Research Article

d-f luminescence of Ce³⁺ and Eu²⁺ ions in BaAl₂O₄, SrAl₂O₄ and CaAl₂O₄ phosphors

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Abstract: Ce^{3^+} and Eu^{2^+} doped alkaline earth aluminates MAl₂O₄ (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 BaAl₂O₄, CaAl₂O₄, and SrAl₂O₄. Photoluminescence spectra and optimal luminescent properties of Ce³⁺ and Eu²⁺ doped MAl₂O₄ phosphors were studied. Relation between Eu^{2^+} and Ce^{3^+} f–d transitions was explained. Spectroscopic properties known for Ce³⁺ 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 Ce³⁺ and Eu²⁺ at different Ba²⁺, Sr²⁺, Ca²⁺ crystallographic sites was discussed. The dependence of emission wavelengths of Ce³⁺ and Eu²⁺ 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: Ce³⁺; Eu²⁺; 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 Ce³⁺ have received remarkable attention owing to their wide

applications in flat panel displays, X-ray imaging, and tri-colour lamps [1]. Ce³⁺ doped phosphors are used for scintillators and fast also as long lasting phosphorescent materials. Jia and co-workers [2] BaAl₂O₄:Ce³⁺ reported luminescence in and $BaAl_2O_4:Ce^{3+},Dv^{3+}$. The photoluminescence in BaAl₂O₄:Mn²⁺,Ce³⁺ was reported by Surivamurthy 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 yettrium 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,

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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 $4f \rightarrow 5d$ transition [6,7]. $BaAl_2O_4:Eu^{2+},Dy^{3+}$ [8] and $BaAl_2O_4:Eu^{2+},Nd^{3+}$ [9] also exhibit long lasting phosphorescence (LLP) properties. Eu^{2+} doped BaAl₂O₄ and SrAl₂O₄ could be promising phosphor materials for plasma display panel (PDP) application [10,11]. SrAl₂O₄ 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 (SrAl₂O₄:Eu²⁺,Dy³⁺) have been reported by Kim *et al*. [17]. CaAl₂O₄:Eu²⁺ 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 BaAl₂O₄, SrAl₂O₄, CaAl₂O₄ phosphors using single-step combustion synthesis at an initiating temperature of 600 $^{\circ}$ 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 Ce³⁺ and Eu²⁺ luminescence in these hosts. Systematic relationship between emission wavelengths of Ce³⁺ 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 Ce³⁺ 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(NO₃)₂), strontium (Sr(NO₃)₂), or calcium (Ca(NO₃)₂) and aluminum (Al(NO₃)₃·9H₂O), with cerium nitrate or europium nitrate, and urea (CO(NH₂)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 Eu²⁺. 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 $^{\circ}$ 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 Eu²⁺ (0.05%-3%) and Ce³⁺ (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-fluriometer 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:

 $\begin{array}{l} 6Al(NO_3)_3 + 3Ba(NO_3)_2 + 20NH_2CONH_2 \rightarrow \\ 3BaAl_2O_4 + 20CO_2 + 32N_2 + 40H_2O \\ 6Al(NO_3)_3 + 3Sr(NO_3)_2 + 20NH_2CONH_2 \rightarrow \\ 3SrAl_2O_4 + 20CO_2 + 32N_2 + 40H_2O \end{array}$

$$6\text{Al}(\text{NO}_3)_3 + 3\text{Ca}(\text{NO}_3)_2 + 20\text{NH}_2\text{CONH}_2 \rightarrow 3\text{CaAl}_2\text{O}_4 + 20\text{CO}_2 + 32\text{N}_2 + 40\text{H}_2\text{O}$$

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 2 θ 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 $P6_322(182)$ and its lattice parameters are a=5.227 Å and c=8.802 Å. It is also confirmed that SrAl₂O₄ possesses monoclinic structrure



Fig. 1 XRD pattern of $BaAl_2O_4$ compared with ICDD No. 73-0202.



Fig. 2 XRD pattern of SrAl₂O₄ compared with ICDD No. 74-0794.



Fig. 3 XRD pattern of $CaAl_2O_4$ compared with ICDD No. 88-2477.

with space group $P2_1(4)$ 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 flow combustion irregular mass during and non-uniform distribution of temperature. Finally, the aluminates derived from the combustion process reflect inherent foamy nature.

