Synthesis and characterization of $CaB_4O_7:Eu^{3+}$ nano-phosphors prepared using solution - combustion method

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Abstract. Calcium borate ($CaB_4O_7:Eu^{3+}$) phosphors with different Ca:B molar ratio and holding Eu concentration constant have been synthesized by a solution combustion method at initial reaction temperature of 500^0C for 15 minutes. The morphology, structure and luminescence properties of the synthesized nanostructures were investigated using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Photoluminescence (PL) spectroscopy. The XRD spectra of all the as prepared samples show monoclinic phase. SEM micrograph show that the surface aspect are nanorod like for low Ca:B mole ratios but the grains become flake-like as the Ca:B molar ratio increased, giving rise to the increase in particle size resulting from agglomeration. PL results analysis showed that as the excitation wavelength increases the luminescence intensity also increases. The PL excitation spectra display broad spectra with a maximum at around 250 nm and narrow lines at around 396 nm. The PL result also shows that the luminescence intensity of these emission spectra increased with increase in Ca: B molar ratios. The narrow emission lines between 590-688 nm are due to transitions Eu^{3+}.

1. Introduction

In the last two decades, a burst of research activities has been devoted to nanomaterials. It has attracted many works in various fields from material science to biotechnologies and genetics [1–3]. Borates with non-centrosymmetric crystal structure are among the most frequently used nonlinear optical materials [4]. Phosphor nanocrystals are exceptionally promising materials in many fields of technology including photonics, luminescent displays, fluorescent lamps, lasers, cathodoluminescence, and biotechnology [5]. Europium ion (Eu^{3+}) is widely used as a luminescent center in a number of phosphors for the exhibited characteristic red emission mainly corresponding to its $^5D_0 \rightarrow {}^7F_2$ transition [6,7]. In the luminescence study of $CaB_4O_7:Eu^{3+}$ nano-phosphors, the Eu^{3+} ion plays an important role as a luminescent probe. Borates doped with trivalent europium ions have excellent efficiencies and appropriate absorption Bands [6]. A great deal of work has been done on Eu^{3+} activation of these hosts [8]. Solution combustion is a well-known method for synthesis of rare earth activated insulating materials at low temperatures ($350\text{-}500^0C$) and very short times (<10 minutes). Wet chemical methods such as sol-gel [9, 10] and polymerized-complex [11] have been used to synthesis $CaB_3O_7:Eu$ red phosphor. Although these methods have more control on size, structure and morphology, conventional solid reaction shows higher luminescence intensity [12]. Combustion synthesis offers many potential advantages over conventional techniques of synthesis, including relatively simple equipment, shorter processing time, lower nergy requirement and higher purity [13]. The initial combustion process used the conventional furnace as heating system. This method was accidentally discovered in 1988 in Prof. Patil's lab in India [14]. In this paper, red phosphor $CaB_4O_7:Eu^{3+}$ have been successfully synthesized at 500^0C by combustion reaction. The effects of urea, boric acid and europium concentration on structural, morphology and Luminescence of $CaB_4O_7:Eu^{3+}$ were studied in detail.

2. Experimental

$Ca_4O_7:Eu^{3+}$ phosphor powders were prepared by a solutions combustion method. All the reagents were of analytical purity, and were used without further purification. In a typical procedure, three glass beaker were used with the same contant of $Eu(NO_3)_3.5H_2O$, (H_3BO_3), $NH_3(ON)H_2$, NH_4NO_3 were mixed and different amount of $Ca(NO_3)_2$ were added. In each glass beaker 15 ml of deionized water was added and the above solutions were stirred for 20 minutes in a 250 ml beaker at room temperature vigorous until everything has dissolved. The solution was later transferred into a crucible, and then the crucible was introduced into a furnace maintained at 500^0C. The solution under-went dehydration followed by decomposition with the evolution of large amounts of gases. The mixture then froths and swells forming foam, which ruptures with a flame and glows to incandescence. During the incandescence the foam further swells to the capacity of the container. The entire combustion process was over in less than 15 min. The crystal structures of the samples were determined with a Bruker D8 Advance X-ray diffractometer with CuK_α (1.5418 Å). The morphologies of the phosphor were characterized with scanning electron microscopy (SEM, Shimadzu SSX-550 Super scan). The Photo luminescent spectra were obtained by using a spectrum analyzer (Varian carry eclipse fluorescence). Emission and excitation spectra were recorded using a spectral slit width of 5 nm.

