



Synthesis and Photoluminescence properties of Eu³⁺ ions doped LiBaPO₄ phosphor

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Abstract

The red orange emitting LiBa_(1-x)PO₄:xEu³⁺ phosphor was successfully synthesized by combustion method. The structure of the prepared LiBaPO₄: Eu³⁺ phosphor was confirmed by powder XRD analysis and its photoluminescence properties has been studied in the range of 200 – 400 nm. The XRD pattern of prepared LiBa_{0.98}PO₄:0.02Eu³⁺ phosphor is well matched with available standard ICDD file. The effect of different concentrations of Eu³⁺ ions in LiBaPO₄ phosphor was studied and optimum PL intensity was obtained at 0.01 mol of Eu³⁺ ion. The photoluminescence (PL) emission spectra of prepared LiBaPO₄:Eu³⁺ phosphor consist of series of sharp line peaks at 596 nm, and 615 nm under the excitation of 393 nm.

Keywords: Photoluminescence, Combustion method, LiBaPO₄:Eu³⁺, SSL

1.0 Introduction

The phosphates with chemical composition ABPO₄ (A and B are mono and divalent cations, respectively) are in a large family of monophosphates with the different structures rigorously depending on the relative ionic size of the A and B ions [1, 2]. These compounds have been considered to be efficient luminescent materials due to their excellent thermal and hydrolytic stability [3, 4]. Recently, Eu²⁺-doped ABPO₄ phosphates have received much attention because of its potential applications as new white light emission diodes (W-LEDs) phosphors, such as KCaPO₄:Eu²⁺ [5], KSrPO₄:Eu²⁺, [6] NaCaPO₄:Eu²⁺, [7] and ABaPO₄:Eu²⁺ (A = Na, K) [8]. The use of combustion synthesis has been developed looking at experiences of last few years in the preparation of luminescent materials, specifically borates, silicates, aluminates, and some oxides. The advantages of using the combustion method are low cost, highly effective as well as time saving approach to produce highly stable particles. Furthermore, under some specific conditions, uniform and narrow distribution of particle with regular size crystallite could be obtained by the combustion method [9]. Inspiring from the above discussion, it was decided to attempt the combustion method for the synthesis of LiBaPO₄ activated with Eu³⁺ as activator.

2.0 Experimental

2.1 Synthesis of Materials and Characterizations

The reputation on combustion synthesis was only due to drawbacks of solid state diffusion method [9]. The AR grade constituent raw materials were used such as lithium nitrate (LiNO_3), barium nitrate (BaNO_3)₂, ammonium dihydrogen orthophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), ammonium nitrate (NH_4NO_3) and urea ($\text{CO}(\text{NH}_2)_2$). The precursors were mixed thoroughly in China clay basins. The stock solution of the dopant Eu_2O_3 was then added into the mixture and later little amount of double distilled water was added into the prepared mixture. The mixture slowly converts into the thick paste. The thick paste was then heated for 5–10 min on hot plate, till it turns into a homogeneous clear solution. The clear solution obtained was then transferred directly to preheated furnaces maintained at temperature of 550°C . The clear solution was warmed and boiled till the evolution of lots of fumes, for 5 min. As the fuel reaches the required temperature for burning, the self-heat generating redox reaction was started. The temperature of environment during the reaction was may be around $1100\text{--}1200^\circ\text{C}$. This sudden high temperature generation from the fuel and oxidizer reaction increases the chances of the formation of fine and stable product. The fine powder of $\text{LiBa}_{(1-x)}\text{PO}_4\text{:}_x\text{Eu}^{3+}$ ($x = 0.001, 0.002, 0.005, 0.01$ and 0.02) were then finally obtained. The powder obtained from the reaction was then calcinated in the microwave furnace at 800°C for 2 hr and suddenly quenched at room temperature. This step was introduced to remove excess of organic impurities and carbon traces remaining in the material after reaction. Also the calcining gives the particles with fine structure due to sudden quenching.

