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Footnote Information		

7

Rapid synthesis and enhancement in down conversion emission properties of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{RE}^{3+}$ ($\text{RE}^{3+}=\text{Y}, \text{Pr}$) nanophosphors

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Abstract $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{RE}^{3+}$ ($\text{RE}^{3+}=\text{Y}, \text{Pr}$) down conversion nanophosphors were prepared at 600 °C by a rapid gel combustion technique in presence of air using boron as flux and urea as a fuel. A comparative study of the prepared materials was carried out with and without the addition of boric acid. The boric acid was playing the important role of flux and reducer simultaneously. The peaks available in the XPS spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ at 1126.5 and 1154.8 eV was ascribed to $\text{Eu}^{2+}(3d_{5/2})$ and $\text{Eu}^{2+}(3d_{3/2})$ respectively which confirmed the presence of Eu^{2+} ion in the prepared lattice. Morphology of phosphors was characterized by tunneling electron microscopy. XRD patterns revealed a dominant phase characteristics of hexagonal BaAl_2O_4 compound and the presence of dopants having unrecognizable effects on basic crystal structure of BaAl_2O_4 . The addition of boric acid showed a remarkable change in luminescence properties and crystal size of nanophosphors. The emission spectra of phosphors had a broad band with maximum at 490–495 nm due to electron transition from $4f^65d^1 \rightarrow 4f^7$ of Eu^{2+} ion. The co-doping of the rare earth ($\text{RE}^{3+}=\text{Y}, \text{Pr}$) ions help in the enhancement of their luminescent properties. The prepared phosphors had brilliant optoelectronic properties that can be properly used for solid state display device applications.

1 Introduction

Advanced luminescent materials find increasing demands in a variety of applications such as display devices, lamps, sensors etc. [1–4]. RE^{3+} activated luminescent materials have fascinated an enormous attention because of their tremendous optical properties and wide ranges of applications [5–7]. Europium activated aluminates phosphors [$\text{M}(\text{Ca}, \text{Sr}, \text{Ba})\text{Al}_2\text{O}_4:\text{Eu}^{2+},\text{RE}^{3+}$] demonstrate a wide emission band of high intensity produced from electronic transitions $4f^7 \rightarrow 4f^65d^1$ of the Eu^{2+} ions. This group of aluminate phosphors possesses several advantages in comparison to traditional sulfide based phosphors as lower chemical toxicity, lack of radioactive elements and high stability.

For the enhancement of photoluminescence intensity and persistency of Eu^{2+} activated aluminates phosphors, researchers generally introduce some RE^{3+} ions (Nd and Dy are most common) which act as coactivators, and this results in enhancement of luminescence as well as after-glow properties [8]. Eu^{2+} is a suitable activator for phosphor materials. As the $f \rightarrow d$ transitions are electric dipole allowed transitions thus broad bands are observed for absorption as well as emission of Eu^{2+} doped host lattices [9]. Also the $5d$ wave function has a huge spatial extension thus transition line is generally widened, and it is influenced by the surrounding of Eu^{2+} ions. Therefore the different lattices environments provide different variation to the optical properties of the Eu^{2+} ions [10]. Under ultraviolet excitation Eu^{2+} doped BaAl_2O_4 emits green light [11], Eu^{2+} doped BaAl_2O_9 reveal a very broadband emission from blue to green light region [12]. Mechanism reveals the photoionization of Eu^{2+} ion and consequently electrons are migrated to traps created by the lattices defects as O^{2-} vacant spaces and possibly also by RE^{3+}

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ions co-activators. The thermal removal of electrons from the traps followed by the process reverse to the storage of the excitation energy leads to Eu^{2+} emission [13].

