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Marí, B.; Singh, K.; Verma, N.; Mollar García, MA.; Jindal, J. (2015). Luminescence properties of the $\text{Eu}^{2+}/\text{Eu}^{3+}$ activated Barium aluminate phosphors with varies Gd^{3+} concentration. Transactions of the Indian Ceramic Society. 74(3):157-161.
doi:10.1080/0371750X.2015.1082932



The final publication is available at

<http://doi.org/10.1080/0371750X.2015.1082932>

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Additional Information

Luminescence Properties of $\text{Eu}^{2+}/\text{Eu}^{3+}$ Activated Barium Aluminate Phosphors with Gd^{3+} Concentration Variation

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[MS received March 09, 2015; Accepted August 10, 2015]

$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}/\text{Eu}^{3+}$ (1 mol %) co-doped with varying concentrations of Gd^{3+} (1, 2, 5 and 10 mol%) were prepared by combustion synthesis method at 600°C. All the compositions were investigated for their structural and photoluminescence properties. Samples prepared in open atmosphere showed the presence of both Eu^{3+} and Eu^{2+} states which indicates the reduction of Eu^{3+} to Eu^{2+} during the preparation of these compounds. The prepared materials at 600°C showed high intense broad peaks around 498 nm corresponding to Eu^{2+} and small peaks in the red region which are attributed to the presence of Eu^{3+} . In the 1000°C annealed compounds, the intensity of the peak at 498 nm got increased. The intensity of this broad band for $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}/\text{Eu}^{3+}$ (1 mol%): Gd^{3+} (1 mol%) was three times than that of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}/\text{Eu}^{3+}$ (1 mol%). Thus second rare earth ion (Gd^{3+}) acted as a good sensitizer and enhanced the photoluminescence intensity. The XRD spectra revealed the presence of hexagonal phase of BaAl_2O_4 as main phase and a small amount of a mixed phase $\text{BaO} \cdot 6.6 \text{Al}_2\text{O}_3$. Doping of Eu^{3+} , Gd^{3+} did not change the crystalline structure of barium aluminate (BaAl_2O_4).

Introduction

Rare earth (RE) ions are used extensively to prepare photoluminescent materials. Among these luminescent materials, the RE doped alkaline earth aluminate phosphor materials have attracted much attention due to their excellent properties like good stability,¹ long persistent behaviour,² high quantum efficiency,³ etc. The metal aluminates can be represented by the general formula MAl_2O_4 (M = Ba^{2+} , Sr^{2+} , Ca^{2+} or Mg^{2+}) which are widely used as host lattice for doping of RE. Among rare earth ions, europium is an attractive activator and has been used in preparation of phosphor materials for an efficient red and blue emission. The europium emission in the phosphor materials is strongly dependent on the host lattice and it is possible to obtain different colours from blue to red. Europium can act as an activator in two forms, Eu^{3+} and Eu^{2+} . Eu^{2+} or Eu^{3+} can be identified from their characteristic photoluminescence spectra.⁴ For many years, optical properties of the trivalent europium (Eu^{3+}) doped materials like borates, oxides, silicates, phosphates, sulfates and fluorides have been studied.⁵⁻⁸ These materials have found their applications in lighting, information display and optoelectronic technology. The photoluminescence properties of RE-doped compounds are highly dependant on composition and local structure of the host. Usually

