



Synthesis and photoluminescence properties of the high-brightness Eu^{3+} -doped $\text{M}_2\text{Gd}_4(\text{MoO}_4)_7$ ($M=\text{Li}, \text{Na}$) red phosphors

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ARTICLE INFO

Article history:

Received 18 August 2011

Received in revised form

19 September 2011

Accepted 20 September 2011

Available online 4 October 2011

Keywords:

Optical materials

Luminescence

Light-emitting diodes

ABSTRACT

A series of red-emitting phosphors Eu^{3+} -doped $\text{M}_2\text{Gd}_4(\text{MoO}_4)_7$ ($M=\text{Li}, \text{Na}$) have been successfully synthesized at 850 °C by solid state reaction. The excitation spectra of the two phosphors reveal two strong excitation bands at 396 nm and 466 nm, respectively, which match well with the two popular emissions from near-UV and blue light-emitting diode chips. The intensity of the emission from $^5\text{D}_0$ to $^7\text{F}_2$ of $\text{M}_2(\text{Gd}_{1-x}\text{Eu}_x)_4(\text{MoO}_4)_7$ phosphors with the optimal compositions of $x=0.85$ for Li or $x=0.70$ for Na is about five times higher than that of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The quantum efficiencies of the entitled phosphors excited under 396 nm and 466 nm are also investigated and compared with commercial phosphors $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ and $\text{Y}_3\text{A}_5\text{O}_{12}:\text{Ce}^{3+}$. The experimental results indicate that the Eu^{3+} -doped $\text{M}_2\text{Gd}_4(\text{MoO}_4)_7$ ($M=\text{Li}, \text{Na}$) phosphors are promising red-emitting phosphors pumped by near-UV and blue light.

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1. Introduction

Recently, a lot of attention has been drawn to research on white light-emitting diodes (LEDs) because of their merits of significant power saving, higher luminous efficiency, and longer lifetime compared with the incandescent or fluorescent lamps. At present, white LEDs fabricated by combining a blue LED chip with a yellow-emitting phosphor ($\text{YAG}:\text{Ce}^{3+}$) is commercially available due to the unsurpassed efficiency such a combination provides [1–3]. However, they exhibit poor color rendering index (CRI) and high correlated color temperature due to the deficiency of red emission. One solution to this problem is to excite red, green and blue phosphors by UV LED. However, current sulfide and oxysulfide for red phosphors suffer chemical instability and decompose at high temperature, whereas Eu^{2+} -doped nitrides phosphors such as CaAlSiN_3 suffer from a relatively difficult preparation process [4]. Red-emitting phosphors with excellent performance are urgently required.

In recent years, Eu^{3+} doped molybdates have received much attention because of their low synthesis temperature, high red-emitting efficiency, and superior chemical stability [5–7]. Recently, the molybdates $\text{M}_2\text{Gd}_4(\text{MoO}_4)_7$ ($M=\text{Li}, \text{Na}$) have been investigated for applications in solid-state laser materials [8–10]. Na_2Gd_4

(MoO_4)₇ is of isomorphism of $\text{Li}_2\text{Gd}_4(\text{MoO}_4)_7$. $\text{Li}_2\text{Gd}_4(\text{MoO}_4)_7$ was first reported by Pandey as ferroelectric and paramagnetic materials [11]. A subsequent publication supposed that $\text{Li}_2\text{Gd}_4(\text{MoO}_4)_7$ has a defect scheelite (space group $I4_1/a$) structure with the formula $\text{Li}_{0.286}\text{Gd}_{0.571}\square_{0.143}\text{MoO}_4$ (\square represents vacancy) [12]. It was assigned to be isostructural to the scheelite CaWO_4 . However, the Ca^{2+} sites in $\text{Li}_2\text{Gd}_4(\text{MoO}_4)_7$ are not fully occupied by Li^+ and Gd^{3+} ions, and 14.3% of them are unoccupied. Moreover, the site symmetry of Gd^{3+} (S_4) lacks inversion center. Therefore, the two compounds could be suitable hosts for Eu^{3+} -doped phosphors with high color purity and brightness by induced $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission. To the best of our knowledge, the synthesis and luminescence properties of Eu^{3+} -doped $\text{M}_2\text{Gd}_4(\text{MoO}_4)_7$ ($M=\text{Li}, \text{Na}$) phosphors have not been reported. In this work, we systematically studied the luminescence behavior of Eu^{3+} -doped $\text{M}_2\text{Gd}_4(\text{MoO}_4)_7$ ($M=\text{Li}, \text{Na}$) and compared their quantum efficiencies with those of commercial phosphors $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ and $\text{Y}_3\text{A}_5\text{G}_{12}:\text{Ce}^{3+}$.

