# Synthesis and role of co-dopants (alkaline earth divalents and halides) on the photoluminescence of $Eu^{2+}$ doped $BaAl_2O_4$ phosphor

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## Abstract

Pure and $Eu^{2+}$ doped $BaAl_2O_4$ phosphors have been synthesized by simple solid-state reaction technique. Synthesized $BaAl_2O_4$ samples were studied using powder X-ray diffraction analysis (XRD), Photoluminescence spectroscopy (PL), Fourier Transform - Infra Red Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM). Alkaline earth divalent (Sr, Ca, Zn, Mg) and halides (F, Cl, Br, I) were used as co-dopants to enhance the PL properties of $BaAl_2O_4:Eu^{2+}$ phosphor. Significant impact of ionic radii of co-dopants on PL properties of the phosphor is reported. Copyright © 2019 VBRI Press.

**Keywords:** $BaAl_2O_4$, europium, alkaline earth divalent and halides, photoluminescence.

## Introduction

From twentieth century, inorganic phosphors were showed their extensive applications in many technological functional devices such as fluorescent lamps (FL), plasma display panels (PDP), flat panel display (FPD), light emitting diodes (LED), computed tomography (CT), X-ray intensifiers and radiation protection dosimetry. Various types of inorganic phosphors include borates, aluminates, silicates, nitrides, tungstates, molybdates, sulphides, alkali halides etc. have been synthesized and studied extensively for above mentioned applications [**1-4**]. Aluminates phosphors have proven its outstanding characteristics as an efficient phosphor candidate due to its lower chemical toxicity, higher chemical and moisture stability [**5-7**]. In phosphors, lanthanides always played fascinating role in designing the desirable luminescence properties [**8**]. Lanthanides doped barium aluminate ($BaAl_2O_4$) phosphor was well known phosphor candidate mainly used in various display, lighting and optoelectronic devices [**9**]. Luminescence properties of $BaAl_2O_4$ phosphor doped with different lanthanides (Eu, Ce, Nd, Gd, Sm, Er, Pr and Tb) has been studied by various researchers [**10-11**]. Similarly, the co-doping effect of alkaline earth divalent ions such as Sr, Ca, Zn, Mg on the photoluminescence properties $BaAl_2O_4$:Eu phosphor has been studied in detail [**12-13**]. An earlier study reported that co-doping of Sr and Ca ions significantly enhanced PL intensity of $BaAl_2O_4$:Ce phosphor [**12**]. Similarly, another report showed that the replacement of $Ba^{2+}$ ions with other ions such as $Sr^{2+}$ and $Ca^{2+}$ in $BaAl_2O_4$:Eu phosphor influenced emission properties of $Eu^{2+}$ [**13**]. In addition, effect of boric acid flux in $BaAl_2O_4$:Eu was also reported [**14**]. Boric acid flux played an important role both in emission center and afterglow characteristics of $BaAl_2O_4$:Eu. Present works made an attempt to enhance the photoluminescence of $BaAl_2O_4$: Eu phosphor by co-doping both alkaline earths divalent ions and halide ions. In this work, we report photoluminescence properties of $BaAl_2O_4$:Eu as a function of alkaline earth divalents (Sr, Ca, Zn, Mg) and halides (F, Cl, Br, I) concentrations. To best of our knowledge the role of halides on the photoluminescence of $BaAl_2O_4$:Eu is not reported yet.

## Experimental

### *Phosphor synthesis procedure*

$BaAl_2O_4$:Eu phosphors were synthesized through simple solid state reaction technique. The precursor salts such as $BaCO_3$, $Al_2O_3$, $Eu_2O_3$ were used to synthesis pure $BaAl_2O_4$ host lattice. For co-doping $CaCO_3$, $SrCO_3$ $MgCO_3$, $ZnCO_3$, $NH_4Cl$, $NH_4Br$, $NH_4F$ and $NH_4I$ were used. All precursors are pure A.R. grade (99.99% pure) and so no need for further purification. Stoichiometric ratios of precursors were weighed, mixed and ground thoroughly with an agate mortar for 15 minutes. Ground samples were fired at temperature around at 1000°C for 2h in a weak reductive atmosphere. The reductive atmosphere was used for the purpose of valence reduction of Eu ion. Carbon powder was used to produce the reductive atmosphere. The annealed powder was cooled down to room temperature very slowly. Finally, white coloured $BaAl_2O_4$ phosphor samples were obtained.

