Photoluminescence properties of Sm$^{3+}$-doped LiY(MoO$_4$)$_2$ red phosphors

YANG Zhiping (杨志平)$^*$, DONG Hongyan (董宏岩), LIU Pengfei (刘鹏飞), HOU Chuncai (侯春彩), LIANG Xiaoshuang (梁晓双), WANG Can (王灿), LU Fachun (鲁法春)

(College of Physics Science and Technology, Hebei University, Baoding 071002, China)

Received 10 October 2013; revised 8 January 2014

Abstract: A series of novel Sm$^{3+}$-doped LiY(MoO$_4$)$_2$ red phosphors under the UV excitation were synthesized by solid state reaction at 800 °C for 7 h. The data measured by X-ray diffraction (XRD) indicated that the samples were all pure phases of LiY(MoO$_4$)$_2$. Their excitation spectra had a broad band ranging from 250 to 350 nm and several sharp peaks. The centers of the peaks were located at about 365 nm ($^4$H$_{5/2}→^4$D$_{3/2}$), 378 nm ($^4$H$_{5/2}→^4$P$_{3/2}$), 406 nm ($^4$H$_{5/2}→^4$F$_{1/2}$), 420 nm ($^4$H$_{5/2}→^4$P$_{5/2}$), 442 nm ($^4$H$_{5/2}→^4$G$_{5/2}$), 471 nm ($^4$H$_{5/2}→^4$I$_{13/2}$) and 482 nm ($^4$H$_{5/2}→^4$I$_{15/2}$), respectively. The strongest emission was excited by 406 nm, and the main emissions were located at 568 nm ($^4$G$_{5/2}→^4$H$_{7/2}$), 610 nm ($^4$G$_{5/2}→^4$H$_{9/2}$), 649 nm ($^4$G$_{5/2}→^4$H$_{11/2}$) and 710 nm ($^4$G$_{5/2}→^4$H$_{13/2}$). Photoluminescence properties were determined for various concentrations of Sm$^{3+}$-doped LiY(MoO$_4$)$_2$ host, and the luminescence intensity had the best value when x=0.02 in LiY$_{1−x}$(MoO$_4$)$_2$:xSm$^{3+}$.

Keywords: red phosphors; rare earths; LiY(MoO$_4$)$_2$; photoluminescence

White light-emitting diodes (w-LED) are emerging as an indispensable solid-state light source for the fourth generation lighting industry and display systems because of their advantages of energy saving, fast response time, environmental-friendliness, and wide optical prospects$^{[1−7]}$. A common way to achieve white LED is to use UV light emitting LED (InGaN chip, 350–410 nm) coated with red, green, blue tri-color phosphors$^{[8]}$. Red emitting phosphor is one of crucial tricolor luminescent materials for white LEDs, but the development of red phosphor is not as successful as green or blue$^{[9,10]}$. Up to now, so many researches have been done on Sm$^{3+}$-doped red phosphors. They all have sharp excitation peaks at around 400 nm and narrow emissions at 590–630 nm, due to characteristic intraconfigurational 4f-4f transitions$^{[11]}$.

Molybdates are considered to be good hosts for luminescent materials due to their excellent thermal and chemical stability, and LiY(MoO$_4$)$_2$ is one important material among the molybdate family, which has great potential applications in various fields, such as phosphors, optical fibers, scintillators, magnets and catalysts$^{[12,13]}$. At present Sm$^{3+}$-doped molybdate phosphors have rarely been studied. In the ultraviolet region and the blue region Sm$^{3+}$ has dense excitation lines (almost from $^4$H$_{5/2}$ to $^4$L$_{15/2}$, $^4$L$_{13/2}$, $^4$K$_{11/2}$), and it can emit 600–650 nm red light$^{[14]}$.

This paper expounded the synthesis conditions, photoluminescence properties, decay time, and chromaticity of the new LiY(MoO$_4$)$_2$:Sm$^{3+}$ red phosphors.

1 Experimental

The Sm$^{3+}$-doped LiY$_{1−x}$(MoO$_4$)$_2$:xSm$^{3+}$ (x=0.0025, 0.005, 0.01, 0.02, 0.04, 0.08, 0.16) phosphors were prepared from the raw materials: Li$_2$CO$_3$, MoO$_3$, Y$_2$O$_3$ (all these are of analytical grade) and Sm$_2$O$_3$ of purity higher than 99.99%. The materials were weighed in stoichiometric proportions, thoroughly mixed and ground by an agate mortar and a pestle for 15 min till they were dispersed. Then the mixtures were heated up to 800 °C in the furnace, and kept at this temperature for 7 h in air atmosphere. When the samples were cooled to room temperature in the furnace, they were ground again into powders for use.