2. Experimental

2.1. Sample preparation

Powder samples $\text{Li}_2(\text{Gd}_{1-x}\text{Eu}_x)_4(\text{MoO}_4)_7$ (LGM: $x\text{Eu}^{3+}$) and $\text{Na}_2(\text{Gd}_{1-x}\text{Eu}_x)_4(\text{MoO}_4)_7$ (NGM: $x\text{Eu}^{3+}$) were prepared by a conventional solid state method. Briefly, the starting material was a mixture of Li_2CO_3 (A.R. 99.9%), Na_2CO_3 (A.R. 99.9%), Gd_2O_3 (99.99%), Eu_2O_3 (99.99%), and Mo_2O_3 (A.R. 99.9%). The stoichiometric amount of raw materials was thoroughly mixed by

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grinding in an agate mortar, heated up to 850 °C and kept at this temperature for 5 h in air.

2.2. Sample characterization

The phase purity of LGM: $x\text{Eu}^{3+}$ and NGM: $x\text{Eu}^{3+}$ phosphors were carefully checked by using powder X-ray diffraction (XRD) analysis on a Bruker D8 Focus diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) operated at 40 kV and 40 mA. The XRD data was collected in a 2θ range from 10° to 80° . The morphology Energy-dispersive X-ray spectroscopy (EDS) of the samples was inspected using a scanning electron microscope (SEM, JEOL JSM-6510) equipped with an energy-dispersive X-ray analyzer (EDX Oxford INCA Model 6498). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured with a Horiba Jobin Yvon Fluoromax-4 Spectrofluorometer. An integrating sphere (F-3018) attached to the Spectrofluorometer was used to carry out the measurements of the Commission Internationale de L'Eclairage (CIE) chromaticity coordinates and photoluminescence quantum efficiency.

3. Results and discussion

3.1. Crystal structure and morphology of the phosphors

XRD patterns of $\text{M}_2\text{Gd}_4(\text{MoO}_4)_7$ ($M=\text{Li}, \text{Na}$) samples with and without dopants sintered at 850 °C for 5 h are shown in Fig. 1. In this work, the concentration of Eu^{3+} is varied from $x=0$ to 0.95, and the XRD patterns of all samples are similar. Here, only the XRD patterns of samples with the optimal doping concentration of LGM:0.85 Eu^{3+} and NGM:0.70 Eu^{3+} are displayed as representatives. All peaks of the as-prepared samples can be assigned to the scheelite phase, indicating that the scheelite structure is retained after doping. The lattice parameters determined from XRD patterns are listed in Table 1. The diffraction peaks shift to lower θ values after doping because of the larger radius of Eu^{3+} compared to that of Gd^{3+} , in accordance with the Bragg equation: $\lambda=2d \sin \theta$ (Fig. 1).

The morphologies and constituent elements of the as-prepared LGM:0.85 Eu^{3+} and NGM:0.70 Eu^{3+} samples were investigated by the SEM and EDS. The sizes of the aggregated particles range from 3 to 8 μm (Fig. 2(a) and (c)). Moreover, a small area of each

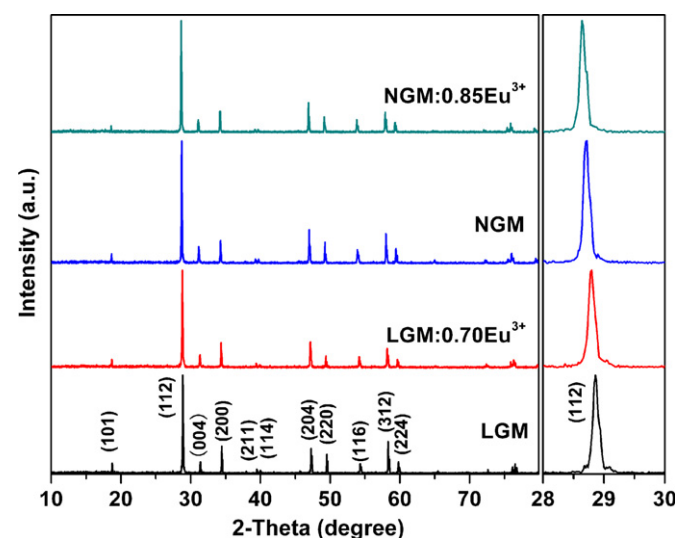


Fig. 1. Powder XRD patterns of LGM, LGM:0.85 Eu^{3+} , NGM and NGM:0.70 Eu^{3+} calcined at 850 °C for 5 h.

