structure is degraded. Since monoclinic possess lower point of symmetry in the structure than orthorhombic [8], $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ addition with increasing of temperature then rises the level of structured asymmetric in phosphor. Furthermore, Eu_2O_3 structure has been found less in phosphor with all synthesis-temperature.

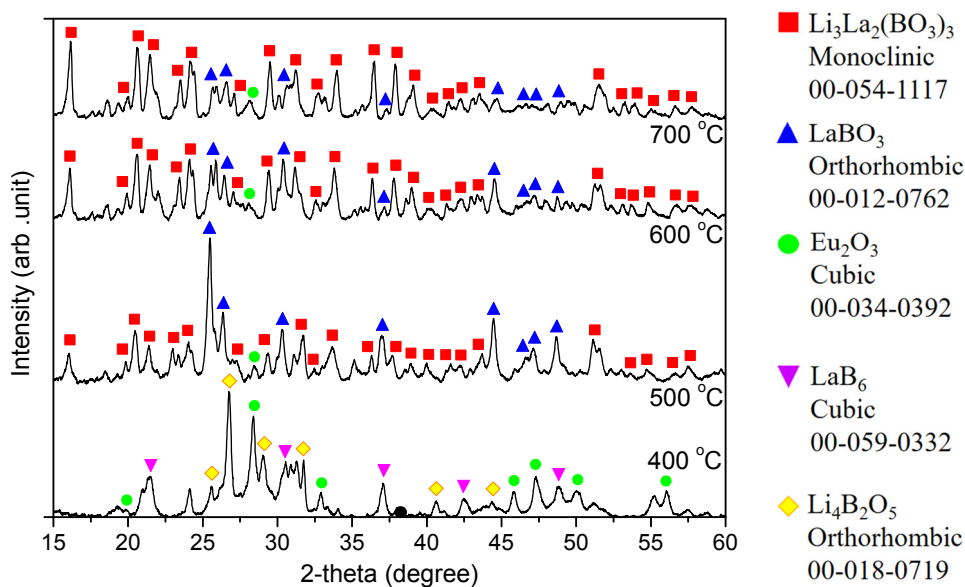


Fig. 1. The XRD result of Eu^{3+} doped lithium lanthanum borate phosphor synthesized with different temperature (red square: $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ monoclinic 00-054-1117, blue up triangle: LaBO_3 orthorhombic 00-012-0762, green circle: Eu_2O_3 cubic 00-034-0392, pink down triangle: LaB_6 cubic 00-059-0332, yellow diamond: $\text{Li}_4\text{B}_2\text{O}_5$ orthorhombic 00-018-0719).

3.2. Absorption spectra

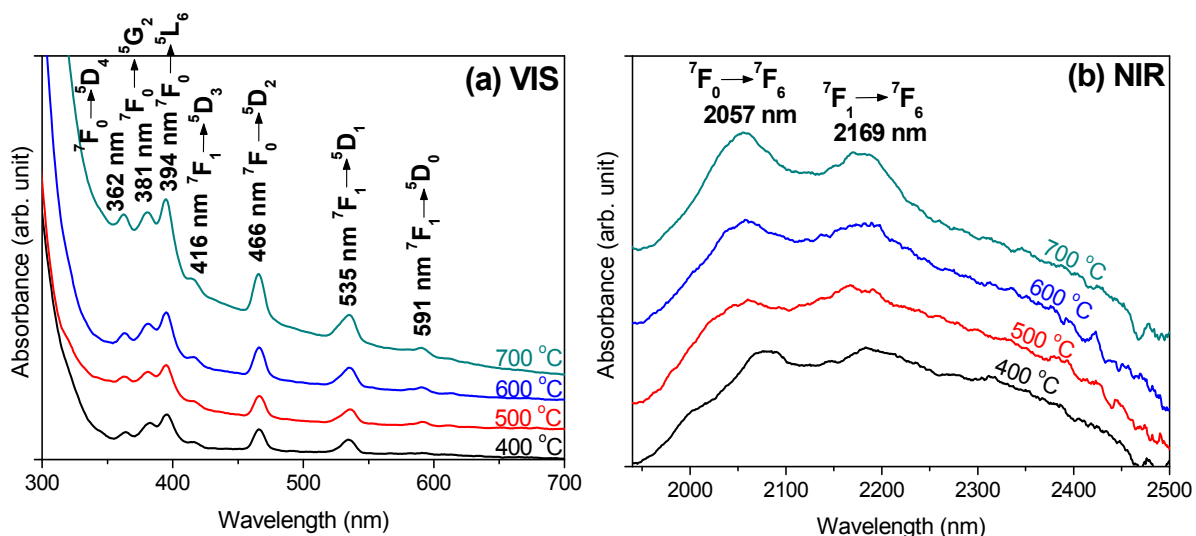


Fig. 2. The absorption spectra in (a) VIS and (b) NIR region of Eu^{3+} doped lithium lanthanum borate phosphor synthesized with different temperature.

