



## PHOTOLUMINESCENT PROPERTIES OF NOVEL RED-EMITTING $\text{Ca}_{2-x}\text{ZnMoO}_6:\text{xEu}^{3+}$ PHOSPHOR

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### ABSTRACT

In this article a novel  $\text{Ca}_{2-x}\text{ZnMoO}_6:\text{Eu}^{3+}$  ( $x=1,3,5,7\& 9\%$ ) red-emitting phosphors have been successfully synthesized by a Combustion Method at  $750^\circ\text{C}$  temperatures and their photoluminescent properties were investigated. The Photoluminescence characteristics of the sample are studied using UV excitation light of 285 nm (i.e. Mo–O charge transfer band). Upon excitation with UV light, the phosphor show a strong red emission line at around 617 nm corresponds to the electric dipole transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  of  $\text{Eu}^{3+}$ , other transition from the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  located at 570–700 nm range are weak. The optimal doping concentration of  $\text{Eu}^{3+}$  ions in  $\text{Ca}_{2-x}\text{ZnMoO}_6$  is about 7 mol% and the phenomenon of concentration quenching occurs when the content of  $\text{Eu}^{3+}$  ions exceeds 7 mol%. The emission intensity increases with increasing of the  $\text{Eu}^{3+}$  up to a particular concentration and then reduces at a higher level. . It was found that the phosphors have a orthorhombic structure with space group Pmm2 and belongs to double perovskite family, in which  $\text{Ca}^{2+}$  ions are coordinated with 12 oxygen, while  $\text{Zn}^{2+}$  and  $\text{Mo}^{6+}$  ions are coordinated with 6 oxygen forming  $\text{ZnO}_6$  and  $\text{MoO}_6$  octahedral respectively. This material appears to be promising red emission which is suitable for lamp industry and display devices.

**Keywords:** Molybdates, Photoluminescence, Phosphor, Combustion Method

### 1. Introduction

A large number of isotropic compounds with perovskite structures, such as double

perovskite oxides, have the established system  $\text{A}_2\text{BB}'\text{O}_6$ , in which  $\text{BO}_6$  and  $\text{B}'\text{O}_6$  octahedra are corner-shared, alternately. The great flexibility of A and B(B') sites in  $\text{A}_2\text{BB}'\text{O}_6$  allows very rich substitutions, and this structure forms cube-octahedral cavities filled by A-site cations [1,2]. Double perovskites with the formula  $\text{A}_2\text{BB}'\text{O}_6$ , where A uses an alkaline earth, B and B' are metal transition magnetic and nonmagnetic ions, and O is oxygen, have been investigated as magnetic materials for many years. For example,  $\text{Ba}_2\text{CrMoO}_6$  has been studied as Insulator-half metal transition driven by M-site doping system [3]. Recently reported magnetic and thermoelectric properties of ordered double perovskite  $\text{Ba}_2\text{FeMoO}_6$  [4]. Complete ordering of Fe and Mo on the B and B' sites of this metallic  $\text{A}_2\text{BB}'\text{O}_6$  double perovskite is predicted to give half-metallic magnetism with restricted majority-spin electrons on the Fe atoms [4]. Recently, the study of  $\text{A}_2\text{BB}'\text{O}_6$ -based materials has increased due to various technological applications, such as inorganic oxide luminescent materials.

The luminescence of rare-earth ions doped in perovskite-type ceramics was once actively investigated in the 1960s and Nineteen Seventies due to the fact of activity in their ferroelectricity, Phase transitions, and semiconducting residences [5]. Recently, many research have shown that the double perovskite structure with a composition of  $\text{A}_2\text{BMO}_6$  (A = Ba, Sr; B = Ca, Zn; M = Mo, W) is activated by trivalent europium ions ( $\text{Eu}^{3+}$ ) [6–9]. Phosphors activated by way of  $\text{Eu}^{3+}$  are considered ideal red sources because of their sharp emission lines in the red region [6–10].  $\text{Eu}^{3+}$ -doped double-perovskite materials have a

