d-f luminescence of Ce$^{3+}$ and Eu$^{2+}$ ions in BaAl$_2$O$_4$, SrAl$_2$O$_4$ and CaAl$_2$O$_4$ phosphors

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d–f luminescence of Ce$^{3+}$ and Eu$^{2+}$ ions in BaAl$_2$O$_4$, SrAl$_2$O$_4$ and CaAl$_2$O$_4$ phosphors

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Abstract: Ce$^{3+}$ and Eu$^{2+}$ doped alkaline earth aluminates MAI$_2$O$_4$ (M = Ca, Sr, Ba) were prepared by single-step combustion synthesis at low temperature (600 °C). X-ray diffraction (XRD) analysis confirmed the formation of BaAl$_2$O$_4$, CaAl$_2$O$_4$, and SrAl$_2$O$_4$. Photoluminescence spectra and optimal luminescent properties of Ce$^{3+}$ and Eu$^{2+}$ doped MAI$_2$O$_4$ phosphors were studied. Relation between Eu$^{2+}$ and Ce$^{3+}$ f–d transitions was explained. Spectroscopic properties known for Ce$^{3+}$ were used to predict those of Eu$^{2+}$ by using Dorenbos’ method. The values thus calculated were in excellent agreement with the experimental results. The preferential substitution of Ce$^{3+}$ and Eu$^{2+}$ at different Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$ crystallographic sites was discussed. The dependence of emission wavelengths of Ce$^{3+}$ and Eu$^{2+}$ on local symmetry of different crystallographic sites was also studied by using Van Uitert’s empirical relation. Experimental results matched excellently with the predictions of Dorenbos’ and Van Uitert’s models.

Keywords: Ce$^{3+}$; Eu$^{2+}$; photoluminescence; X-ray diffraction (XRD); crystal structure

1 Introduction

Sulfide-based phosphors have been used for flat panel displays, cathode ray tubes, and fluorescent lamps. But at high current density, sulfide-based phosphor components degrade rapidly, while oxide-based phosphors doped with rare earth ions are thermally and chemically more stable. They also have good heat resistance in display applications. Hence, recently there is growing interest in oxide-based phosphors.

Aluminate-based phosphors doped with Ce$^{3+}$ have received remarkable attention owing to their wide applications in flat panel displays, X-ray imaging, and tri-colour lamps [1]. Ce$^{3+}$ doped phosphors are used for fast scintillators and also as long lasting phosphorescent materials. Jia and co-workers [2] reported luminescence in BaAl$_2$O$_4$:Ce$^{3+}$ and BaAl$_2$O$_4$:Ce$^{3+}$,Dy$^{3+}$. The photoluminescence in BaAl$_2$O$_4$:Mn$^{2+}$,Ce$^{3+}$ was reported by Suriyamurthy and Panigrahi [3]. In recent, all kinds of lamps and display devices are being replaced by light emitting diodes (LEDs). The first commercial white LEDs have been produced by the combination of blue LED with cerium doped yttrium aluminum garnet (YAG:Ce) phosphor. Divalent europium doped oxide-based phosphors are highly useful owing to their high brightness, tunable emission wavelength from UV to red, low toxicity, and increased chemical and thermal stability. Therefore,
these phosphors are important for industrial and technological applications in fluorescent lamps, LEDs, and emissive displays for computers and mobile telephones [4,5]. The phosphorescence of Eu\(^{2+}\) in most hosts is caused by the 4f→5d transition [6,7]. BaAl\(_2\)O\(_4\):Eu\(^{2+},\)Dy\(^{3+}\) [8] and BaAl\(_2\)O\(_4\):Eu\(^{2+},\)Nd\(^{3+}\) [9] also exhibit long lasting phosphorescence (LLP) properties. Eu\(^{2+}\) doped BaAl\(_2\)O\(_4\) and SrAl\(_2\)O\(_4\) could be promising phosphor materials for plasma display panel (PDP) application [10,11]. SrAl\(_2\)O\(_4\) is one of the foremost promising host materials for fluorescent lamp, light emitting diodes, and persistent luminescent materials [12–16]. The effects of various doping compositions and impurities on the phosphorescence of green-emitting alkaline earth aluminate phosphor (SrAl\(_2\)O\(_4\):Eu\(^{2+}\),Dy\(^{3+}\)) have been reported by Kim et al. [17]. CaAl\(_2\)O\(_4\):Eu\(^{2+}\) is the most important blue phosphor material among the phosphor group which is useful in LLP devices.

