Eu^{3+} Emission in Aluminum Borate Based Phosphor, $Caal_2b_2o_7$

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Abstract

Eu^{3+} doped $CaAl_2B_2O_7$ phosphors were prepared by the solution combustion synthesis technique. The doping content of Eu3+ ions in $CaAl_2B_2O_7:Eu^{3+}$ phosphors are 0.1%, 0.2%, 0.5%, 1%, 2% (molar fraction), respectively. The structures and formation of the phosphors were characterized by XRD. Luminescence properties were analyzed by measuring the excitation and photoluminescence spectra. Photoluminescence (PL) spectroscopy showed that the phosphor could be excited efficiently by UV–vis light from 250 to 410 nm, and exhibit Red emission (615 nm). It is shown that from 1% of doping content of Eu^{3+} ions under 253 nm excitation in $CaAl_2B_2O_7:Eu^{3+}$ phosphors is optimum.

Keywords: Alumino-Borate, Combustion synthesis, XRD, Photoluminescence.

Introduction

Recently, great interest in phosphors has resulted in rapid developments in the promising display and illumination technologies. Borate family compounds have the features of lower preparative temperature and high luminescent efficiency but the thermal stability of borate family compounds is poor. Compounds of the alumino borate family, however, seem to be promising for high luminescent efficiency and good thermal stability. For general lighting, photoluminescent (PL) materials include oxides, silicates, aluminates, alumino silicates, nitrides, borates, etc. [1]. Among these hosts investigated, borates are good candidates as host structure due to their low synthetic temperature, easy preparation and high luminescent brightness. The luminescent properties of Eu^{3+} doped solids have been intensively studied during the past three decades. Eu^{3+} is a well known activated ion. Due to the strong coupling of Eu^{3+} ion with its host lattice, its band type emission can be spectrally tuned from near UV to red region in various host environments [2–4]. Schäfer and Kuzel [5] first described $CaAl_2B_2O_7$ in the study of the ternary $CaO–Al_2O_3–B_2O_3$ system. In their work, the XRD patterns of α - $CaAl_2B_2O_7$ and β - $CaAl_2B_2O_7$ were provided. In 1990, MacDowell [6] reported the formation of α - and β -$MAl_2B_2O_7$ (M= Ca, Sr, Ba) crystallites in glass ceramics with ultra low thermal expansion. Recently, Chang et al. [7] found that Na^+ ion can be substituted into sites within the planes of the linearly coordinated O atoms of $CaAl_2(BO_3)_2O$ leading to the formation of α -$CaAl_2B_2O_7$. You and Hong [8] investigated the luminescent properties of β -$CaAl_2B_2O_7$ doped with Ce^{3+}, Gd^{3+} and Tb^{3+} ions in the UV-visible range. Li et al. [9]. Based on these considerations, urea [$CO(NH_2)_2$] was used as fuel, and the red emitting phosphors $CaAl_2B_2O_7$:Eu^{3+} have been successfully synthesized at 550^0C by a modified solution combustion synthesis method. To enhance the luminescence intensity, synthesis conditions were also investigated and optimized. The effect of phosphor composition on the structure and excitation and emission spectra were investigated at room temperature. Therefore, the luminescent properties of Eu^{3+} in $CaAl_2B_2O_7$ were investigated with the aim to enlarge the fundamental knowledge.

Material and Method

Inorganic borate phosphors were prepared by a modified combustion synthesis method described earlier [10-11], which is a variation of the combustion synthesis. The method based on exothermic reaction in which aluminium nitrate used as oxidizer and urea is used as fuel. The stoichiometric amounts of high purity starting materials, $Ca(NO_3)_2$ (A.R.), $Al(NO_3)_3.9H_2O$ (A.R.), $Eu(NO_3)_2$ (high purity 99.9%), H_3BO_3 (A.R.), $CO(NH_2)_2$ (A.R.) have been used for sample preparation. The starting materials with little amount of DD water were mixed thoroughly in agate mortar to obtain homogeneous solution. The excess water has been removed by slow heating (70^0C) and the solution then transferred directly to the preheated furnace (550°C) for combustion. Following the combustion, the resulting foamy samples were crushed to obtain fine particles and annealed at 750^oC for 2h. The Powder XRD of prepared materials were carried out using Rigaku Miniflex X-ray Diffractometer and compared with the ICDD file. PL & PLE measurements at room temperature were performed on Hitachi F-7000 spectrophotometer in the range 200 –700 nm with spectral resolution of 2.5 nm and PMT voltage of 400 Volts.

