



Eu³⁺→Eu²⁺ reduction in UV emitting BaAl₂B₂O₇ phosphor in oxidizing environment

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Abstract

This paper reports reduction of Eu³⁺→Eu²⁺ in BaAl₂B₂O₇ host prepared in an oxidizing environment by modified solution combustion synthesis technique. The crystal phase and surface morphology of the prepared phosphor have been studied by powder X-ray diffraction (XRD) and FE-SEM images respectively. Photoluminescence emission spectrum of BaAl₂B₂O₇:Eu²⁺ exhibits a strong emission band peaking at 375 nm (UV-A region), upon excitation with 309 nm near UV light. For lower concentrations of Eu²⁺, the emission intensity of BaAl₂B₂O₇:Eu²⁺ was measured. This phosphor could find applications in medical & lamp industry.

Keywords: Alumino-Borate, Combustion synthesis, Photoluminescence (PL).

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1. INTRODUCTION

Ultraviolet light (UV light) is useful for treating various types of skin diseases and skin disorders, such as psoriasis, sun tanning, vitiligo, etc. [1-6]. Photoluminescence materials including oxides, silicates, aluminates, alumino-borates, alumino-silicates, nitrides, borates etc., plays a very important role for the potential applications in ultraviolet devices. Among these hosts, borates are found to be good candidates as hosts due to their low synthetic temperature, easy preparation and high luminescent brightness. These compounds are functionally versatile and can serve as excellent host matrices for efficient luminescence. Recently, researchers have taken interest in alkaline-earth aluminum borates because of their potential applications as luminescence hosts [7-8]. The alkaline-earth aluminum borate, BaAl₂B₂O₇, was first described by Hubner [9] following a study of the ternary system BaO–Al₂O₃–B₂O₃. It has an association of BO₃ triangles, BaO₆ octahedra, and AlO₄ tetrahedra. Its crystal structure was studied in detail by Ye et al. [10]. However, the abnormal reduction of Eu³⁺→Eu²⁺ of BaAl₂B₂O₇ in air atmosphere takes place, when prepared at high temperature. In the present work, we report for the first time the abnormal reduction of Eu³⁺→Eu²⁺.

2. Experimental

The powder samples of Eu²⁺ doped BaAl₂B₂O₇ were prepared by a solution combustion technique which is

described earlier [11-14]. The high purity starting materials, Ba(NO₃)₂ (A.R.), Al(NO₃)₃.9H₂O (A.R.), Eu(NO₃)₃ (high purity 99.9%), H₃BO₃ (A.R.), CO(NH₂)₂ (A.R.) have been used for phosphor preparation. The stoichiometric amounts of the ingredients (Table-1) were thoroughly mixed in an Agate Mortar, adding small volume of double distilled water to obtain an aqueous homogeneous solution. The solution was then transferred into a china basin and slowly heated at lower temperature of 70°C in order to remove the excess water. The solution was then introduced into a preheated muffle furnace maintained at 550 °C. The solution boils foams and ignites to burn with flame; a voluminous, foamy powder was obtained. The entire combustion process was over in about 5 min. Following the combustion, the resulting fine powders were annealed at temperature 800°C for about 90 min. and quenched to room temperature. The prepared materials were characterized by powder XRD using Rigaku Miniflex II X-ray Diffractometer with scan speed of 2°/min. Surface morphology of the calcined particles were observed through scanning electron microscopy (FE-SEM). PL & PLE measurements at room temperature were performed on Hitachi F-7000 Spectrofluorometer with spectral resolution of 2.5 nm.

Table-1: Molar ratio of ingredients used for material preparation

Compound	Molar Ratio
$Ba_{(1-x)}Al_2Eu_xB_2O_7$	$Ba(NO_3)_2:Al(NO_3)_3 \cdot 9H_2O:Eu(NO_3)_3:H_3BO_3:CO(NH_2)_2$ (1-x) : 2 : x : 2 : 6.5 (x = 0.005, 0.007, 0.01, 0.02, 0.03)

3. Result and Discussions

3.1 X-ray Diffraction Pattern

Fig.1 exhibits the powder X-ray diffraction (XRD) patterns of $Ba_{0.98}Al_2B_2O_7:0.02Eu^{2+}$, which is in agreement with ICDD file no.01-086-2168. The $BaAl_2B_2O_7$ host has a rhombohedral crystal structure and lattice parameters $a=b=5.001 \text{ \AA}$ and $c=24.37 \text{ \AA}$. The two possible sites available for the incorporating Eu^{2+} in the $BaAl_2B_2O_7$ lattice are Al^{3+} sites or Ba^{2+} sites. The ionic radius for Eu^{2+} is 1.07 \AA . However, the ionic radii for Al^{3+} are 0.54 \AA that for Ba^{2+} is 1.42 \AA . Eu^{2+} ion have a much larger ionic radius, compared with that of Al^{3+} ion. Therefore Eu^{2+} ions are expected to occupy Ba^{2+} site in $BaAl_2B_2O_7$ crystal structure.