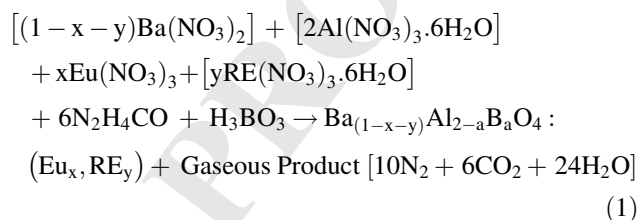
$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ phosphor is most infrequently studied luminescent phosphor because of complicated structure chemistry of BaAl_2O_4 host and size mismatch between Ba^{2+} and Eu^{2+} [14]. In $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ phosphor, Peng and Hong [15] observed first time the reduction of Eu^{3+} to Eu^{2+} when it was calcined at 1400 °C in reducing atmosphere. In current years, a lot of studies have been reported for the preparation of nano phosphor using various route of preparation such as solid state, sol gel spray pyrolysis, combustion route [16], solution phase synthesis [17] and reverse microemulsion [18]. However these methods consume a lot of time and energy as well. This paper reports the rapid combustion technique of preparation of these materials that requires a very short period of time (in minutes). Eu^{2+} doped and RE^{3+} co-doped BaAl_2O_4 have been synthesized by rapid technique and to compare the down conversion property of nanosized crystalline powders. X-ray diffraction was carried out to analyze the phase and crystallinity of material. Effects of the boric acid (flux) on the crystal structure and down conversion properties were also studied.

2 Experimental

2.1 Synthesis of nanophosphors

$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{RE}^{3+}$ blue green nanophosphors were prepared by the rapid gel combustion method, where metal nitrates and urea were used as reactant and fuel, respectively. The raw materials, barium nitrate $\text{Ba}(\text{NO}_3)_2$, aluminium nitrate $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, europium nitrate $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and rare earth nitrates $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (RE may be Y or Pr) used were of analytical grade. All these chemicals were mixed in a fixed stoichiometry corresponding to $\text{Ba}_{(0.98)}\text{Al}_2\text{O}_4:\text{Eu}_{(0.02)}^{2+}$; $\text{Ba}_{(0.96)}\text{Al}_2\text{O}_4:\text{Eu}_{(0.02)}^{2+},\text{Pr}_{(0.02)}^{3+}$; $\text{Ba}_{(0.96)}\text{Al}_2\text{O}_4:\text{Eu}_{(0.02)}^{2+},\text{Y}_{(0.02)}^{3+}$ materials. Urea (NH_2CONH_2) was used as fuel. Here two series were prepared. One series of the phosphors was prepared with only fuel and another series of these phosphors was prepared by using boric acid along with fuel. Boric acid was added in varying ratios (5–25 %) with respect to Eu^{3+} ion in order to optimize homogeneity and maximum brightness (suitable ratio of boric acid was found to be 11 % of its molecular weight for each addition of 0.01 M of Eu^{3+} ion). Urea was used as fuel for the combustion reaction and its amount was calculated balancing total oxidizing and reducing valences of the compounds. The precursors were mixed in small amount of deionized water and were placed into a silica crucible and then this crucible was inserted

into a preheated furnace already set at 600 °C. The reaction started within 2 or 3 min, the mixture boiled and underwent dehydration. Finally the mixture underwent decomposition, resulting in evolution of a large volume of gasses. Then spontaneous ignition occurred resulting in flame type combustion. Then whole process completed in less than 10 min and highly porous white nanopowder was obtained. The voluminous material was taken out and grinded to a very fine powder. The white powder of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ showed bright green luminescence while $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}:\text{RE}^{3+}(\text{Pr}^{3+}/\text{Y}^{3+})$ showed blue green luminescence under the UV light as shown in the Fig. 1b. In an example the chemical reaction that took place in the combustion of the reactant may be represented as follows:



2.2 Characterization of nanophosphors

Photoluminescence excitation and emission spectra were carried out with Fluorimeter SPEX Fluorolog 1680 (USA) equipped with the SPEX 1934 D phosphorimeter having Xenon lamp as excitation source. Phosphors were characterized for presence of oxidation state of europium (either it exist in +2 or +3) with x-ray photoelectron spectroscopy (Model/Supplier:PHI 5000 Versa Prob II). The phase composition and crystal size of the phosphors were analyzed by Xrd patterns using Rigaku Ultima IV X-ray diffractometer, using Ni-filtered $\text{Cu K}\alpha 1$ radiation). Morphology of the powder was determined by using Hitachi F-7500 transmission electron microscope (TEM).

