

**Eu<sup>2+</sup> Emission in Rb<sub>3</sub>ZnBr<sub>5</sub> And Rb<sub>2</sub>ZnBr<sub>4</sub> Phosphors**C.D. Mungmode<sup>a\*</sup>, D.H. Gahane<sup>b</sup>, S.V. Moharil<sup>c</sup><sup>a</sup>M.G. College, Armori, <sup>b</sup>N.H. College, Bramhapuri,<sup>c</sup>Department of Physics, RTM Nagpur University, Nagpur\*Corresponding author: [mungmode.prashant@gmail.com](mailto:mungmode.prashant@gmail.com)**Abstract:**

Eu<sup>2+</sup> activated Rubidium tetrabromozincate, Rb<sub>2</sub>ZnBr<sub>4</sub>:Eu and Rubidium pentabromozincate, Rb<sub>3</sub>ZnBr<sub>5</sub>:Eu, phosphors prepared by a simple wet chemical method have been studied for its photoluminescence (PL). The presence of bands at around 420nm in the PL emission spectra of the phosphor suggests the presence of Eu<sup>2+</sup> in the host compound. Excitation covers near UV region. It is suggested that these phosphors will be useful for applications like solid state lighting, scintillation detectors and X-ray storage using photo-stimulable phosphors.

**Keywords :** Photoluminescence, Bromide, phosphor, Eu<sup>2+</sup>

**1. Introduction:**

The luminescence is very strongly dependent on the host lattice and can occur from the ultraviolet to the red region of the electromagnetic spectrum. The Eu<sup>2+</sup> emission is intense enough to find important industrial applications in, for example, the tricolor low-pressure mercury fluorescence lamps. Eu emission results from two types of transitions: The most common is that due to 4f<sup>6</sup>5d<sup>1</sup>-4f<sup>7</sup>(8S<sub>7/2</sub>). As the position of the band corresponding to 4f<sup>6</sup>5d<sup>1</sup> configuration is strongly influenced by the host, the emission can be anywhere from 365 nm (e.g., in BaSO<sub>4</sub>) to 650 nm (e.g., in CaS). Blasse<sup>[1]</sup> has listed the Eu<sup>2+</sup> doped compounds, which shows that the emission colour of Eu<sup>2+</sup> can vary in a broad range, from ultraviolet to red. Since the 4f-5d transition is an allowed electrostatic dipole transition, the absorption and emission of Eu<sup>2+</sup> is very efficient in many hosts, which makes the Eu<sup>2+</sup> doped phosphors of practical importance. Eu<sup>2+</sup> activated phosphors find use in many applications. BaMgAl<sub>10</sub>O<sub>17</sub>:Eu and Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu are efficient tri-colour lamp phosphors<sup>[2,3]</sup>. Efficient Eu<sup>2+</sup> emission has been obtained in many compounds<sup>[4,5-8]</sup> many of such phosphors have found applications. UV emitting phosphors are useful in erythema and photocopying lamps. Blue color emitting phosphors find applications as lamp phosphors and blue component of CTV phosphor.

Recently, some Eu<sup>2+</sup> activated bromide phosphors are reported<sup>[9,10]</sup>. However, there are not many studies on luminescence of Eu<sup>2+</sup> in bromides. A relatively recent review<sup>[11]</sup> on luminescence of Eu<sup>2+</sup> shows that very few bromides have been covered in luminescence studies. This prompted us to undertake investigations of luminescence of Eu<sup>2+</sup> in some bromides.

