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Photoluminescence properties of a novel red-emitting phosphor Eu^{3+} activated scandium molybdate for white light emitting diodes

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ABSTRACT

A series of red-emitting phosphors of $Sc_2(MoO_4)_3$: x%Eu^{3+} have been successfully synthesized at 800 °C by solid-state reaction. X-ray diffraction, scanning electron microscopy, photoluminescence spectra and decay curves were used to characterize the structures and luminescence properties. In the excitation spectrum, the strongest absorptions of $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ match well with the emission wavelength of the near-ultraviolet InGaN and blue GaN chips. The CIE value of $Sc_2(MoO_4)_3$: 40%Eu^{3+} sample reaches (0.665, 0.334), which is very close to the NTSC standard (0.67, 0.33), demonstrating the highly pure red lights emitted. The decay curves of Eu^{3+}: $^5D_0 \rightarrow {}^7F_2$ emission exhibit a bi-exponential function excited by a 266 nm nanosecond-pulsed laser resulting from the lattice distortion which can speed up electric dipole transition. The good excitation profile and pure red emission indicate $Sc_2(MoO_4)_3$: Eu^{3+} is a promising red-emitting phosphor for its application in commercial white light emitting diodes.

1. Introduction

Due to the high luminescent efficacy, low energy consumption, pollution-free and long lifetime, phosphor-converted white light emitting diodes (LEDs) as a new lighting source are going to replace conventional light sources [1–3]. At present, the commercial white LEDs are the association of a blue chip and yellow phosphor YAG: Ce^{3+} [4,5]. However, Due to the shortage of a red component, the obtained white light displays low color rendering index (CRI) and high color temperature [5,6]. So far, Y_2O_2S: Eu^{3+} is used as primary commercial red phosphor, but it shows the low efficiency and chemical instability [7,8]. It is necessary to develop a novel red phosphor. Eu^{3+} ion as an important activator can emit red fluorescence corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition when located in a noncentrosymmetric site [9]. Thus, many Eu^{3+} doped materials are used as red phosphors for potential application in color displays [2,8,10].

The rare earth doped molybdates as promising host candidates have received much attention owing to the special properties of the MoO_4^{2-} group [11]. The molybdates are very stable and can be synthesized at low temperature. Furthermore, previous investigations have demonstrated that Eu^{3+} doped molybdates exhibit relatively strong absorption in the near-ultraviolet region and intense red emission with good color purity [11–14]. As far as we know, the luminescence characterization of $Sc_2(MoO_4)_3$: Eu^{3+} has not been reported.

In this paper, the $Sc_2(MoO_4)_3$: Eu^{3+} phosphors were obtained by a solid-state reaction. The luminescence properties were investigated and discussed in detail. The results show $Sc_2(MoO_4)_3$: Eu^{3+} material is a promising candidate as red-emitting phosphor for the white LEDs applications.

2. Experimental

The $Sc_2(MoO_4)_3$: x%Eu^{3+} (x = 0–60) samples were prepared by a conventional solid-state reaction. The constituent oxides Sc_2O_3 (99.99%), MoO_3 (99.9%) and Eu_2O_3 (99.99%) purchased from Sigma-Aldrich were employed as the raw materials, which were mixed homogeneously by an agate mortar for 30 min, placed in a crucible with a lid, then sintered at 800 °C for 5 h. Powder X-ray diffraction (XRD) datum was collected using Cu-Kα radiation ($\lambda = 1.54056$ Å) on a Bruker D8 advance diffractometer. Scanning electron microscopy (SEM) image was taken on S-4800 (Hitachi Company) electron microscopes. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a Hitachi F7000 spectrometer equipped with a 150 W xenon lamp. In fluorescence lifetime measurements, the fourth harmonic (266 nm) of an Nd: YAG pulsed laser (Spectra-