trivalent europium salts or europium(III) oxide are the starting materials for synthesis of Eu^{3+} and Eu^{2+} doped oxide materials. So, to prepare the optical materials activated by Eu^{2+} , it is necessary to reduce Eu^{3+} to Eu^{2+} ions. The most common scheme to get Eu^{2+} activated compounds is to calcine Eu^{3+} -containing material in a reducing atmosphere, such as N_2/H_2 or H_2 , or carbon or CO .⁹⁻¹² The irradiation of high energy rays, like X-rays, UV light, etc on Eu^{3+} containing samples^{13, 14} also produce both the oxidation states of europium. $\text{Eu}^{3+}/\text{Eu}^{2+}$ compounds can also be obtained when the Eu-containing samples are prepared in an oxidizing atmosphere, e.g. air or pure O_2 gas.¹⁵ Some special types of lattices are reported in which $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reductions are observed. Some of these crystal lattices are sulphate ($\text{BaSO}_4:\text{Eu}$), borophosphates ($\text{MBPO}_5:\text{Eu}$; M = Ca, Sr, Ba), borates ($\text{SrB}_4\text{O}_7:\text{Eu}$, $\text{BaB}_8\text{O}_{13}:\text{Eu}$) and silicate ($\text{BaMgSiO}_4:\text{Eu}$).¹⁰⁻¹² Few aluminate compounds, like ($\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$)¹⁶ and ($\text{BaAl}_2\text{O}_4:\text{Eu}$),¹⁷ which involve the reduction of Eu^{3+} to Eu^{2+} , have also been reported.

The earlier reported works on $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ show much variation about the photoluminescence (PL) band in the blue green region. The PL emission band appears at 500 nm in ($\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$),^{18, 19} while it appears at 443 nm with a shoulder at 500-510 nm in ($\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$)²⁰ and at 496 nm in the compound ($\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$).²¹ Two emission peaks are observed at 452 and 485 nm in ($\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$) thin film.²² An asymmetric broad band appears at 498 nm in ($\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$) compound prepared at high temperature by solid state reaction. In order to

observe the effect of Gd^{3+} as co-dopant on the PL properties of the $(BaAl_2O_4:Eu)$ compounds, we have synthesized $(BaAl_2O_4:Eu^{2+}/Eu^{3+})$ materials by combustion synthesis method with different concentrations of Gd^{3+} . The $(BaAl_2O_4:Eu^{2+}/Eu^{3+}:Gd^{3+})$ compounds have also been heated at $1000^\circ C$ to observe the annealing effect on the crystal structure and PL properties. The combustion synthesis method has many advantages over other elaborated methods such as: simplicity of experimental set-up, short time of preparation, and low cost due to energy saving. Many times final products are found to be composed of nanosized particles.²³

Experimental

The combustion synthesis method was used to prepare $(BaAl_2O_4:Eu^{2+}/Eu^{3+},Gd^{3+})$ with varying concentrations of Gd^{3+} (1, 2, 5 and 10 mol%). Eu^{3+} concentration was fixed at 1 mol% for all the compositions. High purity $Ba(NO_3)_2$, $Al(NO_3)_3$, $Eu(NO_3)_3$, $Gd(NO_3)_3$ and urea from Sigma Aldrich were used as the starting materials. Materials in stoichiometric ratio for the formation of $BaAl_2O_4:Eu^{3+}:Gd^{3+}$ complex were mixed with a calculated amount of urea and a paste was prepared by adding few drops of deionised water. The urea amount was calculated using total oxidizing reducing valences.²³ The paste was transferred to a furnace preheated at $600^\circ C$, where the material underwent rapid dehydration and combustion, and a voluminous solid was formed with the generation of combustible gases. The solid obtained was again annealed at $1000^\circ C$ for 3 h to increase its crystalline character.

The morphology of the crystals was studied by scanning electron microscope (SEM) using JEOL JSM6300 model operated at 10 kV. Photoluminescence (PL) experiments were performed in backscattering geometry using a He-Cd laser (325 nm) with an optical power of 30 mW for excitation. The emitted light was analyzed by HR-4000 Ocean Optics USB spectrometer optimized for the UV-vis range. For photoluminescence measurements, 0.05 g powder samples were pressed into pellets (10 mm diameter and 1 mm thickness) and then exposed to a 325 nm He-Cd laser. All measurements were carried out at room temperature. The structural characterization was performed by high resolution X-ray diffraction (XRD) using Rigaku Ultima IV diffractometer in the θ - 2θ configuration and using $CuK\alpha$ radiation ($\lambda=1.54184 \text{ \AA}$).

