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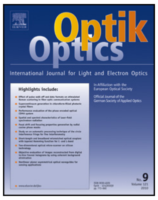

Luminescent property of a novel yellow emitting phosphor $Sr_2ZnMoO_6:Dy^{3+}$

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A yellow emitting phosphor $Sr_2ZnMoO_6:Dy^{3+}$ is synthesized by a solid state reaction at 1250 °C for 4 h, and its luminescent properties are investigated. Its phase formation is carried out with X-ray powder diffraction analysis, and there has no crystalline phases other than Sr_2ZnMoO_6. $Sr_2ZnMoO_6:Dy^{3+}$ can produce yellow emission under the 272 and 387 nm radiation excitation, and the prominent luminescence in yellow (575 nm) due to the $^4F_{9/2}$–$^6H_{13/2}$ transition of Dy^{3+}. For the 575 nm emission, the excitation spectrum present one broad band and some narrow bands, and the peaks locate at 272, 324, 350, 365, 387, 426 and 474 nm, respectively. Its emission intensity is influenced by the Dy^{3+} doping concentration, and the concentration quenching effect is also observed. The CIE chromaticity coordinates values of $Sr_2ZnMoO_6:Dy^{3+}$ show the almost same results with the different Dy^{3+} concentration, and locate in the yellow region.

1. Introduction

In the past few years, trivalent dysprosium ion (Dy^{3+}) doped phosphors have been extensively studied due to its potential application in white light emitting diodes (white LEDs) [1–3]. Usually, Dy^{3+} doped phosphors have an intense blue ($^4F_{9/2}$–$^6H_{15/2}$) and yellow ($^4F_{9/2}$–$^6H_{13/2}$) emissions, and the yellow emission is strongly influenced by the chemical environment surrounding Dy^{3+} due to the $\Delta J = 2(^4F_{9/2} - {}^6H_{13/2})$, while the blue emission ($^4F_{9/2}$–$^6H_{15/2}$) is relatively invariable [4]. Therefore, Dy^{3+} doped phosphors can produce blue, yellow and white emission by tuning the ratio of two dominant emission bands arising from the $^4F_{9/2}$–$^6H_{15/2}$ (blue) and $^4F_{9/2}$–$^6H_{13/2}$ (yellow) transitions of Dy^{3+} [4–6]. Generally, the materials consist of activator and host, in order to obtain the efficient emission, choice of the host is another key factor, and the host must have the excellent physical and chemical stability. Among the compounds, molybdate is good candidate due to its low costs, low synthetic temperature and the stability, etc. [7–15]. For example, the upconversion luminescence of $LiYb(MoO_4)_2:Ho^{3+}$, Tm^{3+} is reported [16]. The synthesization conditions and luminescence of $BaMoO_4:Eu^{3+}$ are studied [17]. $CaLa_2(MoO_4)_4:Eu^{3+}$ is synthesized by the sol–gel method, and its luminescent properties are investigated [18]. The narrow spectral emission $CaMoO_4:Eu^{3+}$, Dy^{3+}, Tb^{3+} phosphor for white LEDs is introduced [19]. $Y_5Mo_2O_{12}:Eu^{3+}$, Sm^{3+} can be excited by near ultraviolet (UV) light, and create red emission [20]. However, there has no reports about the luminescence of Dy^{3+} in Sr_2ZnMoO_6. In this research, $Sr_2ZnMoO_6:Dy^{3+}$ is synthesized, and its luminescent properties are investigated.

2. Experimental

A series of $Sr_{2-x}ZnMoO_6:xDy^{3+}$ (x: mole concentration) are synthesized by a high temperature solid state reaction method. The initial materials, including $SrCO_3$ (A.R.), ZnO (A.R.), MoO_3 (A.R.) and Dy_2O_3 (99.99%) are weighted in stoichiometric proportion, thoroughly mixed and ground by an agate mortar and pestle for more than 30 min till they are uniformly distributed. The obtained mixtures are heated at 1250 °C for 4 h in crucibles along with an atmosphere, and then are naturally cooled to room temperature. In order to measure the characteristics of the phosphor, the samples are grind into powder.

