Novel Eu\(^{3+}\)-doped red-emitting phosphor Gd\(_2\)Mo\(_3\)O\(_9\) for white-light-emitting-diodes (WLEDs) application

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Abstract

A novel red-emitting phosphor Eu\(^{3+}\)-doped Gd\(_2\)Mo\(_3\)O\(_9\) was developed for white-light-emitting-diodes (WLEDs). The phosphors with various Eu\(^{3+}\) concentrations were prepared by solid-state reaction route using Na\(_2\)CO\(_3\) as a flux. The effects of the flux content, sintering temperature and the activator concentration on the crystal structure and luminescent properties were investigated by XRD, emission spectra and excitation spectra. It is found that this phosphor can be effectively excited by C–T band (280 nm), ultraviolet light 395 nm and blue light 465 nm. The wavelengths at 395 and 465 nm are nicely fitting-in with the widely applied output wavelengths of ultraviolet or blue LED chips. The Eu\(^{3+}\)-doped Gd\(_2\)Mo\(_3\)O\(_9\) phosphor may be a better candidate for solid-state lighting applications.

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1. Introduction

As important optical materials, tungstates and molybdates have attracted particular interest because of their importance in practical applications as laser host materials in quantum electronics [1], scintillators in medical devices [2,3] and phosphor materials in fluorescent lamps, cathode ray tubes and X-ray intensifying screens [4]. In the last decades, a large number of rare earth-doped luminescent materials have been extensively investigated. In most cases, the emission of rare earth ions is due to optical transitions within the f manifold. The f-electrons are well shielded from the chemical environment and therefore have almost retained their atomic character [5]. As a consequence, the f–f emission spectra consist of sharp lines. According to the electronic structure of ground state, Eu\(^{3+}\) (4f\(^7\)) is half filled 4f level and therefore, its stability is greater than that of Eu\(^{2+}\) (4f\(^6\)). However, Eu\(^{3+}\) ion is also seen in well-known red phosphors, Y\(_2\)O\(_3\).Eu\(^{3+}\), YVO\(_4\).Eu\(^{3+}\) [6].

In 1997, the first white-light-emitting-diodes became commercially available [7]. There are several ways to gain white light. One is combination of a blue LED with a yellow phosphor, blending the blue light from the LED and yellow light from the phosphor results in white light; another is the UV/violet lights from LED exciting the tri-color phosphors to give white light. However, the phosphors can be effectively excited by blue and/or near ultraviolet (NUV) light are deficient [8–11]. From then on, exploiting phosphors, which can be efficiently excited by blue and/or NUV light, became a very active and interesting research subject. Host candidates such as molybdates and tungstates, attract much attention because of some special properties of MoO\(_4^{2-}\) and WO\(_4^{2-}\) group. Neeraj et al. reported the red phosphors NaM(WO\(_4\))\(_{2-x}\)(MoO\(_4\))\(_x\).Eu\(^{3+}\) (M = Gd, Y, Bi) [7] and Wang et al. reported the red phosphors Ca\(_{1-2x}\)Eu\(_x\)Li\(_x\)MoO\(_4\) [12]. Mental Mo can form different valence of Mo ions with the different preparation methods. Gopalakrishnan reported hydrogen reduction of Ln\(_2\)Mo\(_3\)O\(_{12}\) to Ln\(_2\)Mo\(_3\)O\(_9\) [13].

In this letter, we prepared Eu\(^{3+}\)-activated Gd\(_2\)Mo\(_3\)O\(_9\) by solid-state reaction procedures. Na\(_2\)CO\(_3\) has been widely used in the phosphor preparations by solid-state reaction, and in this study we chose the Na\(_2\)CO\(_3\) as a flux. To our best knowledge,
there is no report on the spectroscopic properties of Eu$^{3+}$-doped Ln$_2$Mo$_3$O$_9$. Various experimental factors affecting the luminescence properties of Gd$_2$Mo$_3$O$_9$:Eu were investigated.

2. Experimental

Phosphors were synthesized through the solid-state reaction technique. According to a certain stoichiometric ratio, the starting materials: gadolinium oxide (Gd$_2$O$_3$, 99.99%), europium oxide (Eu$_2$O$_3$, 99.99%) and molybdenum oxide (MoO$_3$, 99.99%) were weighted. Na$_2$CO$_3$ with purity of 99.9% was used as flux to improve the chemical reaction. After these powders were blended and grounded thoroughly in an agate mortar, the homogeneous mixture was obtained, and then the mixture was put into an alumina crucible and calcined in a muffle furnace at various temperatures from 600 to 1000 °C for 4 h into the intentional sample.

The crystal structure of these phosphors was identified by a Rigaku D-max-II B X-ray diffractometer (XRD) using Cu Kα ($\lambda = 1.54178$) radiation at 40 kV and 100 mA. The excitation and emission spectra of these powder phosphors were recorded with a Hitachi F-4500 using Xe lamp as excitation source. All the measurements were performed at room temperature.