Results and Discussion

X-ray Diffraction Studies

XRD patterns of $BaAl_2O_4:Eu^{3+}(1\%):Gd^{3+}(0, 1, 2, 5, 10\%)$ powder materials at $600^\circ C$ and $1000^\circ C$ are presented in Figs. 1a and 1b, respectively. The XRD patterns correspond to two phases of barium aluminium oxide crystallites. The main phase is hexagonal $BaAl_2O_4$ (JCPDS no. 017-0306), which is found to be retained after doping with Eu^{3+} (1 mol%) and Gd^{3+} (1, 2, 5 and 10 mol%). A small amount of $BaO \cdot 6.6 Al_2O_3$ (JCPDS no. 033-0128) phase is also detected, the amount of which decreases

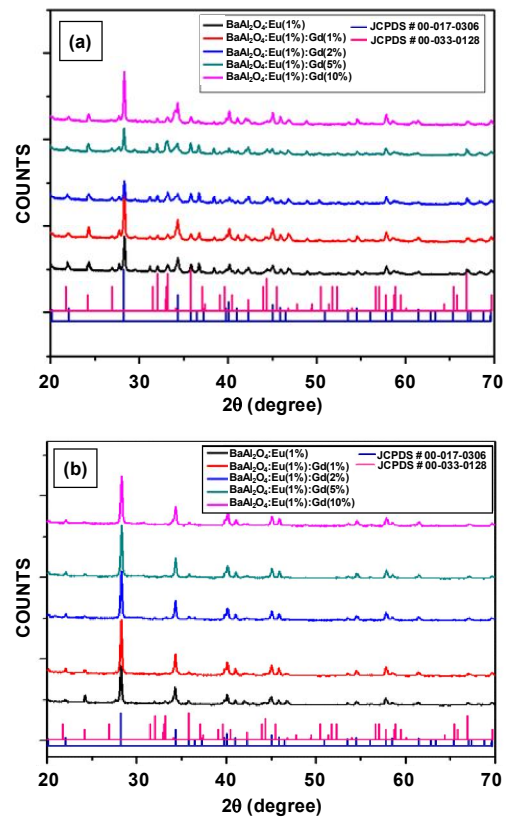


Fig. 1 – XRD patterns of $BaAl_2O_4:Eu^{3+}(1\%):Gd^{3+}(0, 1, 2, 5, 10\%)$ as prepared at (a) $600^\circ C$, (b) $1000^\circ C$

with increasing temperature. The peaks corresponding to hexagonal $BaAl_2O_4$ phase become sharper and larger at $1000^\circ C$. This means that with the increase in temperature, the crystallinity and phase purity increases. The main peaks corresponding to the second phase at $600^\circ C$ appear at 2θ values 22.04° , 24.31° , 26.89° , 31.23° , 32.16° , 31.19° , 32.16° , 46.83° and 49.06° . At $1000^\circ C$ the intensity of these peaks gets decreased and some of the peaks disappear (26.89° , 26.83° , 49.06°). The absence of any cluster phase of Eu_2O_3 or Gd_2O_3 indicates the substitution of all Eu^{3+}/Gd^{3+} ions in $BaAl_2O_4$ lattice.

In the phosphor, divalent barium ions are replaced by trivalent europium or gadolinium ions. Increase in concentration of Gd^{3+} ions from 1 to 10 mol% shows no noticeable effect on the obtained X-ray diffractograms, indicating that the doped ions occupy the primordial Ba^{2+} sites. Evidently, the PL intensity of all the samples at $1000^\circ C$ is more than that at $600^\circ C$, which signifies that the Eu^{3+} and Gd^{3+} are substituted mainly in the $BaAl_2O_4$ phase and not in the second phase.

