

Synthesis and Characterization of $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ nanophosphors Prepared Using Solution Combustion Method.

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The blue emitting $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ phosphors were synthesized by solution-combustion process, and their luminescent properties were studied under 250 and 325 nm excitation. The excitation spectrum showed two broad bands in the range of 200–400 nm: one was the host lattice absorption with the maxima at 320 nm and the other was Ba-O absorption overlapped with the CT band of Eu^{3+} , which indicated that the energy of the host lattice absorption could be efficiently transferred to the Eu^{2+} . The overlapped bands were tended to separate when monitored by different wavelength, which indicated that at least two Ba^{2+} sites were available in $\text{BaB}_8\text{O}_{13}$. The emission spectra peaks at 400 nm assigned to $4f_65d \rightarrow 4f_7$. The Ba:B mole ratios, the Eu concentration and the annealed temperature were found to affect the luminescence property. The Eu moles affect significantly up to an optimum concentrations. There after the cross relation process occurs due to concentration quenching. SEM micrographs of the $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ phosphors at low magnification show agglomerates and high magnification depicts that particle with sizes in nano ranges are the primary sources of agglomerates. XRD patterns analysis of samples with different Ba:B mole ratio when annealed at temperature above (700°C) confirms the existence of pure $\text{BaB}_8\text{O}_{13}$ phase (JCPDS: 74-0674). The variation of Eu concentrations content was found to have no effects on the crystal structure.

Keywords: $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$, Blue phosphor, Solution-combustion, Molar ration, Persistent, Luminescence.

1. Introduction

Eu^{2+} and Eu^{3+} ions exhibit strong photoluminescence in variety of alkaline earth borates and are well known as activators in phosphors [1-4]. The Eu^{2+} -doped phosphors emit blue light, which originated in $4f_65d \rightarrow 4f_7$ transition of Eu^{2+} ions while the Eu^{3+} -doped phosphors emit red light, which originated in $5D_0$

→ $7F_J$ transition of Eu^{3+} ions [5-7]. For example, $\text{BaB}_8\text{BO}_{13}:\text{Eu}^{2+}$ and $\text{BaMgAl}_2\text{O}_4:\text{Eu}^{3+}$ are used as blue and red phosphors, respectively, for plasma display panels [8]. Among various host materials for europium-doped nanocrystals, borates, especially barium borates have attracted much interest because of their rich varieties in structure, high transparency and exceptional optical damage threshold [9]. Barium octaborate $\text{BaB}_8\text{O}_{13}$ is an excellent host material for luminescent ions. The structures of $\text{BaB}_8\text{O}_{13}$ consist of two interlocking three dimensional infinite networks as triborate and pentaborate groups, which form BO_3 triangle and BO_4 tetrahedral units [10-11]. In the $\text{BaB}_8\text{O}_{13}$ lattice, the rare earth ions are isolated from each and therefore exhibit an intense luminescence. In this investigation $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ phosphor was prepared using solution combustion method. The synthesis is based on the exothermic reaction between the fuel (urea) and oxidizer (ammonium nitrate). The material properties were characterized by various techniques. Then, the influence of Eu-doping on the crystallization of the parent glasses was investigated using various techniques and the luminescent properties of the parent glasses and the obtained glass-ceramics were estimated. Under UV excitation (250 nm), $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ shows intense broad emission band peak at 400 nm. The effect of concentration of Ba:B molar ratios and concentration of Eu^{2+} ions and annealing temperature on the PL intensity were also studied.