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Physics, GCR 130) was used as an excitation source, and the signals were detected with a Tektronix digital oscilloscope (TDS 3052).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the undoped and Eu^{3+} doped $Sc_2(MoO_4)_3$ samples. The XRD patterns of the synthesized samples $Sc_2(MoO_4)_3$: x%Eu^{3+} (x = 0-40) are in good agreement with JCPDS card 21-1329 regardless of Eu^{3+} doping concentration, indicating the Eu^{3+} doped samples retain the same crystal structure as that of undoped $Sc_2(MoO_4)_3$. However, when Eu^{3+} doping concentration is increased to 50% and 60%, some new peaks appear which are marked by the black dots as shown in Fig. 1(a), and probably are ascribed to the formation of other molybdate compounds. So in this work we mainly focused on the samples with composition $Sc_2(MoO_4)_3$: x%Eu^{3+} (x = 0–40).

The $Sc_2(MoO_4)_3$ has an orthorhombic structure with space group *Pbcn* (60) and lattice constants $a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$. Fig. 1(c) shows the structure of $Sc_2(MoO_4)_3$ based on the JCPDS card 21-1329. In this structure, Sc^{3+} is sixfold with the large effective ionic radius (0.745 Å) and Mo^{3+} fourfold oxygen coordination with the small radius (0.41 Å). The Eu^{3+} ions own the large ionic radius (0.947 Å) which diverges from that of Mo^{3+} seriously, but it is close to that of Sc^{3+}. The Eu^{3+} ions occupy Sc^{3+} sites to expand the lattice cell volume, making XRD peaks shift to smaller angles as Eu^{3+} concentration increasing, as shown in Fig. 1(b). Shown in Fig. 1(d) is the SEM image for $Sc_2(MoO_4)_3$: 20%Eu^{3+} sample. The phosphor has many crystalline granules with sub-circular shapes and some particles are agglomerated into bulk. The average size of granules estimated is about 500 nm except for the agglomerates, which is suited to make the solid-lighting devices.

The spectroscopic studies of Eu^{3+} ion can be used to investigate the relationship between luminescence and structure of $Sc_2(MoO_4)_3$. The excitation spectrum of $Sc_2(MoO_4)_3$: 20%Eu^{3+} phosphor for monitoring Eu^{3+}: $^5D_0 \rightarrow {}^7F_2$ at 616 nm emission is shown in Fig. 2. It can be seen that the excitation spectrum consists of an intense broad band ranging from 200 to 350 nm and some narrow lines from 350 to 550 nm. The broad band emission can be almost decomposed into two Gaussian bands centered at about 283 nm and 330 nm, which can be attributed to the charge transfer (CT) band of Eu^{3+}—O^{2-} and Mo^{6+}—O^{2-}, respectively [11,12]. Actually, the contribution of two components cannot be distinguished precisely due to spectral overlap [15,16]. The sharp lines correspond to the transitions of Eu^{3+} from the ground state to the upper excited states of 4f^7 configuration, corresponding to $^7F_0 \rightarrow {}^5D_4$, $^7F_0 \rightarrow {}^5L_7$, $^7F_0 \rightarrow {}^5L_6$, $^7F_0 \rightarrow {}^5D_3$, $^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$, respectively [13,17]. The strongest absorptions of $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ match well with the emission wavelength of the near-ultraviolet InGaN and blue GaN chips, indicating the promising application in the commercial white LEDs.

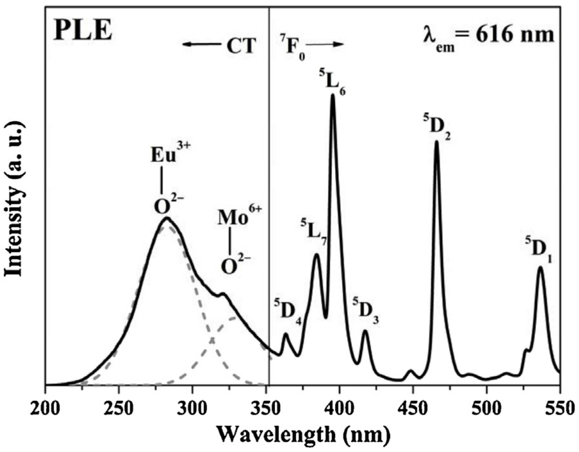

Fig. 2. The excitation spectrum of Eu^{3+}: $^5D_0 \rightarrow {}^7F_2$ at 616 nm emission in $Sc_2(MoO_4)_3$: 20%Eu^{3+} sample.