3. Results and discussion

3.1 Structure and morphology

Fig. 1 shows XRD patterns of CaB_4O_7: Eu^{3+} samples synthesized with different Ca:B molar ratio and Eu ions concentrations. Fig. 1(a) the XRD patterns of the samples are in good agreement with the reference database JCPDS card 83-2025, confirming the composition of the sample to be CaB_4O_7. The obtained product has a monoclinic lattice with the lattice parameters a= 12.34, b= 9.50, c= 7.850. Fig. 1(b) it also shows the monoclinic structure with the single phase. The results also showed that varying the Eu% does not affect the crystal structure of the phosphor. Moreover, the increase of the Eu concentration promotes urea decomposition and causes the more rapid ignition of the mixture, which provides higher temperatures for the reaction [14].

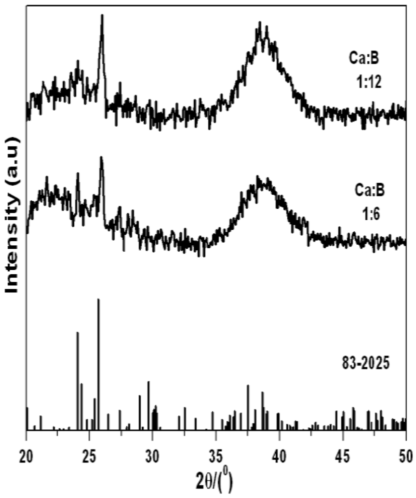

Figure 1. (a) X-ray diffraction

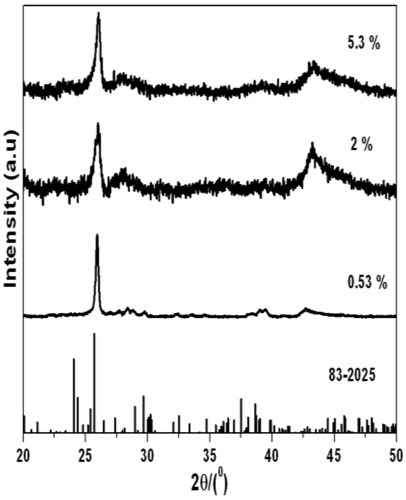

Figure 2. (b) X-ray diffraction

patterns of CaB_4O_7 phosphors for various Ca:B mole ratio.

patterns of CaB_4O_7 for different Eu concentrations.

Fig. 2 shows the SEM images of sample obtained for different Ca:B molar regular structured with well developed edges figure (a and b) and Eu ions concentration values figure (c and d) with plate-like particles. From figure (a,b) the SEM pictures of the $CaB_4O_7{:}Eu^{3+}$ powder reveals nanorod like, agglomerated, porous for low Ca:B molar ratio but the grains become regular structured with well developed edges as the Ca:B molar ratio increased, giving rise to the increase in particle size. As for figure (c,d) the SEM pictures shows the plate-like structure with very narrow edges for low Eu concentration but as the Eu concentration increases it reveals mixed plate-like structure and irregular nanoparticles superimposed on them. It was reported that the flame temperature is responsible for agglomeration [15] and the evolution of large amount gaseous products during combustion produces highly porous voluminous powders [16]. When the ignition of the metal nitrate solution with nitrogen-based fuel starts, localization of the heat on the particle boundaries results in a semi-sintered morphology of particles [17]. In the literature, the observed particle size differences/ microstructure of oxides prepared by solution combustion technique using various fuels is usually explained based on the differences in the number of moles of gases liberated during the reaction.