Table: Molar ratio of ingredients used for material preparation and balanced reaction:

Compound	Molar Ratio
$Ca_{(1-x)}Eu_{(x)}Al_2B_2O_7$	$Ca(NO_3)_2 : Al(NO_3)_3.9H_2O : Eu(NO_3)_2 : H_3BO_3 : CO(NH_2)_2$ $(1-x) : 2 : x : 3 : 4$ (x = 0.001, 0.002, 0.005, 0.01, 0.02) $Ca(NO_3)_2 + 2[x'Al(NO_3)_3.9H_2O] + Eu(NO_3)_2 + DDW + 2H_3BO_3 + 6.5CO(NH_2)_2 \xrightarrow[\text{at 550 C}]{\text{Combustion}} > CaAl_2B_2O_7: xEu^{3+} \rightarrow Gases(NH_3\uparrow + H_2O\uparrow + NO_y\uparrow)$

Result and Discussion

X-ray Diffraction Pattern

The powder XRD pattern (Fig.1) of the host prepared as above was obtained using Rigaku Miniflex II within suitable scan range with the scanning speed of 2.000 deg./min. The pattern is found to be consistent with the ICDD file no. 00-19-0205. The two possible sites for Eu^{3+} incorporating into $CaAl_2B_2O_7$ lattice are the Al^{3+} sites or Ca^{2+} sites. The Ca^{2+} (0.99 Å) ion has a much larger ionic radius, compared with that of Al^{3+} (0.535 Å) ion. However, the ionic radius of Ca^{2+} (0.99 Å) is slightly greater than that of Eu^{3+} (0.947 Å). So it would be expected that Eu^{3+} could replace Ca^{2+} in the crystal lattice.

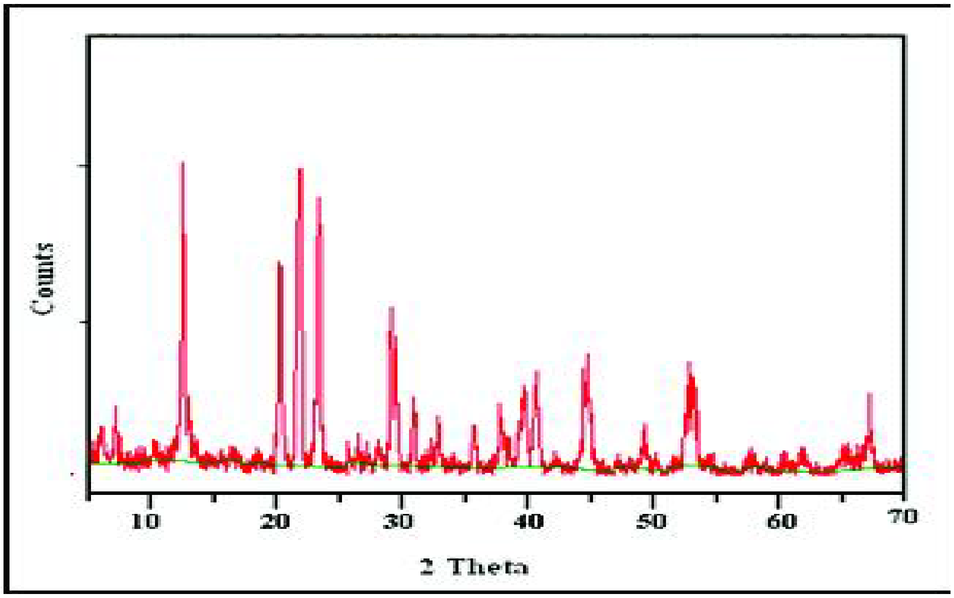

Fig 1: The X-ray powder diffraction pattern of $CaAl_2B_2O_7:Eu^{3+}$.

SEM images of phosphor powder

Fig. 2 show the SEM image of $CaAl_2B_2O_7:Eu^{3+}$ powders prepared at 750°C. It was observed that the microstructure of the phosphor consisted of irregular grains with heavy agglomerate phenomena. The average size of the $CaAl_2B_2O_7:Eu^{3+}$ particles is about 5–15 µm. The results show that $CaAl_2B_2O_7:Eu^{3+}$ phosphor has a good crystalline and a relatively low sinter temperature.

