



# A novel orange emitting bismuth molybdate based phosphor

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## Abstract

A novel orange emitting bismuth molybdate based phosphor ( $\text{Bi}_2\text{MoO}_6:\text{Sm}^{3+}$ ) prepared via a conventional high-temperature solid-state reaction was reported for the first time in the present work. X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and fluorescence spectroscopy (FS) measurements were utilized to investigate their phase purity, structure, and photoluminescence properties. The f–f transitions of  $\text{Sm}^{3+}$  ions were designated in terms of the excitation and emission spectrum. The critical distance as well as concentration quenching mechanism of  $\text{Sm}^{3+}$  ions in  $\text{Bi}_2\text{MoO}_6$  host was also calculated and confirmed, respectively. The decay behaviors of  $\text{Bi}_2\text{MoO}_6:\text{Sm}^{3+}$  phosphors were investigated in detail. The as-prepared phosphors can be effectively excited with a 407 nm light, and exhibit orange emission with decay constant of milliseconds. The above work indicates that the  $\text{Bi}_2\text{MoO}_6:\text{Sm}^{3+}$  phosphors could have potential application in white light-emitting diodes.

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**Keywords:**  $\text{Bi}_2\text{MoO}_6:\text{Sm}^{3+}$ ; Light-emitting diodes; Luminescence; Phosphor

## 1. Introduction

Molybdate based phosphor is a kind of important luminescence material. When the rare earth ions (e.g.  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ) are incorporated, the efficient host sensitization can lead to the strong emission from the rare earth ions due to the energy transfer between molybdate ion and rare earth ions. The broad excitation band can locate in the ultraviolet (UV) region for molybdate phosphors due to the absorption of molybdate ion, which makes it a potential application prospect in solid state lighting region, especially white-lighting emitting diodes (w-LEDs) [1–3]. Many scientists have carried out a lot of work on the luminescence properties and potential application of molybdate based phosphors, in which some novel phosphors were developed. For example, Chen et al. reported an intense reddish-orange emitting phosphor  $\text{Gd}_2\text{MoO}_6:\text{Sm}^{3+}$  potentially useful in  $\sim 370$  nm GaN-based LED through efficient energy feeding by charge transfer absorption of  $\text{MoO}_6^{6-}$  group [1].

Zhao et al. reported a series of red-emitting phosphors  $\text{Eu}^{3+}$ -doped  $\text{M}_2\text{Gd}_4(\text{MoO}_4)_7$  ( $\text{M}=\text{Li}, \text{Na}$ ), which were proved to be with high quantum efficiency and potential application for w-LEDs [2]. In our previous work,  $\text{Y}_2\text{MoO}_6:\text{Eu}^{3+}$  phosphor was also suggested to be potentially a candidate as red phosphor for application in w-LEDs [3]. Thus, the intensive study about the luminescence properties of molybdate based phosphors can promote the development of novel phosphors applied in solid state lighting region.

As one kind of plentiful molybdate compounds, bismuth molybdate [ $\text{Bi}_2\text{MoO}_6$ ] belongs to the so called Aurivillius family of bismuth layered compounds with general formula  $(\text{Bi}_2\text{O}_2)(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})$  [4,5]. For this compound, a lot of attention has been paid to its excellent photophysical properties and photocatalytic activities by many scientists [6–9] such as CO conversion, water splitting, the selective oxidation and ammoxidation of lower olefins, the degradation of organic dyes, and so on. In fact,  $\text{Bi}_2\text{MoO}_6$  can also be chosen to be the host material for phosphor, because  $\text{Bi}^{3+}$  ions can be replaced partly by rare earth ions [10]. But to our knowledge, it is unfortunate that no reports can be found elsewhere on the luminescence properties of  $\text{Bi}_2\text{MoO}_6$  based materials. As one

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efficient activator among rare earth ions,  $\text{Sm}^{3+}$  ion often shows orange light emission in the visible wavelength range due to the transitions from the its excited state  $^4\text{G}_{5/2}$  level to the  $^6\text{H}_J$  ( $J=5/2, 7/2, 9/2$ ) levels and potential application in w-LEDs [1]. So, in the dual drives for developing the novel phosphors in solid state lighting region and exploiting the appliance field for the  $\text{Bi}_2\text{MoO}_6$  based materials, we systematically studied the luminescence behavior of  $\text{Sm}^{3+}$ -doped  $\text{Bi}_2\text{MoO}_6$  in the present work.