Table	1	Comparison	of	crystal	structure	data	of
BaAl ₂	04,	SrAl ₂ O ₄ , and O	CaA	l_2O_4			

	BaAl ₂ O ₄	$SrAl_2O_4$	CaAl ₂ O ₄	
Structure type	Hexagonal	Monoclinic	Monoclinic	
Space group	$P6_{3}22(182)$	$P2_{1}(4)$	$P2_1/c(14)$	
ICDD file No.	73-0202	74-0794	88-2477	
a (Å)	5.227	8.447	7.95	
<i>b</i> (Å)	_	8.816	8.62	
<i>c</i> (Å)	8.802	5.163	10.25	
Number of sites of M^{2+}	2	2	3	
Coordination of M ²⁺ with oxygen	Each with 9-coordination	Each with 9-coordination	One with 9-coordination and other two with 6-coordination	

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Fig. 4 SEM images of (a) $BaAl_2O_4$, (b) $SrAl_2O_4$, and (c) $CaAl_2O_4$.

3. 3 Crystal structure of MAl₂O₄ (M = Ca, Sr, Ba)

The compounds MAl_2O_4 (M = Ca, Sr, Ba) belong to the family of stuffed tridymite structure [21]. The structure corner-sharing AlO₄ tetrahedron has 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 Ba²⁺, Ca²⁺, Sr²⁺ occupy interstitial sites within the tetrahedral framework and achieve the charge balance. The tetrahedral framework is isostructural within the tridymite structure [22]. SrAl₂O₄ undergoes a phase transition from a low temperature monoclinic distorted structure to the hexagonal tridymite structure at 650 °C [23]. CaAl₂O₄ 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 BaAl₂O₄ crystal structure showing two Ba²⁺ sites in the BaAl₂O₄ structure, each with 9-fold coordination [25]. According to the crystal structure, the first Ba²⁺ 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 Ba²⁺ is 1.47 Å [26].

The SrAl₂O₄ host crystallizes in the stuffed tridymite type of structure. SrAl₂O₄ belongs to monoclinic space group structure with $P2_{1}(4).$ The three-dimensional network consists of corner-sharing AlO₄ 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].

CaAl₂O₄ possesses monoclinic structure with space group $P2_1/c(14)$. In this phosphor, Ca²⁺ ions occupy three different lattice sites Ca1, Ca2, and Ca3 [28]. Figure 7 shows unit cell of monoclinic CaAl₂O₄ and polyhedral structures of different sites of Ca²⁺. Sites



Fig. 5 (a) Unit cell of $BaAl_2O_4$; (b) local coordination geometry environment of Ba^{2+} .



Fig. 6 (a) Unit cell of $SrAl_2O_4$; (b) local coordination geometry environment of Sr^{2+} .

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 Ca^{2+} and Ce^{3+} 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 Ce^{3+} doped



Fig. 7 (a) Unit cell of $CaAl_2O_4$; (b) local coordination geometry environment of Ca^{2+} .

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 Ba^{2+} , Sr^{2+} , and Ca^{2+} (Unit: Å)

Site	Ba1	Sr1	Sr2	Cal	Ca2	Ca3
CN	9	9	9	6	6	9
Ba ²⁺ –O, Sr ²⁺ –O,	O2 = 2.866	O4 = 2.559	O8 = 2.990	O3 = 2.310	O10 = 2.293	O7 = 2.805
Ca ²⁺ –O distances	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
	O2 = 2.866	O5 = 3.534	O2 = 2.697			O11 = 3.040
	O1 = 3.016	O6 = 3.113	O1 = 2.772			O2 = 3.175
$R_{ m av}$	2.9162	2.8776	2.8359	2.4241	2.4379	2.7843
$\Delta R = R_{\mathrm{M}^{2+}} - R_{\mathrm{Ce}^{3+}}$	0.2740	0.144	0.144	0.010	0.010	0.016
$r(A) = R_{av} - \Delta R / 2$	2.7791	2.805	2.773	2.419	2.432	2.776

CN: coordination number; R_{av} : average distance; ΔR : 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⁺; $R_{M^{2+}}$: radius of metal cation (Ba²⁺, Sr²⁺, and Ca²⁺).