excitation band ranging from UV to visible light, and they also show extraordinarily environment friendly red luminescence. For that,  $\text{Eu}^{3+}$ -doped double molybdenum (Mo)-based double perovskite oxides have attracted substantial interest for their possibly application as luminescent materials, such as  $\text{Sr}_2\text{MgMo}_x\text{W}_{1-x}\text{O}_6:\text{Eu}^{3+}$  [11],  $\text{Sr}_2\text{Ca}(\text{Mo}/\text{W})\text{O}_6:\text{Eu}^{3+}$  [12],  $\text{Sr}_2\text{CaMoO}_6:\text{Eu}^{3+}$  [13],  $(\text{Ba},\text{Sr})_2\text{CaMoO}_6:\text{Eu}^{3+}$ , two  $\text{Yb}^{3+}$  [14],  $\text{Ca}_2\text{LaMoO}_6:\text{Eu}^{3+}$  ( $\text{M} = \text{Sb}, \text{Nb}, \text{Ta}$ ) [15], and  $\text{A}_2\text{CaMoO}_6$  ( $\text{A} = \text{Sr}, \text{Ba}$ ) [6], respectively. But to our knowledge, little work has been performed on the photoluminescence residences of  $\text{Eu}^{3+}$ -doped  $\text{Ca}_2\text{ZnMoO}_6$  phosphors prepared by means of the Combustion method. In this work, double-perovskite  $\text{Ca}_2\text{ZnMoO}_6:\text{Eu}^{3+}$  phosphors were synthesized by way of Combustion method. The crystalline structure, morphology and luminescence properties of the phosphors were investigated.

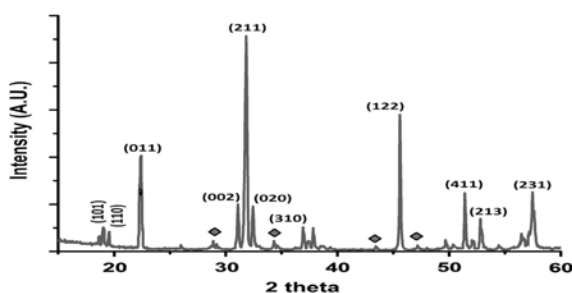
## 2. Experimental:

The  $\text{Ca}_{2-x}\text{ZnMoO}_6:\text{Eu}^{3+}$  ( $x = 1, 3, 5, 7 \& 9$  %) samples were prepared by combustion method.  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.99%),  $\text{Eu}_2\text{O}_3$  (99.99%),  $\text{ZnO}$  (AR, analytical reagent),

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$  (AR) and  $\text{CH}_4\text{N}_2\text{O}$  (AR) were used as the starting materials without further purification and were weighted by stoichiometric ratio. Firstly, Solution (A),  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Eu}(\text{NO}_3)_3$  were obtained by dissolving  $\text{ZnO}$  and  $\text{Eu}_2\text{O}_3$  into the concentrated nitric acid, the excess  $\text{HNO}_3$  was removed by further evaporation. Solution (B) was obtained by dissolving  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 24\text{H}_2\text{O}$  in distilled water. Then the two solutions were fully mixed to get a transparent solution. A weighted amount of Urea ( $\text{NH}_2\text{-CO-NH}_2$ ) were dissolved in the transparent solution as fuel and accelerator, respectively. Then solution (B) was once delivered into above-mentioned solution (A) drop by drop under violently stirring. The mixture was continuously stirred and heated at  $70^\circ\text{C}$  for about 1 h, and then the mixture gel was obtained. The sticky gel was introduced into a preheated muffle furnace with a temperature of  $750^\circ\text{C}$ . By using typical combustion process at  $700^\circ\text{C}$  in this experiment,  $\text{CsAl}(\text{MoO}_4)_2:\text{Eu}^{3+}$  phosphor were prepared. A flame was observed with the formation of foamy powder, the powder so obtained was pale yellow in colour.

