Photoluminescence properties of solid-state Tb^{3+} doped NaY(MoO$_4$)$_2$*

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A series of Tb^{3+} doped NaY(MoO$_4$)$_2$ are synthesized by a solid-state reaction at 550 °C for 4 h, and their luminescent properties are investigated. The phase formation is carried out with X-ray powder diffraction analysis, and there is no other crystalline phase except NaY(MoO$_4$)$_2$. NaY(MoO$_4$)$_2$:Tb^{3+} can produce the green emission under 290 nm radiation excitation, and the luminescence emission peak at 545 nm corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+}. The emission intensity of Tb^{3+} in NaY(MoO$_4$)$_2$ is enhanced with the increase of Tb^{3+} concentration, and there is no concentration quenching effect. The phenomena are proved by the decay curves of Tb^{3+}. Moreover, the Commission International de I'Eclairage (CIE) chromaticity coordinates of NaY(MoO$_4$)$_2$:Tb^{3+} locate in the green region.

In the past several years, the new lighting and display devices, such as light-emitting diodes (LEDs), plasma display panels (PDPs) and field emission displays (FEDs), have been proposed, which leads to great interest in searching novel phosphors for these new applications[1-7]. Tb^{3+} doped materials have been widely used as green emitting phosphor due to their intense $^5D_4 \rightarrow {}^7F_5$ emission in the green spectral region. In order to search the novel green emitting phosphors, many researches have focused on the Tb^{3+} doped materials. Generally, as luminescent materials, the compounds must have the excellent physical and chemical stability[8]. Molybdates have the higher physical and chemical stability and the lower harm to the environment and health[9-11]. Therefore, in order to achieve the efficient emitting phosphor, many researches focused on the luminescent properties of rare earths doped molybdate[12-14]. MLn(MoO$_4$)$_2$ (M: alkali metal; Ln: rare earth) molybdate crystals are attractive host materials because of their good optical properties[15-17]. Moreover, the MLn(MoO$_4$)$_2$ single crystals, which are with a scheelite structure, can be used as the host materials of self-doubling solid-state laser[18-20]. For example, the optical properties of NaY(MoO$_4$)$_2$:Dy^{3+} crystal have been already investigated[21]. Actually, the photoluminescence properties of rare earths in MLn(MoO$_4$)$_2$ are also studied[22], the research results indicate that there is

no concentration quenching of Eu^{3+} in NaLn$_{1-x}$Eu$_x$(MoO$_4$)$_2$ and LiEu(MoO$_4$)$_2$, both materials exhibit the strongest red emission under the 395 nm radiation excitation, and the appropriate Commission International de I'Eclairage (CIE) chromaticity coordinates are close to the NTSC standard values. Moreover, using the hydrothermal synthesis, the excellent luminescent properties of Eu^{3+} or Tb^{3+} doped MLn(MoO$_4$)$_2$ have been achieved[23]. However, to the best of our knowledge, the solid-state synthesis and the luminescence of Tb^{3+} doped NaY(MoO$_4$)$_2$ have not been systematically reported. Therefore, in this paper, Tb^{3+} doped NaY(MoO$_4$)$_2$ phosphors are synthesized by the solid-state method, and the photoluminescence properties are investigated.

A series of NaY$_{1-x}$(MoO$_4$)$_2$:xTb^{3+} (x: mole concentration) samples were synthesized by a high temperature solid state reaction method. The initial materials, including Na$_2$CO$_3$ (A.R.), Y$_2$O$_3$ (A.R.), MoO$_3$ (A.R.) and Tb$_4$O$_7$ (99.99%), were weighted in stoichiometric proportion, thoroughly mixed and ground by an agate mortar and pestle for more than 30 min till they were uniformly distributed. The obtained mixtures were heated at 550 °C for 4 h in crucibles along with an atmosphere, and then were naturally cooled to room temperature. In order to measure the characteristics of the phosphor, the samples were ground into powder.

The phase formation was determined by X-ray diffraction (XRD) in a Bruker AXS D8 advanced automatic diffractometer (Bruker Co., German) with Ni-filtered Cu Kα1 radiation (λ=0.154 06 nm), and a scan rate of 0.02°/s was applied to record the patterns in the 2θ range from 10° to 80°. The steady time resolved photoluminescence spectra and the excitation and emission spectra were detected by a fluorescence spectrophotometer (Hitachi F-4600), and the exciting source was a 450 W Xe lamp. The CIE chromaticity coordinates of the sample were measured by a PMS-80 spectra analysis system. All measurements were carried out at room temperature.

