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JOURNAL OF RARE EARTHS, Vol. 34, No. 1, Jan. 2016, P. 17
JOURNAL OF RARE EARTHS
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Synthesis and luminescence properties of bluish-green emitting $K_2MgSi_3O_8:Eu^{2+}$ phosphor

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Received 23 June 2015; revised 16 October 2015

Abstract: Eu^{2+}-doped $K_2MgSi_3O_8$ phosphors were synthesized by conventional solid-state reaction method. The phase formation of as-prepared samples was characterized by X-ray powder diffraction. The luminescence properties were investigated by the photoluminescence excitation and emission spectra, decay curve and CIE coordinates. The phosphor showed bluish-green emission centered at 460 nm under the excitation of UV and near UV light with the wavelength range of 250–430 nm. Two Eu^{2+} emission centers existed in the $K_2MgSi_3O_8:Eu^{2+}$ phosphor according to the luminescence spectra and the decay curves. The critical quenching concentration of Eu^{2+} doping was determined to be 3.0 mol.% and the concentration quenching mechanism was dipole-dipole interactions between Eu^{2+} ions. These results suggested that $K_2MgSi_3O_8:Eu^{2+}$ was a potential bluish-green phosphor candidate for white UV-LED.

Keywords: $K_2MgSi_3O_8$; phosphors; luminescence; white UV-LED; rare earths

The absorption and emission spectra of Eu^{2+}-doped phosphors usually exhibit broad bands due to the allowed electric-dipole transitions between the $4f^7$ ground state and the $4f^65d^1$ excited state configuration[1,2]. As a typical phosphor, Eu^{2+}-doped alkaline earth silicate phosphors can emit visible light when they absorb ultraviolet or blue (380–460 nm) light from LEDs chips. These phosphors have been investigated a lot due to the significant applications in white light-emitting diodes (W-LEDs). A lot of studies on Eu^{2+}-activated alkaline earth silicate phosphors have been published, such as $Sr_2SiO_4:Eu^{2+}$ [3], $Ca_3Si_2O_7:Eu^{2+}$ [4], $SrCaSiO_4:Eu^{2+}$ [5], $CaAl_2Si_2O_8:Eu^{2+}$ [6], $BaCa_2MgSi_2O_8:Eu^{2+}$ [7], $Ba_2ZnSi_2O_7:Ce^{3+},Eu^{3+},Eu^{2+}$ [8], and so on.

In recent years, Eu^{2+}-doped alkaline and alkaline-earth silicate phosphors have been paid more attention due to the lower calcining temperature and being easier to achieve electric charge balance compared with alkaline earth silicate phosphors for W-LEDs. Many systems have been reported. For example, $Li_2SrSiO_4:Eu^{2+}$ [9], $K_4CaSi_3O_9:Eu^{2+}$ [10], $Na_2Ca_3Si_6O_{16}:Eu^{2+}$ [11], $Li_2Ca_2Si_2O_7:Eu^{2+}$ [12], $Li_4SrCa(SiO_4)_2:Eu^{2+}$ [13], $Na_2Ba_6(Si_2O_7)(SiO_4)_2:Eu^{2+}$ [14], etc. This type of phosphors are one potential candidate in W-LEDs.

In this work, $K_2MgSi_3O_8:Eu^{2+}$ phosphors were first synthesized by conventional solid-state reaction. The structure of samples was measured by powder X-ray powder diffraction (XRD) measurements. The photoluminescence excitation and emission spectra, and the decay curves were investigated. The luminescence intensity measurements were performed as a function of Eu^{2+} concentration. The concentration quenching mechanism was discussed.

1 Experimental

1.1 Preparation of $K_2MgSi_3O_8:Eu^{2+}$ phosphors

$K_2MgSi_3O_8:xEu^{2+}$ (x=0.005–0.07) phosphors were synthesized by conventional solid-state reaction method. The raw materials of K_2CO_3 (A.R.), $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$ (A.R.), SiO_2 (A.R.) and Eu_2O_3 (high purity, 99.99%) were ground together with stoichiometric amount in an agate mortar. First, the mixture was heated at 450 ºC for 5 h. After a second homogenization in the mortar, the sample was heated at 750 ºC for 10 h. After that, the sample was thoroughly mixed and heated again at 950 ºC for 10 h in the flow atmosphere of 95% N_2+5% H_2.

