Synthesis and photoluminescence properties of ultraviolet excited Ba$_2$MgWO$_6$:Sm$^{3+}$ orange-red phosphors

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Abstract. In this work, Sm$^{3+}$-actived Ba$_2$MgWO$_6$ phosphors were prepared through the high temperature solid-state method. The XRD, SEM, photoluminescence spectra and decay curves were surveyed detailly. Under the excitation of 319 nm, the typical Ba$_2$MgWO$_6$:0.01Sm$^{3+}$ phosphor exhibits orange-red emission ranging from 500 to 700 nm with many emission bands ascribed to $^4G_{5/2}$$→$$^6H_{5/2}$ (550-600 nm), $^4G_{5/2}$$→$$^6H_{7/2}$ (600-640 nm) and $^4G_{5/2}$$→$$^6H_{9/2}$ (640-665 nm) transitions of Sm$^{3+}$ ion. The phenomenon of concentration quenching and decay curves suggest the existence of energy transfer between Sm$^{3+}$ ions, and the CIE chromaticity coordinates displays that all the obtained samples are situated in the region of orange-red. All the consequences manifest that Ba$_2$MgWO$_6$:Sm$^{3+}$ orange-red phosphors possess the potential for the application in the white light emitting diodes.

1. Introduction
Due to these unique advantages, such as long performing lifetime, high fluorescence conversion efficiency and safety coefficient, the white light-emitting diodes (WLEDs) are expected to replace the conventional lighting source [1, 2]. Nowadays, the commercial method to obtain white light is coating a blue LED chip with yellow phosphor [3]. Whereas, it still has some disadvantages, including higher correlated color temperature and inferior color rendering index [4]. In order to solve these problems, another approach to acquire high-performance white light is blending an ultraviolet/near-ultraviolet (UV/NUV) LED chip with the red/green/blue phosphors. Compared with the other two phosphors, the application of commercial red-emitting phosphor (Y$_2$O$_2$S:Eu$^{3+}$) is limited by its toxic ingredient and inferior chemical stability as well as photoluminescence properties [5]. Therefore, it is a tough assignment to develop a red or orange-red emitting phosphor with preferable chemical stability and high-efficiency.

Nowadays, the double perovskite compounds have become a hot spot in the research field on account of their diverse structures and physical properties. The tungstate/molybdate phosphors with ordered double perovskite structure have been reported as excellent photoluminescence hosts. Among a variety of double perovskites investigated in the filed of lighting, the literatures about Ba$_2$MgWO$_6$ are focusing on the luminescence properties of Eu$^{3+}$-activated Ba$_2$MgWO$_6$ phosphors [6]. However, as far as we know, there are few reports about the Sm$^{3+}$-actived Ba$_2$MgWO$_6$ phosphors.

In this paper, we synthesized the Ba$_2$MgWO$_6$:Sm$^{3+}$ phosphors with various doping concentration. The phase purity as well as morphology of obtained samples were analysed by the XRD patterns and SEM image, and the luminescence behaviors were investigated through the photoluminescence spectra. Additionally, the concentration quenching phenomenon and decay curves were also carried out to
verify the energy immigration mechanism between Sm$^{3+}$ ions. All the consequences reveal that the Ba$_2$MgWO$_6$:Sm$^{3+}$ phosphors have excellent prospect in the application of WLEDs.

2. Experimental

2.1. Materials and preparation

A variety of Ba$_2$MgWO$_6$:xSm$^{3+}$ (x = 0.003, 0.005, 0.01, 0.02, 0.03 mol) phosphors were synthesized through the high temperature solid-state method. BaCO$_3$, MgO and WO$_3$ with analytically pure as well as Sm$_2$O$_3$(99.99%) were used as the starting materials, meanwhile, 10% excess of MgO was applied. Firstly, all the raw materials are weighed according to the stoichiometric ratio and mixed thoroughly in an agate mortar. After that, the compounds were transferred into a alumina crucible and then calcined in a muffle furnace at 1350°C for 6h. Ultimately, after cooling down to room temperature naturally, the samples were obtained and then grinded into powder for the succedent test.

2.2. Characterization

The crystal structure and phase purity of the as-prepared phosphors were identified by a Rigaku Ultima IV X-ray powder diffractometer. The morphology was characterized using scanning electron microscope (SEM, JEOL, JSM-6701F, Japan). The photoluminescence spectra and decay curves were measured on a Hitachi F-7000 fluorescence spectrophotometer.

