PHOTOLUMINESCENCE STUDIES OF Eu^{3+} DOPED CsAl(MoO$_4$)$_2$ PHOSPHOR

D.H.Gahane[a*], B.V.Tupte[b], M.M. Bhave[b], C.D. Mungmode[c]
[a*]Department of Physics, N.H.College, Bramhapuri (M.S.)– 441206, India.
[b]Department of Physics, SGM College Kurkheda(M.S.) – 441209, India.
[b]Department of Physics, N. H. College, Bramhapuri,(M.S.)-441206 India.
[c]Department of Physics, M.G. College, Armori(M.S.)-441208 India.

A B S T R A C T

Recently double metals molybdate and tungstate with a general formula M$^{\mathbf{I}}$ M$^{\mathbf{III}}$ (M$^{\mathbf{VI}}$ O$_4$)$_2$ (where M$^{\mathbf{I}}$ = Na, K, Rb, Cs, M$^{\mathbf{III}}$ = Al, In, Sc and M$^{\mathbf{VI}}$ =Mo, W) are gaining attentions because their interesting chemical and physical properties. CsAl(MoO$_4$)$_2$ is a member of this family of materials with $P\bar{3}m1$ space group and cell parameters a = 5.551(1) Å, c = 8.037(2)Å . In this article Eu^{3+} activated CsAl(MoO$_4$)$_2$ phosphors were synthesized by combustion methods and their photoluminescence characterization was performed. The photoluminescence spectra results indicate that the excitation spectra of the samples consist of a vast absorption band of 200-350 nm and some sharp traces around 350-500 nm which corresponds to the f-f transitions inside 4f^8 configuration of Eu^{3+}.Upon 285 nm excitation, the phosphor show characteristic fluorescence ^{5}D$_0$→^{7}F$_J$ (J=0, 1, 2, 3, 4) of the Eu^{3+} ions. The electronic transition located at 617 nm corresponding to ^{5}D$_0$→^{7}F$_2$ of Eu^{3+} ions, which is stronger than the magnetic dipole transition located at 595 nm corresponding to ^{5}D$_0$→^{7}F$_1$ of Eu^{3+} ions. Different pathways concerned in emission process have been studied. Concentration quenching has been observed for Eu^{3+} concentration 5 mol%. The phosphor may additionally discover a conceivable application in the display and CFL lamps as one of the phosphor component for white light generation.

Keywords: Photoluminescence, Phosphor, Combustion Method, Crystal Structure

Introduction

Molybdates and tungstates doped with transition metal or rare earth ions are important compounds that are found to have potential in tunable laser applications [1–3]. Recently double metals molybdate and tungstate with a general formula MIMIII(MVIO4)2 (where MI = Na, K, Rb, Cs, MIII = Al, In, Sc and MVI =Mo,W)are gaining attentions because their interesting chemical and physical properties.The Cr3+-doped MIMIII (MVIO4)2 materials have currently receiving a great deal of attention due to their interesting properties in tunable laser applications [4–12]. CsAl(MoO4)2 is a member of this family of materials with P $\bar{3}$m1 space group and cell parameters a = 5.551(1) Å, c = 8.037(2)Å [13] Eu3+ is known to be an efficient activator. Its characteristic energy transfer generates a strong emission with a high color purity.[14,15] Eu3+ has excellent PL properties with various host materials. Among these host materials, double molybdate have shown efficient emitting properties.[16,17] These hosts show efficient charge transfers (CT), because they are transition-metal compounds in their highest oxidation states,[18] and the intense excitation properties in the near UV−blue region were able to be used in GaInN-based LED phosphors.[19]

In the present work, new red-emitting phosphors CsAl$_{1-x}$(MoO$_4$)$_2$:xEu^{3+}(x=0.03,0.05& 0.07) were prepared by Combustion Method and photoluminescence of prepared phosphors is studied.

2. Experimental:

The CsAl1-x(MoO4)2:xEu3+(x=0.03,0.05,0.07) samples were prepared by combustion method. CsNO3 (99.99%), Eu2O3 (99.99%), Al2O3

(AR, analytical reagent), $(NH_4)_6Mo_7O_{24} \cdot 6H_2O$ (AR) and CH_4N_2O (AR) were used as the starting materials without further purification and were weighted by stoichiometric ratio. Firstly, Solution (A), $Al(NO_3)_3$, $Eu(NO_3)_3$ were obtained by dissolving Al_2O_3 and Eu_2O_3 into the concentrated nitric acid, the excess HNO_3 was removed by further evaporation. Solution (B) was obtained by dissolving $CsNO_3$ and $(NH_4)_6Mo_7O_{24} \cdot 24H_2O$ in distilled water. Then the two solutions were fully mixed to get a transparent solution. A weighted amount of Urea $(NH_2-CO-NH_2)$ were dissolved in the transparent solution as fuel and accelerator, respectively. Then solution B was brought into above-mentioned solution A drop through drop under violently stirring. The mixture was continuously stirred and heated at 70 °C 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. By using typical combustion process at 700°C in this experiment, $CsAl_{1-x}(MoO_4)_2:xEu^{3+}$ (x= 0.03, 0.05 & 0.07)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 Crystal Structure $CsAl(MoO_4)_2$

