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Luminescent properties of Dy^{3+} and/or Eu^{3+} doped $Mg_2Al_4Si_5O_{18}$ phosphors and energy transfer between Dy^{3+}/Eu^{3+} ion pairs

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ABSTRACT

A series of Dy^{3+} and/or Eu^{3+} doped $Mg_2Al_4Si_5O_{18}$ phosphors were synthesized by a solid state reaction. The phase, microstructure and luminescent properties of the phosphors were investigated. The XRD patterns and SEM images show that the doping ions have no influence on the phase and microstructure of the phosphors. The Dy^{3+} or Eu^{3+} singly doped $Mg_2Al_4Si_5O_{18}$ phosphors respectively show emission bands of Dy^{3+} or Eu^{3+} ions. Based on the overlap between the emission spectrum of $Mg_2Al_4Si_5O_{18}$:Dy^{3+} with the excitation spectrum of $Mg_2Al_4Si_5O_{18}$:Eu^{3+}, we speculated the possible energy transfer from Dy^{3+} to Eu^{3+} in $Mg_2Al_4Si_5O_{18}$:Dy^{3+}/Eu^{3+} phosphors, which is confirmed by the decreases of Dy^{3+} emission intensity with the increasing Eu^{3+} concentrations. The decreases of decay time of Dy^{3+} emission gave the further evidence to the energy transfer from Dy^{3+} to Eu^{3+}. The energy transfer efficiency increases from 7.35% to 62.41% when the codoped Eu^{3+} concentration increases from 1 mol% to 6 mol%.

1. Introduction

Due to more and more serious energy and environment dilemmas, white light-emitting diodes (WLEDs) are becoming the next generation lighting sources due to their advantages of environmental friendliness, low energy consumption and high performance stability. At present, the most widely used WLEDs are fabricated by the blue light diode and the $Y_3Al_5O_{12}$:Ce^{3+} yellow phosphors, which generally emits white light with disadvantages of low color rendering index (CRI) and high correlated color temperature (CCT) [1,2]. Researchers devote their energies to methods whose can overcome these deficiencies of the current WLEDs. Up to now, one widely accepted method is to compensate red light and the other way is to combine the near-ultraviolet/ultraviolet (NUV/UV) chip with green, blue and green phosphors or single-phased white light phosphors [1–4]. Single-phased white light phosphors can be synthesized by different routes, such as doping a single rare earth ion into appropriate host, combining multiple rare earth ions with red/green/blue emissions or yellow/blue emissions, and codoping ion pairs based on energy transfer between them [5]. And energy transfer, as an effective way to tune the emission color, has been generally applied in luminescent materials [4].

Aluminosilicate has stable crystal structure and excellently chemical/physical stabilities. Moreover, it has been found to be a good host for rare earth ions. Some rare earth ions doped aluminosilicate phosphors, such as $CaAl_2Si_2O_8$:Eu^{2+}/Mn^{2+} [6], $Ca_{12}Al_{10.6}Si_{3.4}O_{32}Cl_{5.4}$:$Eu^{2+}$ [7], $Na_{.34}Ca_{.66}Al_{1.66}Si_{2.34}O_8$:$Eu^{2+}$ [8], $NaAlSiO_4$:Ce^{3+}/Mn^{2+} [9], $(Ca,Sr)_2Al_2SiO_7$:Eu^{3+} [10], $Mg_2Al_4Si_5O_{18}$:Eu^{3+} [11], $Mg_2Al_4Si_5O_{18}$:Mn^{4+} [12] and $Mg_2Al_4Si_5O_{18}$:Eu^{2+}/Mn^{2+} [13] phosphors have been synthesized through different methods. Among various aluminosilicate materials, $Mg_2Al_4Si_5O_{18}$ has a orthorhombic phase with a hexagonal structure, in which, Mg^{2+} ion is coordinated by six O^{2-}, but Si^{4+} and Al^{3+} ions are surrounded by four O^{2-} [11]. Ultimately, the crystal structure is composed of six tetrahedral units $[Si/AlO_4]$ and connected by the $[MgO_6]$ octahedral and $[AlO_4]$ tetrahedra [13]. Except of the use as a host of phosphors, $Mg_2Al_4Si_5O_{18}$ also has been used as high quality refractory material, integrated circuit board, catalyst carrier, ceramic foam and aviation material due to its good thermal shock resistance, dielectric properties, fire resistance and mechanical properties [14–16].

Dy^{3+} and Eu^{3+} are two widely used rare earth ions in phosphors. In general, Dy^{3+} emits three emissions originating from the ${}^4F_{9/2} \rightarrow H_{15/2}$ (blue emission), ${}^4F_{9/2} \rightarrow H_{13/2}$ (yellow emission) and ${}^4F_{9/2} \rightarrow H_{11/2}$ (red emission) transitions and white light can be obtained in Dy^{3+} singly doped phosphors [17]. Normally, the red emission of Dy^{3+} is very weak, which induces the 'cold' characteristic of white light and limits the applications as white light phosphors [18]. And it has been found that the 'warm' white light can be obtained by codoping an ion showing red emission, such as Eu^{3+} [18–21] or Sm^{3+} [22,23]. In this work, we synthesized a series of Dy^{3+} and/or Eu^{3+} doped $Mg_2Al_4Si_5O_{18}$ phosphors. The luminescent properties of the synthesized phosphors were investigated carefully.