Fig. 8 PL spectra for Ce^{3+} activated BaAl₂O₄: (a) excitation spectrum for 386 nm emission of BaAl₂O₄; (b) emission spectra for 308 nm excitation of BaAl₂O₄.



Fig. 9 PL spectra for Ce^{3+} activated $SrAl_2O_4$: (a) excitation spectrum for 371 nm emission of $SrAl_2O_4$; (b) emission spectra for 331 nm excitation of $SrAl_2O_4$.



Fig. 10 PL spectra for Ce^{3+} activated $CaAl_2O_4$: (a) excitation spectrum for 370 nm emission of $CaAl_2O_4$; (b) emission spectra for 300 nm excitation of $CaAl_2O_4$.

 Ce^{3+} is doped above 0.2%, 0.2%, and 0.05% in BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄, respectively.

The ground state (4f¹ configuration) of Ce³⁺ ion splits due to spin orbit coupling into two states namely ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ 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 $4f^1$ state to crystal field split $4f^05d^1$ 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 ²F_{5/2} and ²F_{7/2} 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 Ce^{3+} . He used the terms ε_{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 $\varepsilon_{\rm c}$ 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. ΔS is the Stokes shift between excitation (E^{abs}) and emission (E^{em}) bands. The relation between the red shift D(3+) with crystalline environment is as follows [31,32]:

$$D(3+) = \varepsilon_{\rm C} + \frac{\varepsilon_{\rm CFS}}{r(A)} - 0.234 \text{eV}$$
(4)

where

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

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

$$\Delta S(3+) = E^{\rm abs} - E^{\rm em} \tag{6}$$

Above equations are used for Ce^{3^+} doped 9-coordinated Ba^{2^+} , Sr^{2^+} , and Ca^{2^+} 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 Eu^{2^+} 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 (ΔS) of divalent and trivalent lanthanides as

$$D(2+) = 0.64 \times D(3+) - 0.233 \text{eV}$$
(7)

		BaAl ₂ O ₄		SrAl ₂ O ₄		CaAl ₂ O ₄	
	_	(eV)	(cm^{-1})	(eV)	(cm ⁻¹)	(eV)	(cm^{-1})
	X1	4.036	32467	3.755	30206	4.143	33333
Experimental Ce ³⁺	X2	5.053	40651	4.673	37590	5.033	40486
	M1	3.220	25902	3.350	26953	3.359	27027
	$\mathcal{E}_{\mathrm{CFS}}$	1.017	8181	0.9177	7382	0.8891	7152
Calculated Ce ³⁺	\mathcal{E}_{C}	1.805	14521	2.135	17178	1.761	14170
	D	1.937	15583	2.232	17960	1.848	14871
	ΔS	0.8156	6560	0.4049	3293	0.784	6306
	D	1.077	8666	1.195	9612	0.949	7634
Estimated Eu ²⁺ from Ce ³⁺	ΔS	0.497	4000	0.247	1986	0.478	3845
	M1	2.62	21075 (474 nm)	2.758	22169 (451 nm)	2.774	22314 (448 nm)
Experimental Eu ²⁺	M1	2.56	20593 (485 nm)	2.496	20110 (498 nm)	2.825	22725 (440 nm)

Table 3 Spectroscopic properties of Ce³⁺ and Eu²⁺ in BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄

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

$$\Delta S(2+) = 0.61 \times \Delta S(3+) \tag{8}$$

The energy difference between the lowest $4f^7$ (⁸S_{7/2}) level and the first $4f^6$ (⁷F₀)5d¹ level is lowered from the free electron value when the Eu²⁺ 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 ΔS . The energy of $f \rightarrow d$ absorption and that of the $d \rightarrow f$ emission can be written respectively, as [33]:

$$E^{\rm abs} = E^{\rm free} - D \tag{9}$$

$$E^{\rm em} = E^{\rm free} - D - \Delta S \tag{10}$$

The free ion value of Eu^{2+} is $E^{free} = 4.2 \text{ eV}$ [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 BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄. 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 BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄) as shown in Figs. 11–13. This confirms that the Ce³⁺ and Eu²⁺ preferentially occupy 9-coordinated Ba²⁺, Sr²⁺, and Ca²⁺ sites.