### *Phosphor characterizations*

The X-ray instrument Bruker D2 phase analyser using a Cu $K_\alpha$ radiation (k = 0.154059 nm) at 30 kV and 10 mA was used to study the phase formation of the synthesized sample. FT-IR spectrum of $BaAl_2O_4$ samples was recorded using Bruker Alpha FT-IR spectrometer using KBr pellet method. The photoluminescence measurement of all synthesized samples was carried out using JobinYvon-Fluorolog spectrofluorometer equipped with 450W Xenon lamp at room temperature. Surface morphology of the phosphor sample was examined using SEM instrument Carl Zeiss MA15 / EVO 18.

## Results and discussion

### *XRD analysis of synthesized $BaAl_2O_4$samples*

The powder X-ray diffraction pattern of synthesized $BaAl_2O_4$ samples is shown in **Fig. 1**. The obtained XRD pattern compared with standard JCPDS file.

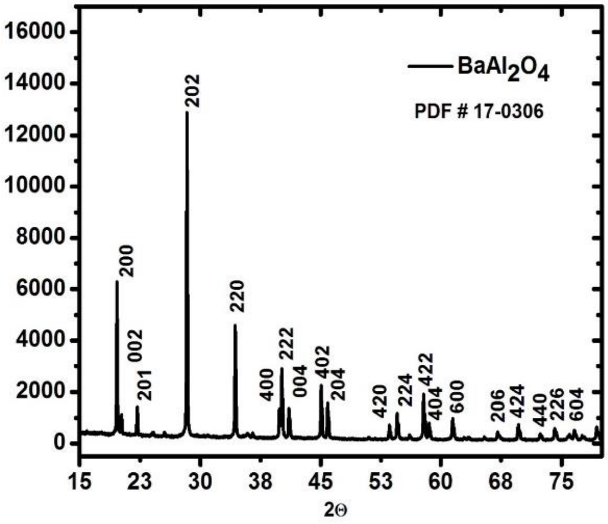

**Fig. 1.** Powder X-Ray diffraction pattern of synthesized $BaAl_2O_4$ host lattice.

All the diffraction peaks of synthesized samples are synchronizing with the standard JCPDS card.no: 17-0306. It dictates that the synthesized $BaAl_2O_4$ belongs to hexagonal crystal system with primitive lattice. It falls under the space group $P6_322$ (182). The lattice parameters of synthesized $BaAl_2O_4$ are a = b = 10.447 and c = 8.794Å. According to the space group $P6_322$ (182), $BaAl_2O_4$ is formed by three-dimensional framework of corner-sharing $AlO_4$ tetrahedra. Each oxygen atom is shared with two aluminium ions so that each tetrahedron has one net negative charge. Charge is balanced by divalent cations in the interstitial sites of tetrahedral framework. Two types of $Ba^{2+}$ sites are available in $BaAl_2O_4$ compound for activators/dopants substitution. The dopants ions are may substitute $Ba^{2+}$ sites via nine co-ordinations (the lattice sites Ba1 (2a) and Ba2 (6c) sites are having $C_3$ and $C_1$ site symmetries respectively) [**5, 12, 15-20**].

### FT-IR analysis

FT-IR spectrum of synthesized $BaAl_2O_4$ is shown in **Fig. 2**. Peaks observed at 632, 809 and 844 $cm^{-1}$ are assigned to bending modes of O – Al – O and symmetric & asymmetric stretching modes of Al – O – Al respectively. Bands around 3447 $cm^{-1}$ and 1635 $cm^{-1}$ are attributed to OH stretching vibration of $H_2O$ molecule in KBr molecule. The additional peaks at 1260, 1746, 2853, 2923, 2959 $cm^{-1}$ may be ascribed to surface absorption of organic molecules presents in the reaction environments during the synthesis of $BaAl_2O_4$ sample [**21-23**].