3 Results and discussion

3.1 X-Ray diffraction analysis of phosphors

Xrd patterns of the prepared materials were obtained for diagnosing the crystal phase and were collected in 2θ range of 15–70°. The XRD diffraction patterns of nano sized BaAl_2O_4 samples prepared at 600 °C are shown in Fig. 2. The resemblance of the resulting diffraction patterns with the reference standard of the BaAl_2O_4 (JCPDS = 82–2001) confirmed the presence of pure hexagonal structure in all phosphors of both the series without any impurities and that small amount of Eu doping and RE^{3+} codoping as well into BaAl_2O_4 did not change the lattice structure. Thus no phase

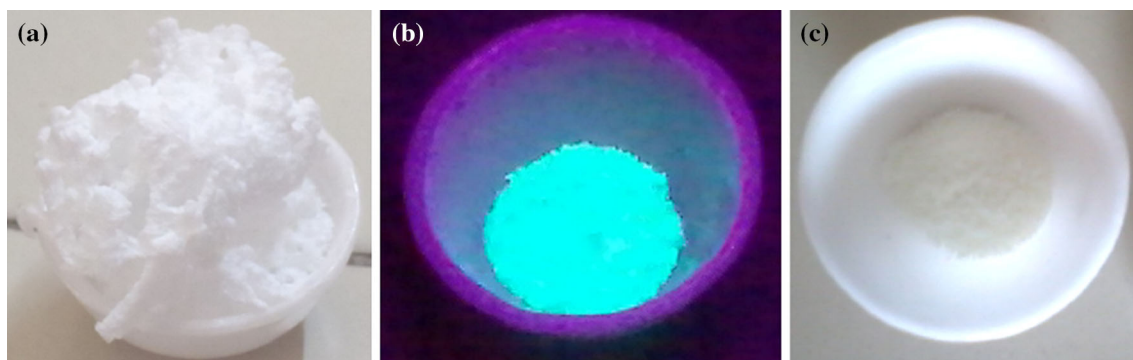


Fig. 1 Showing phosphor in various condition **a** prepared fluffy material **b** material under UV (365 nm) light source **c** material without excitation light source

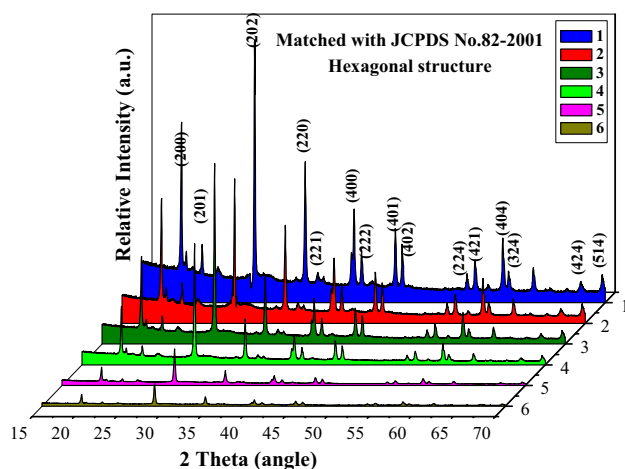


Fig. 2 XRD profile of BaAl_2O_4 doped with Eu^{2+} and various codopants with or without boric acid

157 transformation or any impurity is observed after boric acid
158 addition in sample. However when the higher H_3BO_3 con-
159 tent (more than 15 %) was added in the lattice than a second
160 phase also started to appear as a minor phase in the XRD
161 patterns [19]. But here boric acid used was just 11 % of
162 added Eu concentration hence only single hexagonal phase
163 of BaAl_2O_4 appeared. The peak nearly at 28.3° in all
164 samples was the most intensive and the crystal sizes were
165 calculated through it. The effect of boric acid on the for-
166 mation of BaAl_2O_4 crystals was investigated. The crys-
167 talline qualities as well as crystal size of synthesized
168 phosphors were found improved on the addition of boric
169 acid. XRD diffraction peaks were increased sharply when
170 the boric acid was added, because boric acid facilitated easy
171 incorporation of RE^{3+} ions into the lattice that assisted in
172 the enhancement of the crystallinity, indicating it's stability
173 and a weak effect on the crystal size. The crystal sizes were
174 less than 100 nm and the influence of the boric acid and
175 codopants on the formation of BaAl_2O_4 crystals is shown in
176 Table 1. With the boric acid addition, the FWHM decreased
177 to some extent, implying that BaAl_2O_4 crystals grew to

some extent with the addition of boric acid. The combustion 178
temperature of product with boric acid were much higher 179
than that of precursor without boric acid, as a result, the 180
former exhibited a larger average crystallite size. 181

Further, average particle size (D) of Eu^{2+} doped 182
 BaAl_2O_4 samples without boric acid and with boric acid 183
were calculated from the full width half maximum (β) of 184
the diffraction peaks, using Debye–Scherrer's method: 185

$$D = K\lambda/\beta \cos \theta$$

where ' λ ' is x-ray the wavelength (1.541 \AA), ' θ ' is the 187
Bragg's angle, ' k ' is the constant depending on the grain 188
shape. 189

