Luminescence properties of Eu- and Mn- activated $BaMgP_2O_7$ as a potential red phosphor for white emission

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Abstract

$BaMgP_2O_7$:Eu,Mn phosphors for white emission were synthesized and their luminescent properties were investigated under UV excitation. The phosphor emits two colors: a blue band by Eu^{2+} and a red band by Mn^{2+}. Due to the efficient energy transfer from Eu^{2+} to Mn^{2+}, the red emission positioned at 615 nm is greatly enhanced with increasing Mn^{2+} content up to 17.5 mol%.

1. Introduction

To generate efficient white LEDs using phosphors, there are primarily two approach methods. The first method is to combine the yellow-emitting phosphor of cerium doped yttrium aluminum garnet (YAG:Ce^{3+}) with blue LED chips [1,2]. This method is relatively easy to make white light, but it is known that the white LEDs using YAG:Ce^{3+} phosphor have some drawbacks such as low color rendering index (CRI) and high color temperature [3]. In order to avoid such drawbacks, another approach is to mix a longer wavelength light down-converted from the LED emission using various phosphors with the emission from a near-ultraviolet (UV) LED [4]. The tricolor phosphors based white LEDs show significant CRI, low color temperature and broad color range that originated from blended phosphor. To make suitable white light, built-in phosphors should show good properties [5,6]. So far some yellow, green, and blue phosphors as good candidates of near-UV LED chip for white light generation have been reported. However, there are very few inorganic red phosphors with the compatibility for white LEDs.

In recent, some phosphate-based phosphors have been reported with unconventional properties for white emission. Among these phosphate phosphors, Mn^{2+}-doped phosphates are potential red-emitting materials, which have been proved to be excellent phosphor materials for application in white LEDs. Due to the forbidden transition ($^4T_1$-$^6A_1$) of Mn^{2+}, the Mn^{2+} doped phosphor cannot usually show considerable emission. However, additional doping of Eu^{2+} could generate the energy transfer from Eu^{2+} to Mn^{2+}.

We suggest $BaMgP_2O_7$:Eu,Mn phosphor as a red component for white emission using UV LEDs. In this work, the $BaMgP_2O_7$:Eu,Mn phosphors were synthesized and their photoluminescence properties were characterized. In addition, the doping concentrations of activator and sensitizer were optimized.

2. Experimental

The phosphate phosphors were prepared by conventional solid-state reaction. The starting reagents were high-purity of $BaCO_3$ (99.9%), MgO (99.9%), $MnCO_3$ (99.9%), Eu_2O_3 (99.99%) and $(NH_4)_2HPO_4$ (99.9%). According to the nominal composition of $Ba_{(1-x)}Mg_{(1-y)}P_2O_7$:$x$$Eu^{2+}$,$y$$Mn^{2+}$, the stoichiometric amount of raw materials were mixed in an agate mortar and calcined at 1000℃ for 5 h under the air. Subsequently, the calcined materials were re-ground in the mortar and re-fired at 1000℃ for 5 h under the reductive ambience of 5% H_2/95% N_2 for reduction to Eu^{2+} and Mn^{2+}, respectively.

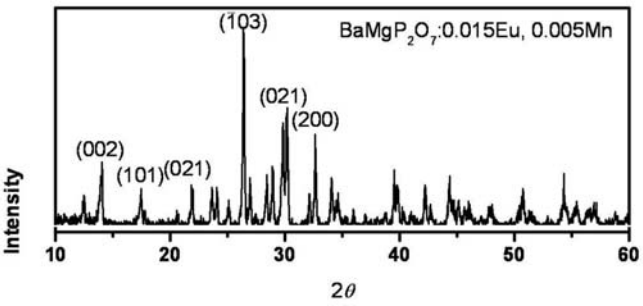

Fig. 1. XRD pattern of $BaMgP_2O_7$:0.015Eu, 0.005Mn phosphor.

The structure of the prepared phosphor was identified by X-ray powder diffraction using a Rigaku DMAX-33 X-ray diffractometer with Cu Kα radiation operated at 40 kV and 40 mA. The measurement of photoluminescence (PL) spectra was performed by using a PSI photoluminescence system equipped with D_2 lamp.

3. Results and discussion

The phosphate compound, $BaMgP_2O_7$ is known to crystallize in monoclinic structure of the space group $P2_1/n$ with the unit cell parameters of a= 5.48 Å, b=8.56 Å, c=12.63 Å, ß = 91.3° and V=593.4 Å^3 [7,8].

In the crystal structure, each Ba^{2+} is coordinated by eight oxygen ions and each Mg^{2+} is coordinated six oxygen ions. With the consideration of ionic sizes of metal cations and coordination number, Ba^{2+} and Mg^{2+} sites should be substituted by Eu^{2+} and Mn^{2+}, respectively. The X-ray diffraction pattern of the Eu^{2+} and Mn^{2+} codoped $BaMgP_2O_7$ phosphor powder is shown in Fig. 1. All the diffraction peaks are indexed

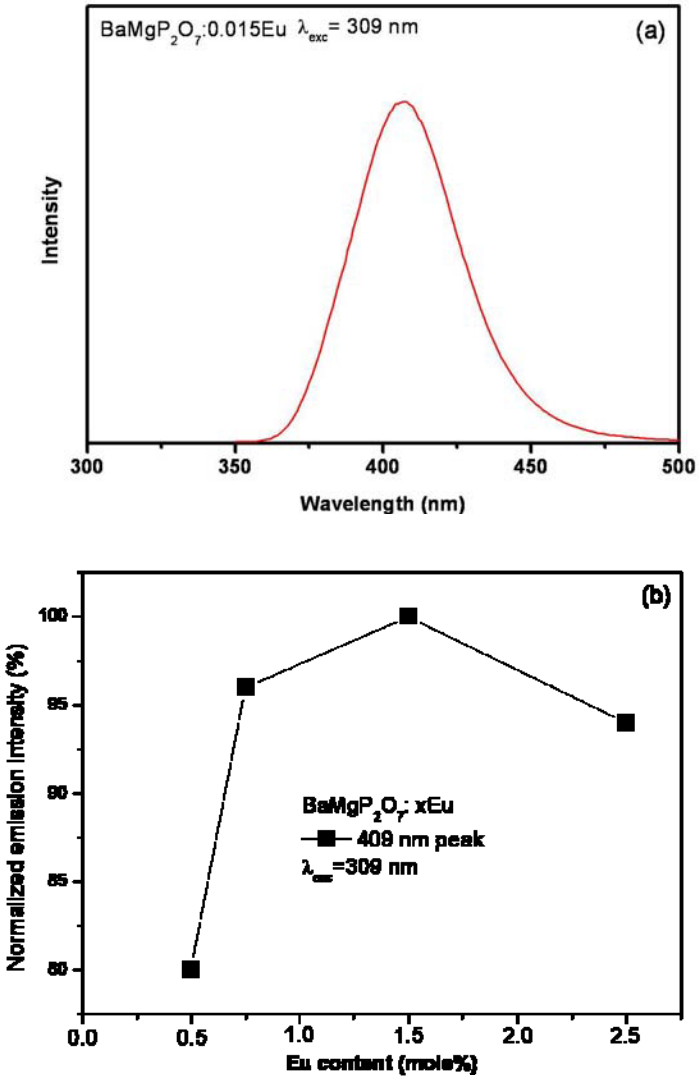

Fig. 2. Emission spectrum of $BaMgP_2O_7$: 0.015Eu (a) and dependence of emission intensity with Eu^{2+} concentration change in $BaMgP_2O_7$:Eu (b).

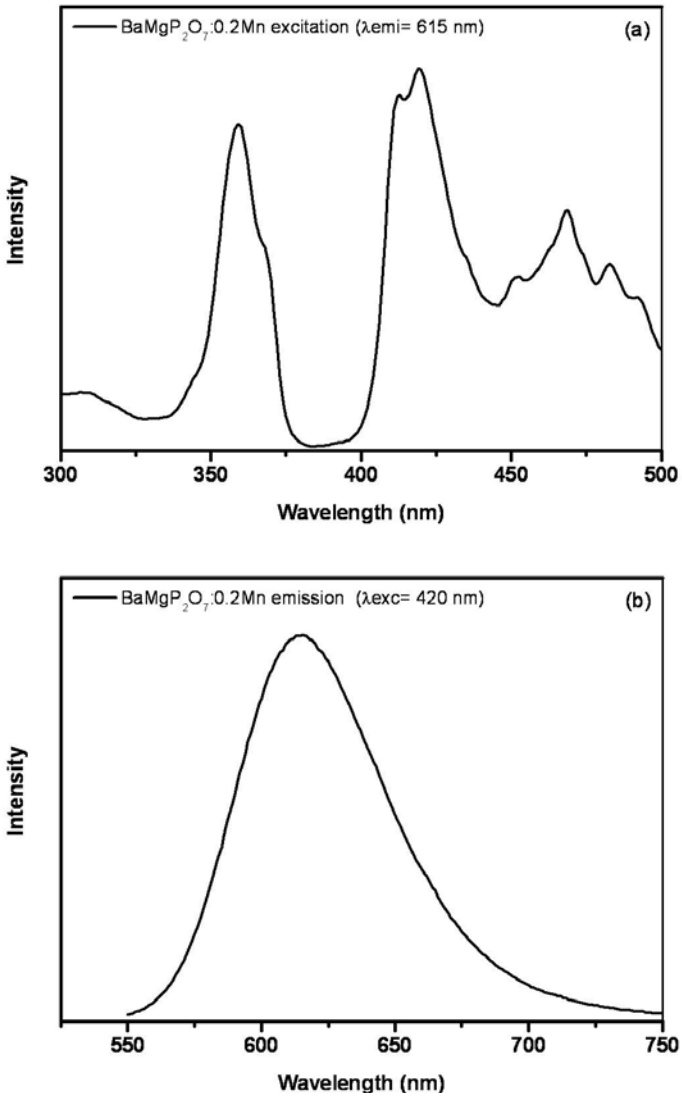

Fig. 3. Excitation spectrum (a) and emission spectrum (b) of $BaMgP_2O_7$:0.2Mn.

based on monoclinic structure and exactly match with JCPDS file No. 50-0363, which indicates that the phosphors are still single phase and the incorporation with Eu^{2+} and Mn^{2+} ions into the $BaMgP_2O_7$ lattice, does not conduct any significant change in crystal structure of the host.

Fig. 2(a) shows the emission spectrum of Eu doped $BaMgP_2O_7$ measured at room temperature. The $BaMgP_2O_7$:Eu phosphor under excitation at 309 nm wavelength exhibits a strong bluish emission band centered at 409 nm, originating from the parity-allowed 4*f*-5*d* transition of Eu^{2+} ion. To investigate optimum concentration of Eu^{2+} in the $BaMgP_2O_7$:Eu system, the concentration of Eu was changed between 0.5 and 2.5 mol%. Fig. 2(b) shows the Eu concentration dependence in emission intensity of the $BaMgP_2O_7$:Eu phosphor. A maximum intensity of the phosphor is achieved at the concentration of 1.5 mol%, and then is decreased at the higher Eu^{2+} concentration. Accordingly, the optimum Eu^{2+} concentration in the $BaMgP_2O_7$:Eu is 1.5 mol%.

