



# WET CHEMICAL PREPARATION AND PHOTOLUMINESCENCE IN $\text{Cs}_2\text{MCl}_4:\text{Eu}^{2+}$ ( $\text{M} = \text{Ba}, \text{Ca}$ ) PHOSPHOR FOR pcLED APPLICATION

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## Abstract

A simple wet chemical synthesis of  $\text{Cs}_2\text{MCl}_4:\text{Eu}^{2+}$  ( $\text{M} = \text{Ba}, \text{Ca}$ ) phosphors is described.

Photoluminescence characterization of prepared phosphors is carried out. Intense blue emission for  $\text{Cs}_2(\text{Ba}_{0.99}\text{Eu}_{0.01})\text{Cl}_4$  phosphor is observed peaking at 443 nm when excited by nUV light, whereas, maximum PL intensity is observed for  $\text{Cs}_2(\text{Ca}_{0.995}\text{Eu}_{0.005})\text{Cl}_4$  phosphor annealed at 875 K centered around 446 nm upon excited by 365 nUV radiations. Emission spectra is attributed to dipole allowed  $4f^6 5d^1 \rightarrow 4f^7$  transition of  $\text{Eu}^{2+}$  dopant ion present in halide crystal. Both the phosphors can be efficiently excited by near Ultra Violet (nUV) radiations. Therefore, these phosphors may be used for pcLED application.

**Keywords:**  $\text{Eu}^{2+}$ , phosphor, LED, photoluminescence

## 1. Introduction

Alkali/ alkaline earth halides have been applied extensively as host lattice using various activators such as  $\text{Cu}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tl}^+$ , Na, etc. [1, 2, 3, 4]. Europium doped alkali halides are extensively investigated due to their potential importance as Thermoluminescence Dosimeters, UV detectors, phosphors for Solid State Lighting, etc. [5, 6]. Europium doped alkaline earth chlorides shows efficient emission of  $\text{Eu}^{2+}$  luminescence [7]. Europium doped cesium bromide phosphor have been reported to show potential X-ray imaging phosphor [8]. Hao et al. proposed use of  $\text{CaCl}_2:\text{Eu}^{2+}$  phosphor for phototherapy lamps

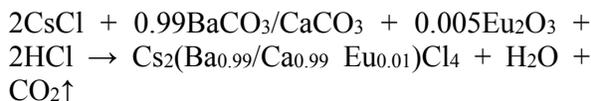
[9]. Several solid solutions of alkaline earth halides are known [10, 11, 12, 13]. Gahane et al. [14, 15] reported synthesis by wet chemical method and efficient luminescence in some  $\text{Eu}^{2+}$  doped alkaline earth iodides, alkaline earth bromides and Alkali-alkaline earth double bromides. Structural characteristics of the x-ray storage phosphors  $\text{Cs}_2\text{BaBr}_4$ ,  $\text{Rb}_2\text{BaBr}_4$ ,  $\text{Cs}_2\text{BaCl}_4$ , and  $\text{Rb}_2\text{BaCl}_4$  are reported by Appleby et al. [16]. They also studied Photoluminescence and Photo Stimulated Luminescence of these phosphors. The phosphors were prepared by solid state route. However, the synthesis of these phosphors takes long time with repeated grinding or extensive ball milling. Recently,  $\text{Eu}^{2+}$  activated  $\text{ABCl}_3$  type hosts like  $\text{KSrCl}_3$ ,  $\text{CsMgCl}_3$ ,  $\text{CsCaCl}_3$ ,  $\text{CsSrCl}_3$ , etc. were synthesized by wet chemical method, confirmed the formation of compounds by XRD characterization and studied luminescence by Gahane et al [17].  $\text{Eu}^{2+}$  emission in all  $\text{ABCl}_3$  type chlorides is very intense comparable to that of commercially available BAM (Sylvania 2466 blue,  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ ). Emission intensities in  $\text{KCaCl}_3$ ,  $\text{KSrCl}_3$ ,  $\text{CsCaCl}_3$  and  $\text{CsSrCl}_3$  are double or more to BAM.

The present work reports on synthesis of  $\text{Eu}^{2+}$  activated  $\text{Cs}_2\text{BaCl}_4$  and  $\text{Cs}_2\text{CaCl}_4$  phosphors using easy and time saving wet-chemical method and their photoluminescence.