The average calculated particle size of the prepared 190
 $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ phosphors are in the range of 80–100 nm. 191
All the details of size calculation are described in the 192
Table 1. 193

3.2 Morphology of phosphors 194

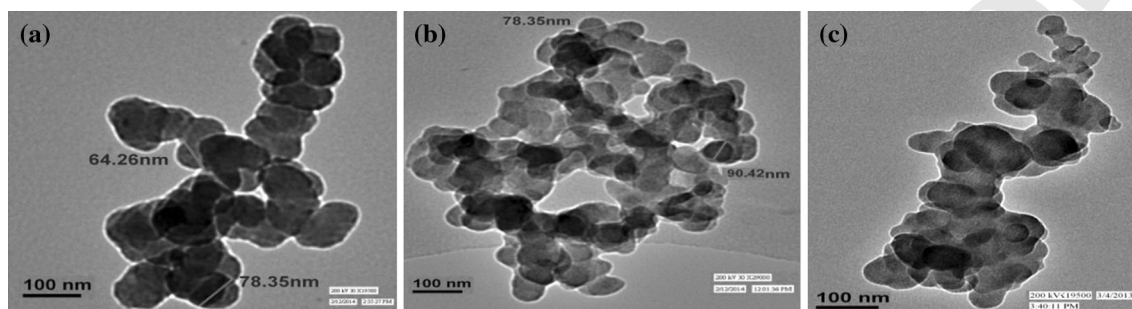
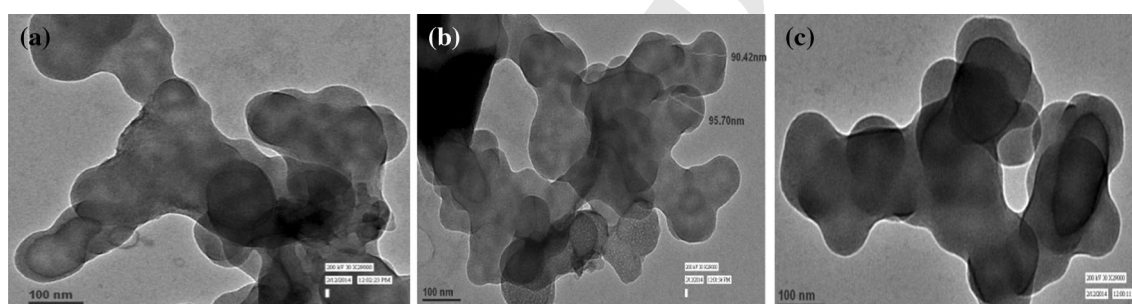
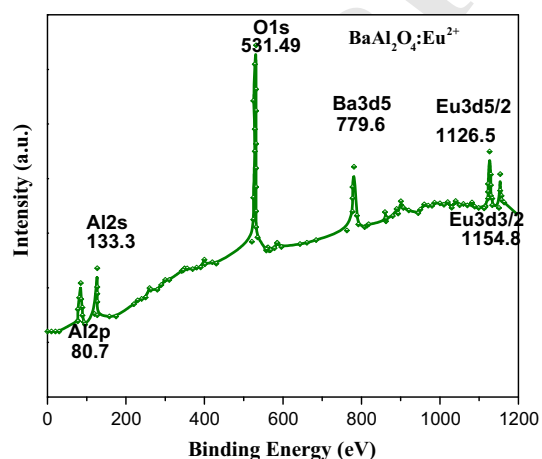
The morphology and crystallinity of the phosphors were 195
analyzed by transmission electron micrographs. Figure 3a, 196
b, c and Fig. 4a, b, c demonstrate the morphology of the 197
 $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$, $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Y}^{3+}$, $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Pr}^{3+}$ 198
nanospheres prepared at 600°C without and with boric 199
acid addition respectively. The BaAl_2O_4 sample prepared 200
at 600°C shows a relatively regular shape, and the average 201
grain size is in the range of 80–100 nm. The samples of 202
 BaAl_2O_4 phosphors prepared with the addition of boric 203
acid were found to be having little increase in crystal size. 204
Thus, after boric acid addition, the particle size slightly 205
increases with change of morphology of BaAl_2O_4 . 206

