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Effect of MoO_4^{2-} partial substitution on optical enhancement of $LaNa(MoO_4)_2:Dy^{3+}$ phosphors for white light emitting diodes

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ABSTRACT

Dy^{3+} doped $LaNa(MoO_4)_2$ phosphors with different anionic groups (SO_4^{2-}, PO_4^{3-} and BO_3^{3-}) substitution were prepared through solid state reaction at 1100 °C. X-ray diffraction patterns of the as-prepared phosphors indicate that all samples have the standard $LaNa(MoO_4)_2$ structure. The photoluminescence spectra consist of a blue emission at 484 nm and a yellow emission at 576 nm, which corresponding to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transitions of Dy^{3+} ions, respectively. The luminescence intensity of $LaNa(MoO_4)_{1.9}(BO_3)_{0.1}:Dy^{3+}$, $LaNa(MoO_4)_{1.8}(PO_4)_{0.2}:Dy^{3+}$ and $LaNa(MoO_4)_{1.9}(SO_4)_{0.1}:Dy^{3+}$ phosphors are 2.8, 1.8 and 3-fold higher than that of $LaNa(MoO_4)_2:Dy^{3+}$ phosphor, respectively. In addition, the luminescence lifetime values of $LaNa(MoO_4)_2:Dy^{3+}$, $LaNa(MoO_4)_{2-x}(BO_3)_x:Dy^{3+}$, $LaNa(MoO_4)_{2-x}(PO_4)_x:Dy^{3+}$, and $LaNa(MoO_4)_{2-x}(SO_4)_x:Dy^{3+}$ are 0.188, 0.189, 0.186 and 0.183 ms, respectively.

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1. Introduction

As a novel lighting source, white light-emitting diodes (LEDs), have attracted much attention because of their superior performance, such as energy-saving, long lifetime, excellent optical properties and environmental-friendly [1–3]. Generally, there are both ways to achieve white LEDs, one is that coating yellow emitting phosphor on a blue LED chip; and the other is that combining near UV-LED chip with red, green and blue phosphors [4–6]. Until now, the former is the most popular method in commercial manufacture of white LEDs because of its lower cost and higher technical maturity [7]. However, the commercial phosphors for white LEDs are still limited in such as $Y_2O_2S:Eu^{3+}$, $YAG:Ce^{3+}$, $SrS:Eu^{2+}$ and $BaMgAl_{10}O_{17}:Eu^{2+}$ [8,9], which hold low luminous efficiency and serious light decay. Therefore, it is urgent to develop some novel phosphors for excellent luminous efficiency and long fluorescence lifetime.

As known, double molybdate $LnA(MoO_4)_2$ (Ln=trivalent rare earth ions; A=alkali metal ions) is a typical scheelite compound and has tetragonal symmetry with space group $I4_1/\alpha$ [10–13]. In $LaNa(MoO_4)_2$ compounds, each unit cell has 2 La^{3+}, 2 Na^+ and 4 MoO_4^{2-}, and every Mo ion is coordinated by four O^{2-} ions in tetrahedral symmetry, which makes MoO_4^{2-} quite stable [14–16]. Up to now, there are only a few researches on Dy^{3+} doped $LaNa(MoO_4)_2$ phosphor [17–19], and its luminescence properties is not excellent enough for white LEDs application. So some efforts are very necessary to improve the luminescence intensity of $LaNa(MoO_4)_2:Dy^{3+}$ phosphors. For example, Xi and colleagues synthesized $Na_5Eu(MoO_4)_{4-x}(PO_4)_x$ phosphors by solid-state reaction, the emission intensity of $Na_5Eu(MoO_4)_{3.96}(PO_4)_{0.04}$ is obviously higher than that of $Na_5Eu(MoO_4)_4$, and is 5.0 times higher than that of commercial $Y_2O_2S:Eu^{3+}$ phosphor [20]. In Zhang's study, the emission intensity of as-prepared pure $NaEu(MoO_4)_2$ and anionic (SO_4^{2-} and SiO_3^{2-})-doped $NaEu(MoO_4)_2$ are also increased obviously [21]. Therefore, different anionic groups substitution of MoO_4^{2-} is a possible way to improve the emission intensity of $LaNa(MoO_4)_2:Dy^{3+}$.

