Synthesis and luminescence properties of novel host-sensitized double perovskite Ba_2MgWO_6 based phosphors

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This work first reports the synthesis and luminescence properties of novel host-sensitized double perovskite Ba_2MgWO_6 based phosphors [Ba_2MgWO_6:Ln (Ln =Sm^{3+}, Dy^{3+})]. The phosphors were synthesized by a solid state reaction at high temperature, and characterized by X-ray diffraction, ultraviolet visible diffuse reflection spectra, photoluminescence spectra and luminescence decay curves. The efficient energy transfer phenomenon from W^{6+}-O^{2-} group to Sm^{3+}/Dy^{3+} was observed, which leads to broadband sensitized reddish-orange/white light of Sm^{3+}/Dy^{3+}, respectively. These results demonstrate that Sm^{3+}/Dy^{3+} ion with low 4f –4f absorption efficiency in ultraviolet region can play a role of activator in reddish-orange/white emitting phosphor, which can be potentially useful in light emitting diode based on ultraviolet chip through efficient energy feeding by charge transfer absorption of W^{6+}-O^{2-} group.

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Keywords: Double perovskite; Ba_2MgWO_6; Energy transfer; Luminescence

1. Introduction

Ba_2MgWO_6, a representative double perovskite compound, has drawn much more attention in recent years because of its interesting physical properties and applications [1−5]. This compound adopts the cubic structure with space group $Fm\bar{3}m$ [3]. Nevertheless, up to now, little research on using Ba_2MgWO_6 as host material to develop novel phosphor has been reported. Previous investigations have showed tungstate phosphors exhibited relatively broad and strong host-related absorption band in the ultraviolet (UV) or near UV region due to the $O^{2-}\rightarrow W^{6+}$ charge transfer band, which is prerequisite to develop novel phosphors applied in white light emitting diodes (LEDs) [6-8]. So, when the luminescent active ion was doped into the Ba_2MgWO_6 host, efficient emission from the active ion upon excitation with UV or near UV light can be obtained due to the host-sensitization effect [9].

Among the rare-earth ions, Sm^{3+} and Dy^{3+} ions were often chose to be luminescent active ion to develop novel phosphors for display and lighting application, because they can produce orange and white emissions corresponding to $^4G_{5/2}\rightarrow{}^6H_J$ (J = 5/2, 7/2, 9/2, and 11/2) and $^4F_{9/2}\rightarrow{}^6H_J$ (J = 15/2, 13/2) transitions, respectively [10−13]. So, Ba_2MgWO_6:Sm^{3+} and Ba_2MgWO_6:Dy^{3+} could be novel orange and white emitting phosphors with broad absorption in UV or near UV region.

Based on the above consideration, in this work, we report the novel Sm^{3+} and Dy^{3+} doped Ba_2MgWO_6 phosphors, which were investigated by the photoluminescence excitation (PLE), photoluminescence emission (PL) spectra, the diffuse reflection spectra, and decay curves.

2. Experimental

Ba_2MgWO_6:Sm^{3+} and Ba_2MgWO_6:Dy^{3+} phosphors were prepared by a solid-state reaction at high-temperature. The doping level of Sm^{3+} or Dy^{3+} is 2 mol% relative to the amount of Ba^{2+} and doping agents. The starting materials were analytical reagent (A.R.) grade $BaCO_3$, MgO, WO_3, 99.99% purity Sm_2O_3, and 99.99% purity Dy_2O_3. The stoichiometric amounts of the starting materials with 10% excess MgO to suppress the formation of $BaWO_4$ as an impurity were firstly mixed and ground thoroughly in an agate mortar. Then they were pre-sintered at 600 °C for 6 h, and re-sintered at 1200 °C for 6 h for 2 times in air atmosphere in a muffle furnace. Finally, the products were obtained after cooling to room temperature naturally and ground into fine powder.

The phase purity of the final products was characterized by a powder X-ray diffraction (XRD) analysis on a Bruker D8 Advance X-Ray Diffractometer with Cu Kα (λ = 1.5405 Å) radiation over the 2θ range 10^o–70^o. Ultraviolet visible (UV–vis) diffuse reflection spectra were measured using a Hitachi UV–vis spectrophotometer (U-3900H) in the range of 250 nm to

800 nm. The PLE/PL spectra and decay curves were recorded by using an FLS980-Combined Fluorescence Lifetime & Steady State Fluorescence Spectrometer (EDINBURGH INSTRUMENTS) with a 450 W xenon lamp and a 100 W μF2 microsecond flash lamp used as the excitation source, respectively. All the above measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of Ba_2MgWO_6:Sm^{3+} and Ba_2MgWO_6:Dy^{3+} phosphors synthesized by solid-state reaction at 1200 ^{0}C for 6 h. All the diffraction peaks of the samples agree well with Joint Committee on Powder Diffraction Standards (JCPDS No. 73-2404), indicating that doping Sm^{3+} and Dy^{3+} ions do not cause any significant change in the host structure, and keep the cubic structure of Ba_2MgWO_6 because of the similar ionic radius of Sm^{3+}/Dy^{3+} and Ba^{2+} ions [14]. Meanwhile, the intense and sharp diffraction peaks also suggest that the as-synthesized phosphors are well crystallized.

