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Flux and concentration effect on Eu^{3+} doped $\text{Gd}_2(\text{MoO}_4)_3$ phosphor

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Abstract: A novel red emitting phosphor $\text{Gd}_2(\text{MoO}_4)_3:\text{Eu}^{3+}$ was prepared by solid reaction, using Gd_2O_3 , Eu_2O_3 and WO_3 as starting materials and NH_4F as flux. The effects of flux content and Eu^{3+} concentration on the crystal structure, morphology and luminescent properties were investigated using XRD, SEM and fluorescent spectrum measurement. The XRD patterns showed that the resultants had the monoclinic structure. With the increase in flux amount, their crystallization significantly improved. The SEM images indicated that the mean size of the phosphor particles was around 2 μm , and agglomeration of the phosphor particles appeared while introducing higher flux amount. The excitation spectra exhibited more intense f-f transitions originating from ground state ${}^7\text{F}_0$ to upper states ${}^5\text{L}_6$ and ${}^5\text{D}_2$ than the charge transfer band. The concentration quenching of Eu^{3+} emission indicated that energy transfer from Eu^{3+} to molybdate host existed even at lower Eu^{3+} concentration.

Keywords: Eu; X-ray diffraction; luminescence; phosphors; crystal structure; rare earths

Recently, molybdates have attracted growing interest due to their potential applications in catalysis, laser, phosphor and ionic conductors^[1-5]. The optical and electric properties of molybdates are structure-dependent. Molybdates can exist in different crystal phases composed of the same and different valences of molybdenum atom. The formation of different phase structures depends on the synthesis approach and stoichiometric ratio of starting materials. In recent years, various preparative methods such as sol-gel^[1], solid state reaction^[5,6], freeze-dried precursor^[2], cation complexation^[3] for powder synthesis and Czochralski technique for the bulky crystal^[4], have been developed.

In this study, we prepared Eu^{3+} -doped $\text{Gd}_2(\text{MoO}_4)_3$ phosphor by using a solid state reaction. Compared with alkaline-metal molybdate, $\text{Gd}_2(\text{MoO}_4)_3$ could accommodate higher concentration of Eu^{3+} . The influence of NH_4F content, which serves as a flux, on their crystal structure, morphology, and fluorescent properties were studied. Compared with the usually commercialized Eu^{3+} -activated phosphors, intense absorption in the NUV (near ultraviolet) and blue region in these molybdate phosphors has been observed. This fact suggests the applications of Eu^{3+} -doped molybdate in the red emitting phosphor to the white light emitting diodes.

1 Experimental

The phosphors $\text{Gd}_2(\text{MoO}_4)_3:\text{Eu}^{3+}$ with various concentration of Eu^{3+} and flux amount of NH_4F were prepared by solid state reaction in air atmosphere. According to a certain stoichiometric ratio, the starting materials Gd_2O_3 (99.99%), Eu_2O_3 (99.99%), MoO_3 (99.99%) and NH_4F (analysis grade) were weighted and well mixed in an agate. Each batch of the mixtures was put into an alumina crucible and then sent to a muffle furnace. After 4 h-calcination at 800 °C, resultant powder with white color was obtained.

X-ray diffraction (XRD) patterns were measured using a RigakuD/max-II B X-ray diffractometer operating at 40 kV and 100 mA. The Cu K α radiation ($\lambda=0.154178$ nm) was used as X-ray source. The SEM (scanning electron microscopy) images were obtained using a KYKY-1000 Scanning Electron Microscope. The excitation and emission spectra of these powder phosphors were recorded using a Hitachi F-4500 fluorescentometer equipped with 150 W Xe lamp as an excitation source. All the measurements were performed at room temperature.

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2 Results and discussion

In order to check the crystal structure of the resultant powder, the XRD patterns for the samples with 0.5wt.%, 3.0wt.% and 7.0wt.% and without fluxes were measured and shown in Fig. 1. The concentration of Eu^{3+} is constant as 2.0 mol% in all samples. All the samples exhibit the same diffraction patterns as appeared in JCPDS card No. 25-0338 corresponding to the intrinsic diffraction patterns of monoclinic structure of $\text{Gd}_2(\text{MoO}_4)_3$. No extra-peaks related to the starting materials Gd_2O_3 , MoO_3 and Eu_2O_3 were observed. The intensity of diffraction peak increases with the increase in flux content in the range less than 3.0wt.%. When the flux content is more than 3.0wt.%, the diffraction peak intensity does not change. This fact implies that addition of more than 3.0wt.% flux is necessary in order to obtain better crystallization.