In this study, $LaNa(MoO_4)_{2-x}(SO_4)_x:Dy^{3+}$, $LaNa(MoO_4)_{2-x}(PO_4)_x:Dy^{3+}$ and $LaNa(MoO_4)_{2-x}(BO_3)_x:Dy^{3+}$ phosphors are prepared by a conventional solid state reaction. Anionic groups (SO_4^{2-}, PO_4^{3-} and BO_3^{3-}) are expected to improve the luminescence properties of these phosphors. The effects of SO_4^{2-}, PO_4^{3-} and BO_3^{3-} substitution on luminescence properties of $LaNa(MoO_4)_{2-x}A_x:Dy^{3+}$ (A=BO_3^{3-}, SO_4^{2-} and PO_4^{3-}) phosphors are discussed in detail, and the optimum concentration of anionic groups for luminescence intensity and lifetime are also investigated.

2. Experimental

$LaNa(MoO_4)_{2-x}(SO_4)_x:Dy^{3+}$ phosphors were synthesized via a traditional solid state method, and the doping amount of Dy^{3+} was determined at 2 mol%. In a typical process, Stoichiometric

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amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Na_2CO_3, La_2O_3, $(NH_4)_2SO_4$ and Dy_2O_3 were taken as $LaNa(MoO_4)_{2-x}(SO_4)_x:Dy^{3+}$ sequentially, these raw materials were blended and ground thoroughly in an agate mortar, and then transferred to an alumina crucible. The homogeneous mixture was calcined in muffle furnace at 1100 °C for 3 h, and then cooled to room temperature. $LaNa(MoO_4)_{2-x}(PO_4)_x:Dy^{3+}$ and $LaNa(MoO_4)_{2-x}(BO_3)_x:Dy^{3+}$ phosphors were prepared by the same operation.

The crystal structure of obtained phosphors were characterized by X-ray diffraction (XRD) performed on 40 kV and 100 mA with Cu K_α radiation ($\lambda=1.5406$ Å), and the photoluminescence (PL) spectra were measured by a Hitachi F-4600 luminescence spectrometer with a 150 W Xe lamp as the excitation source. The luminescence lifetime of obtained samples were investigated by a Fluorolog-3-Tau fluorescence spectrophotometer. Fourier transform infrared spectroscopy (FT-IR) spectra were characterized by Perkin-Elmer 580B IR spectrophotometer using potassium bromide pellet technique. All the characterization results of phosphors were obtained at the room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of $LaNa(MoO_4)_2:Dy^{3+}$ phosphors with different contents of anionic group substitution. It can be seen that all the diffraction peaks of obtained phosphors are perfectly matched with the data of the scheelite-type tetragonal structure (JCPDS No. 24-1103) with $I4_1/\alpha$ lattice symmetry. No impurity peaks are observed in Fig. 1, which because the doping amount of Dy^{3+}, SO_4^{3-}, PO_4^{3-} and BO_3^{3-} is not too large, and also indicate that Dy^{3+}, SO_4^{3-}, PO_4^{3-} and BO_3^{3-} have been successfully entered into the $LaNa(MoO_4)_2$ lattices. With introducing the anionic groups, the characteristic peaks were almost identical and a little higher than that of pure $LaNa(MoO_4)_2$, that because anion groups could reduce synthesis temperature and improve crystallization of $LaNa(MoO_4)_2$ structure. The diffraction peaks of phosphors with SO_4^{2-}, PO_4^{3-} and BO_3^{3-} doping shift a little to larger angle, which can attributed to the substitution of larger sized MoO_4^{2-} sites by the smaller sized SO_4^{2-}, PO_4^{3-} and BO_3^{3-} in the $LaNa(MoO_4)_2:Dy^{3+}$ phosphors.