The detail of stoichiometric molar amount of each precursor used for phosphors synthesis is given in Table 1.

Table 1. Molar ratio of precursors used for material preparation and corresponding chemical reaction.

Compounds	Corresponding reaction with balance molar ratios of precursors
$\text{LiBa}_{(1-x)}\text{PO}_4\text{:}_x\text{Eu}^{3+}$	$\text{LiNO}_3 + (1-x)\text{Ba}(\text{NO}_3)_2 + x(\text{Eu}_2\text{O}_3 + \text{HNO}_3) + \text{NH}_4\text{H}_2\text{PO}_4 + 5\text{CO}(\text{NH}_2)_2 + 7.5\text{NH}_4\text{NO}_3 \rightarrow \text{LiBa}_{(1-x)}\text{PO}_4\text{:}_x\text{Eu}^{3+} + (\text{Gaseous product like } \text{NO}_3, \text{N}_2, \text{CO}_2, \text{ and } \text{H}_2\text{O})$

The structural confirmation of as prepared material was done by XRD method by using Rigaku miniflex II X-ray diffractometer with scan speed of $2.000^\circ/\text{min}$ and $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation in the range 10° to 70° . The PL excitation and PL emission spectra were recorded at room temperature on (Hitachi F-7000) fluorescence spectrometer associated with 450W Xenon discharge lamp in range of wavelength 200 – 700 nm. The measuring parameter such as width of monochromatic slit (1.0 nm), photomultiplier tube (PMT) detector voltage, scan speed (240 nm/min), spectral resolution were kept constant during the entire analysis of materials.

2.2 Structural Confirmation

For the phase confirmation the sample with maximum dopant concentration chosen. The formation of the $\text{LiBa}_{0.98}\text{PO}_4\text{:}_{0.02}\text{Eu}$, sample in the crystalline phase synthesized by combustion method was confirmed by XRD pattern as shown in Fig.1. The XRD pattern of $\text{LiBa}_{0.98}\text{PO}_4\text{:}_{0.02}\text{Eu}$ agreed well with the standard data from ICDD file having file number (00-014-0270) of LiBaPO_4 . Also the XRD pattern show that the formed material was absolutely crystalline and in single phase. The XRD data can be refined to be hexagonal structure and crystallized in the P63 space group. Based on the effective ionic radii it was assumed that the Ba^{2+} was more preferably replaced by Eu^{3+} ions [10].

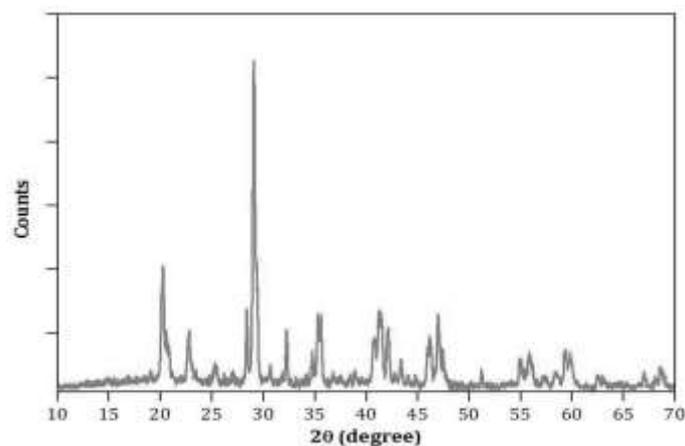


Fig. 1: XRD pattern of the $\text{LiBa}_{0.98}\text{PO}_4:0.02\text{Eu}^{3+}$ phosphor.