Table 1
Lattice parameters ($\alpha=\beta=\gamma=90^\circ$) of the as-prepared LGM, LGM:0.85 Eu^{3+} , NGM and NGM:0.70 Eu^{3+} .

Sample	a (Å)	c (Å)	V (Å ³)
LGM	5.204	11.394	308.548
LGM:0.85 Eu^{3+}	5.216	11.424	310.769
NGM	5.228	11.479	313.735
NGM:0.70 Eu^{3+}	5.238	11.497	315.502

sample was selected for EDS measurement, characterizing the composition of the phosphors, as presented in Fig. 2(b) and (d). It confirms the formation of all samples by the synthesis method herein according to the presence of Na, Eu, Gd, Mo, and O. However, the light Li element was hard to identify by EDS measurement. The atomic ratio of Eu to the sum of Eu and Gd were about 0.84 and 0.69 for LGM:0.85 Eu^{3+} and NGM:0.70 Eu^{3+} , which agrees with that of the starting materials.

3.2. Absorption spectra and luminescence properties of LGM: Eu^{3+} and NGM: Eu^{3+} phosphors

The absorption bands from 250 nm to 370 nm in the absorption spectra of undoped LGM and NGM hosts (Fig. 3(a) and (c)) are attributed to the $(\text{MoO}_4)^{2-}$ group [13]. The broad absorption bands shift to lower energy for the doped samples (Fig. 3(b) and (d)) due to the overlap of $(\text{MoO}_4)^{2-}$ group absorption and the $\text{Eu}^{3+}-\text{O}^{2-}$ charge transfer band (CTB). The sharp peaks in the range from 370 to 600 nm are associated with typical intra-4f forbidden transitions of the Eu^{3+} ions. The room temperature excitation spectra and emission spectra of both LGM:0.85 Eu^{3+} and NGM:0.70 Eu^{3+} are shown in Fig. 4.

Similar to the absorption spectra, the excitation spectra monitored at 617 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) can be divided into two regions: sharp lines associated with the intra-4f transitions and the charge-transfer band [14]. The shape difference between the absorption and excitation spectra in the charge-transfer band is because part of the charge-transfer absorption does not contribute to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission. It can be seen in Fig. 4 that LGM:0.85 Eu^{3+} shows stronger blue and green-yellow excitation (from 440 nm to 550 nm) than NGM:0.70 Eu^{3+} , whereas NGM:0.70 Eu^{3+} shows stronger near-UV excitation (below 440 nm). The strong excitation bands located at 466 nm and 396 nm are attributed to the $^7\text{F}_0 \rightarrow ^5\text{D}_2$ and $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transitions, indicating that Eu^{3+} -doped $\text{M}_2\text{Gd}_4(\text{MoO}_4)_7$ ($M=\text{Li}, \text{Na}$) phosphors can be used as the red phosphor excited by blue or near-UV LED chips.

On excitation with a 466 nm irradiation, the emission line ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) centered at 617 nm dominated in the emission spectra. The photoluminescence (PL) intensity increases with the increase in Eu^{3+} content up to a critical concentration, after which it decreases due to concentration quenching effect. The optimal Eu^{3+} concentration in LGM and NGM are 0.85 and 0.70, and the emission intensity of the two samples is about five times higher than that of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor under blue excitation (Fig. 4). The photoluminescence and concentration quenching behavior will be discussed in detail later.

The emission spectra of LGM: $x\text{Eu}^{3+}$ and NGM: $x\text{Eu}^{3+}$ under 466 nm excitation are similar, as is shown in Fig. 5(a) and (b). Emission peaks at 530–545, 550–560, 579–582, 583–600, 603–635, and 645–660 nm are assigned to the $^5\text{D}_1 \rightarrow ^7\text{F}_1$, $^5\text{D}_1 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, and $^5\text{D}_0 \rightarrow ^7\text{F}_3$ transitions of the Eu^{3+} ions, respectively. The emission intensity of the higher excited state ($^5\text{D}_1$) in the two hosts is very weak compared with the excited state $^5\text{D}_0$ even at low Eu^{3+} concentration. This is different from the host materials with very low phonon energy

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