3.3 X-ray photoelectron analysis 207

The elemental composition in the Eu^{2+} doped BaAl_2O_4 208
phosphor was analyzed by X-ray photoelectron spec- 209
troscopy as shown in Fig. 5. In the present work phosphors 210

Table 1 Crystallite sizes and colour co-ordinates of prepared nanophosphors doping with Eu^{2+} and various codopants without the use of boric acid using Scherrer equation

S. no.	Nanophosphors	FWHM	2θ	Crystal size (nm)
1	$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Y}^{3+}$ (without boric acid)	0.10862	28.33862	83.53012
2	$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Pr}^{3+}$ (without boric acid)	0.10427	28.33152	86.66213
3	$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ (without boric acid)	0.10127	28.32077	88.88462
4	$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ (with boric acid)	0.10027	28.33862	90.03896
5	$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Y}^{3+}$ (with boric acid)	0.09641	28.32083	93.68919
6	$\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Pr}^{3+}$ (with boric acid)	0.09191	28.32191	98.24632

**Fig. 3** TEM micrographs of nanophosphors prepared without boric acid **a** $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$, **b** $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}:\text{Y}^{3+}$, **c** $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}:\text{Pr}^{3+}$ **Fig. 4** TEM micrographs of nanophosphors prepared with boric acid **a** $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$, **b** $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}:\text{Y}^{3+}$, **c** $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}:\text{Pr}^{3+}$ **Fig. 5** X-ray photoelectron spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ phosphors

were characterized by the XPS to analyze mainly the oxidation states of the europium whether it exist in +2 or +3. Peaks of the all the constituents of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ phosphor was consistent with standard corresponding values of intensity of peaks. The peaks consequent to Eu ($3d$), Ba ($3d$), O ($1d$) and Al ($2p$) core levels were recognized in XPS spectra. Ba ($3d$), O ($1s$) and Al ($2p$) were established at binding energy of 779.6 eV, 531.49 eV and 80.7 eV correspondingly. The peak at 1126.5 eV is due to the parent peak of Eu^{2+} ($3d_{5/2}$) and the peak at 1154.8 eV originated from Eu^{2+} ions ascribed to the parent photoelectron peaks of Eu^{2+} ($3d_{3/2}$) [20, 21].

3.4 Photoluminescence properties of nanophosphors

Two apparent absorption peaks between 260 and 400 nm (inset) are available in the absorption spectra of these

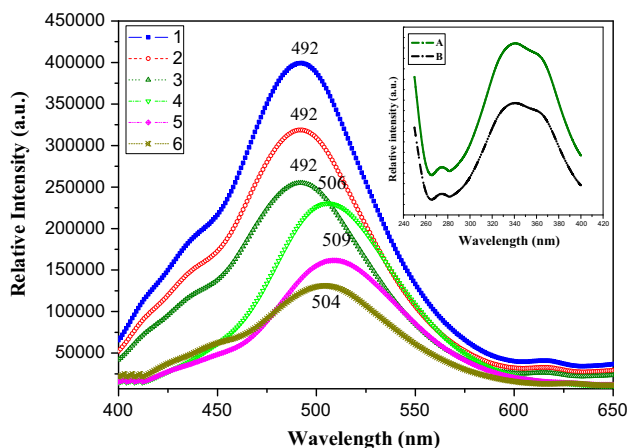


Fig. 6 Emission spectra of 1 BaAl₂O₄:Eu²⁺,Pr³⁺(with boric acid), 2 BaAl₂O₄:Eu²⁺,Y³⁺(with boric acid), 3 BaAl₂O₄:Eu²⁺(with boric acid), 4 BaAl₂O₄:Eu²⁺(without boric acid), 5 BaAl₂O₄:Eu²⁺,Y³⁺(without boric acid), 6 BaAl₂O₄:Eu²⁺,Pr³⁺(without boric acid) and inset shows the Excitation spectra of rare earth doped and codoped BaAl₂O₄ A With boric acid and B without boric acid

226 prepared phosphors as shown in Fig. 6. One is a narrow
 227 peak with low intensity and the other is a broad one with
 228 high intensity in higher wavelength region, analogous to
 229 the crystal field splitting of d-orbital of the Eu²⁺ ions. The
 230 feature of a typical broad band emission in the visible light
 231 range indicates that the dopant ion Eu is in +2 state
 232 (4f⁶5d¹ → 4f⁷ blue green emission) not in trivalent
 233 (4f → 4f, sharp red emission). In BaAl₂O₄, 5d levels of
 234 Eu²⁺ are positioned beneath the ⁶P₁ state of the 4f⁷
 235 configuration. The broad emission band is obtained owing to
 236 the permitted 4f⁶5d¹ → 4f⁷ transition as shown in Fig. 6.