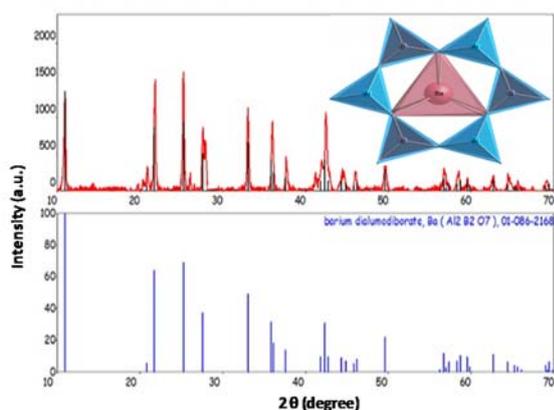


Fig.1. XRD pattern of $Ba_{0.98}Al_2B_2O_7:0.02Eu^{2+}$ phosphor.

3.2 FE-SEM image of $Ba_{0.98}Al_2B_2O_7:0.02Eu^{2+}$

Fig. 2 shows the FE-SEM image of $Ba_{0.98}Al_2B_2O_7:0.02Eu^{2+}$ powder prepared at $800 \text{ }^\circ\text{C}$. The microstructure of the phosphor shows irregular rod like structures with agglomerate phenomena. The result shows that the phosphors have a good crystalline nature at a relatively low sintering temperature.

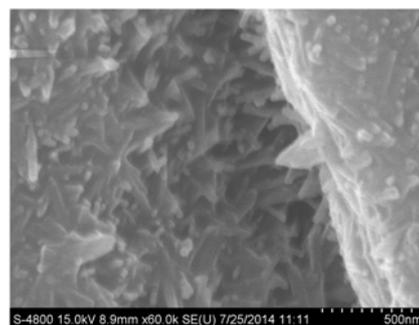


Fig.2. FE-SEM image of $Ba_{0.98}Al_2B_2O_7:0.02Eu^{2+}$ phosphor.

3.2 Photoluminescence Properties

The excitation spectra monitored at 375 nm emission and emission spectra monitored at 309 nm excitation of $Ba_{0.98}Al_2B_2O_7:0.02Eu^{2+}$ are shown in Fig. 3. The excited states of Eu^{2+} may be formed from the $4f^65d$ configuration. The crystal field causes a splitting of the $4f^65d^1$ configuration of Eu^{2+} ions in the phosphor. Therefore the lowest excited state is below the 6P_1 state and only $4f^7 ({}^8S_{7/2})$ to $4f^65d^1$ transitions within the Eu^{2+} ions are observed in excitation and emission [15]. The excitation spectrum consists of a series of bands peaking at 250 nm, 290 nm, 309 nm, 330 nm & 343 nm which correspond to the electric dipole allowed transitions. The emission spectra under 309 nm excitation consist of broad band peaking at 375 nm, which lies in the UV-A region of electromagnetic spectrum as shown in Fig. 4(a). The intensity of Eu^{2+} line at 375 nm was found to increase with dopant concentration. The luminescence intensities of the $Ba_{(1-x)}Al_2B_2O_7:xEu^{2+}$ ($x = 0.005, 0.007, 0.01, 0.02, \text{ and } 0.03$) phosphors were enhanced with increasing Eu^{2+} doping ratio and reached maximum at $x = 2$ mole % as shown in Fig. 4(b). When the Eu^{2+} doping ratio was above optimum concentration, the phosphors luminescence intensity reduced continually, which can be ascribed to the concentration quenching of Eu^{2+} . This quenching process often attributes to energy migration among Eu^{2+} ions, because for an over-doping concentration, the non-radiative relaxation between the neighboring Eu^{2+} ions will enhance. Under the excitation of 241 nm, the phosphor show emission line at 614 nm corresponding to the ${}^5D_0 \rightarrow {}^7F_J$ ($J=0, 1, 2$ and 3) transitions of Eu^{3+} . The optimum concentration of Eu^{3+} for 614 nm line was found to be 0.02 mol, shown in Fig. 5. The dominant emission at 614 nm shows Eu^{3+} sites occupying the barium sites with lower symmetry [16]. The intensity of this line (Eu^{3+}) is found to be very poor as compared to the Eu^{2+} emission line (375 nm). So, it can be concluded that it is possible to prepare the phosphor

$Ba_{0.98}Al_2B_2O_7:0.02Eu^{2+}$ in the absence of reducing atmosphere.

