

## Pholuminescence Properties of Some Molybdate Phosphors Containing Bismuth

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### ABSTRACT

Eu<sup>3+</sup>-doped Molybdate Phosphors Containing Bismuth are prepared by a combustion method and characterized by X-ray diffraction (XRD) patterns, photoluminescence (PL) spectroscopy. PL properties have an impact on factors along with molar ratio of Bismuth (Bi<sup>3+</sup>) and Molybdate (Mo<sup>6+</sup>) ions, dopants concentration are studied. The results show that Molybdate Phosphors Containing Bismuth can act as a useful host for Eu<sup>3+</sup> ions doping, and energy transferring from Bi<sup>3+</sup> to Eu<sup>3+</sup> achieved efficiently hence this phosphor displayed intense red color emission under ultraviolet light excitation.

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

### I. INTRODUCTION

Nowadays, great amply of efforts have been paid for the development of phosphors, due to the extensive applications of white light-emitting diodes (LEDs), as it was known that LEDs had the advantage of low power consumption, high efficiency, long durability, fast response and lack of toxic mercury. [1,2] Among the oxides and sulfides phosphors, molybdates could be a perfect host for rare Earth luminescent material, ascribe to their good thermal and chemical stability. Bismuth molybdate is an important inorganic material due to its perfect luminescent and structural properties, however, it other potential applications in modern fields, such as optical sensors, magnetic nano-device,

biomedical reagent, photocatalysis, organic molecules ammonia-oxidizing agent, and so on forth. [3-6]

The Bi<sup>3+</sup> and RE<sup>3+</sup> ions possess close ionic radii and therefore the Bi-containing compounds could be easily doped with luminescent ions like Eu<sup>3+</sup>, Yb<sup>3+</sup>, etc. It was demonstrated recently that K<sub>2</sub>Bi(PO<sub>4</sub>)(MoO<sub>4</sub>):Eu<sup>3+</sup> is a phosphor for white light-emitting diodes. Yb<sup>3+</sup> and Nd<sup>3+</sup>-doped K<sub>5</sub>Bi(MoO<sub>4</sub>)<sub>4</sub> is considered as a promising material for laser in the near-IR region [7, 8].

Recently, the molybdate family has aroused great interest and been chosen as host materials for new luminescent materials which can be activated in the deep UV region (200–250 nm) based on their good stability, low costs, simple synthesis conditions and good luminescence properties. [9,10,11] However,

most of the reports focus on the luminescence properties of  $\text{Eu}^{3+}$  doped  $\text{CaMoO}_4$  for the applications in white LED. Here in this manuscript, we synthesized rare earth ions  $\text{Eu}^{3+}$  doped  $\text{R}_5\text{Bi}(\text{MoO}_4)_4$  ( $\text{R}=\text{K}, \text{Na}$ ) phosphors, and investigated their luminescence properties in detail.