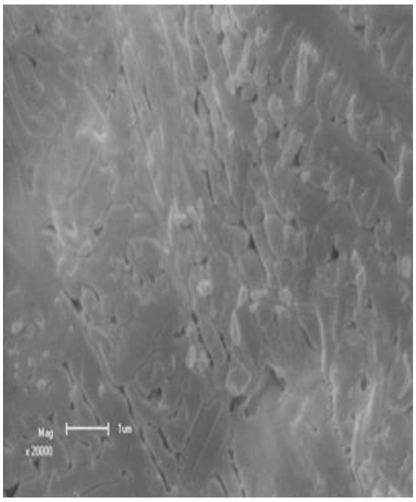

Figure 2. (a) SEM image of $CaB_4O_7{:}Eu^{3+}$ Ca:B 1:6 mole ratio sample.

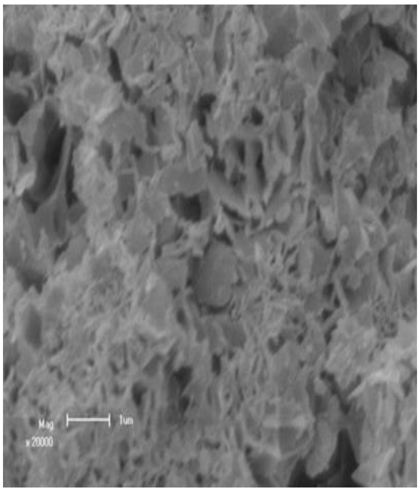

Figure 2. (b) A typical SEM image of samples with 1:12 Ca:B mole ration sample.

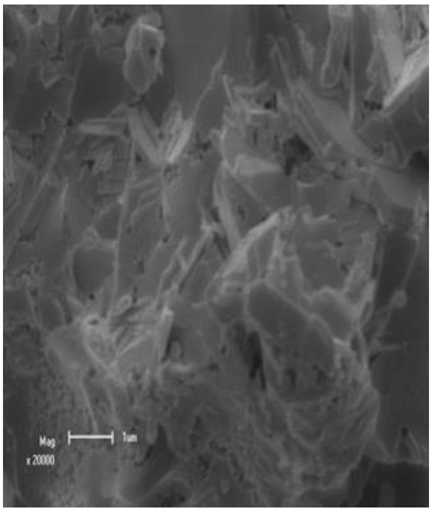

Figure 2. (c) SEM image of CaB_4O_7: Eu3+ samples with 0.53% Eu concentration.

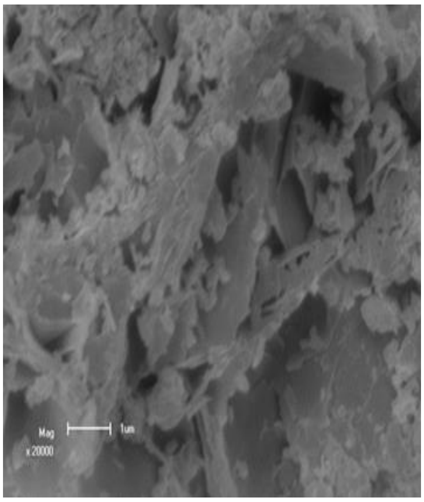

Figure 2. (d) SEM image of samples with 5.3% Eu concentration.