3. Results and discussion

For the solid-state reaction, flux is often used to depress the sintering temperature, shorten the reaction time and improve the crystallization. An idea flux can promote the reaction, strengthen the crystallization and the luminescence properties, and it usually does not react with the raw materials. Na$_2$CO$_3$ is frequently used as flux in solid-state reaction because of its low melting point. In this work, different amount of Na$_2$CO$_3$ was used as flux reagent in the sample preparation to investigate the effect on the crystallization and luminescent properties. Fig. 1 shows the XRD patterns of the samples prepared with different amount of Na$_2$CO$_3$. The intensity of XRD peaks for sample with 3% Na$_2$CO$_3$ is higher than that of the sample with 7% Na$_2$CO$_3$, this fact indicated that 3% Na$_2$CO$_3$ as flux is suitable. Obviously, the XRD pattern of the sample prepared with no flux is different from that of the samples prepared with Na$_2$CO$_3$ as flux reagent. Compared with the JCPDS card, we know that the sample with no flux is $\alpha$-Gd$_2$(MoO$_4$)$_3$ (JCPDS card 25-0338) and the XRD patterns of the samples prepared with Na$_2$CO$_3$ agree well with Gd$_2$Mo$_3$O$_9$ structure (JCPDS card 33-0548). It should be noted that the Mo-valence from the starting material MoO$_3$ to Gd$_2$(MoO$_4$)$_3$ and Gd$_2$Mo$_3$O$_9$ was changed. Probably, this valence change is due to the fact that Mo in MoO$_3$ has highest valence, and tends to be decomposed to form lower-valence molybdenum oxide and desorbs O$_2$ at high temperature. In the case of Na$_2$CO$_3$ flux, the decomposed resultant of Na$_2$CO$_3$, CO$_2$, may lead to an O$_2$-lacking atmosphere, therefore the lower-valence-molybdenum oxide cannot be oxidized again. In the contrary case without flux, the lower-valence-molybdenum will be oxidized. Anyway, in order to obtain the Gd$_2$Mo$_3$O$_9$ phosphor, the solid-state reaction involving the flux Na$_2$CO$_3$ should be doable route. The flux Na$_2$CO$_3$ plays an important role in this reaction. For a more comprehensive understanding of molybdate crystal structures and transform between them, there is still a challenge to the researchers [14,15].

The excitation spectrum for monitoring $^5$D$_0 \rightarrow ^7$F$_2$ emission of Eu$^{3+}$ can be divided into two regions (as shown in Fig. 2): the broad excitation band extending up to 350 nm is attributable to the charge transfer transition of MoO$_4^{2-}$ and Eu–O group, and the narrow peaks located at wavelengths longer than 350 nm can be assigned to the f–f transitions of Eu$^{3+}$. The f–f transitions of Eu$^{3+}$ in excitation spectrum include sharp lines $^7$F$_0 \rightarrow ^5$L$_6$(Eu$^{3+}$) at 395 nm, $^7$F$_0 \rightarrow ^5$D$_2$(Eu$^{3+}$) at 465 nm, and $^7$F$_0 \rightarrow ^5$D$_1$(Eu$^{3+}$) at 535 nm; their intensities are comparable to the broad C–T band (in Fig. 2). For the usual Eu$^{3+}$-doped phosphors the intensity of charge transfer band is much more intense than that of f–f transitions in the excitation spectrum. In Gd$_2$Mo$_3$O$_9$:Eu system, however, the intensity of f–f transitions is almost equal to that of charge transfer band. This abnormal phenomena was also observed in NaM(WO$_4$)$_2$$_x$ (M = Gd, Y, Bi) [7] and AgLnMo$_2$O$_8$ [16]. Probably, this is due to the nature of WO$_4^{2-}$ and MoO$_4^{2-}$ groups.

The emission spectrum of Gd$_{1.8}$Mo$_3$O$_9$:Eu$_{0.203+}$ excited by 280 nm was shown in Fig. 2, it is composed of groups of several sharp lines, which belong to the intrinsic emission of trivalent Eu ion. The weak emission in the vicinity of 590 nm is ascribed to the Eu$^{3+}$ magnetic dipole transition $^5$D$_0 \rightarrow ^7$F$_1$, which is insensitive to the site symmetry. The main emission line around 613 nm is assigned to the Eu$^{3+}$ electric dipole transition of $^5$D$_0 \rightarrow ^7$F$_2$. 

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which is sensitive to the site symmetry. The domain emission peak at 613 nm indicated that the Eu$^{3+}$ located at the lack of inversion symmetry site breaking the parity selection rules. The emission spectra excited by 395 and 465 nm (not shown here) have the same profiles as that excited by 280 nm. Obviously, this phosphor can be excited by C–T band and f–f transition from the excitation spectra and emission spectra. In any cases, it is good sign that this novel phosphor can strongly absorb ultraviolet (395 nm) and visible blue light (465 nm), and transfer the excitation energy to the red radiation. The wavelengths at 395 and 465 nm are nicely in agreement with the widely applied UV or blue output wavelengths of GaN-based LED chips.

