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Photoluminescence properties of a new orange–red emitting Sm^{3+}-doped $Y_2Mo_4O_{15}$ phosphor

Huajuan Deng [a], Ze Zhao [a], Jing Wang [a], Zhoufei Hei [a], Mengxue Li [a], Hyeon Mi Noh [b], Jung Hyun Jeong [b,*], Ruijin Yu [a,*]

[a] College of Science, Northwest A&F University, Yangling, Shaanxi 712100, PR China
[b] Department of Physics, Pukyong National University, Busan 608-737, Republic of Korea

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ABSTRACT

A series of novel $Y_2Mo_4O_{15}$:$x$$Sm^{3+}$ ($(0.01 \le x \le 0.20)$ phosphors for white light-emitting (W-LEDs) were successfully prepared by the solid state reaction technology at 973 K for 12 h. X-ray diffraction and photoluminescence spectra were utilized to characterize the structure and luminescence properties of the as-synthesized phosphors. The emission spectra of the $Y_2Mo_4O_{15}$:Sm^{3+} phosphors consisted of some sharp emission peaks of Sm^{3+} ions centered at 565 nm, 605 nm, 650 nm, and 712 nm. The strongest one is located at 605 nm due to $^4G_{5/2}$–$^6H_{7/2}$ transition of Sm^{3+}, generating bright orange–red light. The optimum dopant concentration of Sm^{3+} ions in $Y_2Mo_4O_{15}$:$x$$Sm^{3+}$ is around 5 mol% and the critical transfer distance of Sm^{3+} is calculated as 23.32 Å. The CIE chromaticity coordinates of the $Y_2Mo_4O_{15}$:0.05Sm^{3+} phosphors were located in the orange reddish region. The $Y_2Mo_4O_{15}$:Sm^{3+} phosphors may be potentially used as red phosphors for white light-emitting diodes.

1. Introduction

Light-emitting diodes (LEDs) have recently attracted attention as novel sources for illuminating light. LEDs have several advantages over fluorescent lights, including a longer operating life, better energy efficiency and a mercury-free composition [1–3]. It is well known that commercial white LEDs are mainly fabricated by combining blue LEDs with a yellow-emitting phosphor (YAG:Ce^{3+}). However, the white light obtained has a poor color rendering, because the yellow emission of YAG:Ce^{3+} lacks any red and blue–green emissions [4,5]. Nitride phosphor has attracted interest for its high stability as a red phosphor, but very high firing temperatures (1500–2000 °C) and nitrogen pressures are required for their synthesis, resulting in an uneasy production and high cost [6,7]. For example, for the synthesis of excellent nitride $CaAlSiN_3$:Eu^{2+} phosphor, high cost of raw nitride powders Ca_3N_2, AlN, Si_3N_4 and EuN are used as the starting materials and severe conditions (e.g. 0.9 MPa, 1800 °C) are inevitably applied at solid state reaction.

Recently, one solution to resolve this problem has been to fabricate a white LED with high color rendering by combining red-, green- and blue-emitting tricolor phosphors with irradiation by a near-UV LED. Therefore, many new red- or orange–red-emitting phosphors doped with Eu^{3+} ion or/and Sm^{3+} have been developed, including Eu^{3+}-doped molybdate and tungstate scheelites [8,9], Eu^{3+}-doped vanadate garnet [10,11], M_2SiO_4:Sm^{3+}(M=Ba, Sr,Ca) [12], $Y_2Si_4N_6C$:Sm^{3+} [13], $Ba_3La(PO_4)_3$:Sm^{3+} [14], $KIn(MoO_4)_2$:Eu^{3+}, Sm^{3+} [15], and $GdAl_3(BO_3)_4$:Sm^{3+}, and Eu^{3+} [16].

It is reported that the excitation band position of the molybdates depends strongly on the structure, in a specific manner, on the coordination number of Mo according to Wiegel and Blasse [17]. Many molybdates take scheelite or scheelite-related structures [18–20]. In the cell, such as $CaMoO_4$ [20], and $CsGd(MoO_4)_2$ [8]. Mo^{6+} ions are coordinated to four oxygen atoms forming MoO_4 tetrahedron. It was found that the host lattices of the compounds have strong absorption of near-UV light; the absorbed energy can then be transferred from the host lattices to doped Eu^{3+} ions, resulting in intensive red light emission [21–23]. The crystal structures of $Y_2Mo_4O_{15}$ were investigated by Gopalakrishnan et.al. and found anomalous negative thermal expansion property in the 25–100 °C range [24]. We noticed that the $Y_2Mo_4O_{15}$ with MoO_4 tetrahedron structure have not been investigated as the Sm^{3+}-activated host lattice. For understanding the wide range excitations and the energy transfers from MoO_4 to Sm^{3+}, we investigated the photoluminescence properties of $Y_2Mo_4O_{15}$:Sm^{3+} phosphors.