The X-ray diffraction (XRD) patterns were performed on a Shimadzu model XRD-6000 X-ray powder diffractometer with Cu Kα ($\lambda=0.154 06$ nm) radiation at 40 kV and 30 mA. The XRD pattern was recorded in the $2θ$ range from 25° to 65°. The emission and excitation spectra of the obtained powders were recorded with a Hitachi F-4600 spectrophotometer, and it was equipped with a 150 W xenon lamp as the excitation source. The scanning speed was 1200 nm/min with a step of 0.2 nm and the response time was 0.05 s.

2 Results and discussion

2.1 Structure of LiY(MoO$_4$)$_2$

The crystal structure of LiY(MoO$_4$)$_2$ is shown in Fig. 1.
LiY(MoO₄)₂ crystallizes in the scheelite-type structure, with space group I41/a and Z=2 (R1=1.7% and 2.7%, respectively). It has a=0.5148 nm, c=1.1173 nm, V=0.29611 nm³. Li is completely disordered on a jointly occupied site. Mean (Y, Li)–O distances are 24.0 and 24.7 nm, respectively. In this compound the unique MoO₄ tetrahedron has four identical Mo–O bonds with lengths of 17.79 nm. The stoichiometry of LiRE(MoO₄)₂ (RE= rare-earth element) compound is discussed and the relation to structure types of other MRE(XO₄)₂ (M=alkali metal, X=Mo, W) compounds is briefly addressed [13,14]. Experimentally measured data are a=0.5128 nm, c=1.1144 nm, V=0.2931 nm³, and they agree well with the standard data. Fig. 2 shows the SEM pictures of LiY₀.₉₈(MoO₄)₂:0.0₂Sm³⁺, which are magnified 500, 5000, 10000, and 20000 times, respectively. The as-synthesized phosphor consisted of the ball-like particles with relative narrow size distribution and apparent agglomeration, so its luminescence intensity is strong.

2.2 X-ray diffraction analysis

Fig. 3 exhibits the X-ray powder diffraction (XRD) patterns of the LiY₁₋ₓ(MoO₄)₂ₓSm³⁺ (x=0.0025, 0.005, 0.01, 0.02, 0.04, 0.08, 0.16) samples and JCPDS card No. 17-0773. The positions and intensities of the peaks agree well with the data reported in the JCPDS standard card (PDF#17-0773) of tetragonal LiY(MoO₄)₂ crystals. They are shown to have pure phases for no impurity phases are observed in the composition. The result definitely indicates that a small amount of Sm³⁺ ions doped into matrix does not change the crystalline structure of the sample.

2.3 Discussion of excitation and emission spectra

Fig. 4 shows the excitation spectra of LiY(MoO₄)₂: 0.0₂Sm³⁺ monitored by 649 nm. It can be seen that there are two parts in the picture. One is a broad excitation band ranging from 250 to 350 nm, which belongs to the Mo–O charge transfer absorption band (CTB); the
other consists of series of sharp peaks, which are located at 365, 378, 406, 420, 442, 471, and 482 nm due to the transitions $^6H_{5/2} \rightarrow ^4D_{3/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4G_{9/2}$, $^4I_{13/2}$ and $^4I_{9/2}$.[15,16]. They are assigned to the $4f \rightarrow 4f$ transition of the Sm$^{3+}$ ion, and the $^6H_{5/2} \rightarrow ^4F_{7/2}$ transition has the strongest intensity. This suggests that the phosphor can be effectively excited by near-UV LED chips (350–420 nm), which is certainly needed for potential applications in W-LEDs.

The emission spectra of the LiY$_{0.98}$(MoO$_4$)$_2$:0.02Sm$^{3+}$ phosphor excited by 406 and 420 nm are shown in Fig. 5. It can be find that there are four emission peaks, including three sharp peaks and a relatively weak peak. These peaks are corresponding to $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{11/2}$[16]. And the strongest emission peak is located at 649 nm due to the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition. Sm$^{3+}$ has a similar radius as Y$^{3+}$, and they are both trivalent cations in LiY(MoO$_4$)$_2$. Luminescence properties are dissimilar when doping Sm$^{3+}$ ion in different hosts. A lot of work has been done about Sm$^{3+}$-doped phosphors. Researches on MMoO$_4$ (M=Ca$^{2+}$, Ba$^{2+}$ and Sr$^{2+}$):Sm$^{3+}$[17], LiBaPO$_4$:Sm$^{3+}$[18], Sr$_5$Bi(PO$_4$)$_3$:Sm$^{3+}$[15] show that the strongest peak is located at about 600 nm in those hosts, while the strongest emission peak of the LiY(MoO$_4$)$_2$:Sm$^{3+}$ phosphor is located at 649 nm, which is closer to the red range. Therefore, LiY(MoO$_4$)$_2$:Sm$^{3+}$ will be a good potential red phosphor. Emission spectra of all the samples excited by 406 nm display a similar profile including four peaks shown in Fig. 6 except the relative intensity. The luminescence intensity enhances with the Sm$^{3+}$ doping concentration increasing but the luminescence intensity decreases when doping excess Sm$^{3+}$ ions. We know that the greatest integrated emission intensity is at the concentration of $x=0.02$, which can be seen from the picture.