The effect of flux content on the luminescent intensity of phosphor Gd$_{1.96}$Mo$_3$O$_9$:Eu$_{0.04}$ under NUV (395 nm) excitation illustrated in Fig. 3. With an increase of the flux content, the luminescent intensities of the phosphor are improved gradually until Na$_2$CO$_3$ amount to 3%. When the flux amount is more than 3%, the luminescent intensity of the phosphor decreases. This fact implies a coherent conclusion that the XRD patterns (Fig. 1) reflect 3% flux could result in best crystallization. So flux amount of 3% is a better choice for synthesizing this phosphor.

Sintering temperature is an important factor affects the luminescent properties of phosphors. Fig. 4 shows the emission spectra of the Gd$_{1.96}$Mo$_3$O$_9$:Eu$_{0.04}$ prepared at different temperatures excited by 395 nm. The emission intensity of phosphor increases with a increase of preparation temperature below 800$^\circ$C and it is inversely above 800$^\circ$C. This result tell us that the temperature lower than 800$^\circ$C, the reaction tends to form Gd$_2$Mo$_3$O$_9$, while the temperature higher than 800$^\circ$C, other compounds different from Gd$_2$Mo$_3$O$_9$ crystal structure may grow. The intensity of PL emission in Gd$_{1.96}$Mo$_3$O$_9$:Eu$_{0.04}$ powders prepared at 800$^\circ$C was stronger than those of other temperatures showed that 800$^\circ$C is the optimized temperature for prepared Gd$_{1.96}$Mo$_3$O$_9$:Eu$_{0.04}$ phosphor.

The radius of Eu$^{3+}$ (0.95 nm) is almost equal to that of Gd$^{3+}$ (0.94 nm), therefore, Eu and Gd can form a solid solution (Gd, Eu)$_2$Mo$_3$O$_9$, this point has been verified by XRD. In order to investigate further the effect of the activator ions on the luminescence properties of the phosphor, the relationship between 613 nm emission intensity and concentration of activator ion Eu$^{3+}$ is showed in Fig. 5. As the wide band excitation and f–f excitation have different excitation mechanisms, when excited by wide band and f–f transition, the samples performed different intensity dependence on Eu$^{3+}$ concentration. The intensity of the samples excited by 280 nm (wide excitation band) approaches maximum at $x = 1$, then concentration quenching occurs, while no concentration quenching appears when the samples were excited by f–f transitions (395 nm and 465 nm). The intensity of the sample excited by 280 nm is higher than that of sample excited by 395 and 465 nm at the same Eu concentration.

Y$_2$O$_2$S-doped with Eu is a well-known red photoluminescent and cathodo-luminescent phosphor. At present, this phosphor is a red candidate for solid-state lighting application. The excitation spectra of Y$_2$O$_2$S:Eu and Gd$_2$Mo$_3$O$_9$:Eu are shown in Fig. 6 (top part). Obviously, the excitation spec-
Excitation spectra of Y$_2$O$_2$S:Eu (curve a) and Gd$_2$Mo$_3$O$_9$:Eu (curve b), and emission spectra under 395 nm UV excitation (curve c for Y$_2$O$_2$S:Eu and curve d for Gd$_2$Mo$_3$O$_9$:Eu).

In conclusion, Eu$^{3+}$-doped Gd$_2$Mo$_3$O$_9$ has been successfully developed by solid-state reaction with Na$_2$CO$_3$ as flux reagent. It is found that this phosphor can be effectively excited by C–T band (280 nm) and ultraviolet light 395 nm and blue light 465 nm (f–f transition) and emits red light (613 nm) with line spectrum. The wavelengths at 395 and 465 nm are nicely fitting-in with the widely applied output wavelengths of ultraviolet or blue LED chips. Appropriate amount of flux can enhance the luminescence intensity and improve crystallization. The result shows that the best flux content is 3%. The emission intensity of the sample prepared at 800 °C was stronger than those of other temperatures showed that 800 °C is the optimized temperature for prepared Gd$_2$Mo$_3$O$_9$:Eu phosphor. The wide band excitation and f–f excitation have different excitation mechanisms, the luminescent intensities of the sample excited by 280 nm approaches maximum at x = 1, then concentration quenching occurs, while no concentration quenching was observed under 395 and 465 nm. Compared with the commercial phosphor Y$_2$O$_2$S:Eu$^{3+}$, as-synthesized phosphor exhibits higher emission intensity when excited at blue (465 nm) and UV (395 nm). The integrated intensity for $^{5}D_{0}\rightarrow^{7}F_{1,2}$ transition of Eu$^{3+}$ is two times higher than that of Y$_2$O$_2$S:Eu$^{3+}$ under 395 nm excitation (see bottom part of Fig. 6).

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