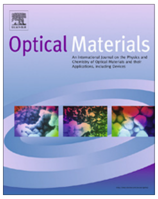
Optical Materials 45 (2015) 28–31

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



Site selective spectroscopic study of an efficient red-emitting phosphor Y_2MoO_6:Eu

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ARTICLE INFO

Article history:
Received 29 December 2014
Received in revised form 8 February 2015
Accepted 24 February 2015
Available online 25 March 2015

Keywords:
Photoluminescence
Site selective spectra
Eu^{3+}
Phosphor

ABSTRACT

Y_2MoO_6:Eu, an efficient red-emitting phosphor for white light emitting diodes, was synthesized by the sol–gel method and investigated by site selective spectroscopy under the selective excitation of a tunable laser. Three kinds of sites occupied by Eu^{3+} ions were confirmed by low temperature emission and excitation spectra in this compound. Lifetime measurements were carried out to identify the emission peaks of Eu^{3+} in each site. The correlation between the site structure and luminescent property of Eu^{3+} were clarified by using selection rules. And energy transfer between different sites was observed and discussed.

1. Introduction

White light emitting diode (WLED) lamps have been expected to be the next generation light sources in the near future due to its high efficiency, long lifetime, and excellent color rendering property [1,2]. White light can be achieved by mixing red, green and blue emission light converted from near-ultraviolet (NUV) light of NUV LED chips. However, under the excitation of NUV light, the most widely used red phosphor Y_2O_2S:Eu suffers from much lower efficiency compared with the green and blue phosphors [3]. So it is urgent to develop brand new red phosphors which can convert NUV light to red emission efficiently. In previous research, Y_2MoO_6:Eu shows efficient absorption of NUV light, and exhibits excellent performance in emission intensity and color purity compared with the commercial phosphor (Y_2O_2S:Eu) in current use, indicating that Y_2MoO_6:Eu could be an novel alternative red-emitting phosphor for solid state lighting [4–7]. The improvement of luminescence for Y_2MoO_6:Eu by doping Li ions was reported by Jin et al. [8]. Recently, the effects of temperature [9], doping concentration [10] and particle size [11] on luminescence properties of Y_2MoO_6:Eu were investigated. But to date, the local structures of Eu ions in Y_2MoO_6 and luminescence properties of each Eu site have not been investigated and discussed in details.

The local structure of the site occupied by dopant ions in a host lattice is an important factor which affects luminescence characteristics of the phosphors. The luminescence property of rare earth ions are strongly influenced by the symmetry and strength of crystal field [12]. In fact, as a result of the simplicity of the emission spectra from the nondegenerate $^5D_0$ level to ^7F_J terminal multiplets, the spectra of Eu^{3+} can be employed as a local structure probe [13–16]. The local site symmetry of lanthanide ions in crystal lattices and the point groups of the molecules are possible to be determined by combining the spectra of Eu^{3+} ions with the selection rules for induced electric dipole (ED) and magnetic dipole (MD) transitions. Seo and co-workers have studied the site occupations and local structures of Eu^{3+} by site selective spectra in oxyfluoride [17], tungstate [18], phosphate [19], borate [20], etc. In the case of Y_2MoO_6:Eu, it is expected that Eu^{3+} substitute for Y^{3+} by considering the ionic radius and valence state. Neutron diffraction investigation suggested that Y_2MoO_6 crystallized with a monoclinic phase which is closely related to the scheelite-type structure [21,22]. In order to clarify the nature of the local environment of Eu^{3+} ions in Y_2MoO_6, their luminescence properties were investigated by site selective spectroscopy and discussed by combining with the structural features of the host lattice in this work. The results could be helpful for the luminescence investigation of RE ions doped in Y_2MoO_6 and other hosts with similar structure.