Synthesis technique highly affects the quality of luminescent material. Use of conventional processes like solid-state reaction and sol–gel method for synthesis of phosphorescence materials involves unavoidable problems such as extremely high temperature and quite long reaction time at high temperature [18]. In comparison, combustion method is relatively simple. Moreover, there are many merits of the combustion synthesis. It is energy-saving and safe. It gets completed only in few minutes (5 min). This synthesis technique avoids steps such as washing, filtration, drying, etc. It has been extensively used to prepare various oxide materials at a relatively low temperature. Therefore, combustion method is a promising technique for synthesis of complex oxide ceramics such as aluminates.

In this study, we have prepared Ce\(^{3+}\) and Eu\(^{2+}\) doped BaAl\(_2\)O\(_4\), SrAl\(_2\)O\(_4\), CaAl\(_2\)O\(_4\) phosphors using single-step combustion synthesis at an initiating temperature of 600 °C with urea as a fuel. The prepared samples were characterized using X-ray diffraction (XRD), photoluminescence (PL) spectroscopy, and scanning electron microscopy (SEM). In this paper, we have reported the concentration quenching behavior of Ce\(^{3+}\) and Eu\(^{2+}\) luminescence in these hosts. Systematic relationship between emission wavelengths of Ce\(^{3+}\) and Eu\(^{2+}\) ions at the same crystallographic site was studied. The spectroscopic properties, crystal field splitting, centroid shift, red shift, and Stokes shift were estimated. Spectroscopic properties known for Ce\(^{3+}\) were used to predict those of Eu\(^{2+}\) by using Dorenbos’ formula [19]. Experimental results matched with the theoretical predictions. The preferential substitution of Ce\(^{3+}\) and Eu\(^{2+}\) ions at different Ba\(^{2+}\), Sr\(^{2+}\), Ca\(^{2+}\) crystallographic sites was explained by using Van Uitert’s empirical relation [20]. The dependence of emission wavelengths of Ce\(^{3+}\) and Eu\(^{2+}\) on the local symmetry of crystallographic site was studied.

### 2 Experimental

The samples were prepared by mixing nitrates of barium (Ba(NO\(_3\))\(_2\)), strontium (Sr(NO\(_3\))\(_2\)), or calcium (Ca(NO\(_3\))\(_2\)) and aluminum (Al(NO\(_3\))\(_3\)·9H\(_2\)O), with cerium nitrate or europium nitrate, and urea (CO(NH\(_2\))\(_2\)) in stoichiometric ratio using a mortar and pestle. The resulting paste for each mixture was then heated in a muffle furnace at an initiating combustion temperature of 600 °C. The paste underwent dehydration and finally decomposed with the evolution of gases (oxides of nitrogen and ammonia). The mixture frothed and swelled, forming the foam that ruptured with a flame. The entire combustion process was completed in less than 5 min. The voluminous combustion ashes of combustion synthesized phosphors were ground using the pestle and mortar to make fine white powders.

Reducing atmosphere was needed for Eu\(^{3+}\). Eu doped sample as described above was taken in alumina crucible and placed in closed stainless still box filled with charcoal. The box was heated at 800 °C for 1.30 h. Incomplete burning of charcoal provided reducing atmosphere. To avoid the contamination from burning charcoal, the crucible was covered by piece of ceramic fiber blanket followed by alumina lid. This method is low cost and simple. Various concentrations of Eu\(^{2+}\) (0.05%–3%) and Ce\(^{3+}\) (0.02%–2%) dopants were tried. The fine powders were characterized further. XRD measurements were performed using Philips PANalytical X’pert Pro diffractometer. XRD pattern of reduced sample was not different from that of the sample without reduction. PL measurements in the spectral range of 220–700 nm were made on Hitachi F-4000 spectro-fluorimeter at room temperature. The morphology was studied using EVO 18 scanning electron microscope with an accelerating voltage of 20 kV and working distance of 8.5 mm.