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* Corresponding authors. Tel.: +82 51 629 6285; fax: +82 51 629 5549.
E-mail addresses: jhjeong@pknu.ac.kr (J.H. Jeong), yuruijin@nwsuaf.edu.cn (R. Yu).

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2. Experimental

A series of powder samples of $Y_{2-x}Mo_4O_{15}$:xSm^{3+} ($x=0.01$, 0.02, 0.05, 0.10, 0.15, and 0.20) were synthesized by a high-temperature solid-state reaction. The starting materials Y_2O_3 (>99.99%), MoO_3 (>99.5%), and Sm_2O_3 (99.99%) obtained from Sigma-Aldrich were thoroughly mixed and ground in an agate mortar. The mixture was fired at 973 K for 12 h in air. After calcination, the samples were naturally cooled down to room temperature and ground for further measurements. The pertinent reaction equation is as follows:

$$(2-x)/2Y_2O_3+4MoO_3+(x/2)Sm_2O_3 \overset{973\ K/12\ h}{\Longrightarrow} Y_{2-x}Mo_4O_{15}:xSm^{3+}.$$

The phase structure of the powders was examined by X-ray diffraction (XRD) on a Philips X'Pert MPD X-ray diffractometer (Philips, Netherlands) with Cu$K\alpha$ radiation ($\lambda=1.5406$ Å) at 40 kV and 30 mA. Structural refinements of X-ray diffractogram were made using the GSAS (General structure analysis system) program [25]. The morphology and size of the phosphor particle were characterized using a scanning electron microscopy (SEM) system JSM-6490, JEOL Company. Diffuse reflection spectra (DRS) are measured on UV–vis–NIR spectrophotometer (V-670, JASCO Corp., Tokyo, Japan) attached to an integral sphere using $BaSO_4$ as reference standard. The PL and PLE spectra were recorded on a Photon Technology International (PTI, USA) fluorimeter with a 60 W Xe-arc lamp.

3. Results and discussion

It is of interest that *Ln* molybdates often exhibit polymorphs due to the flexibility of coordination number and geometry for both Ln^{3+} and Mo^{6+} centers, realizing 6–12 and 4–7 coordinates [26] respectively, with various coordination polyhedra. For this reason, a replacement of *Ln* with other species in *Ln* molybdate sometimes gives rise to a drastic structural and qualitative change [26]. One of such examples is LnIIIMo$_2O_{7.5} \equiv Ln_2Mo_4O_{15}$ compounds, which crystallize in different structures depending on the size of *R* and preparation conditions. The family is categorized into five structures, I: $R=$La (α-form), Ie s$R=$La (β-form), II: $R=$Ce and Pr, III: $R=$Nd–Gd, and IV: $R=$Tb and Ho [27–31]. Considering the large diversity of the *R*–O and Mo–O coordination patterns in the I–IV structures, it seems difficult to discover structural similarity among them [31]. $Y_2Mo_4O_{15}$ belongs to No.14 space group with $P2_1/c$ [30], which is isomorphous with $Ho_2Mo_4O_{15}$ [31].