The crystallite size was calculated by Debye-Scherrer relation using Gaussian fitting for most intense peak at 28.28° (202) in the XRD pattern. The crystallite size for both as prepared and annealed samples is found to be in the 45-55 nm range. Co-doping of Gd^{3+} ions and annealing show no significant effect on crystallite size.

SEM Analysis

The SEM images (Fig. 2) show the morphology of the samples containing particle clusters and flaky aggregates, which is consistent with the combustion derived compounds.²⁴ The flaky aggregates have lots of voids and pores. These voids and pores are formed by escaping gases during the combustion process. The microstructure of the sample reflects the inherent nature of the combustion process. The non-uniform and irregular shapes of the particles can be attributed to the non-uniform distribution of temperature and mass flow in the combustion flame.²⁵

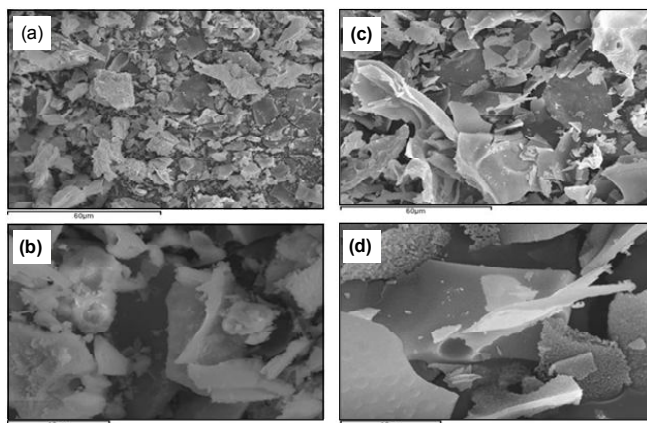


Fig. 2 – SEM images of: (a) & (b) BaAl₂O₄:Eu³⁺(1%):Gd³⁺(1%), (c) & (d) BaAl₂O₄:Eu³⁺(1%):Gd³⁺(5%)

Photoluminescence Properties

The PL spectra of BaAl₂O₄:Eu³⁺(1%):Gd³⁺(0, 1, 2, 5, 10%) materials as prepared at 600° and 1000°C are shown in Figs. 3a and 3b respectively. PL emission spectra of all the prepared compounds show the presence of both valence states of europium (Eu²⁺/Eu³⁺). A high intensity broad band appears around 498 nm with a small shoulder at 442 nm due to Eu²⁺ and very low intensity peaks are observed from 600 to 720 nm, indicating the presence of Eu³⁺. Higher intensity of peak of Eu²⁺ predicts appreciable reduction of Eu³⁺ to Eu²⁺ during preparation of the phosphor material in air. Some conditions are defined in earlier reports,^{10, 11, 26} which should be satisfied for the reduction of Eu³⁺ to Eu²⁺ in compounds prepared in open atmosphere. These conditions are as follows: (i) no oxidizing ion should be present in the host lattice, (ii) the dopant trivalent ion should replace bivalent ion in the crystal lattice, (iii) there should be similarity between the substituted and the dopant cation, (iv) the host compound should have an appropriate structure, composed of tetrahedral anion.

For the present case both Ba²⁺ and Al³⁺ are not oxidizing in nature. As the ionic radii of dopant ion (Eu³⁺ or Eu²⁺) and host lattice ion (Ba²⁺) are similar, Eu³⁺ or Eu²⁺ can substitute Ba²⁺. Also, previous reports have revealed the presence of tetrahedral anion group in these structures.^{10, 27, 28} Thus all required conditions have been