Eu³⁺ doped lithium lanthanum borate phosphor can absorb the photon in visible light (VIS) and near-infrared (NIR) as shown in Fig. 2 (a) and (b), respectively. Each absorption band in spectra located at 362, 381, 394, 416, 466, 535, 591, 2057 and 2169 nm represents the Eu³⁺ energy transition, ⁷F₀→⁵D₄, ⁷F₀→⁵G₂, ⁷F₀→⁵L₆, ⁷F₁→⁵D₃, ⁷F₀→⁵D₂, ⁷F₁→⁵D₁, ⁷F₁→⁵D₀, ⁷F₀→⁷F₆ and ⁷F₁→⁷F₆, respectively [9,10]. From consideration at the band sharpness, phosphor can absorb more these photons with increasing of synthesis-temperature. This should be the result from the structure enhancement of Li₃La₂(BO₃)₃ in powder.

3.3. Emission and Excitation spectra

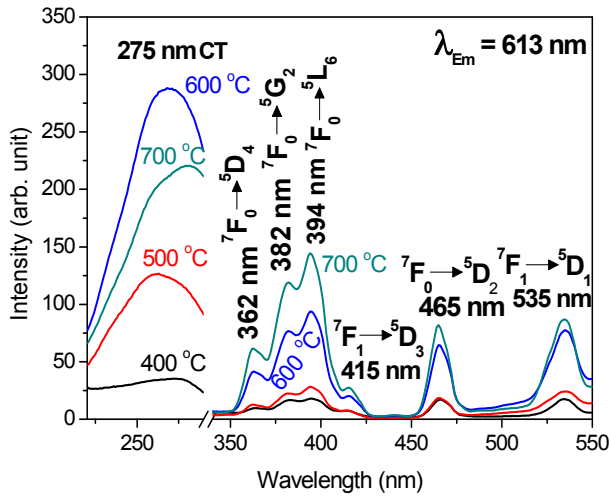


Fig. 3. The excitation spectra with 613 nm emission wavelength of Eu³⁺ doped lithium lanthanum borate phosphor synthesized with different temperature.

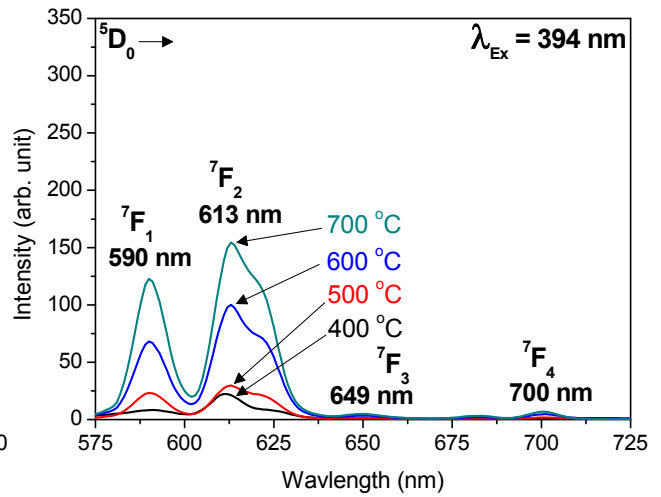


Fig. 4. The emission spectra with 394 nm excitation wavelength of Eu³⁺ doped lithium lanthanum borate phosphor synthesized with temperature.

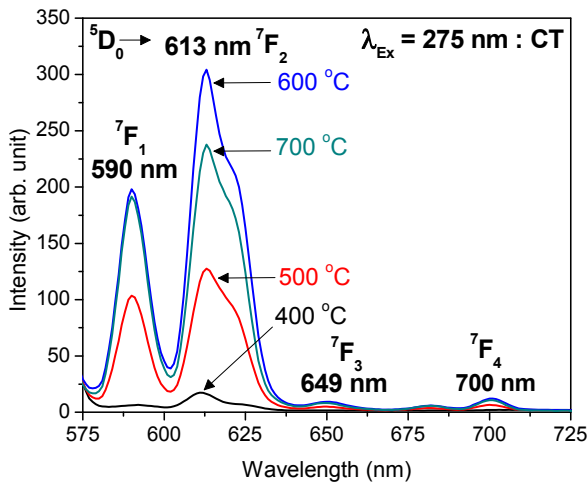


Fig. 5. The emission spectra with 275 nm excitation wavelength of Eu³⁺ doped lithium lanthanum borate phosphor synthesized with different temperature.