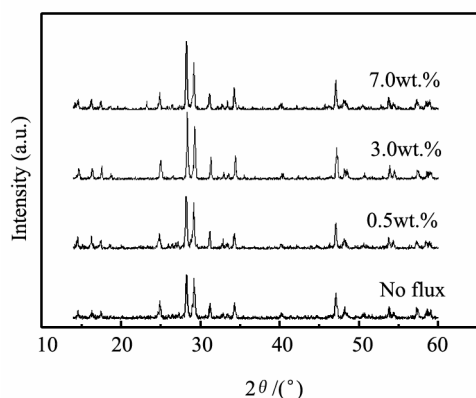


Fig. 1 XRD patterns of $\text{Gd}_{1.96}(\text{MoO}_4)_3:\text{Eu}^{3+}_{0.04}$ with different amount of NH_4F prepared at temperature of 800°C

Fig. 2 exhibits the SEM images for the samples without flux (a) and with 3.0wt.% (b) and 7.0wt.% (c) flux, the doping concentration of Eu^{3+} is 2.0 mol% for all these samples. The samples without flux and with 3.0wt.% flux show a mean particle size around $2\ \mu\text{m}$ and sphere-like shape, and the agglomeration of phosphor particles appears in the sample with 7.0wt.% flux. It is well-known that the phosphor with regular morphology and fine size can improve the slurry properties, packing density and make the luminescence intensity uniform on the device. At this point, addition of 3.0wt.% flux may be proper for the practical application

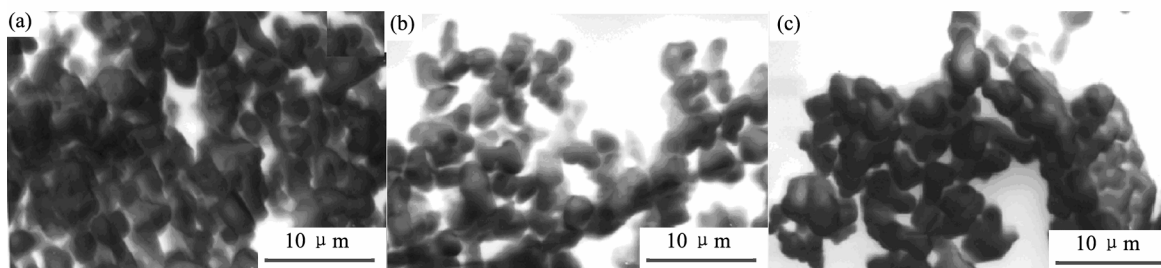


Fig. 2 SEM images of $\text{Gd}_{1.96}(\text{MoO}_4)_3:\text{Eu}^{3+}_{0.04}$ phosphors prepared with (a) no flux, (b) 3.0wt.% NH_4F , (c) 7.0wt.% NH_4F

of the phosphor; meanwhile the XRD results above reflect that the sample with 3.0wt.% flux possesses better crystallization.

The excitation and emission spectra for the sample with only $\text{Gd}_{1.96}(\text{MoO}_4)_3:\text{Eu}^{3+}_{0.04}$ and with the addition of 3.0wt.% flux into its preparation are illustrated in Fig. 3 as curves (a) and (b), respectively. The excitation spectra (monitored at 613 nm emission) composed of a wide band centered at 275 nm and several intense sharp lines. The broad band originates from the overlap of two charge-transfer bands of Mo-O and Eu-O, and the sharp lines are assigned to the intrinsic f-f transitions of Eu^{3+} from the ground state $^7\text{F}_0$ to the excited state $^5\text{L}_6$, $^5\text{D}_2$ and $^5\text{D}_1$. It should be noted that in the excitation spectra, the f-f transition is more intense than the charge transfer bands. It is different from the most Eu^{3+} -doped phosphors. The wavelengths of intense f-f transition peaking at 465 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_2$) and 395 nm ($^7\text{F}_0 \rightarrow ^5\text{L}_6$) match the output wavelengths of commercialized GaN-based light emitting diodes (LEDs). Therefore, this phosphor could be used as a candidate for red emitting component of phosphors for the white LEDs applications, since there is still a lack of satisfactory red emitting phosphor for white LEDs^[7-9].

The emission spectra upon 465 nm excitation in Fig. 3 show an intense emission line centered at 613 nm and several weaker emission lines in shorter wavelength region, and they are corresponding to transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_{0,1}$ and $^5\text{D}_1 \rightarrow ^7\text{F}_0$, respectively. We believe this phosphor would have better color coordinates and color purity meeting the need in practical application in white light emitting diodes.

The circle dots in Fig. 3 represent the dependence of integrated emission intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0, 1, \dots$ and 5) transitions on the flux content introduced into the preparation. It is found that luminescent intensity increases with an increase of flux content in the range less than 3.0wt.%, and then keeps constant with the further increase in flux amount. Therefore, introducing 3.0wt.% flux improves luminescent properties of this phosphor and does not bring any agglomeration of phosphor particles as shown in Fig. 2(c).