3. Results and discussion

Fig. 1. The XRD patterns of Ba$_2$MgWO$_6$:xSm$^{3+}$ (0.003 ≤ x ≤ 0.03) phosphors.

Fig. 1 illustrates the XRD patterns of Ba$_2$MgWO$_6$:xSm$^{3+}$ (0.003 ≤ x ≤ 0.03) phosphors. As shown in Fig. 1, all the positions of diffraction peaks match well with the standard card of Ba$_2$MgWO$_6$ (JCPDS 73-2404), indicating that all the as-prepared samples are pure phases and Sm$^{3+}$ ion has little effect on the formation of crystalline phase. It can be seen that the particles are nearly spherical and have formed obvious agglomeration due to the high sintering temperature.
Fig. 3 (a) The excitation as well as emission spectra of Ba₂MgWO₆:0.01Sm³⁺ phosphor. (b) The emission spectra of Ba₂MgWO₆:xSm³⁺ phosphor with different Sm³⁺ doping concentrations.

Fig. 3 (a) represents the excitation and emission spectrum of Ba₂MgWO₆:0.01Sm³⁺ phosphor monitored at 571 nm and excited by 319 nm, respectively. The excitation spectrum includes a broad band with the center located in 319 nm attributing to the O-W charge transfer band (CTB) and an unobservable peak located at 467 nm, which is ascribed to the Sm³⁺ ion transition of 6H5/2→4I13/2 [7]. The emission spectrum exhibits many emission spectral bands, attributed to the 4G5/2→6H5/2 (550-600 nm), 4G5/2→6H7/2 (600-640 nm) and 4G5/2→6H9/2 (640-665 nm) transitions of Sm³⁺ ion, respectively [8].

The photoluminescence properties of Ba₂MgWO₆:xSm³⁺ phosphors are displayed in Fig. 3(b). The inset shows the optimal Sm³⁺ ions doping concentration is 0.01 mol. The critical distance (Rc) are defined by the equation as following [9]:

$$ R_c = 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3} \quad (1) $$

where V is the volume of unit cell, x_c stands for the optimal doping concentration of activator ion and N is the cations number in the unit cell. For Ba₂MgWO₆:0.01Sm³⁺ sample, the values of V, x_c and N is 532.94 Å³, 0.01 mol and 4, respectively. The value of Rc can be obtained to be about 29.413 Å, much larger than 5 Å. Hence, the concentration quenching mechanism of Sm³⁺ ion can be ascribed to the electric multipole-multipole interaction.

Fig. 4. The decay curves of Sm³⁺ ions in Ba₂MgWO₆:Sm³⁺ phosphors.

The decay curves of Sm³⁺ ions in Ba₂MgWO₆:Sm³⁺ phosphors are illustrated in Fig. 4. All the decay curves are highly consistent with the first-order exponential function defined as below:

$$ I(t) = I_0 + A \exp\left(-\frac{t}{\tau}\right) \quad (2) $$

Here, I(t) and I₀ stand for the emission intensities at time t and t = 0, respectively. A is the fitting constant, τ is the decay lifetimes. The decay lifetime of as-prepared Ba₂MgWO₆:xSm³⁺ phosphors was...
determined to be 2.886, 2.848, 2.682, 2.306 and 2.010 ms, which further verifies the energy transfer between the Sm$^{3+}$ ions.

The CIE chromaticity coordinates of obtained phosphors are depicted in Fig. 5. It is obvious that all the chromaticity coordinates are situated in region of orange-red.

4. Conclusions

In brief, the Ba$_2$MgWO$_6$:Sm$^{3+}$ phosphors were synthesized through the high temperature solid-state method. Under 319 nm excitation, all the samples exhibit orange-red emission and the optimal Sm$^{3+}$ ions doping concentration was determined to be 0.01 mol, and the mechanism of concentration quenching is dominated by electric multipole-multipole interaction. The decay lifetimes of Ba$_2$MgWO$_6$:Sm$^{3+}$ phosphors were calculated to be 2.886-2.010 ms. The CIE chromaticity coordinates of Ba$_2$MgWO$_6$:xSm$^{3+}$ phosphors are situated in the orange-red region. All the consequences above indicate that Ba$_2$MgWO$_6$: Sm$^{3+}$ phosphors are promising candidates for WLEDs.

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