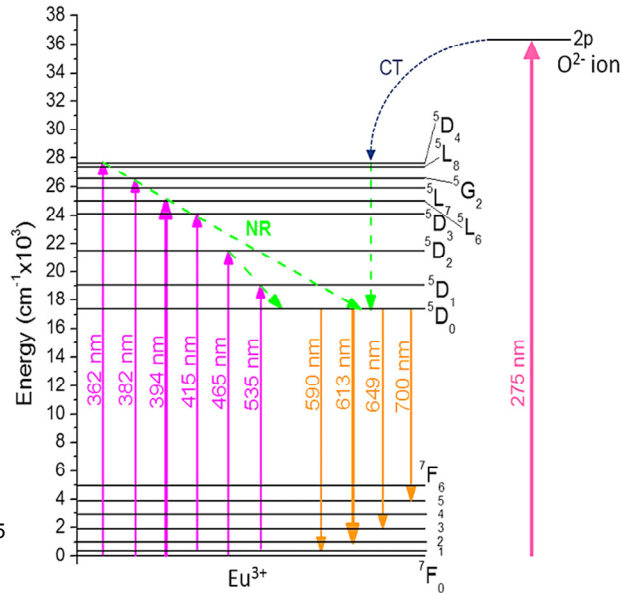


Fig. 6. The energy transition diagram of Eu³⁺ in lithium lanthanum borate phosphor.

This work focuses on the emission with 613 nm because it is the feature luminescence of Eu^{3+} . Therefore, the excitation spectra with this emission wavelength of phosphor were investigated as shown in Fig. 3. There are 7 wavelengths of photon, such as 275, 362, 382, 394, 415, 465 and 535 nm, can excite phosphor to emit the light with 613 nm. The ultraviolet (UV) with 275 nm induce the electrons from 2p orbital of O^{2-} to transfer to 4f orbital of Eu^{3+} , called charge transfer (CT) process [11]. The rest of excitation wavelength is belonged to VIS those make the 4f-4f energy transitions of Eu^{3+} composing of ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_1 \rightarrow {}^5\text{D}_3$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ and ${}^7\text{F}_1 \rightarrow {}^5\text{D}_1$, respectively [9,10]. The UV excitation result to the maximum emission-intensity of 613 nm light. VIS with 394 nm and UV with 275 nm were used to investigate the emission spectra as shown in Fig. 4 and Fig. 5, respectively. Emission spectra from both UV and VIS excitation perform similar emission bands located at 590, 613, 649 and 700 nm. These bands correspond to the Eu^{3+} transitions ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ [9,10]. All CT and Eu^{3+} transition mechanism of excitation and emission spectra are shown in Fig. 6. After excitation with VIS (4f-4f transition) and UV (CT), non-radiative relaxation (NR) decay the Eu^{3+} energy state down to ${}^5\text{D}_0$ luminescence level before it emits the photons as shown in emission spectra. The emission intensity with UV excitation is higher than one with VIS excitation.

The intensity of emission spectra with VIS excitation (Fig. 4) rises with increasing of synthesis-temperature from 400 to 700 °C. It corresponds to the improvement of asymmetric $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ structure as mentioned in XRD result. Eu^{3+} in phosphor was then more surrounded with asymmetric environment via higher temperature. Accordingly to Judd-Oflet theory, this phenomena makes the enhancement of 4f-4f luminescence-transition of Eu^{3+} [12]. For emission spectra with UV excitation (Fig. 5), the structured asymmetry of $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ also improve the emission intensity with higher synthesis-temperature. However, the maximum intensity is in the phosphor prepared at 600 °C. At this condition, the formation level of $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ and LaBO_3 structure is nearby as mentioned in XRD result. This non-dominant structure condition probably causes the low stability of electrons in O^{2-} and make electrons transfer to Eu^{3+} with high probability. It leads to a lot of Eu^{3+} population on luminescence level, ${}^5\text{D}_0$, before it emits the photons with high intensity.

4. Conclusion

The Eu^{3+} doped lithium lanthanum borate phosphors were synthesized with different temperature from 400 to 700 °C. In phosphor, monoclinic $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ structure is formed better with increasing of synthesis-temperature between 500 – 700 °C, while orthorhombic LaBO_3 structure is degraded. At 600 °C, the formation level of both compound structure is close together which shows the non-dominant structure situation. Eu^{3+} in phosphor directly absorb photons in VIS and NIR region. VIS with 394 nm and UV with 275 nm can excited phosphor to perform the strong emission with 613 nm. The emission band via UV excitation possess more light intensity than VIS excitation. Asymmetric structure of $\text{Li}_3\text{La}_2(\text{BO}_3)_3$ enhance the 4f-4f luminescence-transition of Eu^{3+} with both VIS and UV excitation. The emission intensity with VIS excitation then increases with increasing of synthesis-temperature until 700 °C. In contrary, the emission intensity with UV excitation is maximum at 600 °C preparation because the non-dominant structure condition probably induced the O^{2-} - Eu^{3+} CT process occurring with high probability. Phosphor in this work is suitable for using in the ultraviolet-light converter, display, light source and performs an interesting potential for neutron-imaging application.

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