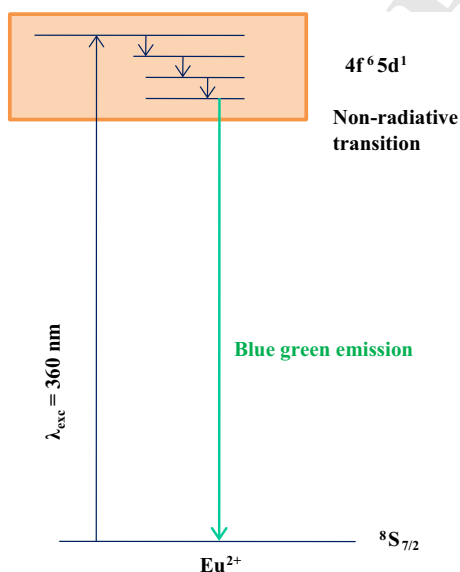


Fig. 7 Mechanism of probable transition of Eu²⁺ ion

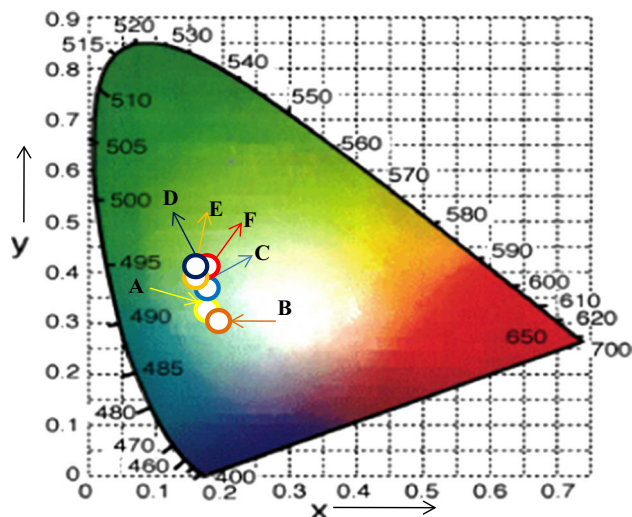


Fig. 8 CIE Chromaticity coordinates of prepared phosphors

Moreover, the 5d ↔ 4f transition is related with the elec- 237
 238 tric dipole change, and the excited state 5d is affected by
 239 crystal field effects. Consequently, the Eu²⁺ emission is too
 240 much reliant on the surrounding environment. The emis-
 241 sion spectrum of BaAl₂O₄:Eu²⁺ and BaAl₂O₄:Eu²⁺,RE³⁺
 242 (Fig. 6) presents a broad band assigned to interconfigura-
 243 tional 4f⁶5d¹ → 4f⁷ transition of Eu²⁺. When lattice is
 244 SrAl₂O₄:Eu²⁺ the emission is green, while in BaAl₂O₄:
 245 Eu²⁺ the emissive color is blue green because of the
 246 emission towards shorter wavelength (~495 nm) in com-
 247 parison to SrAl₂O₄:Eu²⁺ (~512 nm). The reason is that
 248 the Sr²⁺ and Eu²⁺ (0.112 nm) are isovalence and having
 249 nearly same size so no any significant distortion on lattice
 250 structure while substituting Sr²⁺ by Eu²⁺. Although Eu²⁺
 251 and Ba²⁺ are also isovalence but have much difference in
 252 ionic sizes. Due to small ionic radii of Eu²⁺ than Ba²⁺ the
 253 contraction in crystal lattice will occur resulting in the
 254 emission to short wavelength [14, 22].

Emission maxima, peaking at 491–495 nm, were 255
 256 observed attributable to the transitions 4f⁶5d¹ → 4f⁷ of
 257 Eu²⁺. In the emission spectra, however, a low intense
 258 asymmetric emission peak was observed, emitting nearly at
 259 440 nm only in phosphor compounds prepared by using
 260 flux, which is due to two Ba²⁺ sites taken by Eu²⁺ in
 261 BaAl₂O₄ structure. The broad band emission at
 262 491–495 nm is due to the host and the activator interaction,
 263 which can be accredited to the occurrence of an excited
 264 electron in the outer shell of the Eu²⁺ ion [23]. The
 265 mechanism of Eu²⁺ transition is shown in Fig. 7.