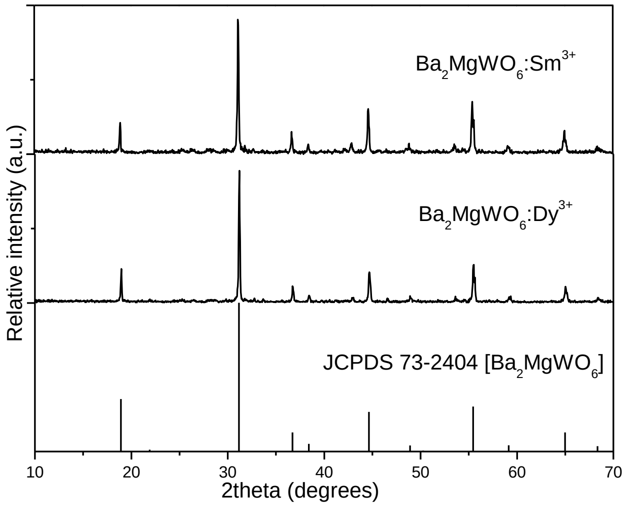

Fig. 1. XRD patterns of Ba_2MgWO_6:Sm^{3+} and Ba_2MgWO_6:Dy^{3+} phosphors

Fig. 2 shows the UV–vis diffusive reflectance spectra of Ba_2MgWO_6:Sm^{3+} and Ba_2MgWO_6:Dy^{3+}, which indicate that the as-prepared phosphors exhibit photo-absorption properties from 250 nm to 400 nm region. Obviously, the broad absorption band peaking at around 300 nm can contribute to the charge transfer transition of O^{2+}→W^{6-} in the host lattice (the host related absorption). Here, the contribution of the O^{2-}→Sm^{3+}/Dy^{3+} charge transfer to the broad band around 300 nm could be excluded, since the O^{2}→Sm^{3+}/Dy^{3+} charge transfer band was usually located in the vacuum ultraviolet region [15]. Furthermore, the characteristic 4f-4f transitions of Sm^{3+} and Dy^{3+} cannot be observed in the spectra due to the weak intensity.

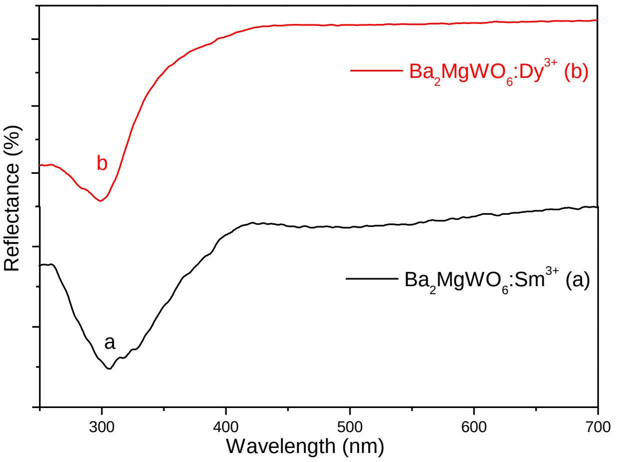

Fig. 2. UV–vis diffusive reflectance spectra of Ba_2MgWO_6:Sm^{3+} (a) and Ba_2MgWO_6:Dy^{3+} (b).

Fig. 3(a) and 3(b) present the excitation spectra of Ba_2MgWO_6:Sm^{3+} and Ba_2MgWO_6:Dy^{3+} phosphors by monitoring the prominent emissions at 642 nm and 481 nm, respectively. Two curves a and b show the similar spectral property, which consist of a strong and broad excitation band dominating at 305 nm, ascribed to the charge transfer absorption band of the W^{6+}-O^{2-} group, and many weak and sharp peaks at 350-450 nm, due to the forbidden 4f-4f transitions of Sm^{3+}/Dy^{3+} ions, respectively. The appearance of the intense charge transfer absorption band of the W^{6+}-O^{2-} group in excitation spectrum of Sm^{3+}/Dy^{3+} suggests that the efficient energy transfer from host to Sm^{3+}/Dy^{3+} occurs. Similar phenomenon can also be found in other Sm^{3+} or Dy^{3+} doped tungstate phosphors, e.g. $CaWO_4$:Dy^{3+} [15], $NaY(WO_4)_2$:Sm^{3+} [16], $NaGd(WO_4)_2$:Sm^{3+} [17], $NaGd(WO_4)_2$:Dy^{3+} [18].

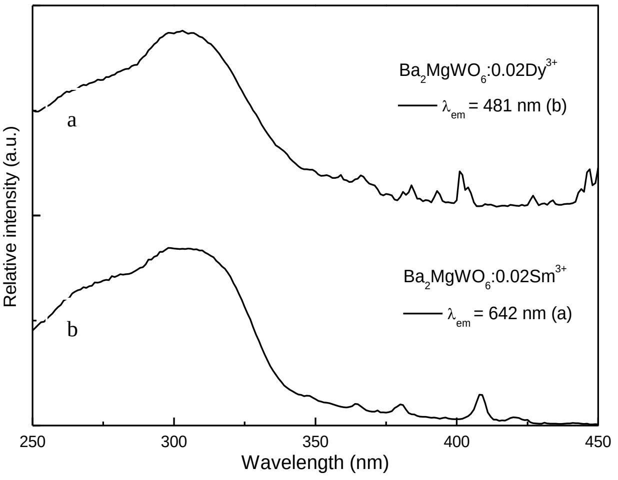

Fig. 3. Excitation spectra of Ba_2MgWO_6:Sm^{3+} (a) and Ba_2MgWO_6:Dy^{3+} (b) phosphors.

Fig. 4(a) and 4(b) present the emission spectra of $Ba_2MgWO_6:Sm^{3+}$ and $Ba_2MgWO_6:Dy^{3+}$ phosphors under excited at 305 nm, respectively. $Ba_2MgWO_6:Sm^{3+}$ exhibits four groups of narrow emissions at 550–730 nm, assigned to the $^4G_{5/2}\rightarrow{}^6H_J$ transitions of Sm^{3+} (J = 5/2, 7/2, 9/2, and 11/2) [10]. $Ba_2MgWO_6:Dy^{3+}$ exhibits three groups of narrow emissions at 400–700 nm, assigned to the $^4F_{9/2}\rightarrow{}^6H_J$ transitions of Dy^{3+} (J = 15/2, 13/2, and 11/2) [19, 20]. Generally speaking, the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition of Dy^{3+} belongs to the hypersensitive transition with J = 2, which is strongly influenced by the local environment of Dy^{3+} in the host [20]. As the emission intensity of $^4F_{9/2}\rightarrow{}^6H_{15/2}$ transition is more than that of the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition, so the Dy^{3+} ion can be located at an almost symmetric position in the matrix.

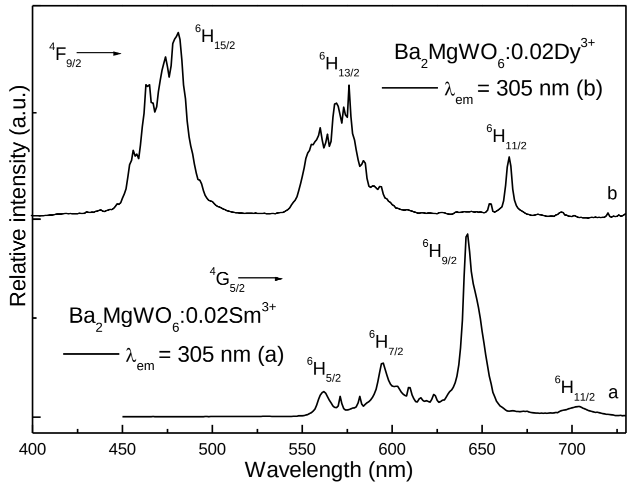

Fig. 4. Emission spectra of $Ba_2MgWO_6:Sm^{3+}$ (a) and $Ba_2MgWO_6:Dy^{3+}$ (b) phosphors

The Commission International de'Eclairage (CIE) chromaticity coordinates of $Ba_2MgWO_6:Sm^{3+}$ (a) and $Ba_2MgWO_6:Dy^{3+}$ (b) phosphors upon 305 nm excitation were calculated to be (0.615, 0.378) and (0.281, 0.306), respectively, as shown in Fig. 5. Obviously, the as-prepared $Ba_2MgWO_6:Sm^{3+}$ and $Ba_2MgWO_6:Dy^{3+}$ phosphors presented reddish orange and white emissions, respectively. The above results demonstrate that Sm^{3+}/Dy^{3+} ion with low 4f–4f absorption efficiency in UV region can serve as the potential activator of reddish-orange/white emitting phosphor, which can be directly excited by UV LEDs, through energy feeding of the W^{6+}-O^{2-} group with allowed charge-transfer absorption and high absorption oscillator strength [9].