Photo Luminescence of CaAl2B2O7:Eu3+

Fig. 3 shows the PL excitation spectra of $CaAl_2B_2O_7:Eu^{3+}$ consists of excitation broad band peaking at 253 nm which corresponds to the $^7F_0 \rightarrow {}^5L_6$ transitions of Eu^{3+} ions. Under 253 nm excitation the emission spectra consists of three main peaks at 615, 580 and 592 nm. Emission band peaking at 615 nm corresponds to the $^5D_0 \rightarrow {}^7F_2$ transitions, 580 nm corresponds to $^5D_0 \rightarrow {}^7F_0$ transitions and 592 nm corresponds to ${}^5D_0 \rightarrow {}^7F_1$ transitions of Eu^{3+} ion. Among these emission peak, 615 n m line is intense as compared to other two (Fig.3). The excitation spectrum from 200 to 450 nm of CAB: Eu monitored at 615 nm is shown in Fig. 3. There is a broad absorption band in the wavelength range 200-300 nm. In the excitation spectrum, the absorption line at 253 nm corresponds to (${}^7F_0 \rightarrow {}^5L_6$) is the strongest one and also the lines at 394 nm corresponds to (${}^7F_1 \rightarrow {}^5L_6$) transitions, 319 nm corresponds to (${}^7F_0 \rightarrow {}^5G_1$) transitions, 362 nm corresponds to (${}^7F_0 \rightarrow {}^5D_4$) transitions, 381 nm corresponds to (${}^7F_1 \rightarrow {}^5D_4$) transitions, 319 nm corresponds to (${}^7F_0 \rightarrow {}^5G_1$) transitions, 414 nm corresponds to (${}^7F_1 \rightarrow {}^5D_3$) transitions, are also observed. Furthermore, ot observe effect of Eu3+ concentration on luminescence intensity, phosphor with different Eu3+ concentration were prepared. Fig. 4 shows the variation of emission intensity with the concentration of Eu^{3+}. It was observed that the critical concentration of Eu^{3+} in $CaAl_2B_2O_7$: Eu^{3+} phosphor is about 1 mol%.

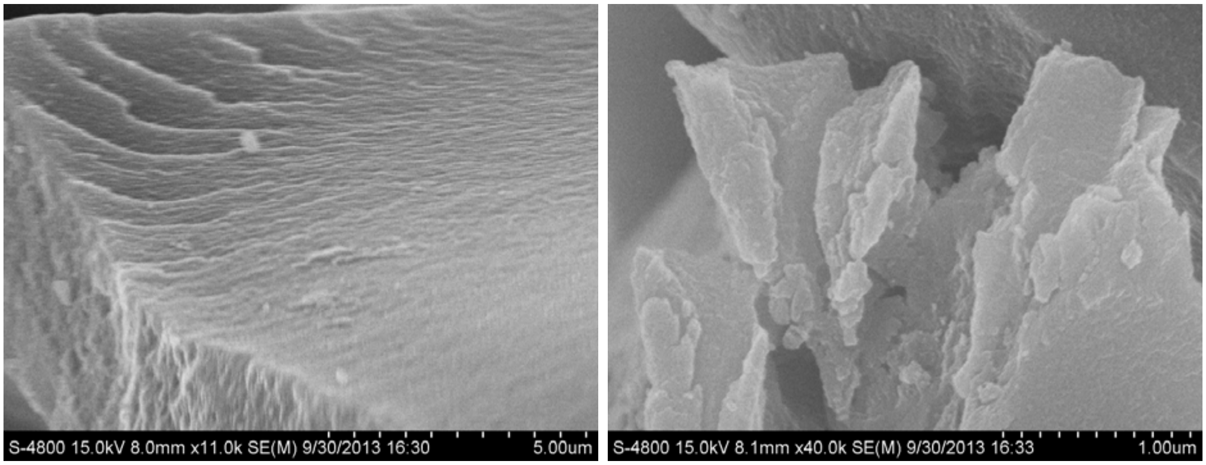

Figure 2 SEM images of $CaAl_2B_2O_7$:Eu^{3+}.