2. Experiment

$\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ phosphor powders were prepared by a solutions combustion method without the use of flux material. To investigate the effect of the Ba/B molar ratios on the structural and PL properties of the $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ phosphor, samples with Ba/B molar ratios of 9, 12 and 18 mole% were prepared under atmospheric pressure without post treatment. The doping concentrations of Eu were fixed at 1.3 mole% and latter varied from 0.5 to 7 mole% respectively of the Ba component. The solutions were prepared by dissolving various amounts of the Boric acid, urea and nitrate precursors of each component into a minimum amount of distilled water. The resulting solution was transferred into a crucible, which was then introduced into a muffle furnace maintained at 500°C for 10-20 minutes. The voluminous and foamy combustion ash was easily milled to obtain the final $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ phosphor powders. XRD patterns of as-synthesized samples were recorded on an x-ray diffractometer with $\text{Cu K}\alpha = 1.5406 \text{ \AA}$, which was operated at 40 kV voltage and 40 mA anode current. Data were collected in 2θ values from 20° to 80° . The morphologies and sizes of the particles were examined using a PHI 700 Nano Scanning Auger Microprobe (Nano SAM) and a Shimadzu model ZU SSX – 550 Superscan scanning electron microscope (SEM). Photoluminescence (PL) measurements were performed at room temperature on a Cary Eclipse fluorescence spectrophotometer (Model: LS 55) with a built-in 150 W xenon lamp as the excitation source and a grating to select a suitable wavelength for excitation.

3. Results and discussions

3.1 Morphological and structural properties

It is well known, that the final surface morphology and structure of a specific sample is significantly influenced by the overall bulk composition of the phosphor powder. The variations in morphology and structural features of the phosphor powders dependence on the bulk composition were therefore closely monitored for the various samples that were prepared with the different Ba:B molar ratios and various Eu ion content. Figure 1(a) shows the representative SEM images of $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ samples obtained for various Ba:B mole rations. As can be seen from figure, the products are mainly large agglomerated

microparticles that appear to contain particles with sizes in nano ranges as primary source. The as-prepared powder reflects the foamy and agglomerate particle nature of the powder. The foamy structure of $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ reflects the inherent nature of the reaction. Theoretical equation assuming complete combustion may be written for blue phosphor $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ using urea as follows:



The equation above can only describe an ideal process. A typical SEM image figure 1 (b) of samples with Eu ions reveals that the sample is composed of more uniform nano particles with relatively less agglomerates. It indicates that the amount of Eu concentration has no obvious influence on the morphology and size. For the solution-combustion synthesis of oxides, metal nitrates are employed as oxidizer and urea is employed as a reducer. Figure 1(c) shows SEM image when annealed at high temperature (700°C) gives large grains size and better crystallization.

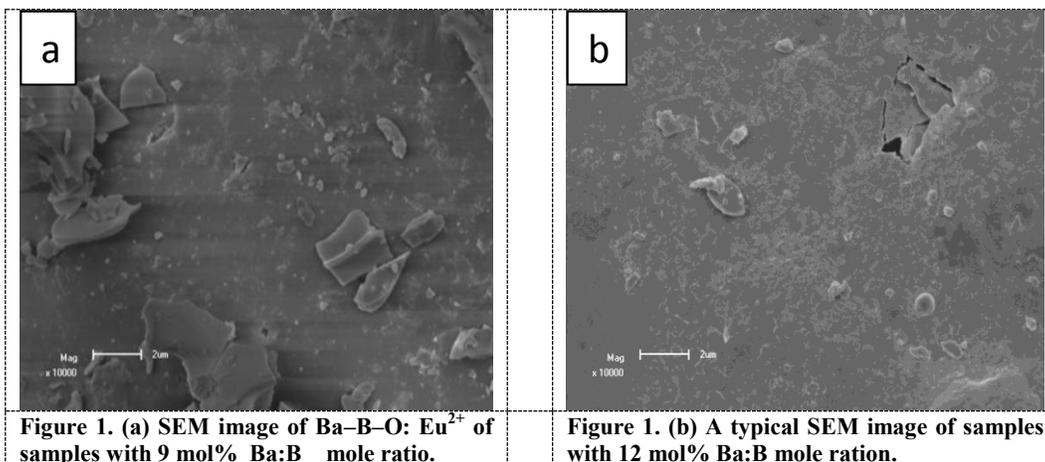


Figure 1. (a) SEM image of Ba-B-O: Eu^{2+} of samples with 9 mol% Ba:B mole ratio.