2.3 Photoluminescence Properties

The excitation and emission spectra of $\text{LiBa}_{(1-x)}\text{PO}_4:x\text{Eu}^{3+}$ phosphor is as presented in the Fig. 2 and Fig. 3 respectively. The excitation and emission spectra of $\text{LiBa}_{(1-x)}\text{PO}_4:x\text{Eu}^{3+}$ ($x = 0.001, 0.002, 0.005, 0.01$ and 0.02) phosphor, were monitored at wavelength 615 nm and 393 nm respectively. The excitation spectra consists of series of lines at $321, 365, 378$ and 393 nm correspond to the ${}^7\text{F}_0 \rightarrow {}^5\text{H}_3, {}^7\text{F}_0 \rightarrow {}^5\text{D}_4, {}^7\text{F}_0 \rightarrow {}^5\text{L}_7$ and ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transitions respectively. Among these peaks, the excitation at 394 nm is the dominant, as shown in Fig. 2. On the other hand emission spectra consist of two sharp peaks 596 nm and 613 nm with one weak peak at 653 nm . The emission at 596 nm corresponds to the ${}^5\text{F}_0 \rightarrow {}^7\text{D}_1$ (magnetic dipole), the emission at 613 nm corresponds to the ${}^5\text{F}_0 \rightarrow {}^7\text{D}_2$ (electric dipole) and weak emission at 653 nm corresponds to the ${}^5\text{F}_0 \rightarrow {}^7\text{D}_3$ transition of Eu^{3+} ions [11]. The PL emission intensity was studied as a function of concentration of Eu^{2+} ($0.1\text{ mol}\%$ to $2.0\text{ mole}\%$). It is observed that 0.01 mol is the optimum concentration of Eu^{3+} ions for the prepared phosphor. The luminescence intensity is found to be decreased when the concentration of Eu^{3+} ions is increased beyond the optimum value, due to well known consequence of concentration quenching.

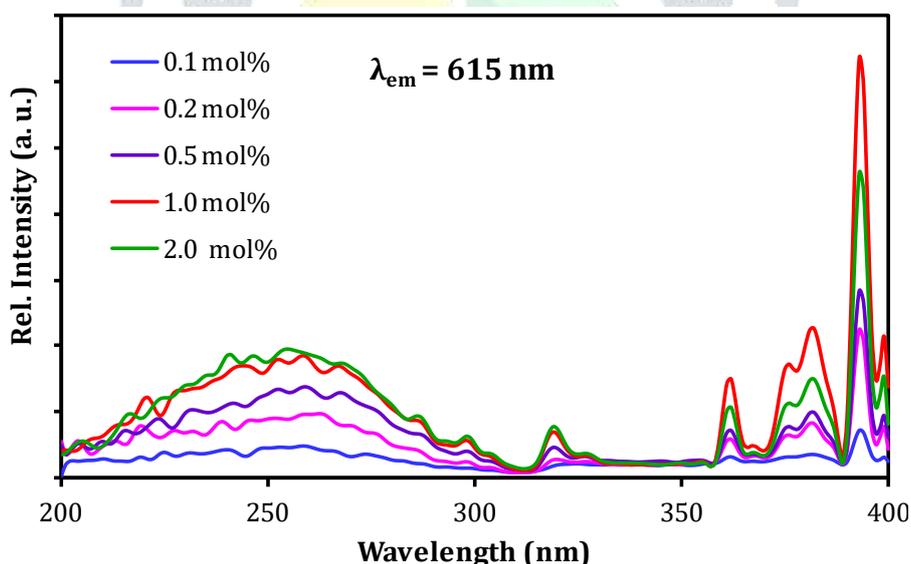


Fig. 2: PL excitation spectra of $\text{LiBa}_{(1-x)}\text{PO}_4:x\text{Eu}^{3+}$ ($x = 0.001, 0.002, 0.005, 0.01$ and 0.02) phosphors