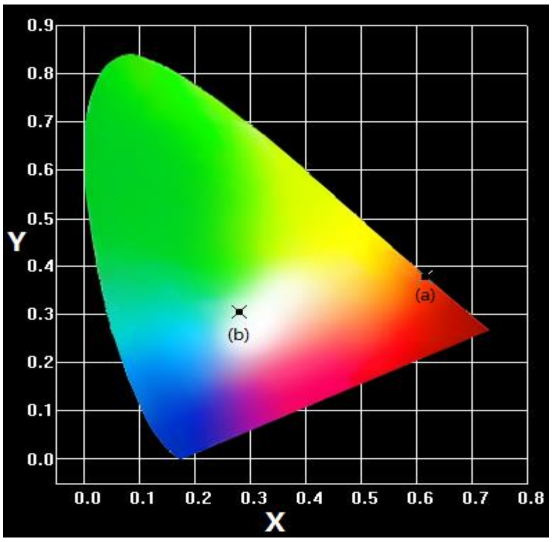

Fig. 5. CIE chromaticity coordinates of $Ba_2MgWO_6:Sm^{3+}$ (a) and $Ba_2MgWO_6:Dy^{3+}$ (b) phosphors

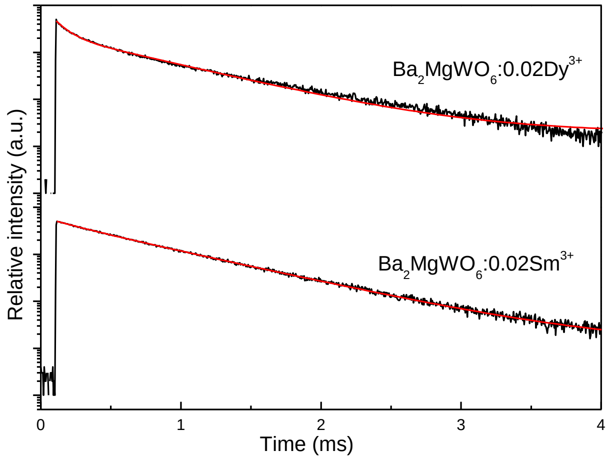

Fig. 6. Decay curves of Sm^{3+} $^4G_{5/2}\rightarrow{}^6H_{9/2}$ emission at 642 nm and Dy^{3+} $^4F_{9/2}\rightarrow{}^6H_{15/2}$ emission at 481 nm

Fig. 6(a) and 6(b) shows the decay curves of Sm^{3+} $^4G_{5/2}\rightarrow{}^6H_{9/2}$ emission at 642 nm and Dy^{3+} $^4F_{9/2}\rightarrow{}^6H_{15/2}$ emission at 481 nm, respectively. The decay curves of are well fitted with a double exponential function as follows [21], $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$, where I is the luminescence intensity; A_1 and A_2 are constants; t is the time; and τ_1 and τ_2 are the lifetimes for the exponential components. Then the average decay time (τ) can be determined by the following formula: $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. So the value of τ was calculated to be about 0.63 ms for Sm^{3+}, and 0.45 ms for Dy^{3+} in Ba_2MgWO_6 host. Generally, phosphors doped with Sm^{3+}/Dy^{3+} activator have a decay time of the order of a millisecond induced by a forbidden transition of Sm^{3+}/Dy^{3+}

according to a spin-selection rule. The above results show that the decay constant is short enough for potential applications in displays and lighting.

4. Conclusions

In summary, novel host-sensitized double perovskite Ba_2MgWO_6 based phosphors [Ba_2MgWO_6:Ln (Ln =Sm^{3+}, Dy^{3+})] were synthesized and investigated. The as-prepared phosphors show the broad excitation band in UV region due to the efficient host-sensitization effect, which is ascribed to energy transfer from W^{6+}-O^{2-} group to Sm^{3+}/Dy^{3+}. Sm^{3+}/Dy^{3+} ion give reddish-orange/white emitting light with a fast decay time of the order of millisecond. The above results show that Ba_2MgWO_6:Ln (Ln = Sm^{3+}, Dy^{3+}) phosphor might have potential application as reddish-orange/white emitting phosphor for w-LEDs based on UV chip.

Acknowledgments

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