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Photoluminescence properties of Sm^{3+}-doped $LiY(MoO_4)_2$ red phosphors

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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 ºC 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 ($^6H_{5/2}\rightarrow{}^4D_{3/2}$), 378 nm ($^6H_{5/2}\rightarrow{}^6P_{7/2}$), 406 nm ($^6H_{5/2}\rightarrow{}^4F_{7/2}$), 420 nm ($^6H_{5/2}\rightarrow{}^6P_{5/2}$), 442 nm ($^6H_{5/2}\rightarrow{}^4G_{9/2}$), 471 nm ($^6H_{5/2}\rightarrow{}^4I_{13/2}$) and 482 nm ($^6H_{5/2}\rightarrow{}^4I_{9/2}$), respectively. The strongest emission was excited by 406 nm, and the main emissions were located at 568 nm ($^4G_{5/2}\rightarrow{}^6H_{5/2}$), 610 nm ($^4G_{5/2}\rightarrow{}^6H_{7/2}$), 649 nm ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) and 710 nm ($^4G_{5/2}\rightarrow{}^6H_{11/2}$). 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 $^6H_{5/2}$ to $^4L_{17/2}$, $^4L_{13/2}$, $^4K_{11/2}$), and it can emit 600–650 nm red light[11].

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_2CO_3, MoO_3, Y_2O_3 (all these are of analytical grade) and Sm_2O_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 ºC 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 diffraction spectroscope with Cu Kα (λ=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.

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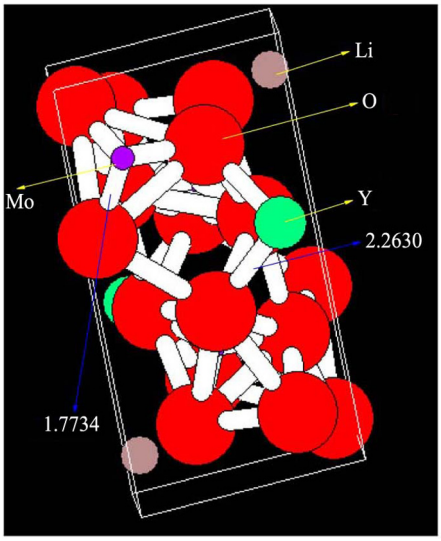

Fig. 1 Crystal structure of $LiY(Mo_2O_4)_2$

$LiY(MoO_4)_2$ 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 nm^3. 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 MoO_4 tetrahedron has four identical Mo–O bonds with lengths of 17.79 nm. The stoichiometry of $LiRE(MoO_4)_2$ (RE= rare-earth element) compound is discussed and the relation to structure types of other $MRE(XO_4)_2$ (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 nm^3, and they agree well with the standard data. Fig. 2 shows the SEM pictures of $LiY_{0.98}(MoO_4)_2$:0.02Sm^{3+}, 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 $LiY_{1-x}(MoO_4)_2$:xSm^{3+} (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 $LiY(MoO_4)_2$ 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 Sm^{3+} 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 $LiY(MoO_4)_2$: 0.02Sm^{3+} 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

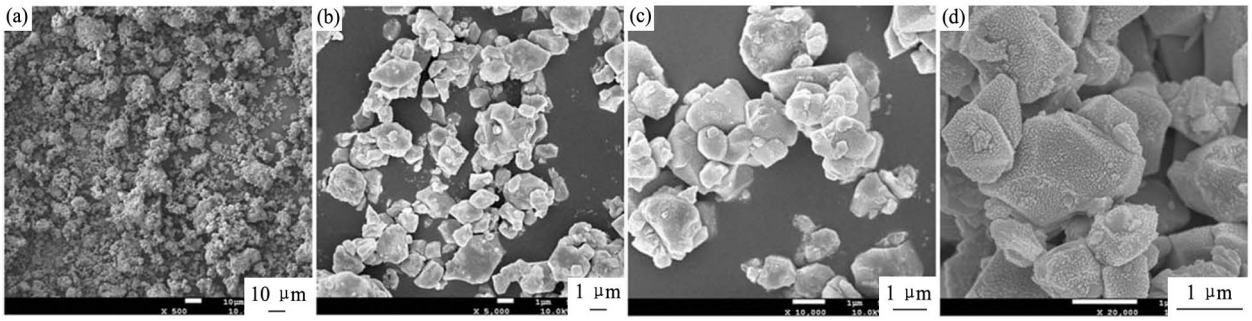

Fig. 2 SEM pictures of $LiY_{0.98}(MoO_4)_2$:0.02Sm^{3+}

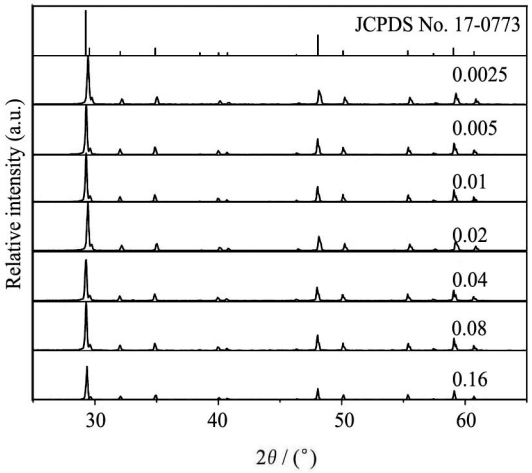

Fig. 3 XRD patterns of $LiY_{1-x}(MoO_4)_2$:xSm^{3+} (x=0.0025, 0.005, 0.01, 0.02, 0.04, 0.08 and 0.16) and JCPDS card No.17-0773

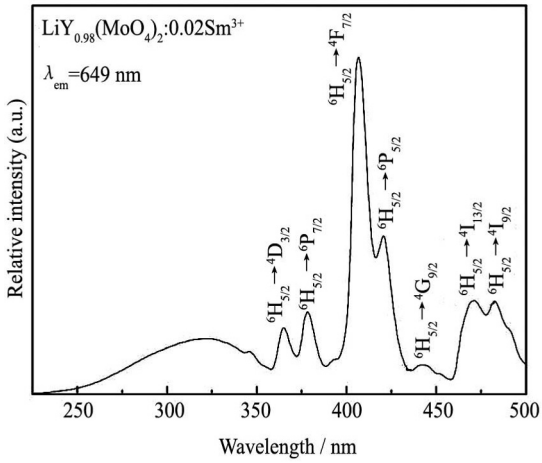

Fig. 4 Excitation spectra of $LiY_{0.98}(MoO_4)_2$:0.02Sm^{3+} monitored at 649 nm