Formation of oxides by the combustion process is represented by following equations:

\[
6\text{Al(NO}_3\text{)}_3 + 3\text{Ba(NO}_3\text{)}_2 + 20\text{NH}_2\text{CONH}_2 \rightarrow 3\text{BaAl}_2\text{O}_4 + 20\text{CO}_2 + 32\text{N}_2 + 40\text{H}_2\text{O} \\
6\text{Al(NO}_3\text{)}_3 + 3\text{Sr(NO}_3\text{)}_2 + 20\text{NH}_2\text{CONH}_2 \rightarrow 3\text{SrAl}_2\text{O}_4 + 20\text{CO}_2 + 32\text{N}_2 + 40\text{H}_2\text{O}
\]
6Al(NO₃)₃ + 3Ca(NO₃)₂ + 20NH₂CONH₂ → 3CaAl₂O₄ + 20CO₂ + 32N₂ + 40H₂O

3 Results and discussion

3.1 X-ray diffraction

The phase formation of samples was checked by XRD. Figures 1–3 show the XRD patterns of BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄. All the observed peaks match excellently with ICDD data file Nos. 73-0202, 74-0794, and 88-2477 respectively, indicating that the high-purity and crystalline samples were obtained in this work. The extra lines in XRD pattern of BaAl₂O₄ are due to unreacted constituents. The doping of Eu²⁺ and Ce³⁺ does not make any noticeable variation of the XRD patterns. The prominent peaks are observed in the diffractograms at around 2θ values of 28.25°, 28.38°, and 29.57° corresponding to (102), (211), and (212) planes for these hosts respectively.

XRD data reveal that BaAl₂O₄ possesses hexagonal structure with space group $P\overline{6}32$ (182) and its lattice parameters are $a = 5.227$ Å and $c = 8.802$ Å. It is also confirmed that SrAl₂O₄ possesses monoclinic structure with space group $P2\overline{1}(4)$ and its lattice parameters are $a = 8.447$ Å, $b = 8.816$ Å, and $c = 5.163$ Å. Compound CaAl₂O₄ possesses monoclinic structure with space group $P2_1/c(14)$ and its lattice parameters are $a = 7.95$ Å, $b = 8.62$ Å, and $c = 10.25$ Å. The results are summarized in Table 1.

3.2 Scanning electron microscopy

Surface morphology of prepared powders was analyzed using SEM. Figure 4 represents the SEM micrographs of the host without any doping. In all three samples, particles tend to agglomerate forming small clusters with non-uniform shapes and sizes. The morphologies of the phosphors are irregular with diameter varying from two to several microns. In addition, there are plate-like structures having cracks and pores. A large number of pores are formed in the combustion derived powders due to large quantity of escaping gases. The plate-like morphology has an advantage in light out-coupling. The irregularity in shapes, sizes, and porosity is due to irregular mass flow during combustion and non-uniform distribution of temperature. Finally, the aluminates derived from the combustion process reflect inherent foamy nature.

| Structure type | BaAl₂O₄ | SrAl₂O₄ | CaAl₂O₄ |
|----------------|---------|---------|---------|
| Space group    | Hexagonal | Monoclinic | Monoclinic |
| ICDD file No.  | 73-0202 | 74-0794 | 88-2477 |
| $a$ (Å)        | 5.227   | 8.447   | 7.95    |
| $b$ (Å)        | 8.816   | 5.163   | 8.62    |
| $c$ (Å)        | 8.802   | 10.25   | 10.25   |
| Number of sites of M²⁺ | 2       | 2       | 3       |
| Coordination of M²⁺ with oxygen | Each with 9-coordination | Each with 9-coordination | One with 9-coordination and other two with 6-coordination |
3.3 Crystal structure of MAl_{2}O_{4} (M = Ca, Sr, Ba)

The compounds MAI_{2}O_{4} (M = Ca, Sr, Ba) belong to the family of stuffed tridymite structure [21]. The structure has corner-sharing AlO_{4} tetrahedron in three-dimensional framework. Each tetrahedron has one net negative charge as each oxygen atom in the tetrahedron is shared with two aluminum atoms. Divalent cations Ba^{2+}, Ca^{2+}, Sr^{2+} occupy interstitial sites within the tetrahedral framework and achieve the charge balance. The tetrahedral framework is isostructural within the tridymite structure [22]. SrAl_{2}O_{4} undergoes a phase transition from a low temperature monoclinic distorted structure to the hexagonal tridymite structure at 650 °C [23]. CaAl_{2}O_{4} has a stuffed tridymite structure but transforms to at least three other polymorphs at high pressure [24].

Figure 5 shows three-dimensional sketch of hexagonal BaAl_{2}O_{4} crystal structure showing two Ba^{2+} sites in the BaAl_{2}O_{4} structure, each with 9-fold coordination [25]. According to the crystal structure, the first Ba^{2+} site (2a) has the multiplicity of two and site symmetry of C3 while the second one (6c) has the multiplicity of six and site symmetry of C1. The sites are similar in average size (d(Ba–O)_{ave} = 2.9162 Å). Ionic radius of 9-coordinated Ba^{2+} is 1.47 Å [26].