3.6 Eu²⁺ luminescence

Figures 11–13 show excitation and emission spectra of phosphors $BaAl_2O_4/SrAl_2O_4/CaAl_2O_4$ doped with Eu^{2+} . Figure 11(a) illustrates the excitation spectrum of $BaAl_2O_4:Eu^{2+}$, 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



Fig. 11 PL spectra for Eu^{2+} activated $BaAl_2O_4$: (a) excitation spectrum for 485 nm emission of $BaAl_2O_4$; (b) emission spectra for 328 nm excitation of $BaAl_2O_4$.



Fig. 12 PL spectra for Eu^{2+} activated $SrAl_2O_4$: (a) excitation spectrum for 498 nm emission of $SrAl_2O_4$; (b) emission spectra for 350 nm excitation of $SrAl_2O_4$.

strongest excitation peak in $BaAl_2O_4:Eu^{2+}$. The excitation spectrum is ascribed to $4f^7 \rightarrow 4f^65d$ 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. 13 PL spectra for Eu^{2+} activated $CaAl_2O_4$: (a) excitation spectrum for 440 nm emission of $CaAl_2O_4$; (b) emission spectra for 329 nm excitation of $CaAl_2O_4$.

and 433 nm, which confirms the presence of two Ba²⁺ crystallographic sites in BaAl₂O₄. The emission spectrum has maximum centered at 485 nm, showing blue luminescence. The emission spectrum is due to $4f^{6}5d \rightarrow 4f^{7}$ transition of Eu²⁺. The PL spectra are in good agreement with the results reported in the literature [11,35,36].

The excitation spectrum of SrAl₂O₄:Eu²⁺ 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 CaAl₂O₄:Eu²⁺ 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 CaAl₂O₄ and SrAl₂O₄ 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 Eu²⁺ doped BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄, 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, $D_r = \frac{R_M(CN) - R_d(CN)}{R_M(CN)}$,

Table 4Percentage difference in ionic radius betweenmatrix cations and doped ions

Doped ion	$R_{\rm d}({\rm CN})$	$R_{\rm M}({\rm CN})$	$D_{\rm r}$ (%)
		$R_{\rm Ba}(9) = 1.47$	18.63
		$R_{\rm Sr}(9) = 1.31$	8.70
Ce ³⁺	1.196(9)	$R_{\rm Ca}(9) = 1.18$	-1.35
		$R_{\rm Ca}(6) = 1$	-19.60
		$R_{\rm Al}(4) = 0.39$	-206.66
		$R_{\rm Ba}(9) = 1.47$	11.56
		$R_{\rm Sr}(9) = 1.31$	0.76
Eu^{2+}	1.3(9)	$R_{\rm Ca}(9) = 1.18$	-10.16
		$R_{\rm Ca}(6) = 1$	-30
		$R_{\rm Al}(4) = 0.39$	-233.33

where CN is the coordination number, $R_{\rm M}$ (CN) is the radius of host cation, and $R_{\rm d}$ (CN) is the radius of doped ion. The value of $D_{\rm r}$ between Ce³⁺ and Ba²⁺, Eu²⁺ and Ba²⁺ on 9-coordinated sites is 18.63% and 11.56% respectively, while the value of $D_{\rm r}$ between Ce³⁺ and Al³⁺, Eu²⁺ and Al³⁺ is -206.66% and -233.33% respectively. Thus, doped ions Ce³⁺ and Eu²⁺ will preferentially substitute the 9-coordinated barium sites. Similar arguments hold for doping of Ce³⁺ and Eu²⁺ ions in strontium and calcium sites.

3.7 Occupancy of Ce³⁺ and Eu²⁺ 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:

$$E = Q \left[1 - \left(\frac{V}{4}\right)^{1/V} 10^{-\frac{n \cdot ea \cdot r}{80}} \right]$$
(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 $(Q = 50000 \text{ cm}^{-1} \text{ for } Ce^{3+} \text{ ion and } 34000 \text{ cm}^{-1} \text{ for } Eu^{2+} \text{ ion})$, *V* is the valence of the active cation (here *V* is +3 for Ce^{3+} and +2 for Eu^{2+}), *n* is the number of anions in the immediate shell about this ion, *ea* is the electron affinity of the coordination radial, and *r* is the radius of the host cation replaced by the activator.