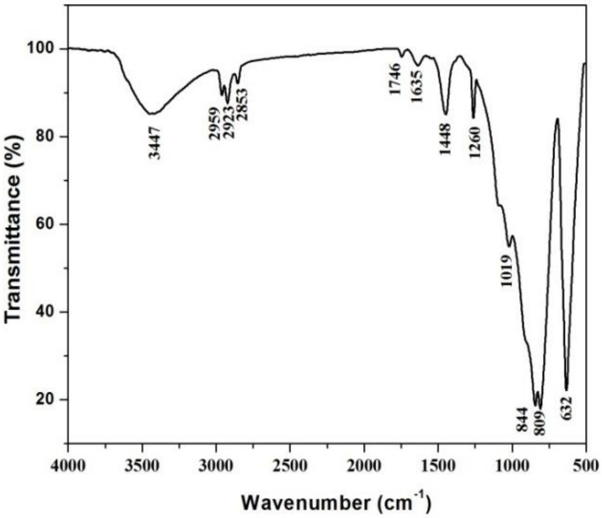

**Fig. 2.** FT-IR spectrum of synthesized $BaAl_2O_4$ samples

### *Photoluminescence (PL) properties of $Eu^{2+}$ doped $BaAl_2O_4$ phosphor*

### *PL excitation and emission*

The representative PL excitation and emission spectra of $Eu^{2+}$ doped $BaAl_2O_4$ phosphor is shown in **Fig. 3**. In the excitation spectrum, the band at 363 nm is attributed to the electronic transition $4f^7 \rightarrow 4f^65d$ of $Eu^{2+}$ ion. By the excitation of 363 nm, the phosphor shows emission band at 499 nm in the green region. This emission band is indexed to the electronic transition $4f^65d \rightarrow 4f^7$ of $Eu^{2+}$ ion. The observed excitation and emission bands are characteristics transition features of $Eu^{2+}$ in $BaAl_2O_4$host lattice [**1-4, 24-26**]. The doped $Eu^{2+}$ ions occupied the $Ba^{2+}$ sites since the coincidence of valence and ionic radii.

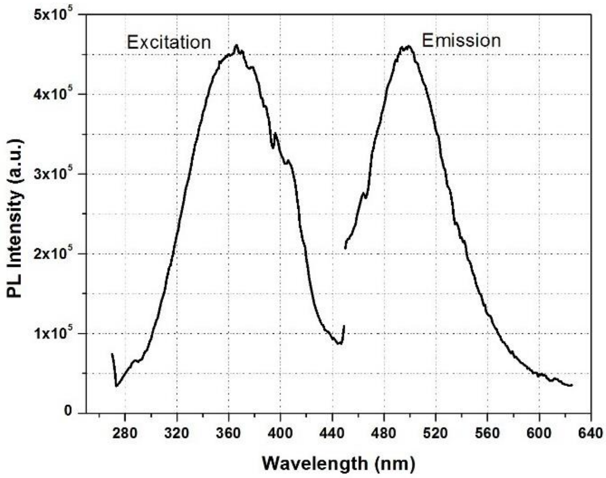

**Fig. 3.** PL excitation and emission spectra of $BaAl_2O_4:Eu^{2+}$phosphor.

### *$Eu^{2+}$ concentration effect*

To study europium concentration effect on PL intensity of the phosphor, europium ion concentration is varied from 1 mol% to 11 mol%. PL intensity is increased up to 8 mol% and afterwards the PL intensity decreased which is shown in **Fig. 4**. The optimal PL intensity is found at 8 mol% of $Eu^{2+}$. The decrease of PL intensity beyond 8 mol% is due to the effect of concentration quenching. It shows that the resonant energy transfer is takes place among the similar or identical $Eu^{2+}$ luminescent centers when increasing the concentration beyond 8 mol%. The excitation energy is dissipated as non-radiative energy from one $Eu^{2+}$ to another $Eu^{2+}$ ion [**1-4, 24**].

### *Role of alkaline earth divalent co-dopants*

Co-doping of alkaline earth divalent cations such as Ca, Sr, Mg and Zn in $BaAl_2O_4:Eu^{2+}$ phosphor could influence the PL properties of the phosphor [**27-28**]. Thus, a series of divalent cations have been utilized to improve the PL intensity of $BaAl_2O_4$:(8mol%)$Eu^{2+}$ phosphor. Co-dopants concentrations are varied from 1 mol% to 6 mol%. Change of PL intensity with respect to co-dopant concentration is shown in **Fig. 5**.