The SrAl_{2}O_{4} host crystallizes in the stuffed tridymite type of structure. SrAl_{2}O_{4} belongs to monoclinic structure with space group P2_{1}(4). The three-dimensional network consists of corner-sharing AlO_{4} tetrahedron containing large voids, in which the Sr^{2+} ions locate on two types of 9-fold coordinated sites which differ only due to slight distortion of their square planes [27] (Fig. 6). Average distances of these 9 oxygen ions are 2.8776 and 2.8359 Å for Sr1 and Sr2 respectively. Ionic radius of 9-coordinated Sr^{2+} is 1.31 Å [26].

CaAl_{2}O_{4} possesses monoclinic structure with space group P2_{1}/c(14). In this phosphor, Ca^{2+} ions occupy three different lattice sites Ca1, Ca2, and Ca3 [28]. Figure 7 shows unit cell of monoclinic CaAl_{2}O_{4} and polyhedral structures of different sites of Ca^{2+}. Sites
Ca1 and Ca2 have the disordered octahedral geometry and site Ca3 forms the tri-capped trigonal anti-prism polyhedron. Sites Ca1 and Ca2 have coordination six and site Ca3 nine [28]. Ionic radius of 9-coordinated Ca2+ and Ce3+ are 1.18 and 1.196 Å respectively.

Distance of each neighboring oxygen anion from the alkaline earth ion at the different sites along with the calculated distances using the formula given by Dorenbos [19] are shown in Table 2 and discussed in the next section.

3.4 Ce3+ luminescence

Figures 8–10 display the excitation and emission spectra of various concentrations of Ce3+ doped BaAl2O4, SrAl2O4, and CaAl2O4 respectively. In BaAl2O4:Ce3+, the excitation band locates in the UV region ranging from 220 to 350 nm with maxima at 246, 292, and 308 nm. On the other hand, the emission spectrum is broad with maximum at 386 nm. In the case of SrAl2O4:Ce3+, the excitation bands range from 250 to 350 nm with two maxima at 266 and 331 nm. The emission peak is observed at 371 nm. For CaAl2O4:Ce3+ sample, the excitation band has two maxima at 247 and 300 nm. The emission band has maximum at 370 nm. In order to obtain optimal luminescent properties, series of these phosphors were synthesized. The concentration quenching occurs when

### Table 2 Distances of neighboring oxygen anions in the different sites of Ba2+, Sr2+, and Ca2+ (Unit: Å)

| Site | Ba1 | Sr1 | Sr2 | Ca1 | Ca2 | Ca3 |
|------|-----|-----|-----|-----|-----|-----|
| CN  | 9   | 9   | 9   | 6   | 6   | 9   |
| O2 = 2.866 | O4 = 2.559 | O8 = 2.990 | O3 = 2.310 | O10 = 2.293 | O7 = 2.805 |
| O1 = 3.016 | O2 = 2.676 | O5 = 2.508 | O1 = 2.399 | O2 = 2.335 | O11 = 2.353 |
| O2 = 2.866 | O7 = 2.732 | O8 = 2.535 | O4 = 2.445 | O1 = 2.601 | O12 = 2.402 |
| O2 = 2.866 | O1 = 2.667 | O6 = 2.556 | O9 = 2.357 | O4 = 2.726 | O8 = 2.903 |
| O2 = 2.866 | O7 = 2.572 | O5 = 3.281 | O6 = 2.350 | O7 = 2.333 | O8 = 2.393 |
| O1 = 3.016 | O3 = 3.522 | O8 = 3.570 | O5 = 2.680 | O5 = 2.337 | O9 = 3.091 |
| O2 = 2.866 | O3 = 2.520 | O4 = 2.609 | O12 = 2.892 | O12 = 2.402 | O11 = 3.040 |
| O2 = 2.866 | O5 = 3.534 | O2 = 2.697 | O2 = 3.175 | O1 = 2.772 | O2 = 3.175 |
| O1 = 3.016 | O6 = 3.113 | O1 = 2.772 | O2 = 3.175 | O2 = 3.175 | O2 = 3.175 |

CN: coordination number; \( R_{av} \): average distance; \( \Delta R \): difference in ionic radius between the replaced and replacing ion; \( r(A) \): measure of the effective distance after correction for lattice relaxation by introduction of Ce3+; \( R_{ca} \): radius of metal cation (Ba2+, Sr2+, and Ca2+).