In BaAl₂O₄, for 9-coordinated Ba²⁺ ions, *r* is 1.47 Å and *ea* is 1.60 eV. The calculated values of *E* using Eq. (11) are 25299 cm⁻¹ (395 nm) for Ce³⁺ and 20928 cm⁻¹ (477 nm) for Eu²⁺. The experimental emission peaks of Ce³⁺ and Eu²⁺ doped BaAl₂O₄ are found at 25902 cm⁻¹

(386 nm) and 20593 cm⁻¹ (485 nm) (Figs. 8(b) and 11(b)), respectively. This confirms the excellent match between theoretical and experimental values. Thus Ce^{3+} and Eu^{2+} occupy 9-coordinated Ba^{2+} site in $BaAl_2O_4$. The calculated theoretical values of energy of the lower d-band edge for Ce^{3+} and Eu^{2+} in the different MAl_2O_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 $SrAl_2O_4$. Hence Ce^{3+} and Eu^{2+} occupy 9-coordinated Sr^{2+} site in $SrAl_2O_4$. In the case of $CaAl_2O_4$, the difference between the calculated and the experimental values is large.

The possible reasons are discussed: Phosphors BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄ 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 Eu²⁺ (1.30 Å) is relatively too large compared to that of Ca²⁺ so the crystallographic distortions will influence the crystal field and emission spectra when Eu²⁺ enters the Ca²⁺ site. In addition experimental results are near to 9-fold coordination geometry of Ca²⁺ ion than the 6-fold coordination. Thus Ce³⁺ and Eu²⁺ will occupy tri-capped trigonal anti-prism polyhedron 9-coordinated Ca3 site in crystal lattice [28].

4 Conclusions

 Ce^{3+} and Eu^{2+} activated aluminate-based phosphors BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄ have been successfully synthesized using a very simple, fast combustion method at low temperature. XRD patterns for prepared phosphors confirmed the monoclinic structure of CaAl₂O₄ and SrAl₂O₄ with space group $P2_1/c(14)$ and

Table 5 Calculated values of position in energy of the lower d-band edge for Eu^{2+} and Ce^{3+} in different hosts

		8		
Compound	п	r	Calculated	Experimental
compound	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	(Å)	energy (cm ⁻¹)	energy (cm ⁻¹)
BaAl ₂ O ₄ :Eu ²⁺	9	1.47	25298 (395 nm)	25905 (386 nm)
BaAl ₂ O ₄ :Ce ³⁺	9	1.47	20927 (477 nm)	20618 (485 nm)
SrAl ₂ O ₄ :Eu ²⁺	9	1.31	20031 (500 nm)	20080 (498 nm)
SrAl ₂ O ₄ :Ce ³⁺	9	1.31	23604 (423 nm)	26954 (371 nm)
CaAl ₂ O ₄ :Eu ²⁺	9	1.18	19257 (519 nm)	27727 (440 nm)
CaAl ₂ O ₄ :Ce ³⁺	9	1.18	22143 (451 nm)	27027 (370 nm)
CaAl ₂ O ₄ :Eu ²⁺	6	1	15763 (634 nm)	27727 (440 nm)
CaAl ₂ O ₄ :Ce ³⁺	6	1	15539 (643 nm)	27027 (370 nm)

 $P2_1(4)$ respectively, while hexagonal structure for $BaAl_2O_4$ with space group $P6_322(182)$. In PL properties, Ce³⁺ doped BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄ 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 Eu²⁺ doped phosphors, emission peaks are at 485, 498, and 440 nm respectively for BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄. Concentration quenching occurred above 2%, 1%, and 2% in Eu²⁺ doped phosphors BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄ respectively. Spectroscopic properties such as crystal field splitting, centroid shift, red shift, Stokes shift were studied systematically for Ce³⁺ and Eu²⁺ doped phosphors. The spectroscopic studies implied that the host crystal structure has great influence on the main emission peaks. The optical properties of Eu²⁺ doped phosphors were correctly predicted from the corresponding properties of Ce^{3+} doped in the same matrix. The site occupancy of Ce³⁺ and Eu²⁺ 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 BaAl₂O₄, SrAl₂O₄, and CaAl₂O₄.

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