Figure 1. (b) A typical SEM image of samples with 12 mol% Ba:B mole ration.

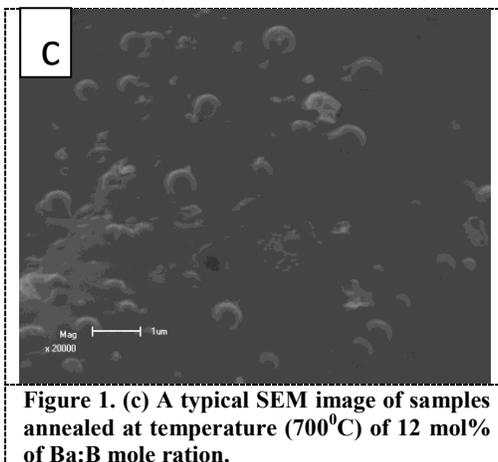


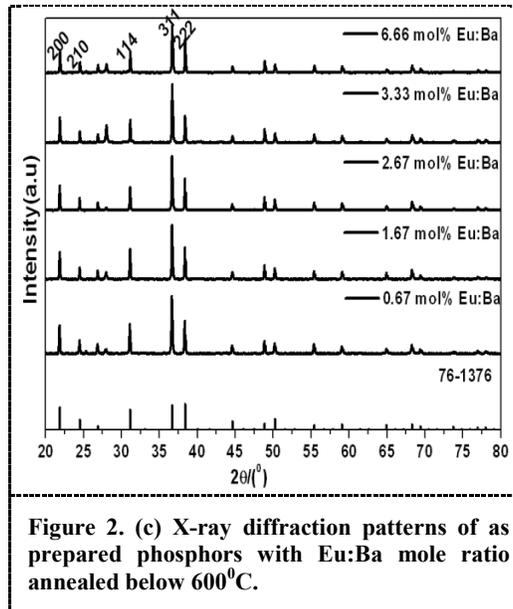
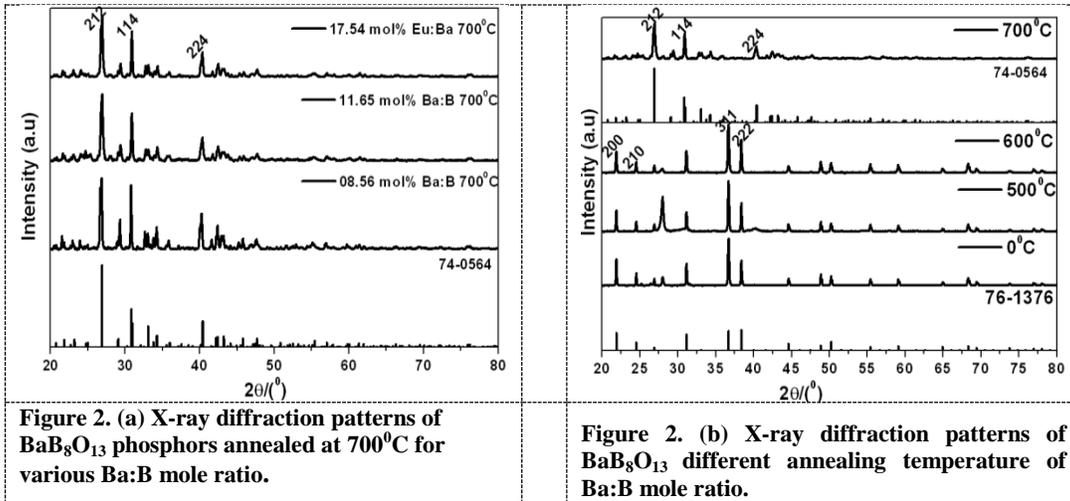
Figure 1. (c) A typical SEM image of samples annealed at temperature (700°C) of 12 mol% of Ba:B mole ration.