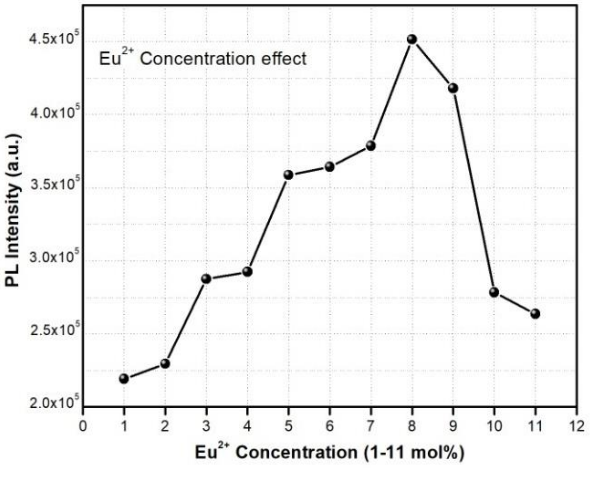

**Fig. 4.** Variation of PL intensity as a function of $Eu^{2+}$ concentration.

The 3 mol % of $Ca^{2+}$ co-doping gives optimal PL intensity when compared to other $Ca^{2+}$ concentrations. The 2 mol % of $Sr^{2+}$ yields highest PL intensity compared to other $Sr^{2+}$ concentrations. In $Mg^{2+}$ co-doping**,** PL intensity starts to decrease from 1 mol % of $Mg^{2+}$ itself. Upto 5 mol % of $Mg^{2+}$ the trend of decrease in PL intensity is observed. Afterwards, slight increase in PL intensity is observed to some extent; however, no significant impact is noticed. In $Zn^{2+}$ co-doped samples optimal PL intensity is found at 3 mol% of $Zn^{2+}$. From the above results, it is well shown that the PL intensity of $BaAl_2O_4:Eu^{2+}$ (8 mol %) phosphor is increased while co-doping the alkali earth divalent metal cations such as Ca, Sr and Mg. These divalent ions have improved the PL intensity of the phosphor appreciably at specific concentrations. At the same moment, the divalent $Zn^{2+}$ suppresses the PL intensity of the phosphor noticeably. Relative PL intensities of divalents co-doped ions and ionic radii of co-dopants are given in **Table 1**. The probable reasons for obtained results are discussed below.

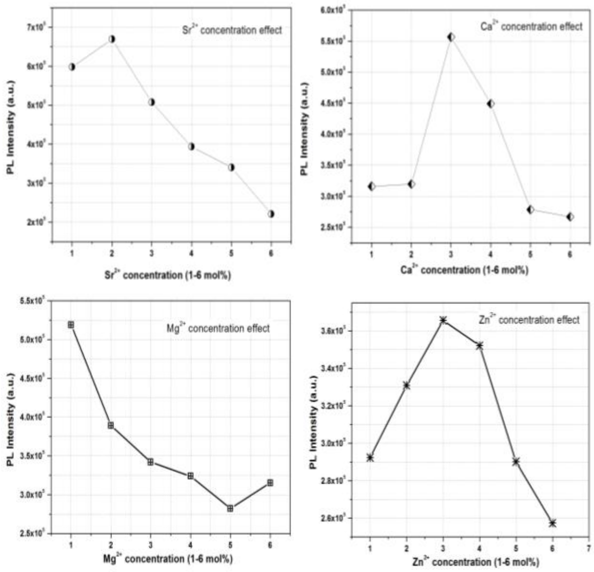

**Fig. 5.** Variation of PL intensity of $BaAl_2O_4:Eu^{2+}$ (8 mol %) phosphor as a function of alkaline earth divalents (Sr, Ca, Mg, Zn) concentration (1-6 mol%).