## II. EXPERIMENTAL

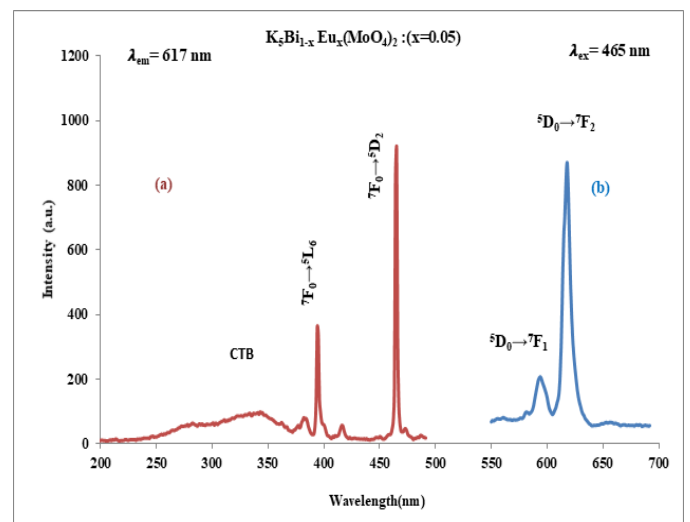
The  $\text{Eu}^{3+}$  activated  $\text{R}_5\text{Bi}_{1-x}(\text{MoO}_4)_4: x\text{Eu}^{3+}$  ( $\text{R}=\text{K}, \text{Na}$ ) (where  $x = 0.05$  mole) phosphors were prepared by the combustion synthesis. The starting AR grade materials (99.99% purity) were taken as Potassium nitrate  $\text{KNO}_3$ , Sodium nitrate ( $\text{NaNO}_3$ ), ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ), Bismuth Oxide ( $\text{Bi}_2\text{O}_3$ ), Europium oxide ( $\text{Eu}_2\text{O}_3$ ) & Urea ( $\text{NH}_2\text{CONH}_2$ ) was used as fuel. In the present investigation, materials were prepared according to the chemical formula  $\text{R}_5\text{Bi}_{1-x}(\text{MoO}_4)_4: x\text{Eu}^{3+}$  ( $\text{R}=\text{K}, \text{Na}$ ). The mixture of reagents was grind together to obtain a homogeneous powder.  $\text{Bi}^{3+}$  and  $\text{Eu}^{3+}$  ions were introduced as a  $\text{Bi}(\text{NO}_3)_3$  and  $\text{Eu}(\text{NO}_3)_3$  solution by dissolving  $\text{Bi}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$  into a dil.  $\text{HNO}_3$  solution. For various compositions of the metal nitrates (oxidizers), the amount of urea (fuel) was calculated maintaining total oxidizing and reducing valences of the components equal to unity, so that the heat liberated during combustion is a maximum. After stirring for about 30 min, the precursor solution was transferred to a furnace which was preheated to 750 °C. Porous products were obtained.

## III. RESULTS AND DISCUSSION

Fig.1(a) and 1(b) shows excitation spectra of  $\text{R}_2\text{Bi}_{0.95}(\text{MoO}_4)_4:0.05\text{Eu}^{3+}$  ( $\text{R} = \text{K}, \text{Na}$ ) doped with 5%  $\text{Eu}^{3+}$  monitoring the emission at 617nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition). The band located between 250 and 350 nm can be attributed to the charge transfer (CT) from  $[\text{MoO}_4]^{2-}$  groups to  $\text{Eu}^{3+}$ . It shows broadening and a

slight red-shift with increasing  $\text{Eu}^{3+}$  content. The red shift of the CT band is caused by the decreasing size of the  $\text{Eu}^{3+}$  sites, upon substitution of  $\text{Bi}^{3+}$  by smaller  $\text{Eu}^{3+}$ , thus resulting in shorter  $\text{Eu}-\text{O}$  bonds, which eases the charge transfer. There are several sets of lines in the range of 350–600 nm which are associated with the typical intra-configurational  $4f^6$  transitions of  $\text{Eu}^{3+}$ .

Lines originating from  $^7\text{F}_0 \rightarrow ^5\text{L}_6$  and  $^7\text{F}_0 \rightarrow ^5\text{D}_2$  transitions are located at 395 and 465 nm, respectively, and are of special interest. The spectral position of these lines match well with the emission spectra of near-UV and blue LEDs, respectively, thus making the synthesized phosphors suitable for solid-state light sources. Moreover, it should be noted that the intensity ratio between  $^7\text{F}_0 \rightarrow ^5\text{L}_6$  and  $^7\text{F}_0 \rightarrow ^5\text{L}_j, ^5\text{G}_j$  is different. We assume that the  $^7\text{F}_0 \rightarrow ^5\text{L}_j, ^5\text{G}_j$  transitions become more probable due to the broadening of the CT-level with increasing  $\text{Eu}^{3+}$  concentration and thus the admixing of the CT-level with those excited terms of the  $[\text{Xe}]4f^6$  ground state configuration, which are energy wise close to the CT state.



**Fig. (1) Photoluminescence spectrum of  $\text{Eu}^{3+}$  activated  $\text{K}_5\text{Bi}_{1-x}\text{Eu}_x(\text{MoO}_4)_4$  ( $x=0.05$ ) Phosphor**  
**(a) Excitation spectra of  $\text{K}_5\text{Bi}_{1-x}\text{Eu}_x(\text{MoO}_4)_4$  ( $x=0.05$ ) for 617 nm emission**  
**(b) Emission Spectra of  $\text{K}_5\text{Bi}_{1-x}\text{Eu}_x(\text{MoO}_4)_4$  ( $x=0.05$ ) for 465 nm excitation.**

The  $O \rightarrow Eu^{3+}$  CT transitions can be manifested only in the case of  $R_5Bi(MoO_4)_4$  ( $R=K, Na$ ), where the bismuth-oxygen polyhedra have  $BiO_6$  structure rather than  $BiO_8$  in three other crystals.