**2. Experimental:**

The precursors used in this work are of AR grade. Samples were prepared by dissolving desired quantities of RbBr, ZnO and Eu<sub>2</sub>O<sub>3</sub> in preheated HBr. Excess acid was then boiled off and the solutions were evaporated to dryness. These resulting powders were dried and annealed for 1 h at 900 K in a reducing atmosphere provided by burning charcoal so as to reduce the activator to divalent state. An alumina crucible containing the compound was placed in another crucible. The annular space was filled with charcoal. A tight fitting lid covered the outer crucible. This treatment was found sufficient to yield bright phosphors exhibiting intense Eu<sup>2+</sup> emission. No nitrogen/H<sub>2</sub> circulation was needed. Compounds formed are hygroscopic and catch moisture if left in open. They are to be stored in tight-capped bottles. The annealed powders were quickly sandwiched between quartz plates and transferred to photoluminescence (PL) cell. Photoluminescence spectra in

the range 220–700nm were recorded on Hitachi F-4000 spectro-fluorimeter with spectral slit width of 1.5 nm. Samples were also found to be stable against UV irradiation that was used for the PL measurements. No changes in spectral positions or intensities were observed during several, successive PL runs.

### 3. Result and Discussion:

As all the results are related to PL of  $\text{Eu}^{2+}$ , general features of the emission are first briefly mentioned.  $\text{Eu}^{2+}$  emission arises from the lowest band of  $4f^65d^1$  configuration to  ${}^8\text{S}_{7/2}$  state of  $4f^7$  configuration. The excitation arises from the transition from  ${}^8\text{S}_{7/2}$  state of  $4f^7$  configuration to the states belonging to  $4f^65d^1$  configuration. The ground state electronic configuration of  $\text{Eu}^{2+}$  is  $4f^7$ . This results in a  ${}^8\text{S}_{7/2}$  level for the ground state. The next  $f^7$  manifold ( ${}^6\text{P}_j$ ) lies approximately  $28,000\text{cm}^{-1}$  higher. The lowest lying  $4f^65d^1$  levels begin near  $34,000\text{cm}^{-1}$  and are labeled  ${}^8\text{H}_j$  for the free ion. The  $4f^65d^1$  levels experience much more crystal field splitting than the  $4f^7$  levels due to the increased spatial extent of the 5d orbitals and often are the metastable state, or the lowest excited state, when the  $\text{Eu}^{2+}$  ion is incorporated in a crystalline host. The effect of the crystal field of octahedral symmetry on the 5d electron is to split the 5d orbitals into two component  $st_{2g}$  and  $e_g$ . For lesser symmetries, the splitting can be as much as five fold. The isotropic part of the exchange interaction between 5d and 4f electrons results in an exchange splitting into states with total spins of  $S = 7/2$  and  $5/2$ . Thus for the absorption spectra of  $\text{Eu}^{2+}$  in the solids, the lowest energy band arises from the state described by the notation  $[4f^6({}^7\text{F}_j)e_g, S = 7/2]^{114}$ . The lowest energy configuration corresponds to the situation where  ${}^7\text{F}_j(4f^6)$  state couples to the 5d  $e_g$  orbital such that all spins are parallel. Spectral positions of these bands vary a great deal from lattice to lattice<sup>115</sup>. The most commonly observed emission is the dipole and spin allowed d-f emission starting from the relaxed  $4f^6({}^7\text{F}_0)5d^1$  level. Due to allowed nature of the transition, d-f emission is intense.