Change of ionic radii of co-dopants is the crucial basis for observation of change of PL intensity of phosphor when co-doping with different divalent ions. When co-doped divalent ions occupy the $Ba^{2+}$ lattice sites, the electrostatic field exerted by those ions is entirely different from actual field inside the crystal lattice. This field effectively influences the crystal field around the luminescent center i.e., $Eu^{2+}$. Change of crystal field strongly affects the electronic states of luminescent center [**13, 14**]. It results the change in PL intensity of the phosphor. Also, those ions create different lattice stresses inside the lattice. This too influences luminescence properties of the phosphor considerably. Ions such as Ca, Sr and Mg favor to the improvement of PL intensity. Nevertheless, Zn doesn't improve the PL intensity of the phosphor. This may be due to particular characteristic nature of that ion. Among, co-dopants employed, Sr shows highest PL intensity compared to other co-dopants. The order of co-dopants for the improvement of PL intensity of phosphor is given by Sr>Ca>Mg. Data such as relative PL intensities of divalents co-doped ions and ionic radii of co-dopants are given in **Table 1**. It shows that the effective role of ionic radii of co-doped divalent ions on PL intensity of the phosphor. Change in PL intensity of phosphors while co-doping with other ion is reported in earlier reports [**27-30**].

**Table 1.** Relative PL intensities of divalent ions $BaAl_2O_4$:$Eu^{2+}$ (8 mol %) co-doped phosphor and ionic radii of co-dopants.

| Sl. No | Phosphor Sample | Ionic radii of ions (pm) | Relative PL intensity (a.u.) |
|---|---|---|---|
| 1 | $BaAl_2O_4$ :$Eu^{2+}$ (8 mol %) | $Ba^{2+}$ - 149<br>$Eu^{2+}$ - 104 | 1.00 |
| 2 | $BaAl_2O_4$ :$Eu^{2+}$ (8 mol %), $Ca^{2+}$ (3 mol%) | $Ca^{2+}$ - 114 | 1.30 |
| 3 | $BaAl_2O_4$ :$Eu^{2+}$ (8 mol %), $Sr^{2+}$ (2 mol%) | $Sr^{2+}$ - 132 | 1.52 |
| 4 | $BaAl_2O_4$ :$Eu^{2+}$ (8 mol %), $Mg^{2+}$ (1 mol%) | $Mg^{2+}$ - 86 | 1.20 |
| 5 | $BaAl_2O_4$ :$Eu^{2+}$ (8 mol %), $Zn^{2+}$ (3 mol%) | $Zn^{2+}$ - 88 | 0.80 |

### *Role of halides*

A series of halides such as $F^-$, $Cl^-$, $Br^-$ and $I^-$ have been used as co-dopants to improve the PL intensity of the phosphor **(Fig. 6)**.

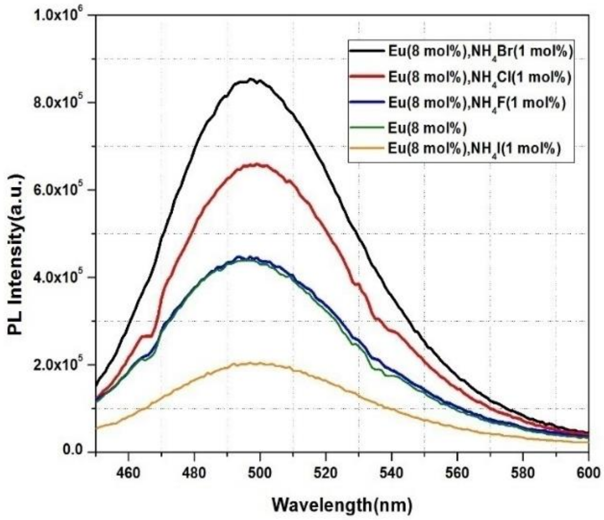

**Fig. 6.** Effect of 1 mol% of halides ($F^-$, $Cl^-$, $Br^-$, $I^-$) on PL intensity of $BaAl_2O_4$:$Eu^{2+}$ (8 mol %) phosphor.