To further investigate BO_3^{3-}, SO_4^{2-} or PO_4^{3-} doping and their effect on enhancement of luminescent intensity, the FT-IR spectra of

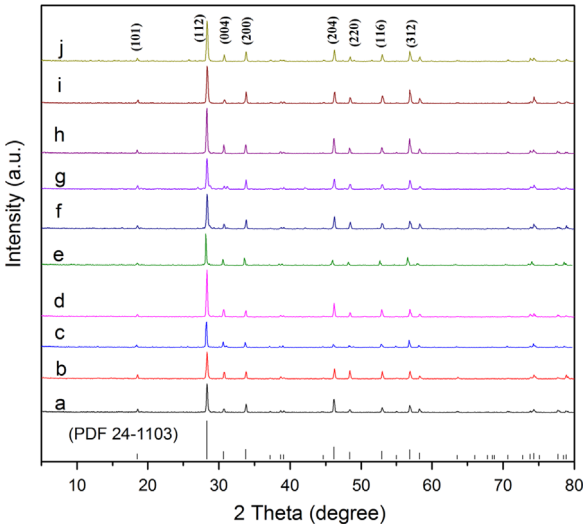

Fig. 1. XRD patterns of Dy^{3+} doped samples: (a) $LaNa(MoO_4)_2$, (b) $LaNa(MoO_4)_{1.9}(SO_4)_{0.1}$, (c) $LaNa(MoO_4)_{1.8}(SO_4)_{0.2}$, (d) $LaNa(MoO_4)_{1.6}(SO_4)_{0.4}$, (e) $LaNa(MoO_4)_{1.9}(PO_4)_{0.1}$, (f) $LaNa(MoO_4)_{1.8}(PO_4)_{0.2}$ and (g) $LaNa(MoO_4)_{1.6}(PO_4)_{0.4}$, (h) $LaNa(MoO_4)_{1.9}(BO_3)_{0.1}$, (i) $LaNa(MoO_4)_{1.8}(BO_3)_{0.2}$, (j) $LaNa(MoO_4)_{1.6}(BO_3)_{0.4}$.

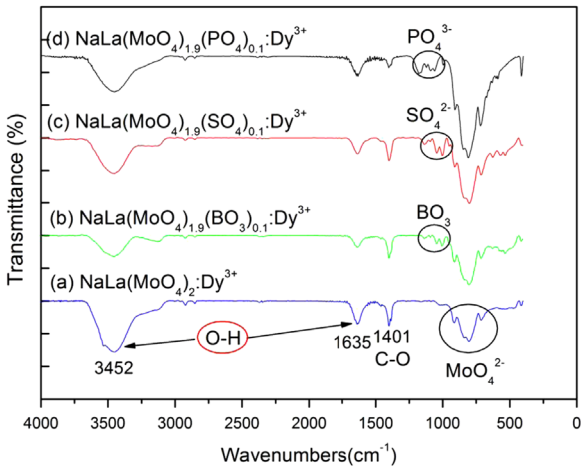

Fig. 2. FT-IR spectra of prepared samples: (a) $LaNa(MoO_4)_2:Dy^{3+}$, (b) $LaNa(MoO_4)_{1.8}(BO_3)_{0.2}:Eu^{3+}$, (c) $LaNa(MoO_4)_{1.8}(SO_4)_{0.2}$ and (d) $LaNa(MoO_4)_{1.8}(PO_4)_{0.2}$.