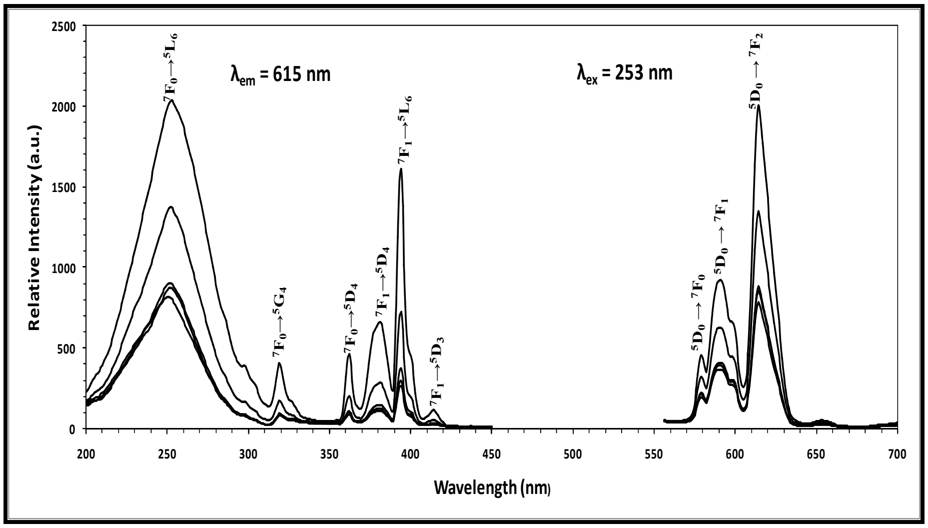

Figure 3 Excitation and Emission spectra of $Ca_{(1-x)}Al_2B_2O_7$:Eu_x^{3+}
(x=0.001,0.002,0.005,0.01,0.02 mol) phosphor.

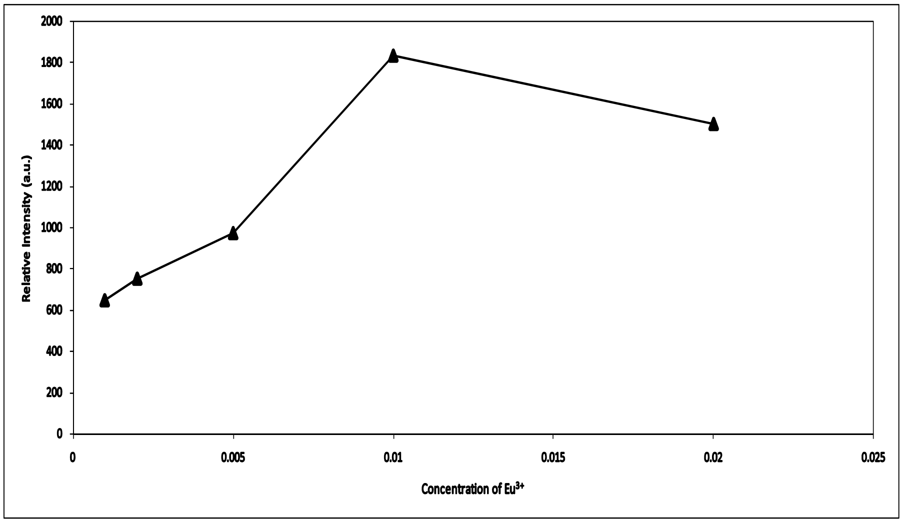

Figure 4: Concentration quenching of Eu^{3+} in $CaAl_2B_2O_7$.

Conclusion

The phosphors $CaAl_2B_2O_7{:}_xEu^{3+}$ have been successfully synthesized by using solution combustion technique. The excitation spectra shows that the intraconfiguration $^7F_1 \rightarrow {}^5L_7$ excitation lines are very stronger than the charge transfer transition from the O_2^- to Eu^{3+}. The PL spectra show the strongest emission at 615 nm corresponding to the electric dipole $_5D^0 – {}_7F^2$ transition of Eu^{3+} in $CaAl_2B_2O_7$ due to the non-centrosymmetric nature of the Eu^{3+} site, which results in pure red color emitting. It is observed that for 1mol% concentration of Eu3+ in $CaAl_2B_2O_7$ phosphor, the emission of 615 nm line is maximum.

References

(1) H.Honingsmann, Clin Exp Dermatol, 2001, 26, 343-350.

(2) L. Scherschun, J.J.Kim, W.H.Lim, J. Am. Acad. Dermatol , 2001, 44, 999-1003.

(3) T.Ota, Y.Hata, A. Tanikawa, M.Amagai, M.Tanaka, T.Nishikawa, Clin. Exp. Dermatol, 2001, 26 ,179-181.

(4) L.J.Warren, S.George, J.Australas.. Dermatol, 1998, 39, 179-182.

(5) V.L. Scha¨ fer, H.J. Kuzel, Neues. Jb. Miner. Monat. 1967, 131.

(6) J.F. MacDowell, J. Am. Ceram. Soc., 1990, 73, 2287.

(7) K.S. Chang, A. Douglas, Keszler Mater. Res. Bull., 1998, 33, 299.

(8) C. Li, Q. Su, J. Alloys Compounds, 2006, 875, 408–412.

(9) R.P.Sonekar, S.K.Omanwar, S.V.Moharil, S.M.Dhopte, P.L.Muthal, V.K.Kondawar, JLumin, 2009, 129, 624-628.

(10) R.P.Sonekar, S.K.Omanwar, S.V.Moharil, S.M.Dhopte, P.L.Muthal, V.K.Kondawar, Opt.Mater., 2007, 30, 622-625.