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2. Materials and method

$Mg_2Al_4Si_5O_{18}$:xmol%Dy^{3+} (x = 2, 4, 6, 8, 10 and 12) and $Mg_2Al_4Si_5O_{18}$:ymol%Eu^{3+} (y = 1, 2, 3, 4, 5 and 6) and $Mg_2Al_4Si_5O_{18}$:10 mol%Dy^{3+}/zmol%Eu^{3+} (z = 1, 2, 3, 4, 5 and 6) were synthesized by a solid state reaction. Chemicals of MgO (99.9%), Al_2O_3 (99.9%), SiO_2 (99.9%), Dy_2O_3 (99.99%) and Eu_2O_3 (99.99%) were used as raw materials. In a typical synthesis, chemicals with stoichiometric ratio were weighted and ground in an agate mortar by adding a little amount of ethyl alcohol. Then, the mixture was transferred into a crucible and calcined at 1400 °C for 8 h in air. After the system cooled to room temperature, the product was ground again for the measurements.

The XRD patterns of the synthesized phosphors were checked by a Rigaku-Dmax 2500 diffractometer. The microstructure was investigated by a scanning electron microscopy (SEM, JEOL JSM-7001F). The excitation and emission spectra were obtained by an Edinburgh Instrument FLS920 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. All of measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 gives the XRD patterns of $Mg_2Al_4Si_5O_{18}$:12 mol%Dy^{3+}, $Mg_2Al_4Si_5O_{18}$:6 mol%Eu^{3+}, $Mg_2Al_4Si_5O_{18}$:10 mol%Dy^{3+}/6 mol%Eu^{3+} and the standard data of JCPDs card no. 85–1541. All of other phosphors have the similar XRD patterns. As shown in Fig. 1, all of diffractions are well according with the standard data of orthorhombic phase $Mg_2Al_4Si_5O_{18}$ and no other diffractions corresponding to impurities can be observed, suggesting the singles phase of the synthesized phosphors and the doping ions do not induce phase change of the host. It is known the ionic radii of Mg^{2+} (CN = 6), Al^{3+} (CN = 4) and Si^{4+} (CN = 4) are 0.720 Å, 0.390 Å and 0.260 Å, but the ionic radii of doping ions are Dy^{3+} (0.912 Å, CN = 6) and Eu^{3+} (0.947 Å CN = 6) [24]. The data on fourfold coordination for Dy^{3+} and Eu^{3+} are current not available. It also has been reported that the Mg^{2+} sites in $Mg_2Al_4Si_5O_{18}$ can be substituted by Ca^{2+} (1.000 Å CN = 6), Sr^{2+} (1.180 Å CN = 6) and Ba^{2+} (1.350 Å CN = 6) [25,26]. This phenomenon indicates that Mg^{2+} sites can be substituted by larger ions and form solid solution. Therefore, Dy^{3+} and Eu^{3+} ions are expected to substitute Mg^{2+} sites in $Mg_2Al_4Si_5O_{18}$ depending on the ionic radii. It can be observed in Fig. 1 that the diffraction peaks of Dy^{3+} and/or Eu^{3+} doped $Mg_2Al_4Si_5O_{18}$ phosphors shift to lower 2θ angels. The larger radii of Dy^{3+} and Eu^{3+} comparing with Mg^{2+} results in the increase of cell volume and thus causes the diffraction peaks to shift to lower 2θ angles [27].

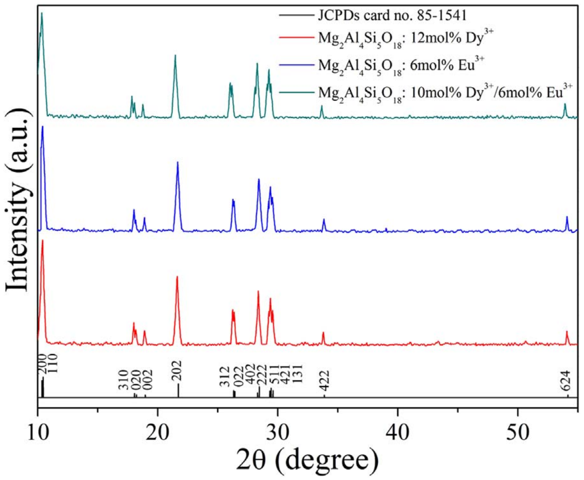

Fig. 1. XRD patterns of Dy^{3+} and/or Eu^{3+} doped $Mg_2Al_4Si_5O_{18}$ phosphors and standard data of JCPDs card no. 85–1541.