3.2 Photoluminescence characteristics

The excitation and emission spectra CaB_4O_7:Eu^{3+} phosphors are shown in Fig. 3. From Fig. 3(a) the excitation spectra of the CaB_4O_7:Eu^{3+} phosphor shows 3 bands from 200-400 nm. The excitation spectra by monitoring $^5D_0\rightarrow{}^7F_2$ emission of Eu^{3+} in CaB_4O_7 can be divided into two regions: the broad excitation band in 220–300 nm regions originates from the charge-transfer transition of the Eu^{3+}–O^{2-} bond (CTB) [18]. The other sharp lines can be assigned, respectively, to the transitions between the ground level $^7F_0$ and the excited levels ^5H_J, $^5D_4$, ^5G_J, $^5L_6$ [19]. The most intense of f-f transitions is $^7F_0\rightarrow{}^5L_0$ band (396 nm). The increase of the amount of the Ca: B molar ratios results in rise of the intensities of both CT and f-f bands. The emission spectra from Fig. 3(a) consist of transitions from $^5D_0$ level of Eu^{3+} ions to lower level of $^7F_4$ (680-700 nm), $^7F_3$ (648-659 nm), $^7F_2$ (608-633 nm), $^7F_1$ (583-603 nm) and the ground state $^7F_0$ (568-580 nm). The $^5D_0$-$^7F_2$ band is observed to be the most intense one (with the maximum at 614 nm) for all Ca: B molar ratios. This $^5D_0 \rightarrow {}^7F_2$ band also possesses a high intensity as a result, summary emission color is red.

Similarly from Fig. 3(b) similar results were observed with the variation of the Eu concentration. Under the excitation of CTB at 240 nm, it can be seen that the red emission lines at 614 nm originating from the electric dipole transition $^5D_0\rightarrow{}^7F_2$ is the dominant luminescence in the spectrum. Sharp red emission indicates that CaB_4O_7: Eu^{3+} is suitable for display phosphors.

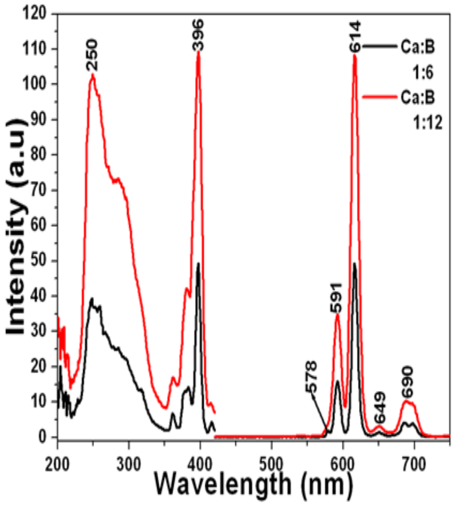

Figure 3. Excitation and emission spectra of CaB_4O_7 for various Ca:B mol ratio excited at 396 nm.

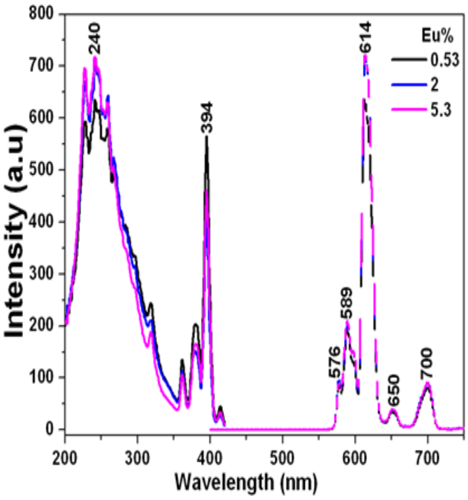

Figure 3. Excitation and emission spectra of CaB_4O_7 at different Eu concentration excited at 240 nm.

4. Conclusion

The $CaB_4O_7:Eu^{3+}$ phosphors with Ca:B molar ratio and Eu ions concentration have been successfully synthesized by the solution-combustion at furnace temperature of 500^0C. XRD analysis of phosphor shows a monoclinic phase. The SEM pictures of the $CaB_4O_7:Eu^{3+}$ powder reveals nanorod like, agglomerated, porous for Ca:B molar ratio but the grains become flake-like as the Ca:B molar ratio increased, giving rise to the increase in particle size. PL results shows the excitation spectra by monitoring $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+} in CaB_4O_7, can be divided into two regions. The luminescent intensity of the $CaB_4O_7:Eu^{3+}$ phosphor increase with increase in both the Ca:B molar ratio and Eu ions concentration.

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