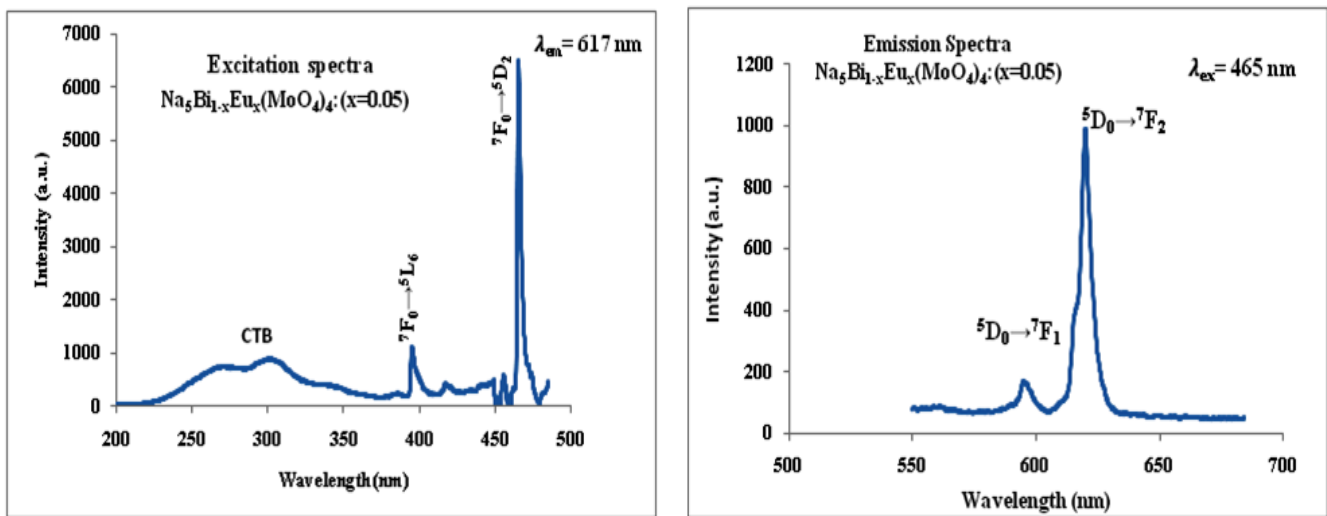


Fig. (2) Photoluminescence spectrum of  $Eu^{3+}$  activated  $Na_5Bi_{1-x}Eu_x(MoO_4)_4$  ( $x=0.05$ ) Phosphor

(a) Excitation spectra of  $Na_5Bi_{1-x}Eu_x(MoO_4)_4$  ( $x=0.05$ ) for 617 nm emission

(b) Emission Spectra of  $Na_5Bi_{1-x}Eu_x(MoO_4)_4$  ( $x=0.05$ ) for 465 nm excitation.