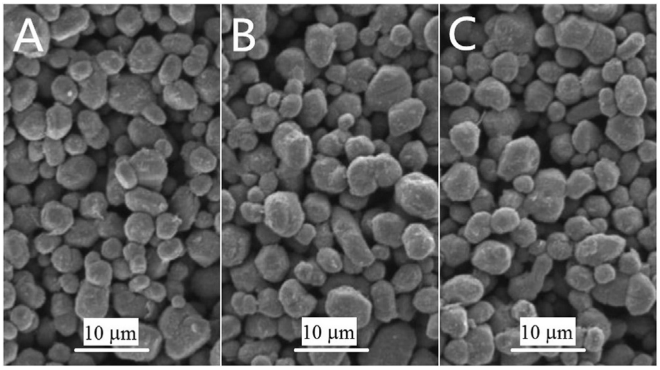

Fig. 2. SEM images of Dy^{3+} and/or Eu^{3+} doped $Mg_2Al_4Si_5O_{18}$ phosphors.

The microstructure of the synthesized phosphors was confirmed by the SEM measurements. Fig. 2 gives the SEM images of $Mg_2Al_4Si_5O_{18}$:12 mol%Dy^{3+}, $Mg_2Al_4Si_5O_{18}$:6 mol%Eu^{3+} and $Mg_2Al_4Si_5O_{18}$:10 mol%Dy^{3+}/6 mol%Eu^{3+} phosphors. It can be seen that irregular microcrystals are obtained in the current synthesis. All of synthesized phosphors have similar microstructure and size range, indicating that the doping ions have no influence on the microstructure of phosphors in the current synthesis. These phosphors with size of micrometers are suitable for fabrication of solid state lighting devices due to their high emission intensities [28].

Fig. 3 presents the excitation and emission spectra of $Mg_2Al_4Si_5O_{18}$:12 mol%Dy^{3+} (A) and $Mg_2Al_4Si_5O_{18}$:6 mol%Eu^{3+} (B) phosphors. As shown in Fig. 3A, the excitation spectrum of $Mg_2Al_4Si_5O_{18}$:12 mol%Dy^{3+} consists of a series of excitation bands in the range of 250–500 nm, which corresponds to the host absorption and the f-f transitions of Dy^{3+}. The weak excitation band peaking at about 300 nm is induced by the host absorption [11]. The other excitation bands peaking at about 324 nm, 350 nm, 364 nm, 387 nm, 426 nm, 453 nm and 469 nm originate from the $^6H_{15/2} \rightarrow {}^4D_{7/2}$, $^6H_{15/2} \rightarrow {}^6P_{7/2}$, $^6H_{15/2} \rightarrow {}^6P_{5/2}$, $^6H_{15/2} \rightarrow {}^4M_{21/2}$, $^6H_{15/2} \rightarrow {}^4G_{11/2}$, $^6H_{15/2} \rightarrow {}^4I_{152}$ and $^6H_{15/2} \rightarrow {}^4F_{9/2}$ transitions of Dy^{3+} [17–19]. Under the excitation at 350 nm, $Mg_2Al_4Si_5O_{18}$:12 mol%Dy^{3+} exhibits three emission bands in the range of 450–700 m with peaks at about 484 nm, 576 nm and 666 nm, which are induced by the $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transitions, respectively [20,22]. As shown in Fig. 3B, the excitation spectrum of $Mg_2Al_4Si_5O_{18}$:6 mol%Eu^{3+} consists of a series of excitation bands in the range of 250–500 nm, which results from the host absorption and charge transfer between Eu^{3+} and O^{2-}, as well as the f-f transitions of Eu^{3+}. The excitation band peaking at about 304 nm is a combination of host absorption and charge transfer between Eu^{3+} and O^{2-} [11]. Other excitation bands peaking at about

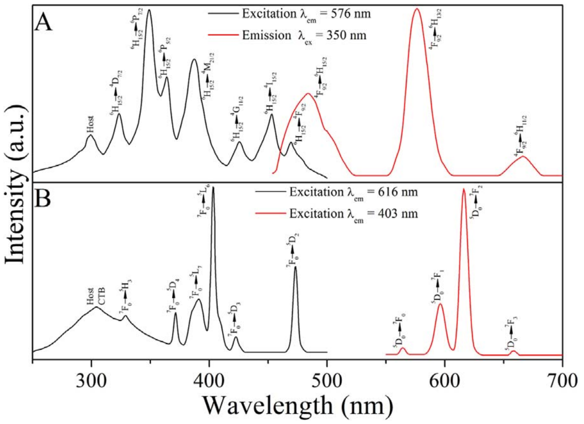

Fig. 3. Excitation and emission spectra of Dy^{3+} or Eu^{3+} doped $Mg_2Al_4Si_5O_{18}$ phosphors.