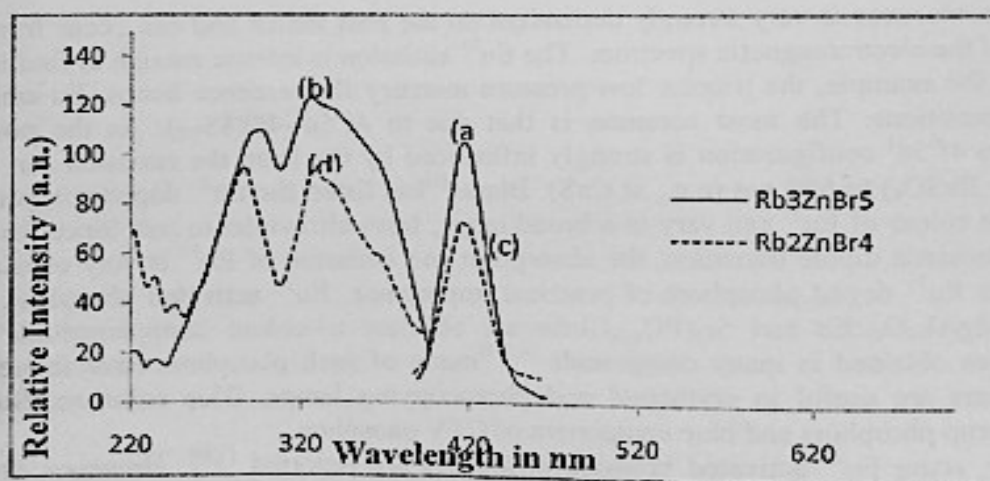


Fig. 1. PL spectra for  $\text{Eu}^{2+}$  activated  $\text{Rb}_2\text{ZnBr}_4$  and  $\text{Rb}_3\text{ZnBr}_5$   
(a) emission in  $\text{Rb}_3\text{ZnBr}_5:\text{Eu}^{2+}$  for 365 nm excitation, (b) excitation for 420 nm emission of  $\text{Rb}_3\text{ZnBr}_5:\text{Eu}^{2+}$ , (c) emission in  $\text{Rb}_2\text{ZnBr}_4:\text{Eu}^{2+}$  for 290 nm excitation, (d) excitation for 419 nm emission of  $\text{Rb}_2\text{ZnBr}_4:\text{Eu}^{2+}$ .

$\text{Rb}_3\text{ZnBr}_5$  crystallizes in orthorhombic system with space group Pnam ( $a = 9.679$ ,  $b = 10.496$ ,  $c = 13.443$ ). Data on PL of  $\text{Rb}_3\text{ZnBr}_5$  are presented in Fig. 1. Intense PL emission is observed for  $\text{Rb}_3\text{ZnBr}_5$  containing 1mol%  $\text{Eu}^{2+}$ , and quenched at 900 K. The intense emission is observed in the violet-blue region with a maximum at 420nm (Fig. 1, curve a). The excitation spectrum (Fig. 1, curve b) shows several unresolved bands; the one around 325 nm being most prominent. Shoulder is also observed around 367 nm. Separation between the longest wavelength excitation band and the emission b and (Stokes shift) is quite small. In fact there is partial overlap of the excitation and emission bands.

Rubidium tetrabromozincate,  $\text{Rb}_2\text{ZnBr}_4$ , belongs to a family of crystals such as  $\text{Rb}_2\text{ZnCl}_4$  with the  $\beta\text{-K}_2\text{SO}_4$  type (orthorhombic Pnam) structure<sup>[13]</sup>. PL data on  $\text{Eu}^{2+}$  activated  $\text{Rb}_2\text{ZnBr}_4$  are included in Fig. 1 (curves c and d). Maximum intensity was observed for the sample containing 1 mol%  $\text{Eu}^{2+}$ , and quenched at 900 K. For 365 nm excitation, emission is observed with a maximum around 420 nm. The excitation curve contains several unresolved bands around 332, 367, and 288 nm. Emission in  $\text{Eu}^{2+}$  activated  $\text{Rb}_3\text{ZnBr}_5$  is more intense than  $\text{Rb}_2\text{ZnBr}_4$ .

Coupled with near UV excitation, these emissions can be useful for solid state lighting using near UV-emitting LEDs. Though the emissions are at shorter wavelengths, these may be converted to useful spectral regions using co-doping or energy transfer from  $\text{Eu}^{2+}$  to another activator such as  $\text{Mn}^{2+}$ . Other important applications could be as scintillation detectors.

#### 4. Conclusions

A simple wet chemical method for the synthesis of  $\text{Eu}^{2+}$  activated  $\text{Rb}_2\text{ZnBr}_4$  and  $\text{Rb}_3\text{ZnBr}_5$  phosphors is described. Efficient luminescence is observed near 420 nm in blue violet region with excitation in the near UV range. More intense emission is observed for  $\text{Rb}_3\text{ZnBr}_5$  than  $\text{Rb}_2\text{ZnBr}_4$ . It is suggested that the efficient luminescence can be used for obtaining phosphors for solid state lighting, scintillation detectors and X-ray storage.

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