The halide co-dopants concentration was fixed as 1 mol%. Among halides, $Br^-$ has greater influence on PL intensity of the phosphor. Next to $Br^-$, the $Cl^-$ and $F^-$ have better influence on PL intensity of the phosphor. Higher the ionic radii of halides generate more stresses on the $BaAl_2O_4$ host lattice. Induced lattice stresses and crystal field has significant impact on oscillator strength of the luminescent center [**13**, **14**]. As a consequence of change of oscillator strength, PL intensity of the phosphor improved significantly. But at the same moment, $I^-$ shows a reverse trend in PL intensity. PL intensity decreased in $I^-$ co-doped $BaAl_2O_4$:$Eu^{2+}$ (8 mol %) phosphor. It may be due to the larger variation of ionic radii of $I^-$. Relative PL intensity values of halides co-doped $BaAl_2O_4$:$Eu^{2+}$ (8 mol %) phosphors are given in the **Table 2**.

**Table 2.** Relative PL intensities of fluxes co-doped phosphor and ionic radii of halide ions.

| Sl. No | Phosphor Sample | Ionic radii of ions (pm) | Relative PL intensity (a.u.) |
|---|---|---|---|
| 1 | $BaAl_2O_4$ :$Eu^{2+}$ (8 mol %) | $Ba^{2+}$ - 149<br>$Eu^{2+}$ - 104 | 1.00 |
| 2 | $BaAl_2O_4$ :$Eu^{2+}$ (8 mol %), $NH_4Br$ (1 mol%) | $Br^-$ - 182 | 1.90 |
| 3 | $BaAl_2O_4$ :$Eu^{2+}$ (8 mol %), $NH_4Cl$ (1 mol%) | $Cl^-$ - 167 | 1.50 |
| 4 | $BaAl_2O_4$ :$Eu^{2+}$ (8 mol %), $NH_4F$ (1 mol%) | $F^-$ - 119 | 1.10 |
| 5 | $BaAl_2O_4$ :$Eu^{2+}$ (8 mol %), $NH_4I$ (1 mol%) | $I^-$206 | 0.45 |

### Morphology analysis

Morphology and grain sizes of $BaAl_2O_4$:$Eu^{2+}$(8 mol %), NH4Br (1 mol%) phosphor is shown in **Fig. 7**. Different magnified images show that the morphology of phosphor appears as flakes like structure. These flakes are having irregular dimensions in the range 2 – 5 µm. The phosphor grains are highly agglomerated due to surface reactivity.

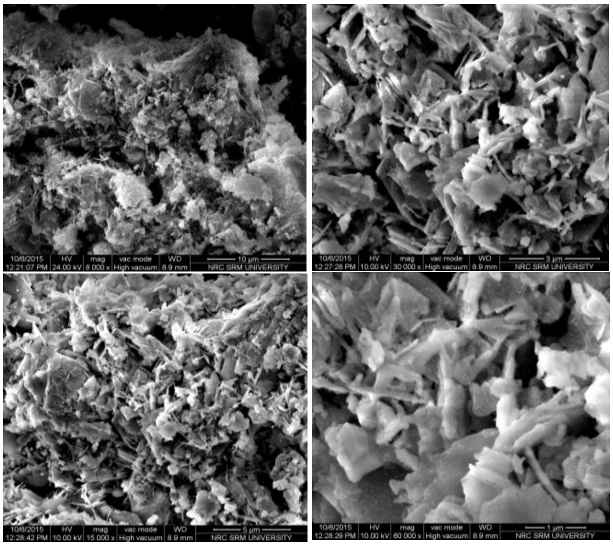

**Fig. 7.** SEM images of $BaAl_2O_4$:$Eu^{2+}$ (8 mol %), $NH_4Br$ (1 mol%) phosphor.

## Conclusion

Pure and $Eu^{2+}$ doped $BaAl_2O_4$ phosphor were synthesized using simple solid-state reaction at 1000 ºC for 2 hours. No additional processes were carried out during phosphor synthesis. PL excitation of the phosphor was found at 363 nm in the near UV region and the intense bluish-green emission observed at 499 nm. Optimal PL intensity was obtained at 8 mol% of $Eu^{2+}$. Further, PL intensity of the phosphor was enhanced by co-doping alkaline earth divalents and halides. $Sr^{2+}$ in alkaline earth divalents and $Br^-$ in halides were increased the PL intensity appreciably. From the results, it is found that ionic radii of co-dopants played a significant role in tuning the PL properties of $BaAl_2O_4$:$Eu^{2+}$. Finally, it is concluded that the studied phosphor may find potential application in modern optical devices.

### Acknowledgements

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