## 2. Experimental

Powder samples  $\text{Bi}_{2(1-x)}\text{Sm}_{2x}\text{MoO}_6$  were prepared by a conventional solid state method at high temperature. In this work, the doping level of  $\text{Sm}^{3+}$  is varied from  $x=0.005$  to 0.05. Briefly, the starting material is a mixture of stoichiometric reactants such as analytical reagent (A.R.) grade  $\text{MoO}_3$ ,  $\text{Bi}_2\text{O}_3$  (A.R.) and  $\text{Sm}_2\text{O}_3$  (99.99%). The mixture was ground thoroughly in an agate mortar, and was pre-fired at 723 K for 6 h in air atmosphere. After a second homogenization in the mortar, the samples were heated up to 1173 K and kept for 8 h at this temperature. Finally, the products were cooled to room temperature (RT) and ground into fine powder for the next characterization of materials.

The XRD patterns of the final products were collected in  $2\theta$  range from  $10^\circ$  to  $70^\circ$  on a D8 Advance X-Ray Diffractometer at 40 kV and 20 mA in order to check the phase purity and structure of the as-prepared products. The Fourier transform infrared (FT-IR) spectrum was measured in a Bruker TENSOR 27 FT-IR spectrometer. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra as well as decay curves were measured with a fluorescence spectrometer (HITACHI F-7000) equipped with a 150 W xenon lamp as the excitation source. All the measurements were performed at RT.

## 3. Results and discussion

The XRD patterns of the  $\text{Bi}_{2(1-x)}\text{Sm}_{2x}\text{MoO}_6$  ( $x=0.005, 0.01, 0.015, 0.02, 0.03$  and 0.05) samples sintered at 1173 K for 8 h are plotted in Fig. 1, which are similar to each other and in agreement with the Joint Committee for Powder Diffraction

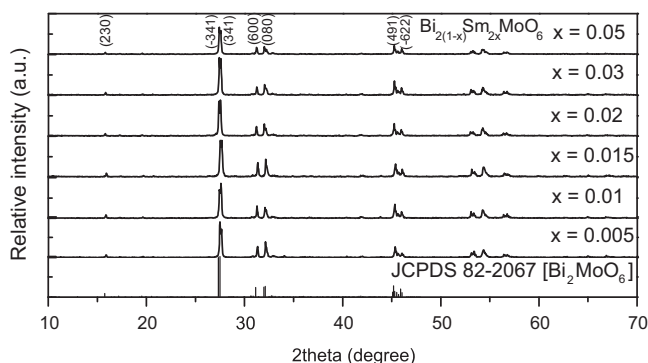


Fig. 1. XRD patterns of the  $\text{Bi}_{2(1-x)}\text{Sm}_{2x}\text{MoO}_6$  ( $x=0.005, 0.01, 0.015, 0.02, 0.03$  and 0.05) samples.