Caesium aluminium dimolybdate $CsAl(MoO_4)_2$, belongs to the glaserite kind family of double molybdates . The room temperature phase of $CsAl (MoO_4)_2$ was developed in the trigonal space group P $\overline{3}$m1 (No. 164), as for many different double molybdates of the glaserite structure.[20-24] The shape consists of $[AlMo_2O_8-]n$ layers perpendicular to the trigonal c-axis, with the caesium cations between the layers Fig.1. Each layer is constructed up from MoO_4 tetrahedra and AlO_6 octahedra; every octahedron shares its six corners with six MoO_4 tetrahedra. The extra low-temperature experiments do not exhibit any changes in the powder-diffraction diagram, for that reason indicating no symmetry modifications and the absence of a phase transition. The low-temperature lattice parameters are as follows: a = 5.525 (2), c = 7.966 (3) Å at 110 K and a = 5.513 (3),c = 7.954 (4) Å at 40 K. The lattice parameter a adjustments linearly with temperature, while the temperature dependence of the parameter c is quadratic.
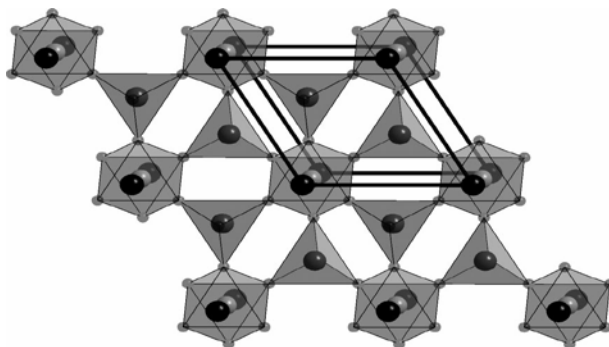

Fig.1 View of CsAl(MoO4)2, approximately down the c axis.

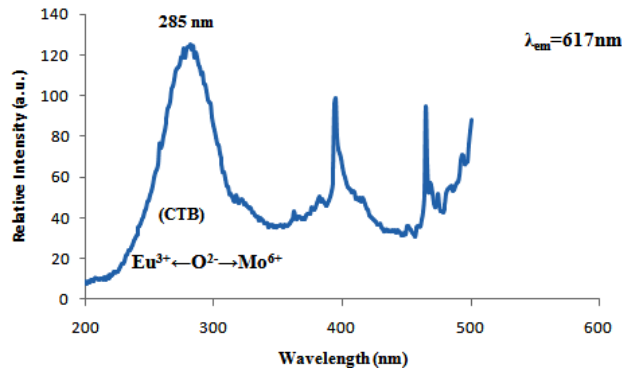## 3.2 PL Characteristics of $CsAl_{1-x}(MoO_4)_2:xEu^{3+}$ (x=0.03,0.05 &0.07)Phosphor:

Fig 2. Excitation spectra of $CsAl_{1-x}(MoO_4)_2:xEu^{3+}$ (x=5%) phosphor

Fig. 2 shows the excitation spectra of $CsAl(MoO_4)_2$: Eu^{3+} was monitored at excitation 617 nm. The host $CsAl(MoO_4)_2$ has a broad absorption band from 230 to 350 nm with peak at about 285 nm which are assigned to the charge-transfer state (CTS) band of $Mo^{6+}-O^{2-}$ [25]. When Eu^{3+} ions are doped into the $CsAl(MoO_4)_2$, the CTS of $Eu^{3+}-O^{2-}$ appears and the absorption edge of $Mo^{6+}-O^{2-}$ CTS band shifts to a longer wavelength, which may be caused by the increment of covalency of Mo-O bond due to the incorporation of Eu^{3+} [26].
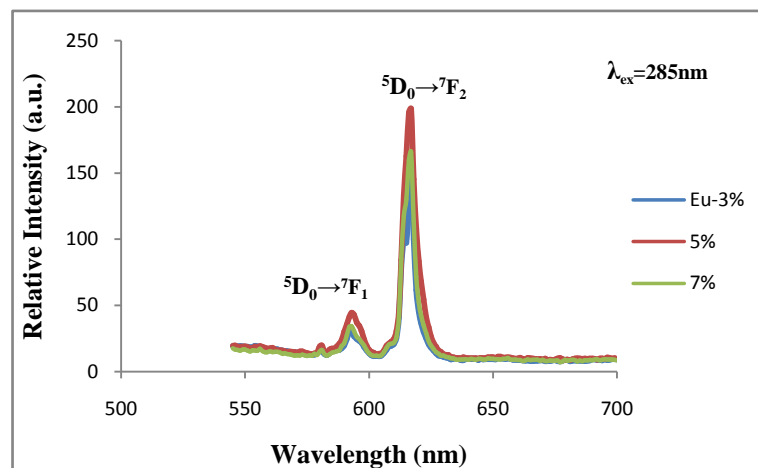

Fig. 3 Emissions spectra of $CsAl_{1-x}(MoO_4)_2:xEu^{3+}$ (x=3,5 & 7 %) phosphor

The emission spectrum of $CsAl_{1-x}(MoO_4)_2$: xEu^{3+}(x=0.03,0.05&0.07) is shown in **Fig. 3** Apparent emission spectrum of $CsAl(MoO_4)_2$: Eu^{3+} phosphor under the excitation of 285 nm consists of narrow and strong emission band at 617 nm and a number of small emission bands. The main emission band should be identified as the transition from splitting level $^5D_0 \rightarrow ^7F_2$ of Eu^{3+}. The emission spectra must be identified as the transitions $^5D_0 \rightarrow ^7F_j$. The spectra which are attributable to the transitions $^5D_0 \rightarrow ^7F_j$ consist of some bands according to the number of stark components of 7Fj, The number of stark components of Eu^{3+} in CsAl(MoO4)2 crystal follows 2J+1 rule. The bands due to the transition $^5D_0 \rightarrow ^7F_1$ are 581, 588, 593, and 599 nm, transition $^5D_0 \rightarrow ^7F_2$ are 620 and 630 nm and transition $^5D_0 \rightarrow ^7F_3$ are 650 and 658 nm [27]. It is expected that Eu^{3+} in $CsAl(MoO_4)_2$ or in RE of which the crystal structure correspond to $CsAl(MoO_4)_2$ crystal emit a narrow 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 $^5D_0 \rightarrow ^7F_2$ of Eu^{3+} ions. In PL emission, we have observed that the luminescence intensity increased with the increasing Eu^{3+} concentration.

3.3 Effect of Eu^{3+} Doping on Photoluminescence Properties

The effect of Eu^{3+} ions doping on the luminescence properties was studied. **Fig 4.** is photoluminescence spectra of samples with different Eu^{3+} doping. It can be seen that luminescence intensity of $CsAl_{1-x}(MoO_4)_2:xEu^{3+}$ (x=0.03,0.05 & 0.07) composite increases with the increase of the amount of Eu^{3+} ions. When the doping amount of Eu^{3+} ion is 3%, the luminescence properties

are the best. When the doping amount of Eu^{3+} ion is more than 5%, the amount of Eu^{3+} ions doping will continue to increase, the intensity of the luminescence will decreases. This quenching process is often attributable to the fact that the energy of electron in an excited state will be transmitted to the quenching center more easily when the concentration of Eu^{3+} has reached a certain value [28–29]. What is more as the concentration of Eu^{3+} ions increases, a slight shift of the CT band maximum towards longer wavelength can be observed. It can be related to reduction of the average crystallite size with increasing concentration of Eu^{3+} ions doped into the host lattice.
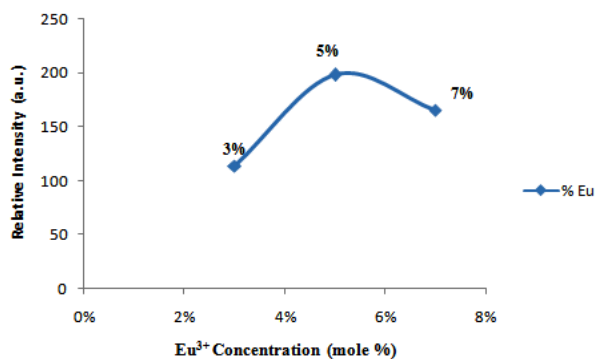

Figure 4. Luminescence intensity of $Ca_{2-x}ZnMoO_6:xEu^{3+}$ (x=1,3,5,7 & 9%) as function of Eu^{3+} concentration.

Conclusion

The PL spectra show the strongest emission at 617 nm corresponds to the $5D0 \rightarrow 7F2$ transition of Eu3+, which outcomes in bright red colour emitting phosphor used for display devices and lamp industries CaAl1-x(MoO4)2:xEu3+ (x=0.03,0.05 & 0.07) had been effectively prepared through Combustion Method .Upon 285nm excitation the phosphor indicates an extreme photoluminescence emission peak at 617 nm due to the electric dipole (ED) transition 5D0→7F2 of Eu 3+ ions and other shoulder peaks at 595 nm. The CsAl(MoO4)2 crystal structure used to be recognized as follows : trigonal system , sp.gr. $P\bar{3}m1$[No.164] , a = 5.525 (2), c = 7.966 (3) Å at 110 K and a = 5.513 (3),c = 7.954 (4) Å at 40 K and ρcalc=3.49 g/cm3. The

photoluminescence result shows this phosphor as a promising red light emitting phosphor and is useful in LEDs and other display devices.

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