## 3. Result and Discussion:

### 3.1. X-ray diffraction of $\text{Ca}_2\text{ZnMoO}_6$



**Fig. 1. XRD pattern of  $\text{Ca}_2\text{ZnMoO}_6$  synthesized at  $750^\circ\text{C}$ .**

**Fig. 1** illustrates the XRD pattern of  $\text{Ca}_2\text{ZnMoO}_6$  synthesized at  $750^\circ\text{C}$ . The acquired XRD pattern is properly matched with scheelite Molybdate  $\text{CaMoO}_4$  (JCPDS File No. 29-0351). It exhibits the formation of desired orthorhombic phase of material. This arises due to vaporization of some amount of Zn at excessive temperature.  $\text{Ca}_2\text{ZnMoO}_6$  has orthorhombic structure with space group  $\text{Pmm}2$  and belongs to double perovskite family, in which  $\text{Ca}^{2+}$  ions are coordinated with 12 oxygen, while  $\text{Zn}^{2+}$  and  $\text{Mo}^{6+}$  ions are coordinated with 6 oxygen forming  $\text{ZnO}_6$  and

$\text{MoO}_6$  octahedra respectively.  $\text{ZnO}_6$  and  $\text{MoO}_6$  octahedra are ordered in crystal structure in such a way that they form FCC shape and each share corner of octahedral as shown in inset of **Fig. 1**.

### 3.2 PL Characteristics of $\text{Ca}_{2-x}\text{ZnMoO}_6:\text{xEu}^{3+}$ Phosphor:

**Figs. 2–3** show the excitation and emission spectrums of  $\text{Eu}^{3+}$  doped  $\text{Ca}_2\text{ZnMoO}_6$  phosphor using inorganic materials taking nitrate form. Under excitation 285nm monitored for recording PL spectra.

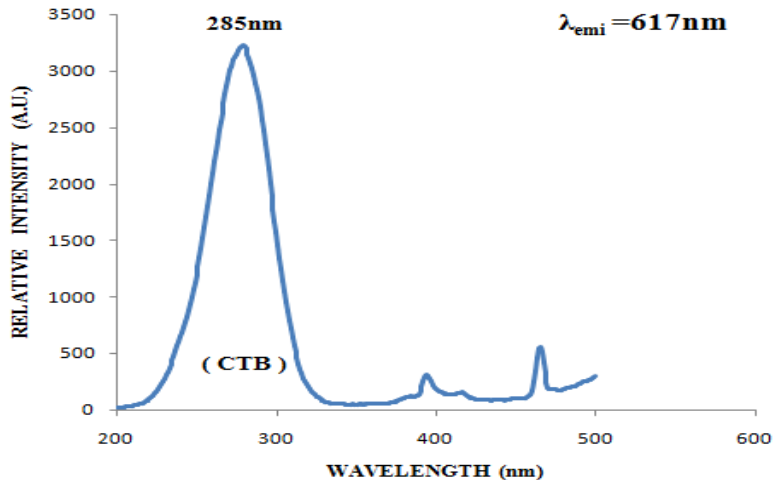


Fig 2. Excitation spectra of  $\text{Ca}_{2-x}\text{ZnMoO}_6:\text{xEu}^{3+}$  ( $x=5\%$ ) phosphor.