As boric acid facilitated the easy incorporation of RE³⁺ 266
 267 ions into the host lattice that helps in the enhancement of
 268 their optical properties. While without adding boric acid,
 269 the use of codopants showed a remarkable lowering effect
 270 on luminescence properties as well as on crystallinity

Author Proof

Table 2 Colour co-ordinates of nanophosphors showing their emissive colour region

S. no.	Nanophosphors	Colour coordinates	
		X	Y
A	BaAl ₂ O ₄ :Eu ²⁺ (with boric acid)	0.17778	0.34673
B	BaAl ₂ O ₄ :Eu ²⁺ ,Y ³⁺ (with boric acid)	0.23353	0.28916
C	BaAl ₂ O ₄ :Eu ²⁺ ,Pr ³⁺ (with boric acid)	0.20225	0.30038
D	BaAl ₂ O ₄ :Eu ²⁺ ,Pr ³⁺ (without boric acid)	0.17124	0.39434
E	BaAl ₂ O ₄ :Eu ²⁺ ,Y ³⁺ (without boric acid)	0.17725	0.37213
F	BaAl ₂ O ₄ :Eu ²⁺ (without boric acid)	0.18995	0.40053

271 because of the presence of RE³⁺ ions on the surface of
 272 lattice which caused hindrance for Eu²⁺ to absorb and emit
 273 light. The crystal field strength is increased with increase of
 274 crystallinity on boric acid addition and the increase in
 275 crystal sizes of phosphors resulted in increase of average
 276 optical path. Both these effects caused the red shift in
 277 emission band. Boric acid is resulted as an outstanding flux
 278 to assist the dissemination of material. Therefore, B₂O₃ is
 279 generally added in the preparations of Eu doped MAI₂O₄
 280 (Ca, Sr, Ba) phosphors to lower the forming temperature.
 281 Furthermore, the flux enforces the dopant and codopant
 282 ions to replace the M²⁺ site in the lattice. This increases the
 283 dopant and codopant ions concentration in the metal alu-
 284 minate lattice and causes steep increase in the photolumi-
 285 nescence properties. Further, the dissolved B³⁺ ions
 286 replace aluminium ions at tetrahedral positions. This sub-
 287 stitution results in the shrinkage of host lattice and improve
 288 the hole trapping capability of RE³⁺ ions due to coming
 289 closer to dopant ions as size of host lattice is decreased, so
 290 it further increases the afterglow intensity. According to
 291 Tukia and Kutty, the added B₂O₃ is substituted in AlO₄
 292 framework of SrAl₂O₄, resulting in the enhancement of
 293 luminescence intensity at low concentration [19, 24, 25].
 294 H₃BO₃ showed a vigorous role in enhancing the lumines-
 295 cence from the phosphor materials as H₃BO₃ has very good
 296 solubility with the oxide materials employed [26].

297 The emissive colours were analyzed and confirmed by
 298 using the Commission Internationale de Eclairage (CIE)
 299 chromaticity co-ordinate diagram. The color co-ordinates
 300 for the prepared phosphors are shown in Fig. 8. The CIE
 301 diagram clearly shows the shifting of emissive color of
 302 BaAl₂O₄ phosphors from green to bluish green region on
 303 adding flux (Table 2).

304 4 Conclusion

305 BaAl₂O₄:Eu²⁺,RE³⁺ down conversion nanophosphors
 306 were efficiently synthesized by rapid gel combustion
 307 technique. The nanophosphors were prepared using boric

acid as flux and without boric acid. Photoluminescence
 spectra showed that by the use of flux, intensity of phos-
 phors enhanced sharply. Codoping of rare earth ions (Y and
 Pr) alongwith Eu²⁺ further enhanced the down conversion
 intensity of the materials. CIE diagram illustrated the
 shifting of emissive color of phosphors towards the bluish
 green region incorporating of boric acid. XRD pattern main
 diffraction peaks indexed well with hexagonal crystalline
 phase. Crystallite size calculation by Sherrer equation
 showed the increment in size of particles of phosphors
 synthesized in presence of flux and this is also well con-
 firmed by TEM images. The BaAl₂O₄:Eu²⁺,Pr³⁺
 nanophosphor showing bright luminescence (at 492 nm)
 could be efficiently in further display and solar
 applications.

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