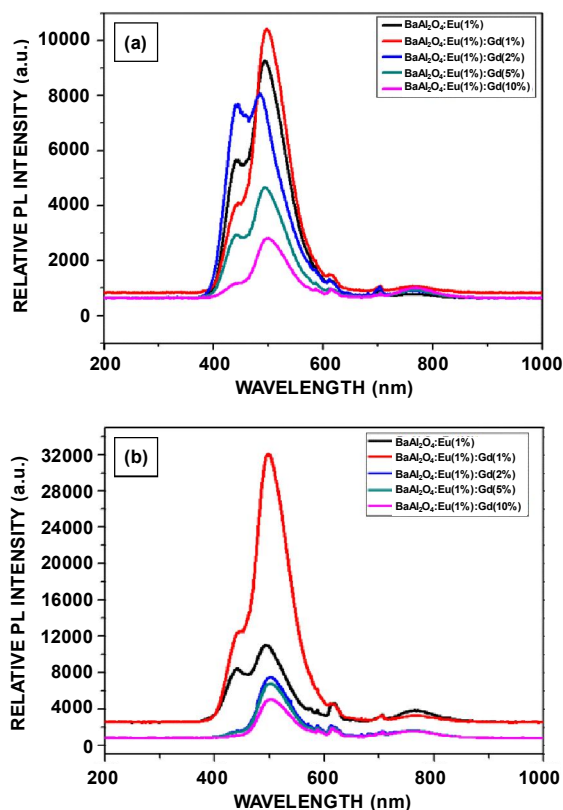
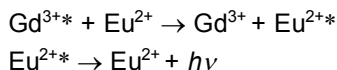


Fig. 3 – PL emission spectra of BaAl₂O₄:Eu³⁺(1%):Gd³⁺(0, 1, 2, 5, 10%) as prepared at (a) 600°C ($\lambda_{exc}=325$ nm), (b) 1000°C ($\lambda_{exc}=325$ nm)

satisfied for the reduction of Eu³⁺ to Eu²⁺ in BaAl₂O₄:Eu compounds.²⁴ The reduction of Eu³⁺→Eu²⁺ may occur due to charge compensation.¹⁶ When trivalent Eu³⁺ ions are doped into BaAl₂O₄, they replace Ba²⁺; three Ba²⁺ should be replaced by two Eu³⁺ to balance the charge. Hence one vacancy defect with two negative charges and two positive defects (Eu_{Ba}) are created. The vacancy defect acts as donor and Eu_{Ba} defect acts as acceptor. Consequently by thermal stimulation, the electron is transferred from vacancy defect to Eu_{Ba} sites and Eu³⁺ gets reduced to Eu²⁺. This mechanism has been reported earlier,¹⁷ in which BaAl₂O₄:Eu compounds were synthesized by solid state reaction.

The broad emission peak at 498 nm is attributed to 4f⁶5d¹→4f⁷ transition of Eu²⁺, which is a dipole allowed transition.^{24, 29} The position of the emission peak does not change noticeably with the addition of Gd³⁺ in BaAl₂O₄ lattice but it affects the intensity of PL emission peak at 498 nm. The intensity increases with the addition of 1 mol% Gd³⁺ ions, but further increase of Gd³⁺ ions (2-10 mol%) decreases the intensity. This decrease in intensity may be due to concentration quenching. With the increase in co-dopant concentration above 1 mol%, the efficient energy transfer process between Gd³⁺ ions increases. This leads to the suppression of energy transfer process from Gd³⁺ to Eu²⁺. In this way energy sinks in the lattice.³⁰ The emission spectra of annealed compounds at 1000°C show the same PL behaviour, however, the intensity of 498 nm band

increases three folds for BaAl₂O₄:Eu³⁺(1%):Gd³⁺(1%) than that for BaAl₂O₄:Eu³⁺(1%). This increase in brightness indicates that the energy absorbed by Gd³⁺ ions can be transferred efficiently to Eu³⁺ due to some energy matching. So Gd³⁺ performs the function of sensitizer. The energy transfer may occur as follows:



The ⁶P_{7/2} level of Gd³⁺ is very close to 4f⁶5d state of Eu²⁺, which results in the energy transfer from Gd³⁺ to Eu²⁺ through non radiative resonance, which can enhance the luminescence of Eu²⁺.³⁰ Some other lattices have also been reported which involve energy transfer from Gd³⁺ to Eu²⁺.^{31, 32} Thus increase in brightness by the addition of Gd³⁺ ion up to 1 mol% is due to the sensitizing action of Gd³⁺. This type of energy transfer between Gd³⁺ and Eu²⁺ has also been reported,³³ which shows the energy transfer through cross-relaxation from Gd³⁺ to Eu²⁺.