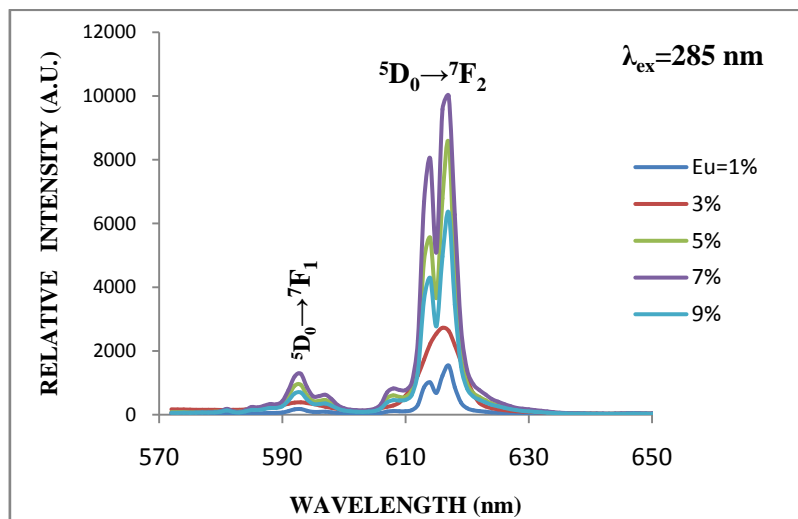


Fig 3. Emissions spectra of  $\text{Ca}_{2-x}\text{ZnMoO}_6:\text{xEu}^{3+}$  ( $x=1,3,5,7 \& 9\%$ ) phosphor

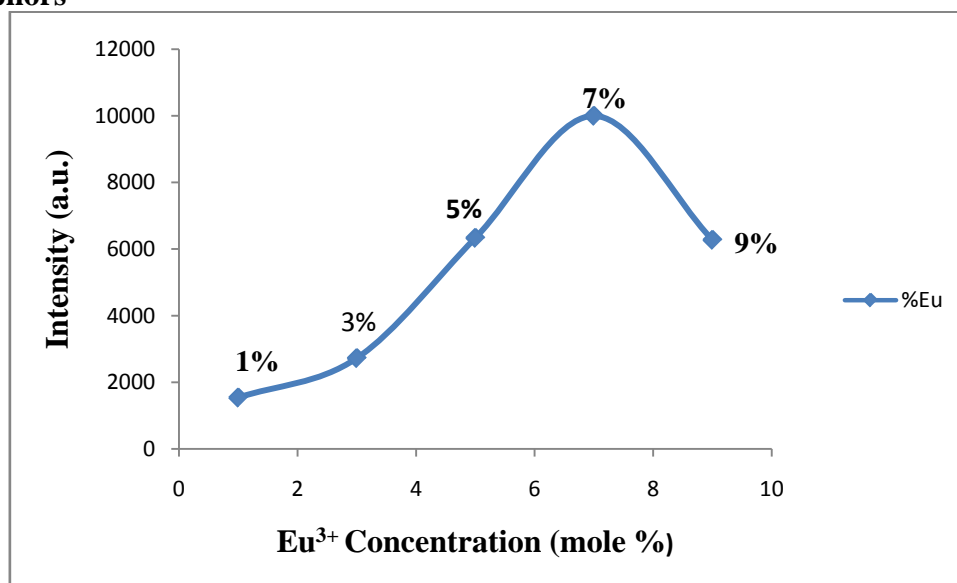
Fig 2. shows the excitation spectra  $\text{Ca}_{2-x}\text{ZnMoO}_6:\text{xEu}^{3+}$  ( $x=0.01,0.03,0.05,0.07 \& 0.09$ ) was monitored at excitation 617 nm and it consists of a broad band with peak at about 285 nm which are assigned to the transitions within  $4f^6$  configuration of  $\text{Eu}^{3+}$  ions. The broader band peaking at 285 nm is ascribed to a combination of a charge transfer (CT) transition from the 2p orbital of oxygen to the 3d orbital of molybdate in the  $(\text{MoO}_4)^{2-}$  group and an  $\text{O}^{2-} - \text{Eu}^{3+}$  charge transfer band [16–18]. The emission spectrum of  $\text{Ca}_2\text{ZnMoO}_6:\text{Eu}^{3+}$  is shown in Fig 3. Apparent emission spectrum of  $\text{Ca}_2\text{ZnMoO}_6:\text{Eu}^{3+}$  phosphor under the excitation of 285 nm consists of narrow and strong emission band at 617 nm and a number of tiny emission bands. The main emission band should be recognized as the transition from splitting level  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  of  $\text{Eu}^{3+}$ . The emission

spectra must be recognized as the transitions  $^5\text{D}_0 \rightarrow ^7\text{F}_j$ . The spectra which are attributable to the transitions  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  consist of some bands according to the number of stark components of  $^7\text{F}_j$ . The number of stark components of  $\text{Eu}^{3+}$  in  $\text{Ca}_2\text{ZnMoO}_6$  crystal follows  $2J+1$  rule. The bands due to the transition  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  is 593nm and transition  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  is 617 nm [19]. It is confidently expected that  $\text{Eu}^{3+}$  in  $\text{Ca}_2\text{ZnMoO}_6$  or in RE of which the crystal structure correspond to calcium zinc molybdate crystal emit a fine and strong emission band at 617 nm under the excitation of UV light. The hypersensitive band at 617 nm can be attributed to the electric dipole transition  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  of  $\text{Eu}^{3+}$  ions. The emission wavelengths of these 4f-4f transitions are only moderately influenced by way of the environment of the lanthanide

ions since the partially filled 4f shell is properly shielded by the filled 5s and 5p orbitals [20, 21]. In PL emission, we have observed that the

luminescence intensity increased with the increasing  $\text{Eu}^{3+}$  concentration

### 3.3 The effect of $\text{Eu}^{3+}$ concentration on the red emission of $\text{Ca}_{2-x}\text{ZnMoO}_6:\text{xEu}^{3+}$ (x=1,3,5,7 & 9%) phosphors



**Figure 4. Luminescence intensity of  $\text{Ca}_{2-x}\text{ZnMoO}_6:\text{xEu}^{3+}$  (x=1,3,5,7 & 9%) as function of  $\text{Eu}^{3+}$  concentration.**

Generally speaking, the doping concentration of luminescent centers has a significant effect on the phosphor performance. Therefore, it is necessary to confirm the optimum doping concentration. For the  $\text{Ca}_2\text{Zn}_{1-x}\text{MoO}_6:\text{xEu}^{3+}$  (x = 0.01, 0.03, 0.05, 0.07 and 0.09) phosphors, the effect of  $\text{Eu}^{3+}$  doping concentration on the relative intensity of the electric dipole transition ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ) is shown in the inset of **Fig. 4**. As can be seen, the emission intensity initially increases, then reaches a maximum at 7 mol%  $\text{Eu}^{3+}$ , and finally decreases with further increasing  $\text{Eu}^{3+}$  doping concentration. Thus, the optimal doping concentration of  $\text{Eu}^{3+}$  in  $\text{Ca}_2\text{Zn}_{1-x}\text{MoO}_6:\text{xEu}^{3+}$  phosphors is just about 7 mol%.

### 4. Conclusion

In summary, novel Double perovskite molybdate  $\text{Ca}_2\text{Zn}_{1-x}\text{MoO}_6:\text{xEu}^{3+}$  (x = 0.01, 0.03, 0.05, 0.07 and 0.09) phosphors were synthesized successfully by Combustion method. The structure and photoluminescence properties of the samples have been investigated. The XRD pattern exhibits the formation of mentioned phosphor; however some much less severe impurity peaks of  $\text{CaMoO}_4$  were seen in diffraction pattern. An intense broad band from 250 to 450 nm, which

matches well with the emission wavelength of near-UV LEDs chips, is observed in the excitation spectrum.  $\text{Ca}_2\text{ZnMoO}_6:\text{Eu}^{3+}$  shows an intense red emission at 617 nm under the excitation of 285 nm. The optimal doping concentration of  $\text{Eu}^{3+}$  in  $\text{Ca}_2\text{ZnMoO}_6$  is about 0.07 and the energy transfer type among  $\text{Eu}^{3+}$  ions in  $\text{Ca}_2\text{ZnMoO}_6:\text{Eu}^{3+}$  phosphors is exchange interaction. Therefore, the  $\text{Ca}_2\text{ZnMoO}_6:\text{Eu}^{3+}$  red phosphors may have a potential application for lamp industry and display devices.

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