In order to further investigate the influence of flux content on the luminescent property of phosphor, the O/R ratios (in-

egrated intensity ratio of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions) for all the samples with different flux contents are calculated and plotted in Fig.4 as a function of flux content. It is seen that the ratio increases first and then keeps constant when the flux content is more than 3.0wt.%. This fact implies that when the flux content is less than 3.0wt.%, the Eu^{3+} ions may not completely decomposes, in other words, Eu_2O_3 cluster may exist in the powders. This result again supports the conclusion above that 3.0wt.% flux is appropriate for preparing the $\text{Gd}_2(\text{MoO}_4)_3:\text{Eu}^{3+}$ phosphor. The insert in Fig.4 shows a comparison between the emission spectra for the samples with 0.5wt.% and 7.0wt.%. The spectra were normalized by the emissive intensity of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$. The intensity for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition in the sample with 0.5wt.% flux is more intense than that of the sample with 7.0wt.% flux. The intense ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition in the sample with 0.5wt.% indicates that Eu^{3+} ions occupy the sites with higher symmetry. The starting material Eu_2O_3 exists as a cubic phase, whose symmetry is higher than that of Eu^{3+} in the resultant

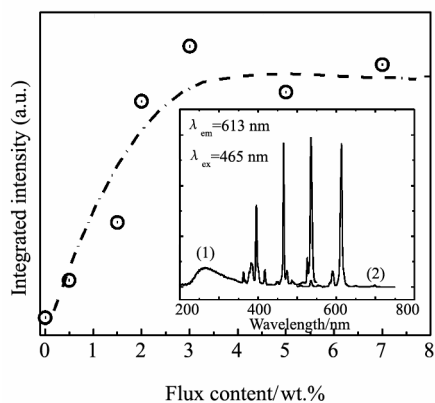


Fig.3 Dependence of integrated emission intensity on the flux content, (while) under 395 nm excitation

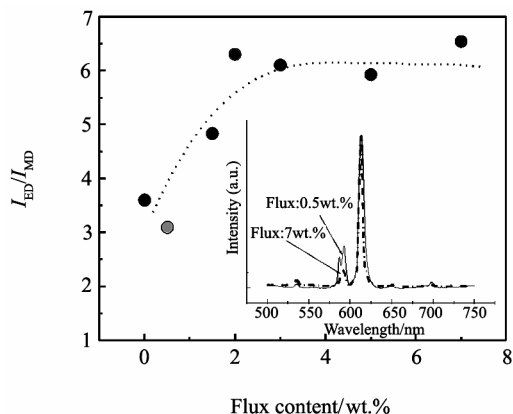


Fig.4 Relationship between emitting intensity ratio of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and flux content, the insert plotting the emission spectra for the samples with different content of flux, and 2.0 mol% of Eu^{3+}

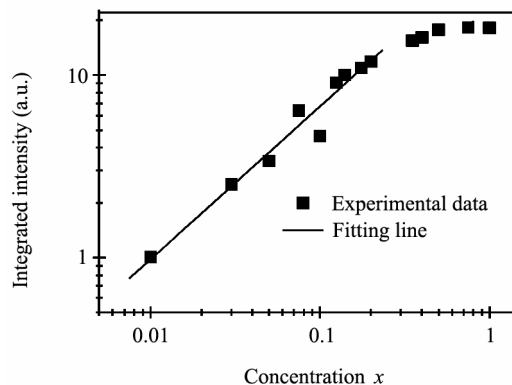


Fig.5 Effect of Eu^{3+} ion concentration on the emission intensity of $\text{Gd}_2(\text{MoO}_4)_3:\text{Eu}^{3+}$ phosphor under 395 nm excitation (The solid square dots are the experimental data, the continuous line is the fitting line)

powder $\text{Gd}_2(\text{MoO}_4)_3$, with a monoclinic structure as shown in Fig.1. This fact coincides with the conclusion derived above from Fig.3.

The doping concentration is one of the important factors influencing the performance of luminescent materials. Therefore, the activator concentration should be optimized experimentally. A set of phosphor samples with various concentrations and 3.0wt.% of flux was produced. The integrated luminescent intensity was calculated over the detectable emissions originating from ${}^5\text{D}_0$ level. Fig.5 shows the relationship between the luminescent intensity and Eu^{3+} concentration in a double log coordinate system. The Eu^{3+} concentration, x , is described by $\text{Gd}_{2-x}(\text{MoO}_4)_3: x\text{Eu}^{3+}$. The solid square dots represent the experimental data. The sample with concentration 30.0 mol% Eu^{3+} ($x=0.6$), which displays the highest emission, would be a proper choice for this phosphor system. In order to investigate the concentration quenching, a linear fitting was done to the experimental data in the lower concentration range by using the function $y=ax+b^{[10]}$. The linear parameter a was obtained to be 0.84, which is closer to 1. This fact proves that the weak energy transfer exists at even lower doping concentration. This energy transfer is assigned to the back energy transfer from the Eu^{3+} ions to the molybdate host and is weaker than the energy transfer from molybdate host to the Eu^{3+} due to the large energy mismatch between host absorption and emission of Eu^{3+} ions^[4].

3 Conclusion

A novel red emitting phosphor Eu^{3+} -doped $\text{Gd}_2(\text{MoO}_4)_3$ was successfully prepared by using solid state reaction. The effects of flux content on the crystal structure, morphology and luminescent properties were investigated using XRD,

SEM and fluorescent spectra. A proper flux content (3.0 wt%) significantly improved crystallization, eliminated agglomeration of phosphor particle and enhanced the luminescent performance of phosphor. Finally, the study on doping concentration indicated the occurrence of weak energy transfer from Eu^{3+} ions to molybdate host and suggested a proper doping concentration around 30 mol%.

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