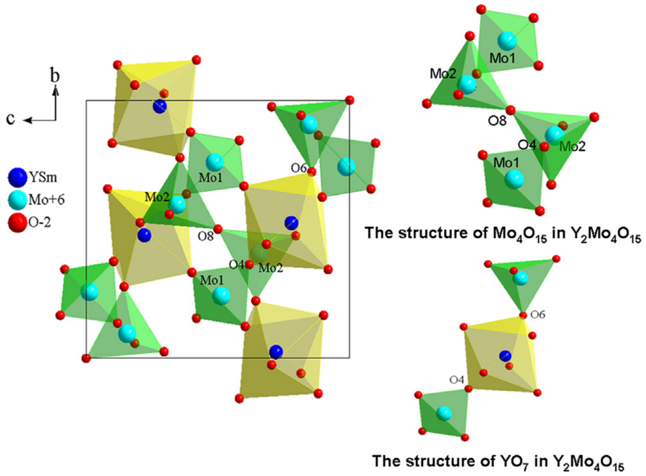

Fig. 1. $Y_2Mo_4O_{15}$ cells and the coordination environments therein (the blue balls are yttrium atoms, the red ones are oxygen atoms, and the turquiose ones are Mo atoms). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 1 (on the bottom right) shows the coordination environment of the Y, Mo1, and Mo2 atoms. Y atoms take 4*e* Wyckoff sites with C_1 point symmetry, and are coordinated to seven O-neighbors. The shape of YO_7 polyhedron is approximated to a monocapped trigonal prism. On the upper right of Fig. 1, the Mo1O_4 and Mo2O_4 polyhedra share a corner at the O4 atom. Furthermore, Mo2O_4 and the another Mo2O_4 are corner-shared by one O8 atom which lies on a center of symmetry. As a result, the oxodimolybdate $Mo(2)_2O_7$ polyhedron and two $Mo(1)O_4$ tetrahedra joined together by sharing O8 atoms to construct an entire tetrameric Mo_4O_{15} cluster. Fig. 1 (on the left) shows the whole framework of this $Y_2Mo_4O_{15}$ crystal structure. The framework is constructed by the MoO_4 groups. Each $Y(Sm)^{3+}$ is coordinated with seven oxygen to constitute singly capped trigonal prism with the bond distances of 2.2514(3) to 2.3224(2) Å. Mo(1) and Mo (2) centers are almost tetrahedron with Mo–O bond lengths from 1.689(3) to 1.878(2) Å. The Mo_4O_{15} cluster and monocapped trigonal prismatic YO_7 polyhedra units are connected by edge- and corner-sharing in the crystal lattice.

Some typical XRD patterns of $Y_{2-x}Mo_4O_{15}$:xSm^{3+} samples ($x=0.02$, 0.05, and 0.10) powder samples are demonstrated in Fig. 2. The standard card of $Y_2Mo_4O_{15}$ (JCPDS 53-0358) is also given for comparison. All the diffraction peaks of samples were found to be in good agreement with those of the standard card, indicating that the samples are single-phased and the crystal structure is not significantly changed when the dopant ions incorporated into the host. Considering the similar valence states, coordination numbers and ionic radius of Y^{3+} (VII) (96 pm), Sm^{3+} (VII) (102 pm) [32], we deduce that Sm^{3+} ion substitutes for Y^{3+} ion in the host. To investigate the crystal structure, the full Rietveld refinement was performed on the representative sample $Y_{2-x}Mo_4O_{15}$:xSm^{3+} ($x=0.05$) by using GSAS software, which converged to $R_p=14.35\%$, and $R_{wp}=11.17\%$, and $\chi^2=2.36$ (see Fig. 3). The refined positions and the lattice parameters of all atoms of $Y_{1.95}Sm_{0.05}Mo_4O_{15}$ are listed in Table 1. This compound has lattice parameters of $a=6.8316(2)$, $b=9.5802(2)$ Å, $c=10.5225(2)$ Å, $\beta=105.519(2)^\circ$, $V=663.59(6)$ Å^3, which are consistent with the unit-cell parameters given by the literature [33]. Furthermore, Table 2 lists the lattice parameters of a series of $Y_{2-x}Mo_4O_{15}$:xSm^{3+} ($x=0.01$, 0.02, 0.05, 0.10, 0.15, and 0.20) phosphors calculated by Jade-5.0 software. Evidently, the unit cell volume increases with increasing Sm^{3+} concentrations in the range of $x=0.01$–0.20, suggesting that the larger radius of the Sm^{3+} ion.

The morphologies of the $Y_2Mo_4O_{15}$:Sm^{3+} were inspected using a scanning electron microscope (SEM). Fig. 4 shows the

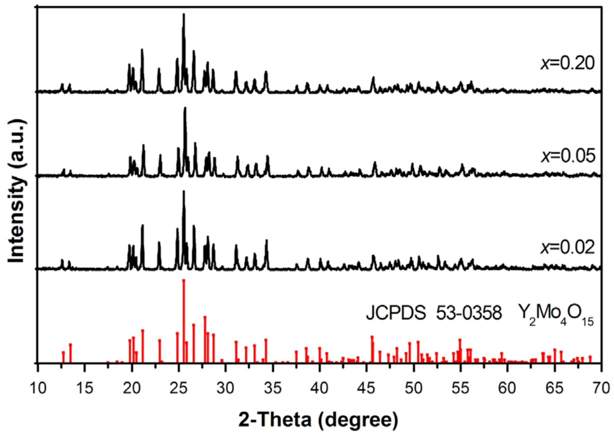

Fig. 2. XRD patterns of three representative $Y_{2-x}Mo_4O_{15}$:xSm^{3+} samples ($x=0.02$, 0.05, and 0.20).