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Ce³⁺ is doped above 0.2%, 0.2%, and 0.05% in BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄, respectively. The ground state (4f⁰ configuration) of Ce³⁺ ion splits due to spin orbit coupling into two states namely 2F⁵/₂ and 2F⁷/₂ with separation of nearly 2000 cm⁻¹. The excited state (5d configuration) of Ce³⁺ ion is split into two to five components due to crystal field effect. The excitation bands in these hosts are due to the transition from typical 4f⁰ state to crystal field split 4f⁰5d¹ state of Ce³⁺. The emission of these phosphors is due to transitions from the lowest crystal field split components of the ²D state to the ²F⁵/₁₂ and ²F⁷/₁₂ levels of ground state. The transition in both the cases is fully allowed, as 5d→4f transition is parity allowed. The 5d level of free Ce³⁺ ion is at 6.35 eV above the 4f ground state. The luminescence is very strongly dependent on the host lattice. It varies from UV to the visible region.

The differences in the photoluminescence spectra of these samples are discussed in terms of effect of crystal structures on Ce³⁺ energy levels. From the emission spectra of different compounds, Dorenbos [19,29,30] derived the semi-empirical relation for predicting PL spectra of Ce³⁺. He used the terms $\varepsilon_{\text{CFS}}$, which is defined as the crystal field splitting (CFS) that is the energy difference between the maxima of the highest and lowest 5d band in the spectra, and $\varepsilon_C$, which is defined as the centroid shift that is the shift of the average of the 5d configuration [19]. $D(n⁺)$ is the red shift of the lowest 5d excitation level as compared to that of free $n$-valent ion. $\Delta S$ is the Stokes shift between excitation ($E_{\text{abs}}$) and emission ($E_{\text{em}}$) bands.

The relation between the red shift $D(3⁺)$ with crystalline environment is as follows [31,32]:

$$D(3⁺) = \varepsilon_C + \frac{C_{\text{CS}}}{r(A)} - 0.234 \text{eV} \quad (4)$$

where

$$r(A) = R_{av} - \Delta R / 2 \quad (5)$$

$R_{av}$ is the average distance from ion to ligand and $\Delta R$ is the correction for lattice relaxation when dopant enters the sites. The Stokes shift can be calculated as

$$\Delta S(3⁺) = E_{\text{abs}} - E_{\text{em}} \quad (6)$$

Above equations are used for Ce³⁺ doped 9-coordinated Ba³⁺, Sr²⁺, and Ca²⁺ sites in these phosphors. All the evaluated data are listed in Table 3.

In the next section, these spectroscopic properties are used to predict those of divalent lanthanide Eu²⁺ in the same host at the same site.

### 3.5 Prediction of Eu²⁺ levels from Ce³⁺

Dorenbos [32] established the relation between red shift ($D$) and Stokes shift ($\Delta S$) of divalent and trivalent lanthanides as

$$D(2⁺) = 0.64 \times D(3⁺) - 0.233 \text{eV} \quad (7)$$
Table 3  Spectroscopic properties of Ce$^{3+}$ and Eu$^{2+}$ in BaAl$_2$O$_4$, SrAl$_2$O$_4$, and CaAl$_2$O$_4$

|                  | BaAl$_2$O$_4$   | SrAl$_2$O$_4$   | CaAl$_2$O$_4$   |
|------------------|-----------------|-----------------|-----------------|
|                  | (eV) (cm$^{-1}$) | (eV) (cm$^{-1}$) | (eV) (cm$^{-1}$) |
| Experimental Ce$^{3+}$ |                 |                 |                 |
| X1               | 4.036 32467     | 3.755 30206     | 4.143 33333     |
| X2               | 5.053 40651     | 4.673 37590     | 5.033 40486     |
| M1               | 3.220 25902     | 3.350 26953     | 3.359 27027     |
| Calculated Ce$^{3+}$ | 1.917 8181     | 0.9177 7382     | 0.8891 7152     |
| $\varepsilon_C$  | 1.805 14521     | 2.135 17178     | 1.761 14170     |
| $D$              | 1.937 15583     | 2.232 17960     | 1.848 14871     |
| $\Delta S$       | 0.8156 6560     | 0.4049 3293     | 0.784 6306      |
| Estimated Eu$^{2+}$ from Ce$^{3+}$ |             |                 |                 |
| M1               | 2.620 21075 (474 nm) | 2.758 22169 (451 nm) | 2.774 22314 (448 nm) |
| Experimental Eu$^{2+}$ |             |                 |                 |
| M1               | 2.560 20593 (485 nm) | 2.496 20110 (498 nm) | 2.825 22725 (440 nm) |

X1 and X2 are the first and second excitation maxima. M1 is the first emission maximum.