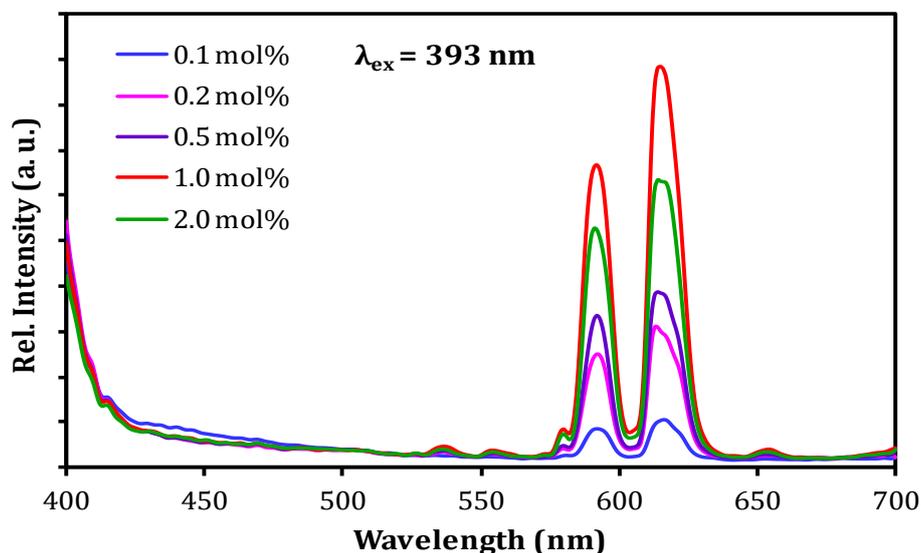


Fig. 3: PL emission spectra of $\text{LiBa}_{(1-x)}\text{PO}_4:x\text{Eu}^{3+}$ ($x = 0.001, 0.002, 0.005, 0.01$ and 0.02) phosphors

3.0 Conclusions

The polycrystalline $\text{LiBa}_{(1-x)}\text{PO}_4:x\text{Eu}^{3+}$ phosphor was effectively prepared by combustion method. The XRD pattern of prepared $\text{LiBa}_{0.98}\text{PO}_4:0.02\text{Eu}^{3+}$ phosphor is good settlement with the ICDD standard file with card no. 00-014-0270. The PL excitation spectra, was monitored at 615 nm and emission spectra was monitored at 393 nm. The outcome of this phosphor provides the support for the probable and potential application in red-orange emitter in many applications in fluorescent area including solid state lighting (SSL).

References

- [1]. W. J. Tang, D. H. Chen, J. Am. Ceram. Soc. 92 (2009), 1059.
- [2]. Y. Chen, J. Wang, M. Zhanga, Q. Zenga RSC Adv., 7, (2017), 21221.
- [3]. R. Yuan Yang, Y. Ming Peng, Y. Kuin Su J. Elect. Mat., 42, (2013) 129.
- [4]. C. C. Lin, Z. R. Xiao, G. Y. Guo, T. S. Chan, R. S. Liu, J. Am. Chem. Soc. 132 (2010), 3020.
- [5]. T. S.Chan, R. S. Liu, I. Baginskiy, Chem. Mater. 20 (2008), 1215.
- [6]. C. B. Palan, K. A. Koparkar, N. S. Bajaj, S. K. Omanwar, Res. Chem. Intermed. 42 (2016), 7637.
- [7]. Y. S.Tang, S. F. Hu, C. C. Lin, N. C. Bagkar, R. S. Liu, Appl. Phys. Lett. 90, (2007), 151108.
- [8]. C. X. Qin, Y. L. Huang, L. Shi, G. Q. Chen, X. B. Qiao, H. J. Seo, J. Phys. D: Appl. Phys. 42 (2009), 185105.
- [9]. M. Ben Amara, M. Vlasse, G. Le Flem, P. Hagenmuller, Acta Crystallogr., Sect. C 39 (1983), 1483.
- [10]. C. B. Palan, N. S. Bajaj, A. Soni, M. S. Kulkarni, S. K. Omanwar, Bull. Mater. Sci., 38 (2015), 1527.
- [11]. N. S. Bajaj, S. K. Omanwar, Opt. Mater. 35, (2013) 1222.
- [12]. L. Elammari, M. El Koumiri, I. Zschokke-Gr€anacher, B.Elouadi, Ferroelectrics 158 (1994), 19.