The phase formation of $NaY_{1-x}(MoO_4)_2:xTb^{3+}$ is determined by the XRD pattern, and a similar diffraction pattern is observed for each sample. As a representative, Fig.1 shows the XRD pattern of $NaY(MoO_4)_2:0.2Tb^{3+}$. Comparing the diffraction data with the standard JCPDS card (No.82-2369), the results indicate that there is no difference between the doped sample and the pure $NaY(MoO_4)_2$. It means that the phase formation of $NaY(MoO_4)_2$ is not influenced by a little amount of Tb^{3+}, and the impurity ions are incorporated into the host successfully. $NaY(MoO_4)_2$ has a tetragonal crystal structure with a space group $I_{41}/a(88)$, and the cell parameters are a=b=0.519 89 nm, c=1.132 99 nm and Z=2.
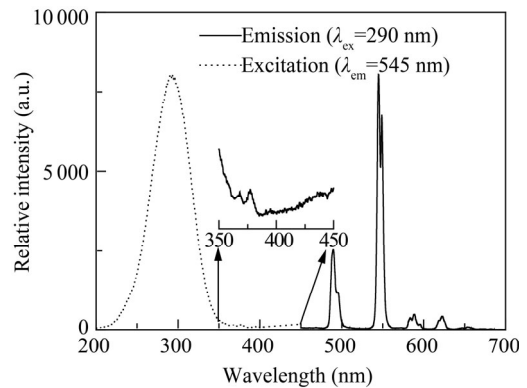

(a) $NaY(MoO_4)_2:0.2Tb^{3+}$
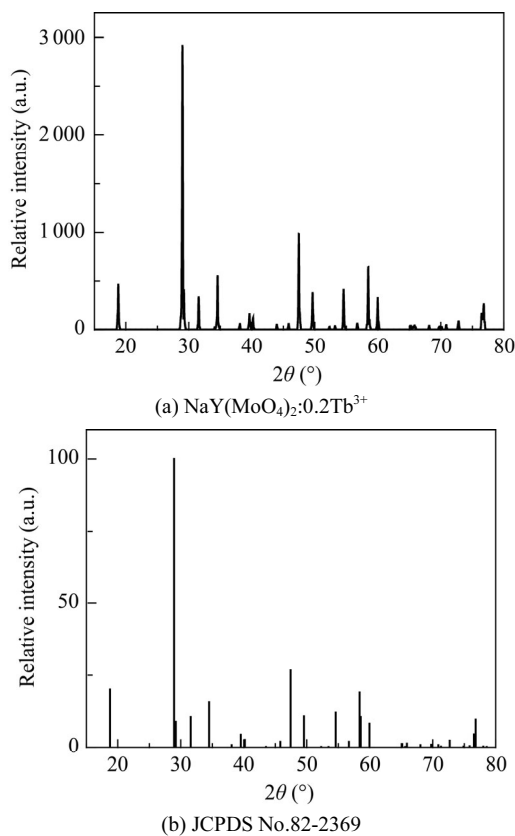
(b) JCPDS No.82-2369

Fig.1 XRD pattern of $NaY(MoO_4)_2:0.2Tb^{3+}$ and the standard data of $NaY(MoO_4)_2$ (JCPDS No.82-2369)

As shown in Fig.2, $NaY(MoO_4)_2:Tb^{3+}$ has several emission bands under the 290 nm radiation excitation, and Fig.3 shows the corresponding $^5D_4 \rightarrow {}^7F_J$ (J=6, 5, 4, 3,

2, 1) transitions of Tb^{3+}. The emission bands at λ_{ex}=290 nm show a splitting pattern, such as the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} at 545 nm and 549 nm[10]. The $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} leads to two peaks, and the intensity of the peak at 545 nm is stronger than that at 549 nm. For the emission bands, the green emission transition of $^5D_4 \rightarrow {}^7F_5$ is dominant among the all, so the phosphor can produce green emission. For the 545 nm emission of $NaY(MoO_4)_2:Tb^{3+}$, the excitation spectrum consists of a strong and broad band from 200 nm to 350 nm with a maximum at about 290 nm, which also corresponds to the charge-transfer transitions within the MoO_4^{2-} groups. It indicates that the same situations are still kept for Tb^{3+} doped $NaY(MoO_4)_2$ phosphors, i.e., an efficient energy transfer also occurs from MoO_4^{2-} to Tb^{3+}.

Moreover, the inset of Fig.2 shows that there are some weaker excitations in the longer wavelength region, which are ascribed to the 4f-4f transitions of Tb^{3+}. Generally, the wavelength of the available ultraviolet (UV) LED ranges from 365 nm to 405 nm. LEDs emitting UV light around 300 nm are also commercially available, although the efficiency of these chips is still low. The UV LED (from 230 nm to 340 nm) can efficiently excite $NaY(MoO_4)_2:Tb^{3+}$, and it is found to be an effective green emitting phosphor for UV-based LEDs.