$\Delta S(2+) = 0.61 \times \Delta S(3+)$  \hspace{1cm} (8)

The energy difference between the lowest 4f$^7$ ($^8$S$_{7/2}$) level and the first 4f$^6$ ($^7$F$_0$)5d$^1$ level is lowered from the free electron value when the Eu$^{2+}$ ion is brought into a crystal environment. The effect of the host crystal on this energy difference is expressed by the red shift $D$ and the Stokes shift $\Delta S$. The energy of f$\rightarrow$d absorption and that of the d$\rightarrow$f emission can be written respectively, as [33]:

\[
E^{\text{abs}} = E^{\text{free}} - D \\
E^{\text{em}} = E^{\text{free}} - D - \Delta S
\]  \hspace{1cm} (9, 10)

The free ion value of Eu$^{2+}$ is $E^{\text{free}} = 4.2$ eV [34]. We determined red shift (Eq. (7)) and Stokes shift (Eq. (8)) of divalent lanthanide (Eu$^{2+}$) using the free ion value of Eu$^{2+}$, red shift and Stokes shift of trivalent lanthanide (Ce$^{3+}$) (Table 3). Using the data from Eqs. (7) and (8) in Eq. (10), we calculated emission energy in europium doped BaAl$_2$O$_4$, SrAl$_2$O$_4$, and CaAl$_2$O$_4$. Emission bands are obtained at 474, 451, and 448 nm respectively for 9-coordinated site. We notice that the calculated values of emission energies are in good agreement with experimental emission spectrum (485, 498, and 440 nm, respectively for BaAl$_2$O$_4$, SrAl$_2$O$_4$, and CaAl$_2$O$_4$) as shown in Figs. 11–13. This confirms that the Ce$^{3+}$ and Eu$^{2+}$ preferentially occupy 9-coordinated Ba$^{2+}$, Sr$^{2+}$, and Ca$^{2+}$ sites.

### 3.6 Eu$^{2+}$ Luminescence

Figures 11–13 show excitation and emission spectra of phosphors BaAl$_2$O$_4$/SrAl$_2$O$_4$/CaAl$_2$O$_4$ doped with Eu$^{2+}$. Figure 11(a) illustrates the excitation spectrum of BaAl$_2$O$_4$:Eu$^{2+}$, which consists of three peaks at 270, 328, and 397 nm. The intensity of 328 nm peak is 5 times greater than that of 270 nm peak. It is the strongest excitation peak in BaAl$_2$O$_4$:Eu$^{2+}$. The excitation spectrum is ascribed to 4f$^6$$\rightarrow$4f$^5$5d transition of Eu$^{2+}$. The emission spectrum is the same for different excitation wavelengths centered at 270, 328, and 397 nm. This shows that emission spectrum does not depend on the excitation wavelengths. The emission spectrum has two well resolved peaks at 485

Fig. 11 PL spectra for Eu$^{2+}$ activated BaAl$_2$O$_4$: (a) excitation spectrum for 485 nm emission of BaAl$_2$O$_4$; (b) emission spectra for 328 nm excitation of BaAl$_2$O$_4$.

Fig. 12 PL spectra for Eu$^{2+}$ activated SrAl$_2$O$_4$: (a) excitation spectrum for 498 nm emission of SrAl$_2$O$_4$; (b) emission spectra for 350 nm excitation of SrAl$_2$O$_4$. 

![Image](image-url)
and 433 nm, which confirms the presence of two Ba$^{2+}$ crystallographic sites in BaAl$_2$O$_4$. The emission spectrum has maximum centered at 485 nm, showing blue luminescence. The emission spectrum is due to $4f^65d\rightarrow4f^7$ transition of Eu$^{2+}$. The PL spectra are in good agreement with the results reported in the literature [11,35,36].

The excitation spectrum of SrAl$_2$O$_4$:Eu$^{2+}$ is broader consisting of two peaks at 230 and 350 nm. The bluish green emission has maximum at 498 nm which is in good agreement with measurement of Palilla et al. [11] who found the band at 500 nm. Excitation spectrum of CaAl$_2$O$_4$:Eu$^{2+}$ shows two peaks at 275 and 329 nm. It shows blue luminescence having peak at 440 nm. This is exactly the same as that reported by Palilla et al. [11] and close to the result of Kim et al. [37]. Observation of single emission band in CaAl$_2$O$_4$ and SrAl$_2$O$_4$ indicates emission from one site only. This seems to be in contrast to the crystallographic data [38,39], that there are three Ca$^{2+}$ and two Sr$^{2+}$ sites of very low symmetry, respectively. In order to obtain optimal luminescent properties of Eu$^{3+}$ doped BaAl$_2$O$_4$, SrAl$_2$O$_4$, and CaAl$_2$O$_4$, a series of these phosphors were synthesized. The concentration quenching occurs when Eu$^{2+}$ is doped above 2%, 1%, and 2% in these hosts respectively.

The maximum acceptable percentage difference ($D_r$) in ionic radii between doped and substituted ions must not exceed 30% [40,41]. The calculations of the radius percentage difference ($D_r$) between the doped ions (Ce$^{3+}$, Eu$^{2+}$) and the possible substituted ions (Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$, Al$^{3+}$) are summarized in Table 4. The values are based on the formula, $D_r = \frac{R_d(CN) - R_s(CN)}{R_M(CN)}$, where CN is the coordination number, $R_M$(CN) is the radius of host cation, and $R_d$(CN) is the radius of doped ion. The value of $D_r$ between Ce$^{3+}$ and Ba$^{2+}$, Eu$^{2+}$ and Ba$^{2+}$ on 9-coordinated sites is 18.63% and 11.56% respectively, while the value of $D_r$ between Ce$^{3+}$ and Al$^{3+}$, Eu$^{2+}$ and Al$^{3+}$ is −206.66% and −233.33% respectively. Thus, doped ions Ce$^{3+}$ and Eu$^{2+}$ will preferentially substitute the 9-coordinated barium sites. Similar arguments hold for doping of Ce$^{3+}$ and Eu$^{2+}$ ions in strontium and calcium sites.

3.7 Occupancy of Ce$^{3+}$ and Eu$^{2+}$ at different crystallographic sites from emission wavelengths

To understand the relationship between emission wavelength and sites of Ba$^{2+}$, Ca$^{2+}$, Sr$^{2+}$ occupied by Ce$^{3+}$ and Eu$^{2+}$, we used Van Uitert's empirical formula [20]. Van Uitert calculated the positions of the lower d-band edge for Ce$^{3+}$ and Eu$^{2+}$ ions using the following empirical formula:

$$E = Q \left[ 1 - \left( \frac{V}{4} \right)^{1/3} \right]^{\frac{n\alpha r}{10}}$$  \hspace{1cm} (11)

where $E$ is the position in energy of the lower d-band edge for Ce$^{3+}$ and Eu$^{2+}$ in three-dimensional structure, $Q$ is the energy edge of the lower d-band for the free ions ($Q = 50000$ cm$^{-1}$ for Ce$^{3+}$ ion and $34000$ cm$^{-1}$ for Eu$^{2+}$ ion), $V$ is the valence of the active cation (here $V = +3$ for Ce$^{3+}$ and +2 for Eu$^{2+}$), $n$ is the number of anions in the immediate shell about this ion, $\alpha$ is the electron affinity of the coordination radial, and $r$ is the radius of the host cation replaced by the activator.

In BaAl$_2$O$_4$, for 9-coordinated Ba$^{2+}$ ions, $r$ is 1.47 Å and $\alpha$ is 1.60 eV. The calculated values of $E$ using Eq. (11) are 25299 cm$^{-1}$ (395 nm) for Ce$^{3+}$ and 20928 cm$^{-1}$ (477 nm) for Eu$^{2+}$. The experimental emission peaks of Ce$^{3+}$ and Eu$^{2+}$ doped BaAl$_2$O$_4$ are found at 25902 cm$^{-1}$

![Fig. 13](image-url) PL spectra for Eu$^{2+}$ activated CaAl$_2$O$_4$: (a) excitation spectrum for 440 nm emission of CaAl$_2$O$_4$; (b) emission spectra for 329 nm excitation of CaAl$_2$O$_4$.  

Table 4 Percentage difference in ionic radius between matrix cations and doped ions

| Doped ion | $R_d$(CN) | $R_s$(CN) | $D_r$ (%) |
|-----------|------------|------------|-----------|
| Ce$^{3+}$ | 1.196(9)   | 1.476(9)   | 18.63     |
| Eu$^{2+}$ | 1.3(9)     | 1.476(9)   | 11.56     |

- **Table 4** Percentage difference in ionic radius between matrix cations and doped ions

**Fig. 13** PL spectra for Eu$^{2+}$ activated CaAl$_2$O$_4$: (a) excitation spectrum for 440 nm emission of CaAl$_2$O$_4$; (b) emission spectra for 329 nm excitation of CaAl$_2$O$_4$.  