The phase formation is determined by X-ray diffraction (XRD) in a Bruker AXS D8 advanced automatic diffractometer (Bruker Co., German) with Ni-filtered Cu Kα 1 radiation ($\lambda = 0.15405$ nm), and a scan rate of 0.02°/s is applied to record the patterns in the 2θ range from 10° to 80°. The excitation and emission spectra are detected by a fluorescence spectrophotometer (Hitachi F-4600), and the exciting source is a 450 W Xe lamp. The Commission International

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de l'Eclairage (CIE) chromaticity coordinates of the phosphors are measured by a PMS-80 spectra analysis system. All measurements are carried out at room temperature.

3. Results and discussion

3.1. Phase formation

The phase formation of $Sr_{2-x}ZnMoO_6$:$x$$Dy^{3+}$ is determined by the X-ray diffraction pattern, and a similar diffraction pattern is observed for each sample. As a representative, Fig. 1 shows the XRD patterns of Sr_2ZnMoO_6:0.01Dy^{3+}, Sr_2ZnMoO_6:0.04Dy^{3+} and Sr_2ZnMoO_6:0.15Dy^{3+}, respectively. Compared the diffraction data with the standard JCPDS card (No. 74-2474), the results indicate that there has no difference between the doped impurity Sr_2ZnMoO_6:Dy^{3+} and the pure Sr_2ZnMoO_6. It means that the phase formation of Sr_2ZnMoO_6 is not influenced by a little amounts of Dy^{3+}, and the doped Dy^{3+} ions are incorporated into the host successfully. The right of Fig. 1 presents the enlarged reflection peaks at $2\theta = 31.794^\circ$, from which we can see that the diffraction peaks shift to a larger 2θ value with the increase of the Dy^{3+} content. This phenomenon can be ascribed to the smaller Dy^{3+} ions substituting for larger Sr^{2+} ions. Sr_2ZnMoO_6 has a cubic crystal structure, with a space group Fm-3m(2 2 5), the cell parameters $a = b = c = 0.7954$ nm.

3.2. Luminescence of Sr_2ZnMoO_6:Dy^{3+}

Fig. 2 shows the emission and excitation spectra of $Sr_{1.96}ZnMoO_6$:0.04Dy^{3+}. Under the 272 and 387 nm radiation excitation, Sr_2ZnMoO_6:Dy^{3+} has the same emission bands expect for its emission intensity, and the peaks locate at 487, 575 and 663 nm which are assigned to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (487 nm), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm) and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (663 nm) transitions of Dy^{3+}, and some emission bands show a splitting pattern, such as the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition of Dy^{3+} (478 and 487 nm) [4–6]. For the emission bands, the yellow emission transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ is dominant among the others, hence, Sr_2ZnMoO_6:Dy^{3+} can produce yellow emission under the UV radiation excitation. For the 575 nm emission, the excitation spectrum has one broad band and a series of narrow bands. The broad band locates at 272 nm which is assigned to the O^{2-}–Dy^{3+} charge transfer band (CTB). The other peaks locate at 324, 350, 365, 387, 426, 452 and 474 nm belong to the intrinsic f–f transition of Dy^{3+} from the ground state $^6H_{15/2}$ to the excited state $^4L_{19/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$, respectively [4–6]. Though the intensity of CTB is stronger than that of others. However, the 387 nm excitation peak has a stronger intensity, hence Sr_2ZnMoO_6:Dy^{3+} can also create an obvious yellow emission under the 387 nm radiation excitation.

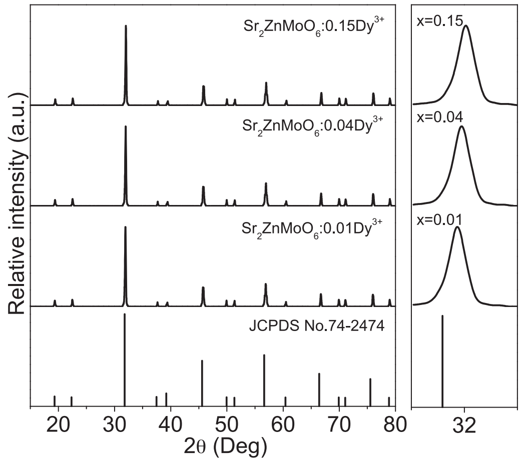

Fig. 1. XRD pattern of Sr_2ZnMoO_6:Dy^{3+} with the standard data of Sr_2ZnMoO_6 (JCPDS No. 74-2474). The right: the enlarged diffraction peak at $2\theta = 31.794^\circ$.