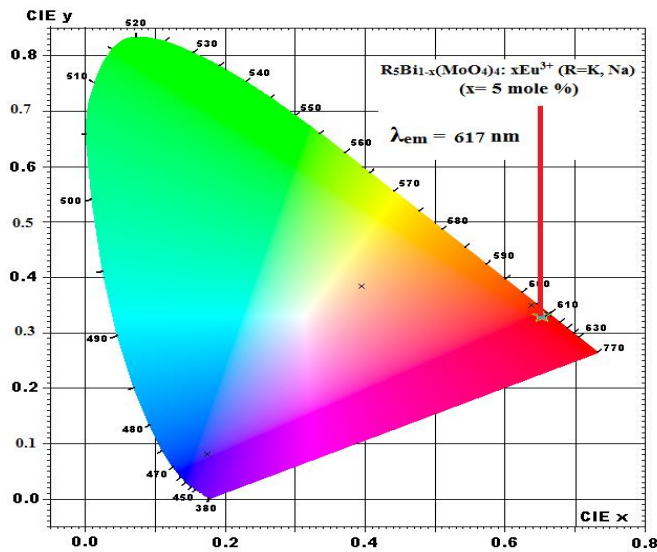
The excitation band of  $Eu^{3+}$  PL in  $R_5Bi(MoO_4)_4$  ( $R=K, Na$ ) with peak position near 300 nm can be tentatively ascribed to  $O \rightarrow Eu^{3+}$  CT transitions. The spectral position of this band corresponds to positions the CT excitation bands of the  $Eu^{3+}$  PL usually observed in the molybdate hosts. The emission spectra of  $R_2Bi_{0.95}(MoO_4)_4:0.05Eu^{3+}$  ( $R = K, Na$ ) samples doped with 5%  $Eu^{3+}$  under 465 nm excitation are depicted in Fig.2(a) and 2(b). The strongest emission lines located at 617nm are ascribed to the  $^5D_0 \rightarrow ^7F_2$  transition. The intensity of lines originating from  $^5D_0 \rightarrow ^7F_1$  (595 nm) is much weaker if compared to  $^5D_0 \rightarrow ^7F_2$  transition.  $^5D_0 \rightarrow ^7F_2$  is an electric dipole transition, [12,13] which requires a lower symmetry on the respective  $Eu^{3+}$  sites.

It is known that the emission of  $Bi^{3+}$  ions at low temperatures, originates from  $^3P_0 \rightarrow ^1S_0$  transitions. At higher temperatures the emission occurs mainly from the higher level  $^3P_1$  and transition  $^3P_1 \rightarrow ^1S_0$  becomes allowed due to spin-orbit coupling of  $^3P_1$  and  $^1P_1$  states. Generalizing the data on the luminescence properties of  $Bi^{3+}$  ions in oxygen coordination we can note that the spectral position of the PL bands depends on number of

the oxygen ions in the nearest surrounding, the symmetry of this surrounding, and the presence of defects, first of all the oxygen vacancies in it. Dependence between these structural characteristics and Stokes shift of luminescence was found too [14]. Analysis of this dependence leads to the conclusion that the described above emission components should be attributed to the transitions in  $Bi^{3+}$  ions in polyhedral oxygen coordination -  $[BiO_8]^{13}$ -groups.

The bismuth ions in  $K_5Bi(MoO_4)_4$  and  $Na_5Bi(MoO_4)_4$  hosts have eight oxygen's in the nearest surrounding form irregular 8-vertex polyhedra  $BiO_8$ . However, three nonequivalent positions of Bi ions exist in  $K_5Bi(MoO_4)_4$  and  $Na_5Bi(MoO_4)_4$  lattice, and each of them is characterized by a specific geometric structure of  $BiO_8$  polyhedron [14, 15]. At the same time, it is well known that spectral properties of  $Bi^{3+}$ -related emissions in molybdate hosts strongly depend on the configuration of the nearest oxygen surrounding [16]. Taking into account these facts, two spectral components of  $K_5Bi(MoO_4)_4$  and  $Na_5Bi(MoO_4)_4$  emission can be tentatively attributed to the emission

of the  $\text{Bi}^{3+}$ -related centers which originate from three nonequivalent lattice positions of the bismuth ions.



**Fig. (3): CIE chromaticity diagram for  $\text{R}_2\text{Bi}_{0.95}(\text{MoO}_4)_4:0.05\text{Eu}^{3+}$  (R = K, Na) phosphor.**

Fig. (3) shows the CIE chromaticity diagram for the emission spectra of  $\text{R}_2\text{Bi}_{0.95}(\text{MoO}_4)_4:0.05\text{Eu}^{3+}$  (R = K, Na) phosphors. The CIE chromaticity coordinates (x, y) of the  $\text{R}_2\text{Bi}_{0.95}(\text{MoO}_4)_4:0.05\text{Eu}^{3+}$  (R = K, Na) phosphors upon 465 nm excitation wavelength lie at  $x = 0.678$  and  $y = 0.322$  which are very close to the standard chromaticity coordinate values of NTSC ( $x = 0.670$ ,  $y = 0.330$ ). Hence, the CIE diagram illustrates that the obtained phosphor particles show red emissions when excited by a single wavelength ( $\lambda_{\text{ex}} = 465$  nm) and thus the obtained results confirm that the combustion method prepared  $\text{R}_2\text{Bi}_{0.95}(\text{MoO}_4)_4:0.05\text{Eu}^{3+}$  (R = K, Na) phosphors is a promising red emitting components for white LEDs.