Standard (JCPDS) File 82-2067 [ $\text{Bi}_2\text{MoO}_6$ ], indicating that the doped  $\text{Sm}^{3+}$  ions did not cause significant changes in the host structure. In fact, it has been known that  $\text{Bi}_2\text{MoO}_6$  often exhibits at least three polymorphs (labeled as  $\gamma$ ,  $\gamma'$ , and  $\gamma''$  here) for a long time. The  $\gamma$  phase is with orthorhombically distorted tetragonal structure stable at the low temperature, the  $\gamma'$  phase is with monoclinic structure stable at high temperature, and the  $\gamma''$  phase is the metastable intermediate between  $\gamma$  phase and  $\gamma'$  phase with tetragonal structure [4,11–13]. In view of a thermodynamic model proposed by Kodama and Watanabe [14], the transition from low to intermediate temperature in ambient pressure forms occurs reversibly at 843 K, and from intermediate to high temperature forms slowly and irreversibly at 877 K. So, the monoclinic structure for the  $\text{Bi}_{2(1-x)}\text{Sm}_{2x}\text{MoO}_6$  ( $x=0.005, 0.01, 0.015, 0.02, 0.03$  and 0.05) samples can be obtained at 1173 K based on the high temperature form of  $\text{Bi}_2\text{MoO}_6$ .

Fig. 2 shows the FT-IR spectrum of the  $\text{Bi}_{2(1-x)}\text{Sm}_{2x}\text{MoO}_6$  ( $x=0.015$ ) sample. The strong absorption bands with multiple peaks below  $935\text{ cm}^{-1}$  ( $860, 806, 690,$  and  $640\text{ cm}^{-1}$ ) are attributed to the Mo–O stretching vibration absorption in  $\text{MoO}_4^{2-}$  tetrahedron [15], suggesting that the crystalline phase of pure  $\text{Bi}_2\text{MoO}_6:0.015\text{Sm}^{3+}$  has formed after sintering at 1173 K. Generally, the position of the Mo–O stretching vibration absorption is often located in the region ( $\leq 1000\text{ cm}^{-1}$ ); our result is compared with that of other molybdate compounds [3,15,16].

Fig. 3 shows the excitation (a) and emission (b) spectra of  $\text{Bi}_{2(1-x)}\text{Sm}_{2x}\text{MoO}_6$  ( $x=0.015$ ) phosphor. By monitoring the emission at 605 nm, the excitation spectrum is obtained and consists of a group of sharp transitions around 370–420 nm due to the  $4f \rightarrow 4f$  transitions of  $\text{Sm}^{3+}$  with a prominent peak at 407 nm ( $^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}$  transition of  $\text{Sm}^{3+}$  ion). Compared with excitation characteristics of  $\text{Sm}^{3+}$  ion in other molybdates such as  $\text{SrMoO}_4$  [17] and  $\text{Gd}_2\text{MoO}_6$  [1,18], an interesting phenomenon can be noted. That is, we did not observe the broad excitation band in Fig. 3(a). Usually,  $\text{O}^{2-} \rightarrow \text{Sm}^{3+}$  and  $\text{O}^{2-} \rightarrow \text{Mo}^{6+}$  charge-transfer (CT) states often lead to a broad excitation band in the excitation spectrum for molybdate

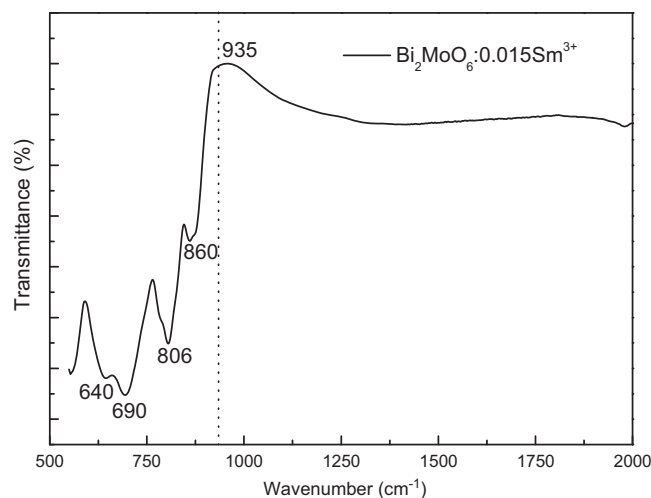


Fig. 2. FT-IR spectrum of the  $\text{Bi}_{2(1-x)}\text{Sm}_{2x}\text{MoO}_6$  ( $x=0.015$ ) sample.

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