Fig.2 Emission and excitation spectra of $NaY(MoO_4)_2$: $0.2Tb^{3+}$ (λ_{ex}=290 nm, λ_{em}=545 nm)
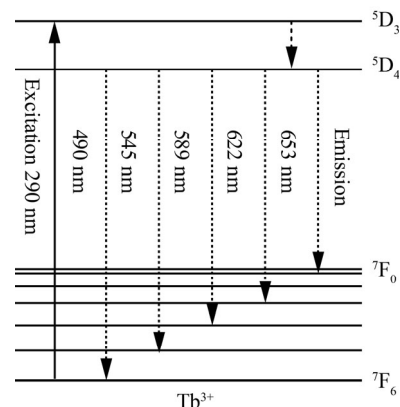
Fig.3 The schematic diagram of representative energy levels and emission transitions for $NaY(MoO_4)_2:Tb^{3+}$

In order to achieve the best doping content of Tb^{3+}, a series of $NaY_{1-x}(MoO_4)_2{:}xTb^{3+}$ (x=0.01–0.25) were synthesized. As shown in Fig.4, with the increase of Tb^{3+} doping content, the emission intensity is continuously enhanced, and there is no concentration quenching effect in our experimental region.
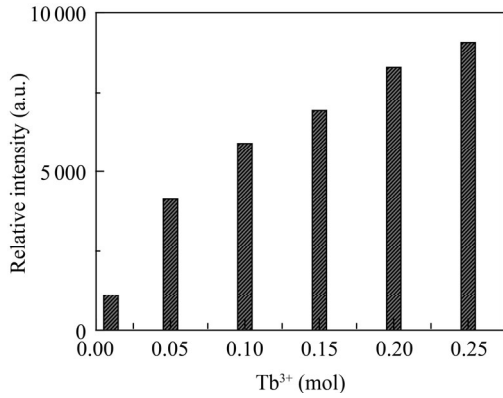

Fig.4 Emission intensities of $NaY(MoO_4)_2{:}xTb^{3+}$ as a function of Tb^{3+} concentration (λ_{ex}=290 nm)

In order to further validate the effect of the Tb^{3+} doping content on the emission intensity of the phosphors, the fluorescence decay curves of 545 nm emission for $NaY_{1-y}(MoO_4)_2{:}xTb^{3+}$ (x=0.01–0.25) under 290 nm excitation are also measured, and the results are shown in Fig.5. For the single exponential decay, it can be expressed as[24]

$$I=I_0\exp(-t/\tau), \tag{1}$$

where I_0 and I are intensities at zero time and time t, respectively, and τ is the lifetime for transition. The lifetime for the $^5D_4{\rightarrow}^7F_5$ of Tb^{3+} is calculated with different Tb^{3+} doping contents, and the results are shown in Tab.1. The results show that the decay time of $NaY_{1-x}(MoO_4)_2{:}xTb^{3+}$ has the similar values with the increase of Tb^{3+} doping content. This phenomenon indicates that there ought to be no concentration quenching effect of Tb^{3+} in the $NaY(MoO_4)_2$ host.
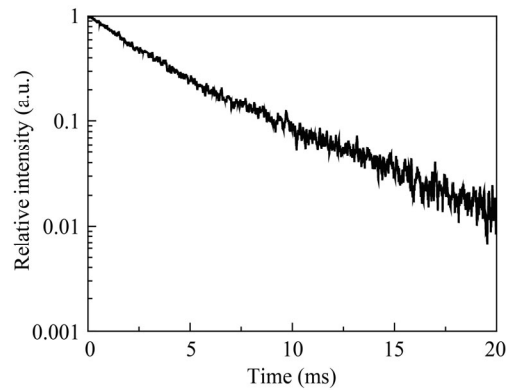
The CIE chromaticity coordinate is one of the important factors for evaluating the performance of phosphors[25]. The CIE chromaticity coordinates of $NaY_{1-x}(MoO_4)_2{:}xTb^{3+}$ (x=0.01–0.25) (λ_{ex}=254 nm) in CIE-1931 chromaticity
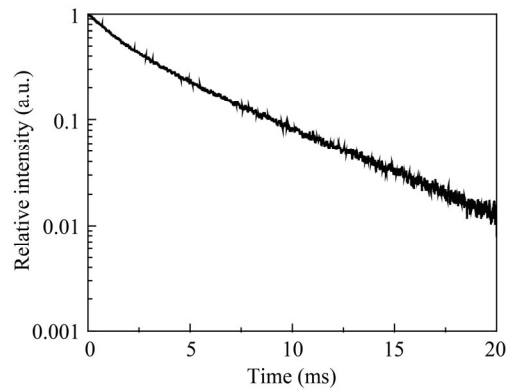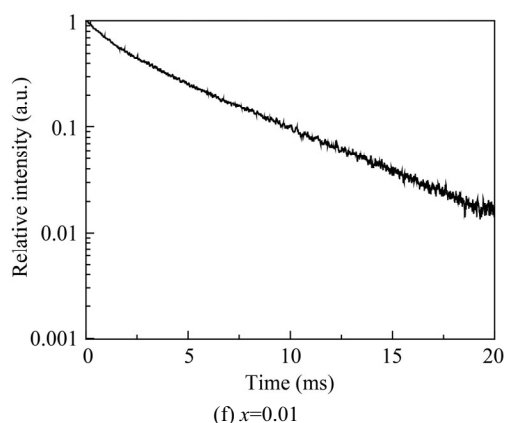