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The Ba\(^{2+}\) and Sr\(^{2+}\) ions are large enough to fit in the O\(^{2-}\) stuffed tridymite structure. This structure consists of BaAl\(_2\)O\(_4\), SrAl\(_2\)O\(_4\), and CaAl\(_2\)O\(_4\) have been successfully

The calculated theoretical values of energy of the lower d-band edge for Ce\(^{3+}\) and Eu\(^{2+}\) in the different MA\(_2\)O\(_4\) hosts are given in Table 5.

The results show that the main emission peaks are close to the experimental values in the case of SrAl\(_2\)O\(_4\). Hence Ce\(^{3+}\) and Eu\(^{2+}\) occupy 9-coordinated Sr\(^{2+}\) site in SrAl\(_2\)O\(_4\). In the case of CaAl\(_2\)O\(_4\), the difference between the calculated and the experimental values is large.

The possible reasons are discussed: Phosphors BaAl\(_2\)O\(_4\), SrAl\(_2\)O\(_4\), and CaAl\(_2\)O\(_4\) belong to family of stuffed tridymite structure. This structure consists of close-packing of alkaline earth ions and oxygen ions. The Ba\(^{2+}\) and Sr\(^{2+}\) ions are large enough to fit in the O\(^{2-}\) packing as the ionic radii of Ba\(^{2+}\) (1.47 Å), Sr\(^{2+}\) (1.31 Å), and O\(^{2-}\) (1.35 Å) are roughly equivalent, while ionic radius of Ca\(^{2+}\) (1.18 Å) is too small, so that distortion will result. On the other side, the ionic radius of Eu\(^{2+}\) (1.30 Å) is relatively too large compared to that of Ca\(^{2+}\), so the crystallographic distortions will influence the crystal field and emission spectra when Eu\(^{2+}\) enters the Ca\(^{2+}\) site. In addition experimental results are near to 9-fold coordination geometry of Ca\(^{2+}\) ion than the 6-fold coordination. Thus Ce\(^{3+}\) and Eu\(^{2+}\) will occupy tri-capped trigonal anti-prism polyhedron 9-coordinated Ca\(^{3+}\) site in crystal lattice [28].

4 Conclusions

Ce\(^{3+}\) and Eu\(^{2+}\) activated aluminate-based phosphors Ba\(_2\)O\(_2\), SrAl\(_2\)O\(_4\), and CaAl\(_2\)O\(_4\) have been successfully synthesized using a very simple, fast combustion method at low temperature. XRD patterns for prepared phosphors confirmed the monoclinic structure of CaAl\(_2\)O\(_4\) and SrAl\(_2\)O\(_4\) with space group P2\(_1\)/c(14) and P2\(_1\)(4) respectively, while hexagonal structure for BaAl\(_2\)O\(_4\) with space group P6\(_3\)22(182). In PL properties, Ce\(^{3+}\) doped BaAl\(_2\)O\(_4\), SrAl\(_2\)O\(_4\), and CaAl\(_2\)O\(_4\) samples showed a broad emission band centered at 386, 371, and 370 nm with concentration quenching above 0.2%, 0.2%, and 0.05% respectively. In Eu\(^{2+}\) doped phosphors, emission peaks are at 485, 498, and 440 nm respectively for BaAl\(_2\)O\(_4\), SrAl\(_2\)O\(_4\), and CaAl\(_2\)O\(_4\). Concentration quenching occurred above 2%, 1%, and 2% in Eu\(^{2+}\) doped phosphors BaAl\(_2\)O\(_4\), SrAl\(_2\)O\(_4\), and CaAl\(_2\)O\(_4\) respectively. Spectroscopic properties such as crystal field splitting, centroid shift, red shift, Stokes shift were studied systematically for Ce\(^{3+}\) and Eu\(^{2+}\) doped phosphors. The spectroscopic studies implied that the host crystal structure has great influence on the main emission peaks. The optical properties of Eu\(^{2+}\) doped phosphors were correctly predicted from the corresponding properties of Ce\(^{3+}\) doped in the same matrix. The site occupancy of Ce\(^{3+}\) and Eu\(^{2+}\) were studied at different crystallographic sites using empirical relations of Dorenbos’ and Van Uitert’s. The Ce\(^{3+}\) and Eu\(^{2+}\) ions prefer to occupy 9-coordinated sites in BaAl\(_2\)O\(_4\), SrAl\(_2\)O\(_4\), and CaAl\(_2\)O\(_4\).

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