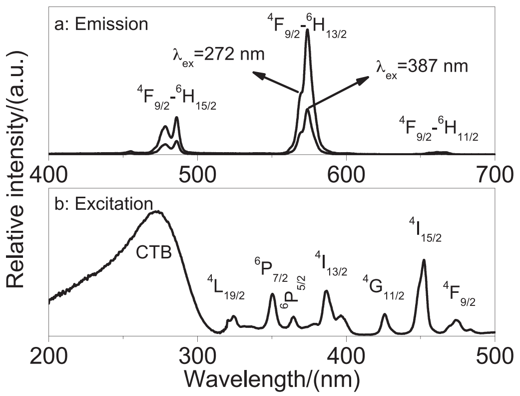

Fig. 2. Emission and excitation spectra of Sr_2ZnMoO_6:Dy^{3+} ($\lambda_{ex} = 272$ nm and 387 nm).

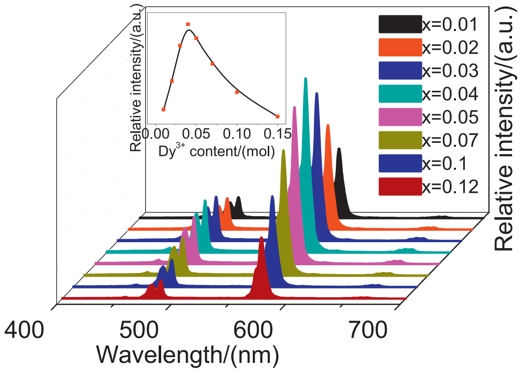

Fig. 3. Emission spectra of Sr_2ZnMoO_6:$x$$Dy^{3+}$ with the different Dy^{3+} concentration (x) ($\lambda_{ex} = 387$ nm). The inset: the yellow emission intensity ($^4F_{9/2}$–$^6H_{13/2}$) as function of Dy^{3+} concentration (x) ($\lambda_{ex} = 387$ nm).

In order to achieve the best doping concentration of Dy^{3+}, a series of $Sr_{2-x}ZnMoO_6$:$x$$Dy^{3+}$ ($x = 0.01$–0.15) are synthesized, and the emission spectra are shown in Fig. 3. It can be seen from Fig. 3, the phosphors have the same spectral profile with the different Dy^{3+} doping concentration, and the integrated emission intensity ratios of $^4F_{9/2}$–$^6H_{13/2}$ to $^4F_{9/2}$–$^6H_{15/2}$ for all the samples are calculated to be about a constant value 3.2, which demonstrates that Dy^{3+} introduction dose not result in an obvious change of the crystal structure and the crystal field environment surrounding Dy^{3+} ions even at such a high doping level as 0.15.

The inset of Fig. 3 shows that the yellow emission intensity ($^4F_{9/2}$–$^6H_{13/2}$) increases with increase Dy^{3+} concentration (x), and it maximizes at about $x = 0.04$, and then decreases with increasing x. It means there has the concentration quenching effect of Dy^{3+} in Sr_2ZnMoO_6 [21]. The concentration quenching is mainly caused by the nonradiative energy transfer among Dy^{3+} ions, which usually occurs as a result of an exchange interaction, radiation reabsorption, or a multipole–multipole interaction [22].

It is necessary to obtain the critical distance (R_c) that is the critical separation between the donor (activator) and acceptor (quenching site). According to the report of Blasse [23], if the activator is introduced solely on Z ion sites, where x_c is the critical concentration of the activator ion, N is the number of Z ions in the unit cell, and V is the volume of the unit cell, then there is on the average one activator ion per V/x_cN. The critical transfer distance