$LaNa(MoO_4)_{1.8}(SO_4)_{0.2}:Dy^{3+}$ and $LaNa(MoO_4)_{1.8}(BO_3)_{0.2}:Dy^{3+}$ and $LaNa(MoO_4)_{1.8}(PO_4)_{0.2}:Dy^{3+}$ phosphors are presented in Fig. 2. For both spectra of samples, the broad absorption band at about 3452 cm^{-1} is attributed to the stretching vibration of O–H, and the weak absorption band at 1635 cm^{-1} is ascribed to the bending vibration of O–H, which belong to physically absorbed water on the phosphor surface. A narrow peak appeared at 1401 cm^{-1} is the vibration absorption of C–O bond from the adsorbed carbon dioxide. The typical absorption peaks at 911, 803 and 710 cm^{-1} which are assigned to stretching vibration of O–Mo–O in MoO_4^{2-} tetrahedron. With BO_3^{3-} doping, the strong peaks appeared at 1137, 1050 and 1014 cm^{-1} are caused by BO_3^{3-} vibration (Fig. 2(b)); in Fig. 2(c), the doping of SO_4^{2-} result in the vibration peaks at about 1128, 1041 and 1005 cm^{-1}; and the doping of PO_4^{3-} result in the vibration peaks at about 1172, 1093 and 1058 cm^{-1} in Fig. 2(d), respectively. Conclusively, the FT-IR spectra further confirm that anion groups (SO_4^{2-}, BO_3^{3-} and PO_4^{3-}) exist in $LaNa(MoO_4)_{1.8}(SO_4)_{0.2}$, $LaNa(MoO_4)_{1.8}(BO_3)_{0.2}$ and $LaNa(MoO_4)_{1.8}(PO_4)_{0.2}$ structure and have entered into the lattices, which are in good agreement with the XRD results. After anion groups doping, the corresponding peaks became strong and distinct with higher energy phonons that would improve the emission intensity of the Dy^{3+} transitions.

Fig. 3 depicts the excitation spectra ($\lambda_{em}=576$ nm) and emission spectra ($\lambda_{ex}=388$ nm) of $LaNa(MoO_4)_{2-x}(BO_3)_x:Dy^{3+}$ phosphors. The excitation spectra of $LaNa(MoO_4)_{2-x}(BO_3)_x:Dy^{3+}$ phosphors are composed of a broad band and some sharp peaks. The broad bands from 230 nm to 350 nm can be described as the charge transfer band (CTB) of Mo–O, the sharp lines at 352 nm, 366 nm, 388 nm, 427 nm, 452 nm, 475 nm are responsible for $^6H_{15/2}\rightarrow{}^6P_{7/2}$, $^6H_{15/2}\rightarrow{}^6P_{5/2}$, $^6H_{15/2}\rightarrow{}^4M_{21/2}$, $^6H_{15/2}\rightarrow{}^4G_{11/2}$, $^6H_{15/2}\rightarrow{}^4J_{15/2}$ and $^6H_{15/2}\rightarrow{}^4F_{9/2}$ transition of Dy^{3+}, respectively. The schematic of energy transfer of Dy^{3+} ions is designed. Under excitation, the 4f electron of Dy^{3+} ions is excited into the $^6P_{7/2}$, $^6P_{5/2}$, and $^4M_{21/2}$ levels, and quickly transit to $^4F_{9/2}$ level via non-radiative transition and resonance transfer the energy, then quickly relax energy by radiative transition when transit to $^6H_{13/2}$ and $^6H_{15/2}$ level of Dy^{3+}, which results in the emission of Dy^{3+} (the electron transition from $^4F_{9/2}$ to $^6H_{13/2}$ and $^6H_{15/2}$ with energy emission at 582 nm and 484 nm). Under the excitation at 388 nm, the strong emission peak at 576 nm corresponding to $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition of Dy^{3+} ions, while the relatively weak emission peak at 484 nm is ascribed to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ transition of Dy^{3+} ions. The $^4F_{9/2}\rightarrow{}^6H_{13/2}$ hypersensitive transition is ascribed to the electric dipole transition, which is strongly influenced by the crystal field

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