(b) x=0.2

(c) x=0.15

(d) x=0.1

(a) x=0.25

(e) x=0.05

(f) *x*=0.01
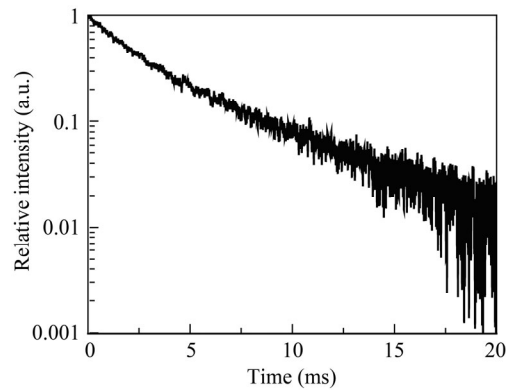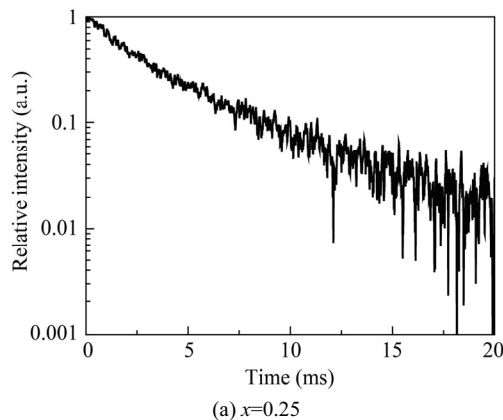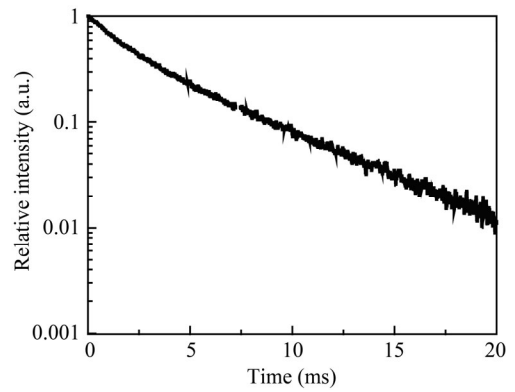
Fig.5 The decay curves of NaY$_{1-x}$(MoO$_4$)$_2$:*x*Tb^{3+} (*x*=0.01, 0.05, 0.1, 0.15, 0.2 and 0.25) (λ_{ex}=290 nm)

diagram are measured and shown in Tab.1. The results present that the CIE chromaticity coordinates keep the similar values with the increase of *x*, and almost locate in the green region.

Tab.1 Decay time of NaY$_{1-x}$(MoO$_4$)$_2$:*x*Tb^{3+} at λ_{ex}=290 nm and CIE chromaticity coordinates of NaY(MoO$_4$)$_2$:*x*Tb^{3+} at λ_{ex}=254 nm

x (mol)	0.01	0.05	0.1	0.15	0.2	0.25
Time (ms)	3.593 43	3.436 50	3.331 16	3.221 72	3.106 17	3.013 49
CIE (*X*, *Y*)	(0.269, 0.597)	(0.271, 0.599)	(0.270, 0.598)	(0.271, 0.597)	(0.269, 0.601)	(0.271, 0.598)

A series of Tb^{3+} doped NaY(MoO$_4$)$_2$ were synthesized by the solid-state reaction at 550 °C for 4 h. NaY(MoO$_4$)$_2$:Tb^{3+} can create green emission under the UV radiation excitation. The emission intensities of Tb^{3+} in NaY(MoO$_4$)$_2$ can be enhanced with the increase of impurity concentration, and there is no concentration quenching phenomenon. The results can be proved by the decay curves of Tb^{3+} in NaY(MoO$_4$)$_2$. The CIE chromaticity coordinates of NaY(MoO$_4$)$_2$:Tb^{3+} locate in the green region, and present the similar values with the increase of impurity concentration. The results indicate that the material may have the potential application in white LEDs.

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