#### IV. CONCLUSION

In summary,  $\text{Eu}^{3+}$  doped Molybdate containing Bi compounds  $\text{K}_5\text{Bi}(\text{MoO}_4)_4$ ,  $\text{Na}_5\text{Bi}(\text{MoO}_4)_4$  were successfully synthesized under combustion method and photoluminescence properties were studied. Upon excitation with UV light and blue light, the as-prepared products show a strong red emission at 617 nm

corresponding to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition of  $\text{Eu}^{3+}$ . Observed intrinsic PL mainly originates from the excitation transitions in Bi-oxygen polyhedrons followed by the related backward radiation transitions. Excitation energy transfer from the host to  $\text{Eu}^{3+}$  ions was observed for all investigated Eu-doped compounds. The Eu-doped samples at nUV and UV excitation reveal narrow lines of  $\text{Eu}^{3+}$  related emission grouped around the main lines peaking at 595 nm and 617 nm which originate from intra-configurational  $4f_6$  transitions in  $\text{Eu}^{3+}$  ions (radiative transitions from the excited  ${}^5\text{D}_0$  level to  ${}^7\text{F}_j$  ( $j = 0, 1, 2, 3, 4$ ) manifolds of the ground state). The results indicate that the Molybdate containing Bi compounds doped with  $\text{Eu}^{3+}$  phosphor is a promising candidate as a red component.

#### V. REFERENCES

- [1]. C. Shivakumara and R. Saraf, *Opt. Mater.* 42 (2015) 178.
- [2]. N. Zhang, D. J. Wang, L. Li, Y. S. Meng, X. S. Zhang and N. Ming, *J. Rare Earth.* 24 (2006) 294.
- [3]. C. S. Guo, J. Xu, S. F. Wang, L. Li, Y. Zhang and X. C. Li, *Cryst. Eng. Commun.* 14 (2012) 3602.
- [4]. E. Vila, J. E. Iglesias, J. Galy and A. Castro, *Solid State Sci.* 7 (2005) 1369.
- [5]. T. T. Fang and T. F. Ko, *J. Am. Ceram. Soc.* 86 (2003) 1453.
- [6]. R. B. Licht, D. Vogt and A. T. Bell, *J. Catal.* 339 (2016) 228.
- [7]. M. Voda, R. Balda, I. Saez de Ocariz et al., *J. Alloys Compd.*, 275-278, 214 (1998).
- [8]. H. Canibano, G. Boulon, L. Palatella et al., *J. Luminescence*, 102-103, 318 (2003).
- [9]. S. X. Yan, J. H. Zhang, X. Zhang, S. Z. Lu, X. G. Ren, Z. G. Nie, and X. J. Wang, *J. Phys. Chem. C* 111, 13256 (2007).
- [10]. Y. Jin, J. H. Zhang, S. Z. Lu, H. F. Zhao, X. Zhang, and X. J. Wang, *J. Phys. Chem. C* 112, 5860 (2008).

- [11]. Y. G. Su, C. F. Du, Q. Y. Jia, L. Lv, Q. L. Liu, and X. J. Wang, *J. Nanosci. Nanotechnol.* 11, 9855 (2011).
- [12]. G. Blasse and B. C. Grabmaier, *Luminescent Materials*, SpringerVerlag, Berlin, 1994.
- [13]. W. M. Yen, S. Shionoya and H. Yamamoto, *Phosphor Handbook*, CRC Press/Taylor and Francis, Boca Raton, 2007.
- [14]. G. Blasse, A. C. van der Steen, *Solid State Comm.*, 31, 993 (1979).
- [15]. Zatovsky, K. Terebilenko, M. Slobodyanik et al., *J. Solid State Chem.*, 180, 3351 (2007).
- [16]. B. Romero, S. Bruque, M. A. G. Aranda, J. E. Iglesias, *Inorg. Chem.*, 33, 1869 (1994).
- [17]. C. Timmermans, G. Blasse, *J. Solid State Chem.*, 52, 222 (1984).