All the luminescence intensities of the samples were tested in the same condition. A Sm$^{3+}$ will take the place of an Y$^{3+}$, then forming a luminescence center when doping Sm$^{3+}$ in the host. Luminescence intensity is enhanced with the Sm$^{3+}$ doping concentration increasing because of the increasing number of luminescence centers. However, beyond the critical concentration, the intensity gradually decreases as the Sm$^{3+}$ concentration increases because of the concentration quenching. And the concentration quenching is mainly caused by the nonradiative energy transfer among Sm$^{3+}$ ions.

When the electric multipolar interaction is involved in the energy transfer, there are four types of interactions, which are exchange interaction, dipole-dipole (d-d), dipole-quadrupole (d-q), and quadrupole-quadrupole (q-q) when the values are 3, 6, 8 and 10, respectively[19]. It is necessary to clarify which type of interaction is involved in the energy transfer. According to the theory of Dexter, there is a simplified equation shown as follows[19]:

$$l_{x} = l_{x0} \frac{k \beta (x)^{6/3}}{1 + \beta (x)^{6/3}}$$

(1)

where $l$ is the luminescence intensity, $x$ is the series of activator concentration, and $k$ and $\beta$ are the constants during the same host, the same excited state. Eq. (1) can be modified (logarithmic transformation) as follows[20]:

$$\log l_{x} = \log l_{x0} + k \beta \frac{6}{3} \log x$$

(2)

Fig. 7 shows the relation between $\log l_{x}$ and $\log x$ in LiY(MoO$_4$)$_2$:Sm$^{3+}$ phosphor ($\lambda_{ex}=406$ nm). From the
slope of Eq. (2), the electric multipolar character can be obtained by the slope (–θ/3) of the plot. It can be seen that the dependence of log(I/x) on lxg is linear and the slope is −1.87. So the value of θ is 5.61, which is very close to the theoretical value 6 for the electric d-d interaction. It suggests that the d-d interaction is the main mechanism for the concentration quenching of 4F7/2 → 4F5/2 transition of Sm3+ in the LiY(MoO4)2:Sm3+ phosphor.

Fig. 8 depicts the Commission International de l’Eclairage (CIE) chromaticity coordinates of LiY1−x(MoO4)2:xSm3+ phosphors excited at 406 nm. All the samples with different Sm3+ concentrations have almost the same color as shown in the picture, and it also suggests that the color keeps constant with the Sm3+ concentration increasing. Though the most intense emission corresponding to 5D3→4H9/2 transition is red (649 nm), the phosphor also emits reddish orange light when excited by 406 nm because of the existence of the emissions corresponding to 5D3→4H9/2 (568 nm), 5G4→4H15/2 (610 nm) and 5G4→4H11/2 (710 nm). The CIE chromaticity coordinates of LiY0.98(MoO4)2:0.02Sm3+ phosphor is (0.613, 0.383), which is quite close to that of commercial red Sr2Si5N8:Eu2+ phosphors (0.620, 0.370). The decay curves (λex=406 nm, λem=649 nm) of Sm3+ in the LiY1−x(MoO4)2:xSm3+ phosphors were measured as shown in Fig. 9 and the lifetime data are presented in the inset of that picture. It is obvious that with the increasing amount of Sm3+ ions, the lifetime of Sm3+ ions gradually decreases.

3 Conclusions

In summary, the LiY(MoO4)2:Sm3+ red phosphors doped with different concentrations of Sm3+ ions were synthesized by high temperature solid state reaction. And the experimental reaction conditions (800 °C and 7 h) were easily implemented. The emission had the best relative intensity when excited at 406 nm. Besides it had in the output wavelength range of UV InGaN-based light-emitting diodes chip. Its strongest emission peak was located at 649 nm, which was better than the other Sm3+-doped phosphors whose strongest emission peaks were at about 600 nm. The optimal doping concentration of Sm3+ ions was 2 mol.%. CIE coordinates of the samples were quite close to that of the commercial red Sr2Si5N8:Eu2+ phosphors (0.620, 0.370), and it was almost kept constant with the Sm3+ concentration increasing. The lifetime decreased with the increasing amount of Sm3+ ions. All these results suggested that LiY(MoO4)2:Sm3+ may be a potential candidate for LED application.

References:


