Luminescence studies of $Ba_{1-x}Mg_{2-y}(PO_4)_2$:xEu^{2+}, yMn^{2+} phosphor

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ABSTRACT

The phosphors $BaMg_2(PO_4)_2$ doped with Eu^{2+} and Mn^{2+} solely or doubly were prepared by solid state reaction, and their luminescent properties were also investigated. Under the excitation of 322 nm, it has been observed a broad blue emission band centered at 417 nm and a red emission band centered at about 665 nm, resulting from Eu^{2+} and Mn^{2+}, respectively. Resonance-type energy transfers from Eu^{2+} to Mn^{2+} were discovered by directly overlapping the emission spectra of Eu^{2+} and the excitation spectra of Mn^{2+}. According to the changes of relative intensities of Eu^{2+} and Mn^{2+} emission, efficiencies of energy transfer were calculated. Based on the principle of energy transfer, the relative intensities of blue and red emission could be tuned by adjusting the contents of Eu^{2+} and Mn^{2+}.

1. Introduction

As we know, Mn^{2+} ion is an efficient activator with wide emission band ranging from 500 to 700 nm in various host materials [1]. It has a weak emission because its d–d absorption transition is spin forbidden when Mn^{2+} is solely doped. In general, the method to enhance the emission intensity of Mn^{2+} is by introducing sensitizer Eu^{2+} because of its high efficiency for both excitation and emission in many hosts. Typically, Eu^{2+} can transfer its absorbed energy fully or partly to Mn^{2+}, consequently orange-reddish or single-phase-full-color phosphors can be obtained [2–4]. Hence, Eu^{2+} and Mn^{2+} co-doped luminescent materials have been studied extensively over the past few years [5,6]. For instance, Kim et al. first proposed that Eu^{2+} and Mn^{2+} co-doped $Ba_3MgSi_2O_8$ could be used as single-phase full-color phosphors for fabrication of a warm white-light emitting diode [7]. Recently, Liu et al. further reported that by adding Si_3N_4 to compensate the green light emission, the phosphors $Ba_3MgSi_2O_8$: Eu^{2+}, Mn^{2+} could emit white-light with CIE chromaticity coordinate (0.2605, 0.3084) [8]. Furthermore, Xiao et al. first synthesized phosphor $Ba_2Ca(B_3O_6)_2$:Eu^{2+}, Mn^{2+} which exhibit a tunable color emission by adjusting the ratio of Eu^{2+} and Mn^{2+} appropriately, and also investigated the energy transfer mechanisms [9].

In recent years, the luminescent properties of phosphate materials have been widely investigated because of the advantages such as excellent thermal and chemical stability [10,11]. Especially, many Eu^{2+} and Mn^{2+} co-doped phosphate materials have been studied, such as $Sr_2Mg_3P_4O_{15}$ [12], $Ca_{10}K(PO_4)_7$ [13] and $BaMgP_2O_7$ [14], and so on. Currently, the compounds $AB_2(PO_4)_2$ (A = Ca, Sr, Ba; B = Mg, Zn) have been considered to be efficient luminescent hosts. Guo et al. have prepared the phosphor $SrMg_2(PO_4)_2$:Eu^{2+}, Mn^{2+} with blue and red two emission bands [15]. Jeong et al. reported that $Sr_{1-x}Zn_{2-y}(PO_4)_2$:Eu_x^{2+}, Mn_y^{2+} phosphor could used for UV-based white-LEDs [16]. Moreover, our experimental group have synthesized the phosphors $(Ca/Ba)Zn_2(PO_4)_2$ and investigated the luminescent properties. To the best of our knowledge, no paper has been published on the preparation of Eu^{2+} and Mn^{2+} doubly activated $BaMg_2(PO_4)_2$ phosphors. Based on these considerations, in this paper, we reported the preparation of phosphors $BaMg_2(PO_4)_2$:Eu^{2+}, Mn^{2+} and discussed the energy transfer mechanism between Eu^{2+} and Mn^{2+}.

2. Experimental

2.1. Synthesis of $BaMg_2(PO_4)_2$:Eu^{2+}, Mn^{2+} phosphor

Eu^{2+} or Mn^{2+} singly doped and Eu^{2+} and Mn^{2+} co-activated $BaMg_2(PO_4)_2$ phosphors were prepared by solid state reaction technique. The starting materials, including $BaCO_3$, $MnCO_3$, $Mg(OH)_2·4MgCO_3·5H_2O$, $NH_4H_2PO_4$ and Eu_2O_3 of purity higher than 99.9%, were weighted in stoichiometric proportions, thoroughly mixed and ground by an agate mortar and pestle for 30 min till they were well distributed. Then the grinded powder which was placed in a small covered aluminum crucible was put in a large crucible. The space between the two crucibles was filled with carbon powder to reduce the Eu^{3+} migrating into the Eu^{2+} in the heating process. The large crucible with its contents was calcined at 1050 °C for 4 h, and the samples were obtained. Finally cool the samples to room temperature and grind them into powder for measure.

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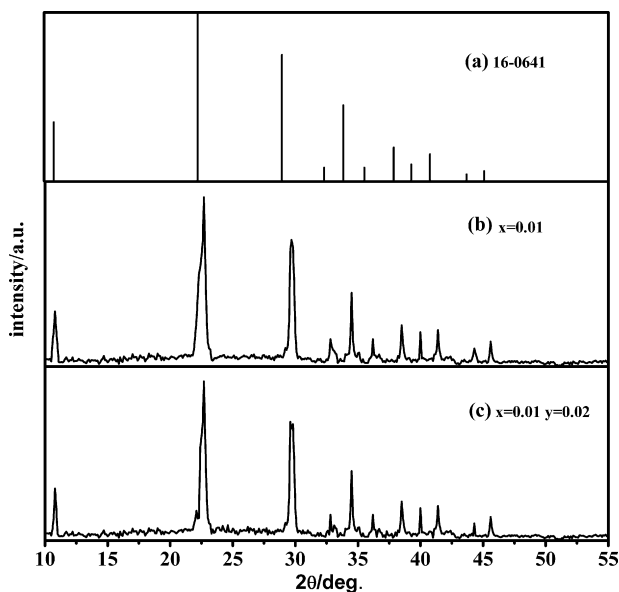E-mail address: mashuyuan841210@sina.com (S. Ma).

Fig. 1. (a) BaMg$_2$(PO$_4$)$_2$ (JCPDS 16-0641), (b) the XRD pattern of Ba$_{0.99}$Mg$_2$(PO$_4$)$_2$:Eu^{2+} and (c) the XRD pattern of Ba$_{0.99}$Mg$_{1.98}$(PO$_4$)$_2$:0.01Eu^{2+}, 0.02Mn^{2+}.

2.2. Characterizations of BaMg$_2$(PO$_4$)$_2$:Eu^{2+}, Mn^{2+} phosphor

The crystalline phases of the as-prepared phosphors were collected by powder X-ray diffraction spectroscopy (XRD6000 Shimadzu) with Cu Kα (λ = 0.15406 nm) radiation operating at 40 kV and 40 mA, and the XRD patterns were recorded in the range of 10° ≤ 2θ ≤ 55°. The emission and excitation spectra were measured using Hitachi F-4600 fluorescence spectrophotometer equipped with a 450 W xenon lamp. The scan speed was 240 nm/min with a step of 0.2 nm and the response time was 0.05 s. For comparison, all measurements were performed at room temperature with the identical instrumental parameters.

3. Results and discussion

3.1. Phase analysis

The phase purity and the crystal structure of samples were characterized by powder X-ray diffraction. Since the XRD patterns of all samples are the same as each other in our experiments, only the XRD patterns of Eu^{2+} singly doped and Eu^{2+}, Mn^{2+} co-activated BaMg$_2$(PO$_4$)$_2$ phosphors are illustrated in Fig. 1. Curve (a) shows the Joint Committee on Powder Diffraction Standards (JCPDS 16-0641). Curves (b) and (c) present the patterns of Ba$_{1-x}$Mg$_2$(PO$_4$)$_2$:xEu^{2+} and Ba$_{1-x}$Mg$_{2-y}$(PO$_4$)$_2$:xEu^{2+}, yMn^{2+}, respectively. Comparing curve (a) with (b) and (c), it is found that the diffraction peaks are found to be consistent with the standards card, but only the peaks shift a little to right. Results indicate that the dopants do not induce a significant change in the crystal structure and no purity phase has been observed in the samples, clearly suggesting that the activator and co-activator have been incorporated in the lattice. Considering the effect of ionic sizes of cations, it is predicted that Eu^{2+} and Mn^{2+} are proposed to occupy the Ba^{2+} and Mg^{2+} sites, respectively, because the ionic radii of Eu^{2+}(1.17 Å) and Mn^{2+}(0.67 Å) are close to that of Ba^{2+}(1.35 Å) and Mg^{2+}(0.72 Å).

3.2. Excitation and emission spectra of Eu^{2+} or Mn^{2+} solely doped BaMg$_2$(PO$_4$)$_2$

The emission and excitation spectra of Eu^{2+} or Mn^{2+} singly activated phosphors were investigated. A broad excitation band in the range of 225–400 nm centered at 322 nm is observed in Fig. 2. This excitation band is attributed to the 4f^7 ground state to the 4f^{6}5d^1 excited state of Eu^{2+}. The phosphor BaMg$_2$(PO$_4$)$_2$:Eu^{2+} under the
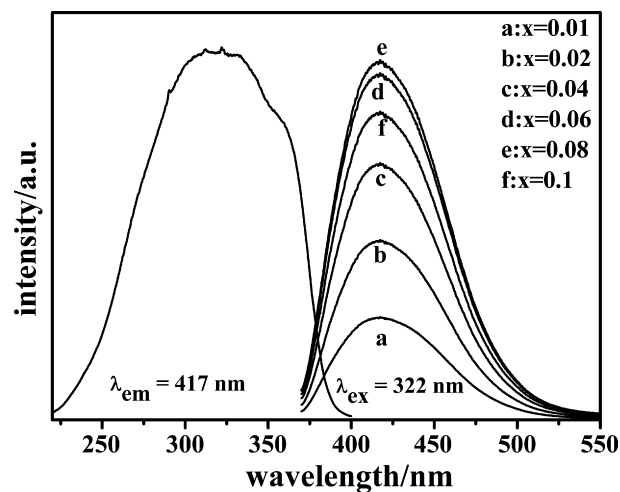

Fig. 2. The emission and excitation spectra of samples Ba$_{1-x}$Mg$_2$(PO$_4$)$_2$:xEu^{2+} (x = 0.01–0.1).

excitation of 322 nm exhibits a strong emission band. Fig. 2 presents the emission spectra of Ba$_{1-x}$Mg$_2$(PO$_4$)$_2$:xEu^{2+} (x = 1–10%). A blue-purple emission band is located at about 417 nm corresponding to the typical 4f^{6}5d^1(t$_{2g}$) → 4f^7(^{8}S$_{7/2}$) transition of Eu^{2+}, and no characteristic emission peaks from Eu^{3+} are observed, implying that Eu^{3+} ions have been reduced to Eu^{2+} completely in our experiments. The emission intensities of the phosphors vary with the content Eu^{2+}, while with increasing the concentration, the intensity increases until the intensity reaches a maximum at 0.08, and thereafter the intensity is decreased. The decrease in the emission intensity occurs as a result of concentration quenching. As the content of Eu^{2+} ions is increased, the distance between Eu^{2+} ions becomes closer, resulting in a higher probability of energy transfer among these ions.

It is well known that divalent Mn^{2+} has a broad band, the position of which depends strongly on the crystal field of the host materials. Generally, tetrahedrally coordinated Mn^{2+} ions (weak crystal field) exhibit a green emission; octahedrally coordinated Mn^{2+} ions (strong crystal field) give an orange to red emission. For the case of BaMg$_{2-y}$(PO$_4$)$_2$:yMn^{2+}, the spectral distribution of the emission spectra exhibits a broad band locating at around 662 nm, which is due to the typical ^{4}T$_1$(^{4}G) → ^{6}A$_1$(^{6}S) transition of Mn^{2+}. Fig. 3 shows the emission spectra of phosphors BaMg$_{2-y}$(PO$_4$)$_2$:yMn^{2+} with the content y ranging from 0.02 to 0.16. The emission intensity increases with the

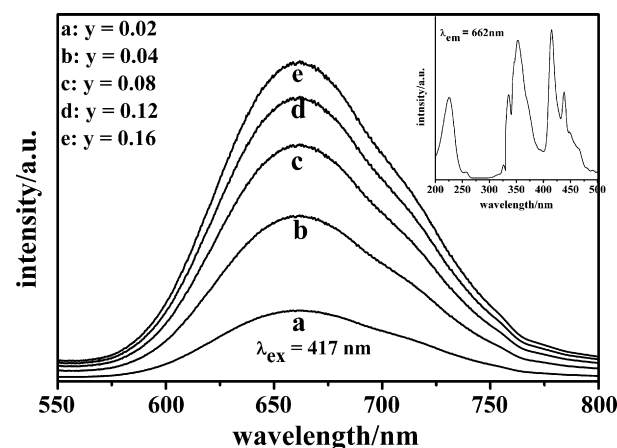**Fig. 3.** The emission spectra of samples BaMg$_{2-y}$(PO$_4$)$_2$:yMn^{2+} (y = 0.02, 0.04, 0.08, 0.12, 0.16) and inset of the figure is the excitation spectra BaMg$_{1.96}$(PO$_4$)$_2$:0.04Mn^{2+}.

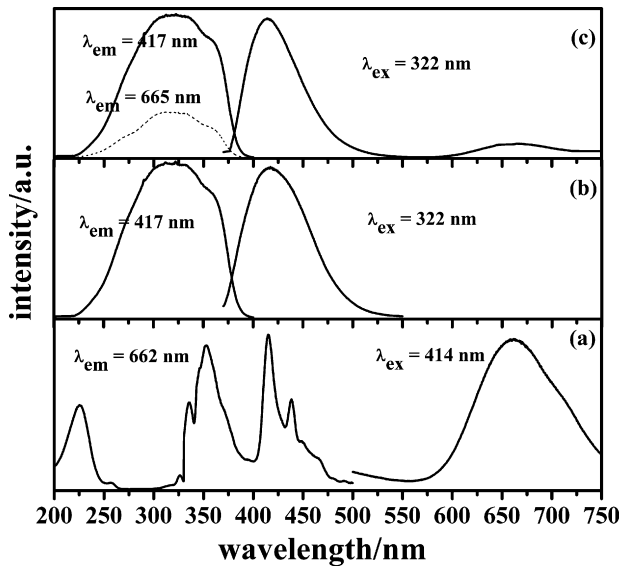**Fig. 4.** The emission and excitation spectra of $Ba_{0.98}Mg_2(PO_4)_2$:0.02Eu^{2+} (a), $BaMg_{1.96}(PO_4)_2$:0.04Mn^{2+} (b) and $Ba_{0.98}Mg_{1.96}(PO_4)_2$:0.02Eu^{2+}, 0.04Mn^{2+} (c).

Fig. 5. The emission spectra of phosphors $Ba_{0.96}Mg_{2-y}(PO_4)_2$:0.04Eu^{2+}, yMn^{2+} for different Mn^{2+} concentrations: $y = 0$, 0.02, 0.04, 0.08, 0.12, respectively, and dependence of the energy transfer efficiency η_T on Mn^{2+} concentration y.

increase of Mn^{2+} concentration, and no concentration quenching appears in our experimental range. The excitation spectra of $BaMg_{1.96}(PO_4)_2$:0.04Mn^{2+} illustrated in the inset of Fig. 3 consists of several bands centered at 225, 335, 353, 416 and 438 nm, respectively. The peaks at 335, 353, 416 and 438 nm are assigned to the transitions from $^6A_1(^6S)$ to $^4E(^4D)$, $^4T_2(^4D)$, $^4T_2(^4G)$ and $^4T_1(^4G)$ levels of Mn^{2+}, respectively.

3.3. Luminescent properties of Eu^{2+} and Mn^{2+} co-doped BaMg$_2$(PO$_4$)$_2$

Resonance-type energy transfer generally plays a central role in the Eu^{2+} and Mn^{2+} co-doped host matrix, such as BaMg$_2$Si$_2$O$_7$ [17],

BaZnP$_2$O$_7$ [18] and Ca$_5$MgSi$_3$O$_{12}$ [19], and so on. The Eu^{2+} or Mn^{2+} singly doped BaMg$_2$(PO$_4$)$_2$ phosphor emits blue or red light, so it is possible to obtain a phosphor with double color emission by the introduction of Eu^{2+} and Mn^{2+} if energy transfer exists. In order to prove our design, we investigate the system of Eu^{2+} and Mn^{2+} co-doped BaMg$_2$(PO$_4$)$_2$ phosphor. The emission and excitation spectra of BaMg$_2$(PO$_4$)$_2$:Eu^{2+}, BaMg$_2$(PO$_4$)$_2$:Mn^{2+} and BaMg$_2$(PO$_4$)$_2$:Eu^{2+}, Mn^{2+} are displayed in Fig. 4 in a comparable way. Comparing the emission spectra of BaMg$_2$(PO$_4$)$_2$:Eu^{2+} with the excitation spectra of BaMg$_2$(PO$_4$)$_2$:Mn^{2+}, it is observed that a significant spectral overlap is found at the region of 400–500 nm, suggesting that energy transfer could be take place in the host. As expected in Fig. 4(c),
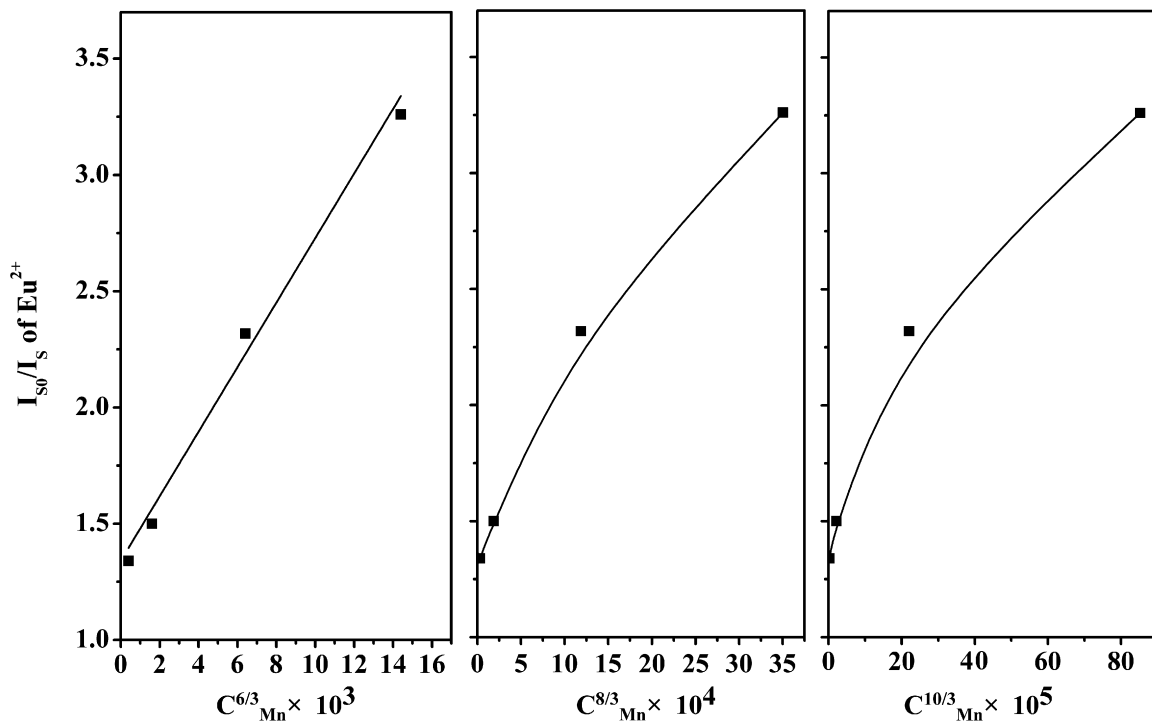

Fig. 6. Dependence of I_{S0}/I_S of Eu^{2+} on (a) $C^{6/3}$, (b) $C^{8/3}$ and (c) $C^{10/3}$.

there are blue and red double color emission bands in the emission spectra of Eu^{2+} and Mn^{2+} co-doped $BaMg_2(PO_4)_2$ phosphor. The excitation spectra monitored at 417 and 665 nm both have strong absorption band ranging from 225 to 400 nm. It is clearly shown that the two excitation spectra are the same except the relative intensity and also proven the existence of energy transfer from Eu^{2+} to Mn^{2+}.

The variations in the emission intensities of Eu^{2+} and Mn^{2+} with the content of Mn^{2+} are investigated. Fig. 4 shows the emission spectra of phosphors $Ba_{0.96}Mg_{2-y}(PO_4)_2$:$0.04Eu^{2+}$, yMn^{2+} ($y=0$, 0.02, 0.04, 0.08, 0.12) under the excitation of 322 nm. It can be seen that when the concentration of the activator Mn^{2+} is altered, no shift of red emission peak is observed. With increasing Mn^{2+} concentration, the relative intensity of blue emission decreases drastically, whereas that of the red emission increases gradually. This could be an evidence that the effective energy transfer exists in the Eu^{2+} and Mn^{2+} co-activated $BaMg_2(PO_4)_2$ system. The energy transfer efficiency (η_T) from Eu^{2+} to Mn^{2+} has been discussed by Paulose et al. and can be calculated by the following formula [20]:

$$\eta_T = 1 - \frac{I_S}{I_{S0}}, \tag{1}$$

where I_{S0} and I_S are the luminescence intensities of the sensitizer (Eu^{2+}) with and without activator (Mn^{2+}) present. The η_T from Eu^{2+} to Mn^{2+} in $Ba_{0.96}Mg_{2-y}(PO_4)_2$:$0.04Eu^{2+}$, yMn^{2+} is calculated as a function of Mn^{2+} concentrations y and is presented in the inset of Fig. 5. The value η_T is found to be increased with increasing Mn^{2+} concentration.

Based on Dexter′s energy transfer formula of multipolar interaction and Reisfeld's approximation, the following relation can be obtained [21]:

$$\frac{\eta_0}{\eta} \propto C^{n/3}, \tag{2}$$

where η_0 and η are the luminescence quantum efficiency of Eu^{2+} in the absence and presence of Mn^{2+}, respectively; the values of η_0/η can be approximately calculated by the ratio of related luminescence intensities (I_{S0}/I_S); C is the concentration of Mn^{2+}; and $n=6$, 8 and 10 corresponded to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The I_{S0}/I_S–$C^{n/3}$ plots are further presented in Fig. 6(a)–(c), and only when $n=6$, the linear relation was found, implying that $ET_{Eu \to Mn}$ is the dipole–dipole mechanism. According to above results, it draws conclusions that energy transfer between Eu^{2+} and Mn^{2+} exists in the phosphors $BaMg_2(PO_4)_2$:Eu^{2+}, Mn^{2+}, and the ratio of blue to red emission can be adjusted by tuning the concentrations of Eu^{2+} and Mn^{2+}.

4. Conclusions

In conclusion, a series of phosphors Eu^{2+} and Mn^{2+} singly or doubly doped $BaMg_2(PO_4)_2$ were synthesized and their optical properties were studied. The spectroscopic data indicated that the energy transfer from Eu^{2+} to Mn^{2+} took place in the host $BaMg_2(PO_4)_2$. And the energy transfer in the phosphor $BaMg_2(PO_4)_2$:Eu^{2+}, Mn^{2+} has been demonstrated to be a resonant type via a dipole–dipole mechanism. Furthermore, adjusting the concentrations of Eu^{2+} and Mn^{2+} could tune the relative intensity of blue and red emission. Eu^{2+} and Mn^{2+} co-doped $BaMg_2(PO_4)_2$ was a promising double colors emission phosphor.

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