## 1. Experimental

$\text{Eu}^{2+}$  activated  $\text{Cs}_2\text{MCl}_4:\text{Eu}^{2+}$  ( $\text{M} = \text{Ba}, \text{Ca}$ ) samples are prepared by wet chemical method dissolving stoichiometric amount of metal carbonates ( $\text{CaCO}_3/\text{BaCO}_3$ ),  $\text{CsCl}$  and  $\text{Eu}_2\text{O}_3$  in

HCl. Excess acid was then boiled off and the solutions are evaporated to dryness. The reaction proceeds as below.



All starting materials used are AR grade manufactured by Merk. The resulting product was dried at 475 K for 2 h in the air, after this, it is crushed to fine powder and, then, annealed for 1 h at various temperature in a reducing atmosphere provided by burning charcoal so as to reduce the  $\text{Eu}^{2+}$  state. An alumina crucible containing the compound was placed in another crucible. The annular space was filled with activated charcoal. A tight fitting lid covered the outer crucible. This treatment is found sufficient to yield bright phosphor exhibiting intense  $\text{Eu}^{2+}$  emission. The heat-treated samples were quickly sandwiched between the fused quartz plates and shifted to the photoluminescence (PL) cell for characterization. The photoluminescence spectra are recorded in the range of 220–700 nm on a Hitachi F-4000 spectrofluorimeter under the spectral resolution of 1.5 nm.

## 2. Result and Discussion

### (a) $\text{Cs}_2\text{BaCl}_4:\text{Eu}^{2+}$ :

Ternary halide  $\text{Cs}_2\text{BaCl}_4$  crystalizes with the  $\text{Th}_3\text{P}_4$  body-centered cubic structure (Fig. 1), space group I-43d (220), where Cs and Ba cations randomly occupy the Th sites in a 2:1 ratio [18]. Cs and Ba atoms are randomly distributed amongst the (12a) positions and the halide atoms occupy the (16c) positions.

Fig. 2 (curve b) shows photoluminescence excitation spectra of  $\text{Cs}_2(\text{Ba}_{0.99}\text{Eu}_{0.01})\text{Cl}_4$  for 440 nm emission. Broad excitation spectra covers wavelength from UV to visible region. It contains several unresolved bands; the bands around 280 nm and 340 nm are most prominent. Phosphor can be efficiently excited by near UV (nUV) radiations. Fig. 2 (curve a) presents PL emission spectrum of  $\text{Cs}_2(\text{Ba}_{0.99}\text{Eu}_{0.01})\text{Cl}_4$  phosphor quenched at 723 K. Photoluminescence spectra consists of a strong broad band lies in blue region with Full Width at Half Maxima (FWHM) equal to 53.1 nm. Upon excitation with 365 nm light, intense blue emission is observed peaking at 443 nm for 1 nm slit width.

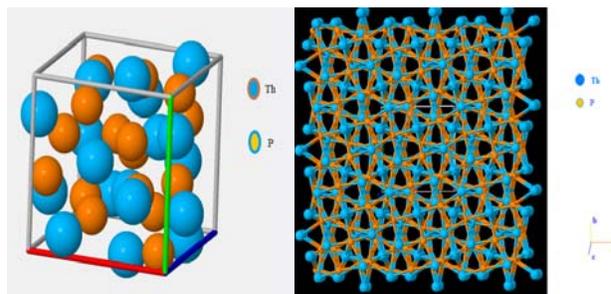


Figure 1: Unit Cell and Crystal Structure of  $\text{Th}_3\text{P}_4$  [19]

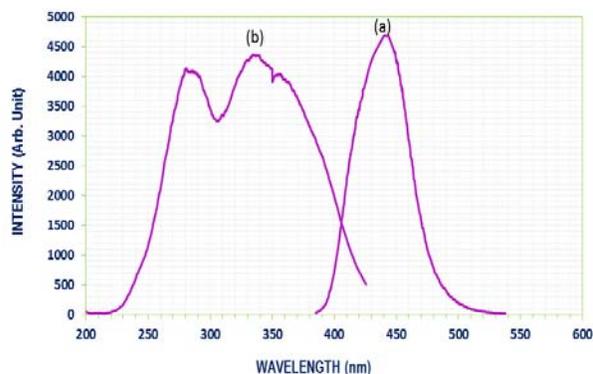


Figure 2: Photoluminescence spectra of  $\text{Cs}_2(\text{Ba}_{0.99}\text{Eu}_{0.01})\text{Cl}_4$

(a) Emission spectra of  $\text{Cs}_2(\text{Ba}_{0.99}\text{Eu}_{0.01})\text{Cl}_4$  under 365 nm excitation. (b) Excitation spectra of  $\text{Cs}_2(\text{Ba}_{0.99}\text{Eu}_{0.01})\text{Cl}_4$  for 440 nm emission.

Emission spectra is attributed to dipole allowed  $4f^6 5d^1 \rightarrow 4f^7$  transition of  $\text{Eu}^{2+}$  dopant ion present in halide crystal [20]. Highly intense PL spectra may be due to lower symmetry of the crystal. Emission peak observed in present work (443 nm) is in good agreement with the literature value (441 nm) [16].

### (b) $\text{Cs}_2\text{CaCl}_4:\text{Eu}^{2+}$ :

$\text{Cs}_2\text{CaCl}_4$  belongs to high - Tc cuprate family. Fig. 3 presents photoluminescence spectrum of  $\text{Cs}_2(\text{Ca}_{0.995}\text{Eu}_{0.005})\text{Cl}_4$  phosphor. The emission spectrums of  $\text{Cs}_2(\text{Ca}_{0.995}\text{Eu}_{0.005})\text{Cl}_4$  phosphor annealed at different temperature are shown by curve a, b and c in Fig. 3. The emission intensity increases with increase in annealing temperature up to 875 K and then after it decreases as shown in inset. Maximum PL intensity is observed for the phosphor annealed at 875 K centered around 446 nm upon excited by 365 nUV radiations. The emission width (FWHM) is observed to be 21 nm. The emission peak is blue shifted from 448.5 nm to 440 nm with increase in annealing

temperature from 675 K to 975 K. This may possibly because of increase in crystal field splitting due to increased crystallinity with increasing annealing temperature. Fig. 3 (curve d) presents excitation spectrum of  $\text{Cs}_2(\text{Ca}_{0.995}\text{Eu}_{0.005})\text{Cl}_4$ . Several overlapping bands are observed near UV region; those around 360 nm and 380 nm being the most prominent. This shows that phosphor can be efficiently excited by nUV radiations claiming the candidature for blue component of Near UV LED.

The emission maxima is slightly red shifted from 443 nm for  $\text{Cs}_2(\text{Ba}_{0.99}\text{Eu}_{0.01})\text{Cl}_4$  to 446 nm for  $\text{Cs}_2(\text{Ca}_{0.995}\text{Eu}_{0.005})\text{Cl}_4$  upon excitation by 365 nm radiation. This can be explained on the basis of crystal field splitting which is increased due to substitution of Ca atoms in place of Ba atoms.

Both,  $\text{Cs}_2\text{BaCl}_4:\text{Eu}^{2+}$  and  $\text{Cs}_2\text{CaCl}_4:\text{Eu}^{2+}$  phosphors showed highly efficient blue emission when excited by nUV light. Hence, these phosphors may be used as blue phosphors for phosphor converted light emitting diode (pcLED) application.

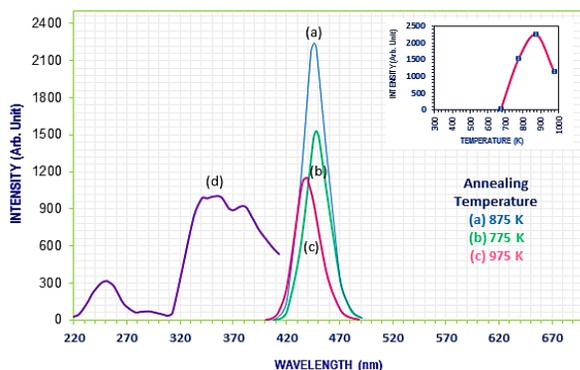


Figure 3: Photoluminescence spectra of  $\text{Cs}_2(\text{Ca}_{0.995}\text{Eu}_{0.005})\text{Cl}_4$  phosphor. (a), (b), (c) Emission spectra of  $\text{Cs}_2(\text{Ca}_{0.995}\text{Eu}_{0.005})\text{Cl}_4$  under 365 nm excitation. (d) Excitation spectra of  $\text{Cs}_2(\text{Ca}_{0.995}\text{Eu}_{0.005})\text{Cl}_4$  for 440 nm emission. The inset shows the variation of the emission intensity with annealing temperature (K).

### 3. Conclusion

$\text{Eu}^{2+}$  activated Alkali-alkaline earth double chlorides,  $\text{Cs}_2\text{BaCl}_4:\text{Eu}^{2+}$  and  $\text{Cs}_2\text{CaCl}_4:\text{Eu}^{2+}$ , are synthesized by simple wet chemical method. Highly efficient emission in blue region is observed for both phosphors when excited by nUV radiation. Phosphors showed excellent response in nUV region. Hence, these phosphors present candidature as blue phosphor for pcLED application.

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