2. Experiment

Y_2MoO_6:Eu samples were prepared by sol–gel method. All the chemicals are of analytical-grad reagents. $RE(NO_3)_3$ standard solutions (RE = Y, Eu, 10 mmol in total), 45 mmol citric acid and

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http://dx.doi.org/10.1016/j.optmat.2015.02.034
0925-3467/

0.714 mmol $(NH_4)_6Mo_7O_{24}·4H_2O$ were mixed in the desired ratio. Under magnetic stirring for 30 min, the mixtures were heated in an 80 °C water bath. Then the obtained gel was prefired at 600 °C for 1 h followed by sintering at 1200 °C for 2 h. The crystalline phases of the synthesized samples were identified via X-ray diffractometer (XRD, MAC Science Co. Ltd. MXP18AHF), with nickel-filtered Cu Kα radiation in the range of $2\theta = 10–70°$, at 40.0 kV and 200.0 mA. The morphology of the samples were observed with field emission scanning electron microscopy (FE-SEM, Sirion 200, FEI). A tunable OPO (optical parametric oscillator) laser system with the tunable range from 410 nm to 2200 nm, the pulse duration of 7 ns and the repetition rate of 20 Hz, was used as the excitation source for the luminescence spectra and decay curves measurements. The emission of the sample was dispersed by a Jobin–Yvon HRD1 double monochromator and detected by a Hamamatsu R928 photomultiplier. The signal was analyzed by an EG&G 7265 DSP lock-in amplifier and stored into computer memories. The decay curves were recorded with a Tektronix TDS2024 digital storage oscilloscope. Low temperature measurements were carried out by keeping the sample temperature at 20 K in a closed cycle helium cryostat.

3. Results and discussion

The crystal structures of the as-prepared samples were identified by XRD. As shown in Fig. 1(a), all diffraction peaks can be indexed by the standard powder diffraction file card No. 52-650 and no other impurity peak is detected, indicating that pure phase Y_2MoO_6 has been synthesized. The SEM image (Fig. 1(b)) shows that the as-prepared powder sample is composed of microparticles with size of hundreds of nanometer.

According to the previous study, the Mo–O charge transfer excitation band located at 300–410 nm [5,6]. Fig. 2(a) presents a global view of the low temperature emission spectrum of Y_2MoO_6:Eu sample under excitation of 355 nm. Five groups of sharp lines between 578 and 720 nm are observed and can be attributed to $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) transitions of Eu^{3+} respectively. And the strong emission intensity indicates that the energy transfer from host to Eu^{3+} is efficient. The $^5D_0 \rightarrow {}^7F_1$ transition is magnetic dipole allowed, and its intensity is generally accepted to be fairly constant for Eu^{3+} in different crystal field [23]. While the $^5D_0 \rightarrow {}^7F_2$ transition is a forced electric dipole transition, the intensity of $^5D_0 \rightarrow {}^7F_2$ is hypersensitive to the degree of noncentrosymmetry of the Eu^{3+} site in a material. As shown in Fig. 2(a), the intensity of $^5D_0 \rightarrow {}^7F_2$ transition is stronger than that of $^5D_0 \rightarrow {}^7F_1$, indicating the absence of the inversion center for the site occupied by Eu^{3+} ions. Since $^5D_0$ is nondegenerate, the structure of the $^5D_0 \rightarrow {}^7F_J$ emission spectra is determined by the splitting of ^7F_J caused by the local crystal field. For Eu^{3+} ions in the site with low symmetry, the degeneracy of the ^7F_J levels are lifted completely and can be split into $2J + 1$ energy levels (three for $^7F_1$, and five for $^7F_2$). However, we observe more than three emission lines corresponding to $^5D_0 \rightarrow {}^7F_1$ transition in Fig. 2(a), implying the presence of more than one Eu^{3+} site in the host.

The excitation spectra were recorded by monitoring $^5D_0 \rightarrow {}^7F_2$ emission bands with the strongest peak at 611.5 nm at 20 K. As shown in Fig. 2(b), sharp excitation peaks were detected around 465, 528, and 579 nm, arising from $^7F_0 \rightarrow {}^5D_{2,1,0}$ transitions respectively. The nondegenerate $^5D_0 \rightarrow {}^7F_0$ transition is usually used to deduce the number of Eu^{3+} sites in the samples. But in Fig. 2(b), only one $^7F_0 \rightarrow {}^5D_0$ transition peak can be found. This may because the energy differences of $^7F_0 \rightarrow {}^5D_0$ transition in different Eu^{3+} sites are too small to be distinguished.