Fig. 3 shows the excitation spectra of $Sc_2(MoO_4)_3$ powders doped with different Eu^{3+} concentrations. The CT intensities of Eu^{3+}—O^{2-} and Mo^{6+}—O^{2-} both increase with Eu^{3+} concentration increasing. Moreover, there is a significant broadening of the CT band. As Eu^{3+} concentration increasing, the crystal field change caused the electron cloud expansion effect [2] and shorter Eu^{3+}—O^{2-} distance both have a direct influence on the CT band shape [18]. In the Eu^{3+} transitions region, where excitations from the $^7F_0$ to higher excited levels occur, the successive increased intensity also has been noted.

The emission spectra of $Sc_2(MoO_4)_3$ powders doped with different Eu^{3+} ion concentrations are presented under 395 nm near-ultraviolet light excitation corresponding to Eu^{3+}: $^7F_0 \rightarrow {}^5L_6$ transition in Fig. 4. The $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3, 4) transitions of Eu^{3+} ion are observed [17]. The $^5D_0 \rightarrow {}^7F_1$ transition around 595 nm belongs to the magnetic dipole transition and its intensity is almost independent on the local environment of Eu^{3+} ions [9]. The $^5D_0 \rightarrow {}^7F_2$ transition around 616 nm is from the electric dipole

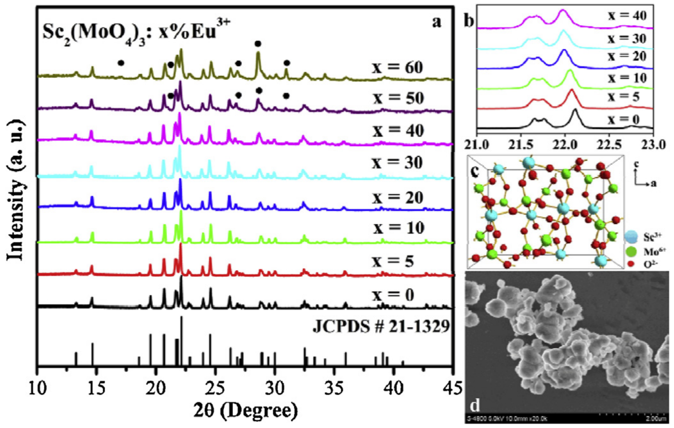

Fig. 1. (a) XRD patterns for phosphors with the nominal compositions of $Sc_2(MoO_4)_3$: x%Eu^{3+} (x = 0-60). (b) Enlarged peaks distributed in various XRD patterns. (c) Structure of $Sc_2(MoO_4)_3$. (d) SEM image of $Sc_2(MoO_4)_3$: 20%Eu^{3+} sample.

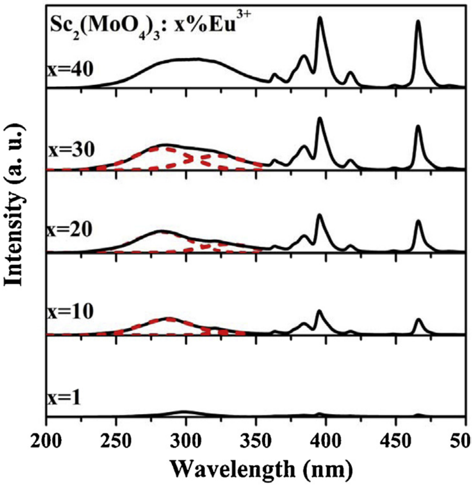

Fig. 3. Excitation spectra of $Sc_2(MoO_4)_3$ doped with different Eu^{3+} concentrations (λ_{em} = 616 nm).