Figure 2 gives the XRD pattern of Eu^{2+} doped $\text{BaB}_8\text{O}_{13}$ as-prepared and annealed phosphors for several Ba:B mole ratios and varying amount of Eu content. All the as prepared samples annealed up to 600°C shows the presence of significant amount of $\text{Ba}(\text{NO}_3)_2$. All diffraction peaks of samples annealed at

temperature above 700°C corresponds to the tetragonal phase of BaB₈O₁₃ (JCPDS no. 74-0564) structure. Comparing the given XRD patterns, the positions and intensities of the main peaks are nearly the same. No diffraction line resulted from the source materials and other impurity crystal structures. Figure 2 (b) shows the behaviour of temperature influence on the structure of BaB₈O₁₃. Further, the crystal structure of BaB₈O₁₃ showed no obvious change after Eu²⁺ doping. The average structural unit distance was estimated from the full width at half maximum of the diffraction peak by the Scherrer equation:

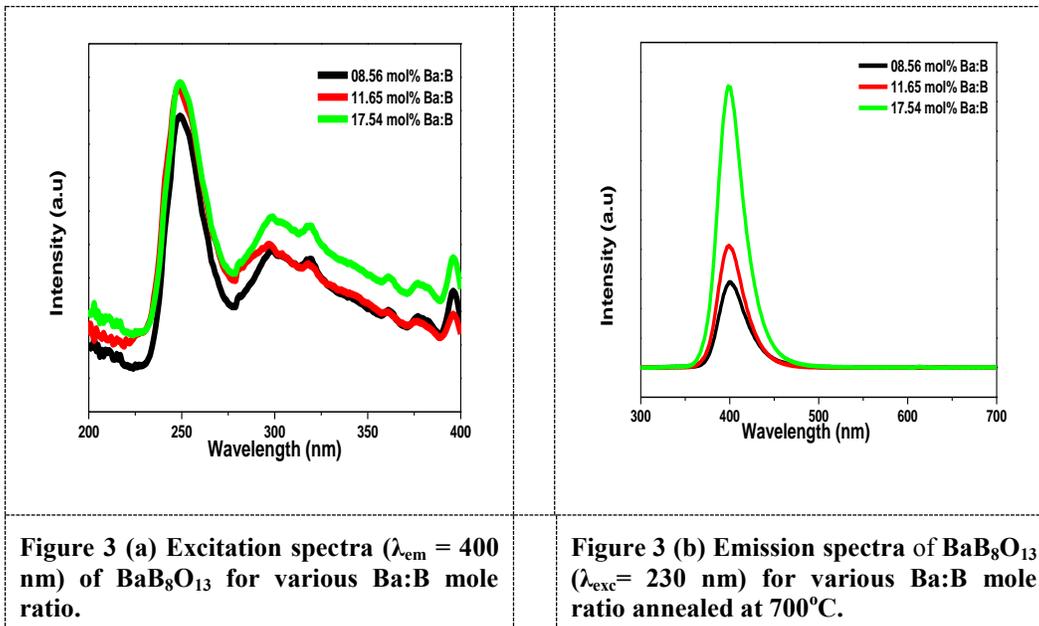
$$D = \frac{k\lambda}{B \cos \theta}$$

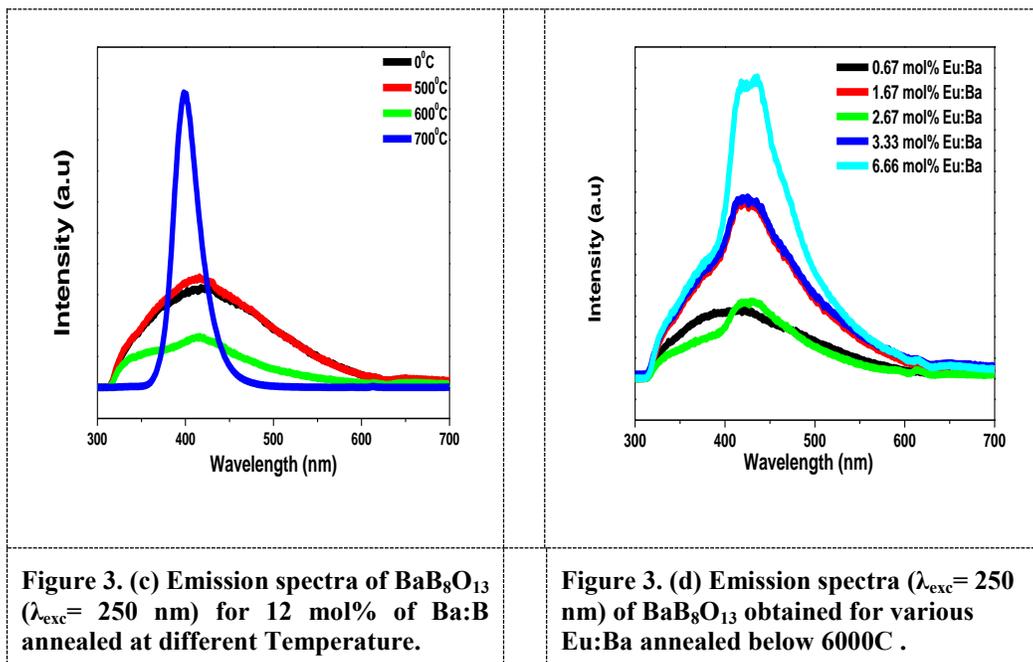
Where D is the mean crystallite diameter, k (0.89) is the Scherrer constant, λ is the X-ray wavelength (1.5406 Å) and B is the full width half maximum (FWHM) of the BaB₈O₁₃:Eu²⁺ diffraction peak. The average crystallite sizes (D) of the annealed BaB₈O₁₃:Eu²⁺ particles is about 14.13 nm calculated using the most intense reflection at $2\theta = 26.88^\circ$.



3.2 Optical properties

The excitation and emission spectra of $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ are shown in figure 3. From figure 3(a) the Eu^{2+} ion shows strong UV absorption and efficient emission in $\text{BaB}_8\text{O}_{13}$. Variation of Ba:B mole ratios has no significant effects on the structure. Excitation spectra show strong excitation bands attributed to a charge transfer band (CTB) of Eu^{2+} band in the short UV region (250 nm) and broad