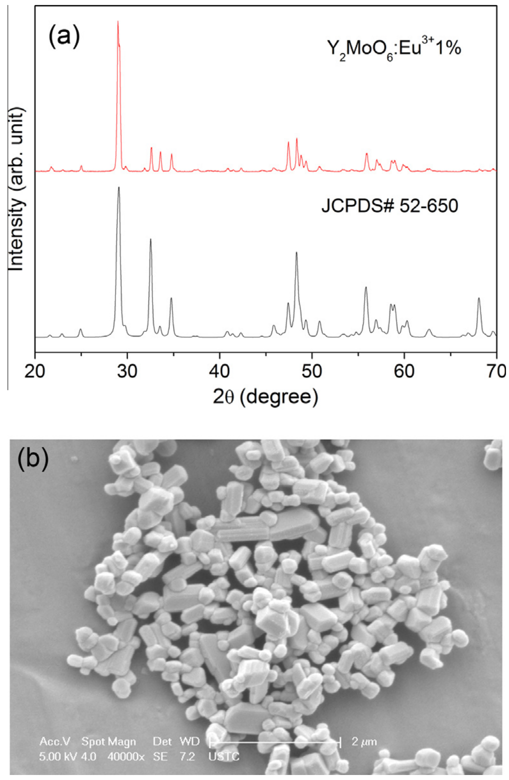

Fig. 1. (a) XRD pattern of Y_2MoO_6:1% Eu^{3+} powder sample and the standard data of Y_2MoO_6 (JCPDS No. 52-650). (b) SEM image of the as-prepared sample.

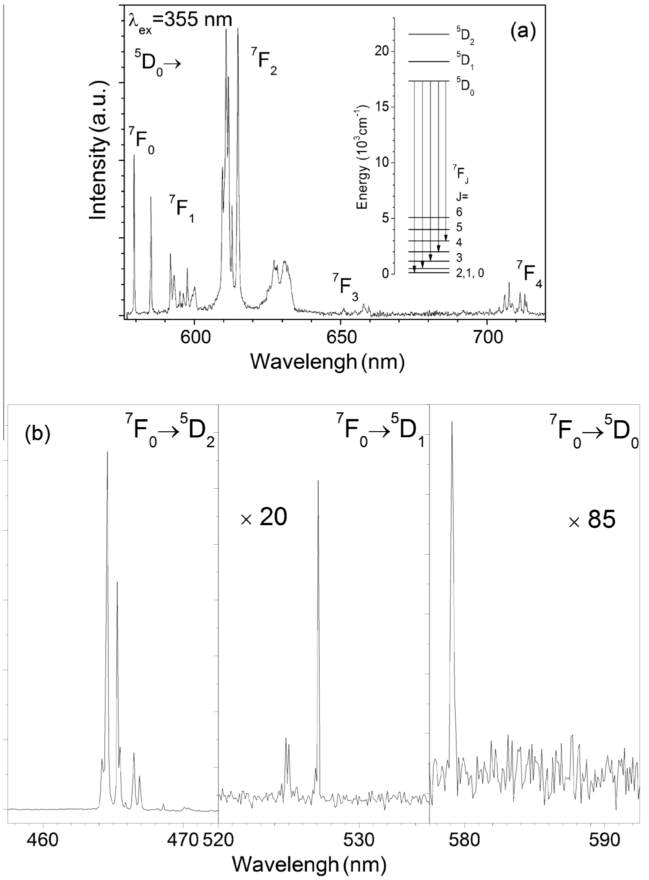

Fig. 2. (a) Emission spectrum of Y_2MoO_6: 1% Eu at 20 K. Inset: Energy level scheme of Eu^{3+}. (b) Excitation spectrum monitoring $^5D_0 \rightarrow {}^7F_2$ fluorescence at 611.5 nm of Y_2MoO_6: 1% Eu at 20 K.