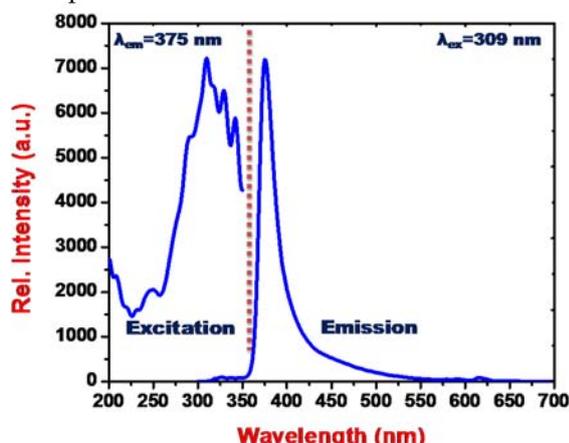


Fig. 3. Excitation and emission spectra of $Ba_{0.98}Al_2B_2O_7:0.02Eu^{2+}$ phosphor.

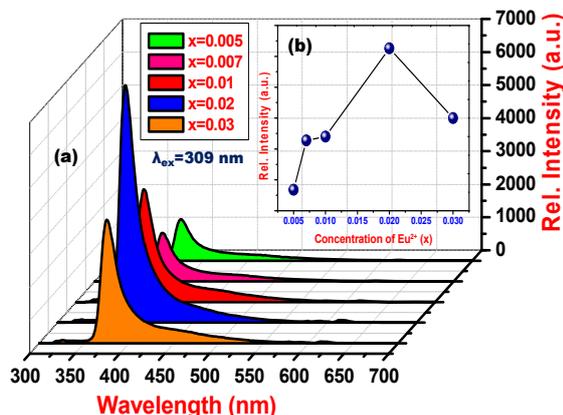


Fig. 4. (a) Dependence of the PL intensities of $Ba_{(1-x)}Al_2B_2O_7:xEu^{2+}$ at $\lambda_{ex}=309$ nm at different Eu^{2+} concentrations. (b) The top inset shows the influence of the concentration on the emission intensity of $Ba_{(1-x)}Al_2B_2O_7:xEu^{2+}$ phosphor ($x=0.005, 0.007, 0.01, 0.02,$ and 0.03).

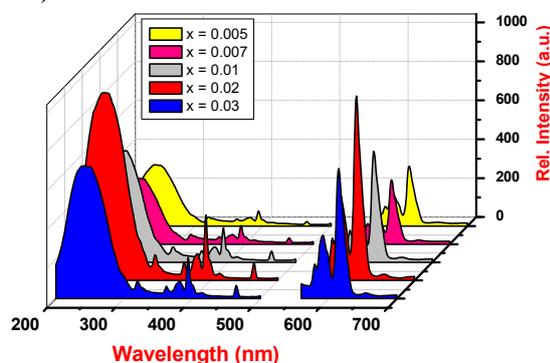


Fig. 5. Photoluminescence spectra of $Ba_{(1-x)}Al_2B_2O_7:xEu^{2+}$ phosphor ($x=0.005, 0.007, 0.01, 0.02,$ and 0.03) at room temperature. The excitation spectrum was

recorded at the maxima of the corresponding emission band (614 nm), and the emission spectrum was recorded under the excitation of 241 nm.

3. CONCLUSIONS

The phosphor $BaAl_2B_2O_7:Eu^{2+}$ was successfully synthesized using modified solution combustion synthesis method in open air environment. The emission band peaking at 374 nm, due to Eu^{2+} ions, under the excitation of 309 nm, lies in the UVA region of EM spectrum. This emission band can be used in treating skin disease like psoriasis in medical field. Low intensity emission line at 614 nm, due to non-reduction of some Eu^{3+} ions, was observed under the excitation of 241 nm.

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