Fig. 3 presents the excitation and emission spectra of the $BaMgP_2O_7$:0.2Mn phosphor. The excitation and emission intensities of the $BaMgP_2O_7$:Mn phosphor are relatively low. It is known that the d-d absorption transition of Mn^{2+} is forbidden so that its excitation efficiency is very low [9]. The $BaMgP_2O_7$:Mn phosphor under the 420 nm excitation shows a red emission band positioned at 615 nm, due to the $^4T_1$-$^6A_1$ transition of Mn^{2+} ions. By comparison Fig. 3 with Fig. 2(a), it is realized that the Mn^{2+} absorption and Eu^{2+} emission are spectrally overlapped at the region of 400 nm to 475 nm indicating efficient energy transfer from Eu^{2+} ions to Mn^{2+} ions in $BaMgP_2O_7$ host matrix.

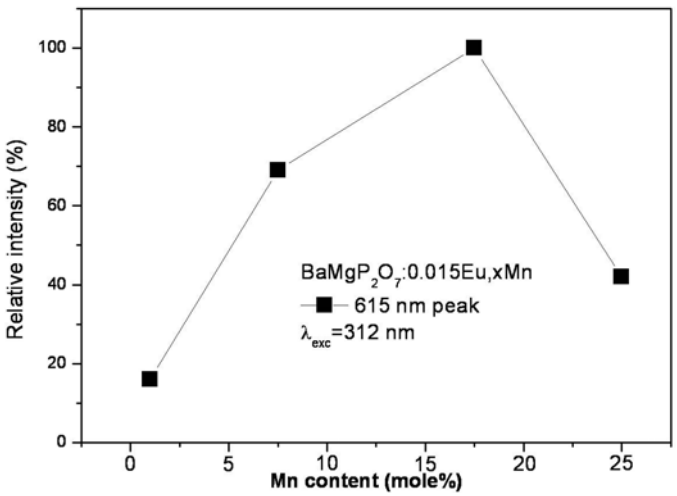

Fig. 4. Dependence of emission intensity upon concentration of Mn^{2+} ions in $BaMgP_2O_7$:0.015Eu, 0.2Mn.

Fig. 4 exhibits the dependence of emission intensity according to concentration changes of Mn^{2+} in $BaMgP_2O_7$:0.015Eu,Mn composition. With increasing Mn^{2+} concentration up to 17.5 mol%, the relative intensity of the red emission band at 615 nm increases gradually. This is an obvious evidence that effective energy transfer from Eu^{2+} to Mn^{2+} in the $BaMgP_2O_7$:Eu,Mn system takes place. On the other hand, after the red emission reaches maximum at the concentration of 17.5 mol% and then is decreased with the higher Mn^{2+} concentration, indicating the concentration quenching.

4. Summary

The synthesis of the Eu^{2+} and Mn^{2+} codoped $BaMgP_2O_7$ phosphors were attempted by the solid state reaction. The crystalline phase, photoluminescence and energy transfer in $BaMgP_2O_7$:Eu,Mn phosphors were investigated. Strong blue emission of Eu^{2+} peaked at 409 nm in $BaMgP_2O_7$:Eu^{2+} and faint emission of Mn^{2+} positioned at 615 nm in $BaMgP_2O_7$:Mn^{2+} were observed under UV excitation. The absorption spectrum of Mn^{2+} and emission spectrum of Eu^{2+} are significantly overlapped at the wavelength region of 400 nm to 475 nm, indicating efficient energy transfer from Eu^{2+} ions to Mn^{2+} ions in $BaMgP_2O_7$ host. Through the energy transfer, the red emission by Mn^{2+} in the $BaMgP_2O_7$:Eu,Mn was enhanced with increasing Mn content. The optimum concentration of Eu^{2+} was 1.5 mol%. Also, the optimum concentration of Mn^{2+} at the 1.5 mol% Eu in the $BaMgP_2O_7$:Eu,Mn was 17.5 mol%. Accordingly, $BaMgP_2O_7$:Eu,Mn phosphor can be a promising phosphor with intense red emitting component for generation of white emission using an UV-LEDs.

5. References

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