The PL peaks due to Eu³⁺ ions in as prepared and annealed compounds are very weak and observed between 600 and 720 nm. These lines are assigned to the transition from ⁵D₀ to ⁷F_J (J = 1, 2, 3, 4). The observed peaks are attributed to ⁵D₀→⁷F₁ (587 nm), ⁵D₀→⁷F₂ (612 nm), ⁵D₀→⁷F₄ (multiplet 682, 695, 707 nm). Generally, the Eu³⁺ spectrum is dominated by ⁵D₀→⁷F₂ transition. It is a hyper sensitive transition, which is highly influenced by the surrounding environment. The dominant peak at 612 nm shows the lower symmetry environment. The Gaussian fitting of the emission curve of BaAl₂O₄:Eu(1%) shows that the emission peak in the blue green region is the combination of a low intensity peak at 434 nm and a high intensity peak at 499 nm (Fig. 4). The low intensity peak appears as a shoulder of the high intensity peak.

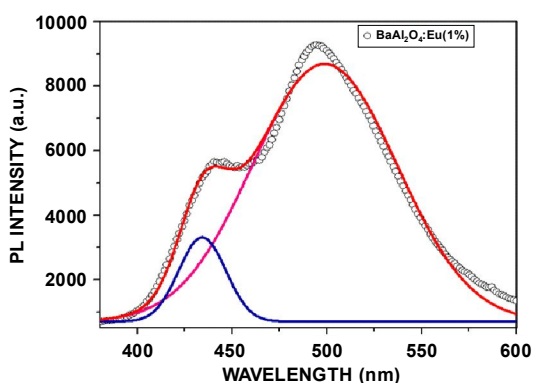


Fig. 4 – Gaussian fitting of PL emission spectra for BaAl₂O₄:Eu³⁺(1%) ($\lambda_{\text{exc}}=325$ nm)

Conclusions

BaAl₂O₄:Eu²⁺/Eu³⁺(1%) compounds co-doped with varying concentrations (1, 2, 5 and 10 mol%) of Gd³⁺ were synthesized by combustion synthesis method. The X-ray diffraction study showed the presence of hexagonal phase

of BaAl₂O₄ and a mixed phase of Ba O! 6.6 Al₂O₃. The mixed phase was diminished on annealing at 1000°C for 3 h. The crystallinity and phase purity of the compounds increased on annealing. On doping with Eu³⁺ and co-doping with Gd³⁺, hexagonal phase of BaAl₂O₄ was retained. SEM images showed particle clusters and flaky aggregates with lots of voids and pores. All the prepared compounds showed the most intense peak around 498 nm due to Eu²⁺. Thus, there was appreciable reduction of Eu³⁺ to Eu²⁺ during preparation of compounds in open air. Intensity of the band at 498 nm was increased on annealing. The annealed compound of BaAl₂O₄:Eu²⁺/Eu³⁺(1%):Gd³⁺(1%) showed three folds increased intensity of this band than that of BaAl₂O₄:Eu²⁺/Eu³⁺(1%). Thus Gd³⁺ acted as a good sensitizer and enhanced the photoluminescence intensity significantly.

Acknowledgements: This work was supported by the Generalitat Valenciana through grant PROMETEUS 2009/2013 and the European Commission through Nano CIS project (FP7-PEOPLE-2010-IRSES ref. 269279).

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