band maximum at 325 nm, attributed to host excitation band. This is good evidence that the Eu ions exist as Eu^{3+} and Eu^{2+} inside the two as-made $\text{BaB}_8\text{O}_{13}$ phosphors. The emission spectra peaks at 400 nm assigned to $4f_65d \rightarrow 4f_7$. In order to investigate the energy migration different samples doped with different Ba:B mole ratios and concentrations of Eu^{2+} ions were prepared under the same conditions. The concentration dependence of the emission intensity of prepared Eu^{2+} doped $\text{BaB}_8\text{O}_{13}$ phosphors annealed at 700°C are showed in figure 3(b). Figure 3(c) shows the temperature influence that annealing at different temperature changes the sharp of the sample, annealing up to 600°C is for $\text{Ba}(\text{NO}_3)_2$ at (700°C) is for $\text{BaB}_8\text{O}_{13}$ as it was seen on XRD. The intensity of sample changes as the annealing temperature increase changing also the structure of the phosphor. Figure 3(d) shows variations of Eu concentrations significantly affect the initial luminescent intensity with an increase in Eu^{2+} . It can be observed the Ba: B mole ratio changes the luminescence property of the phosphors.





4. Conclusions

The BaB₈O₁₃:Eu³⁺ phosphor was successfully synthesized by solution combustion method. The particle homogeneity and luminescence intensity improved by sol-combustion process. The particle like morphology was obtained for various Ba/B ratios. Porosity (at large magnification)–due to production of super-heated gases (N₂, CO₂) escaping from the reaction. The XRD results show the pure BaB₈O₁₃ phase obtained when annealed at 700°C. The position of the emission peak in blue domain does not change but intensity change with Eu concentrations. Addition of Eu concentrations up to optimum value improves luminescence and afterglow.

Acknowledgements

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