1.2 Characterizations

The XRD patterns of samples were measured on a Rigaku D/Max-2000 diffractometer operating at 40 kV, 30 mA with Bragg-Brentano geometry by using Cu Kα radiation (λ=0.15418 nm). A PerkinElmer LS-50B luminescence spectrometer and a Hitachi F-4500 fluorescence spectrophotometer were used to record the excita-

Foundation item: Project supported by the First Phase Project of Jiangsu College Brand Construction (PPZY2015B178), Qing Lan Project of Jiangsu Province and the Higher Occupation Colleges in Jiangsu Province Domestic Senior Visiting Scholar Program Project (2014FX006)

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DOI: 10.1016/S1002-0721(14)60572-X

tion and emission spectra. The luminescence decay curves were tested by the third harmonic (355 nm) of a pulsed Nd:YAG laser (Spectron Laser Sys. SL802G).

2 Results and discussion

2.1 XRD characterization

The samples were characterized by powder XRD measurements. The XRD patterns of the $K_2MgSi_3O_8$:xEu^{2+} (x= 0.005–0.07) are shown in Fig. 1. It can be observed that the XRD patterns of samples match the PDF2 standard card number 19-0973 ($K_2MgSi_3O_8$) well in the International Center for Diffraction Data (ICDD) database. No impurity lines were detected, and all the reflected lines could be well indexed to a $K_2MgSi_3O_8$ single phase.

2.2 Photoluminescent properties

The excitation and emission spectra of $K_2MgSi_3O_8$: $0.03Eu^{2+}$ at room temperature are presented in Fig. 2. The emission spectrum shows a broad emission band ranging from 370 to 580 nm with a maximum of 460 nm. It can be ascribed to $4f^65d^1 \rightarrow 4f^7$ electric transition of Eu^{2+} ions. The excitation spectra show the broad absorption bands covered from 250 to 430 nm. It can be attributed to 4f–5d electric transition of Eu^{2+} ions. This means that the phosphor can match well with the emission light of UV-LED chips (360–400 nm)[14].

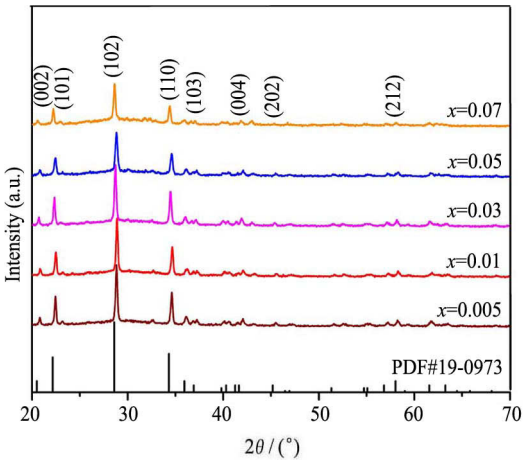

Fig. 1 XRD patterns of $K_2MgSi_3O_8$:xEu^{2+} (x=0.005, 0.01, 0.03, 0.05, 0.07) and in comparison with standard card PDF: 19-0973

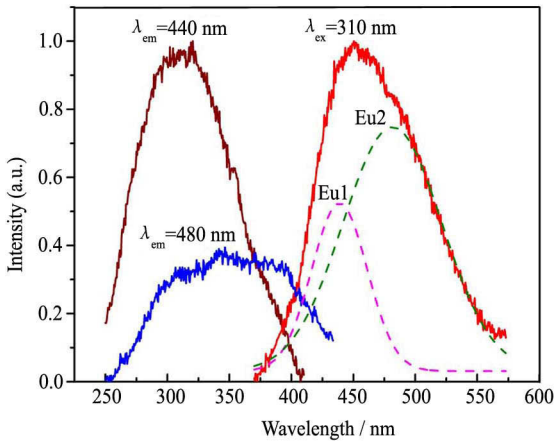

Fig. 2 Excitation and emission spectra of $K_2MgSi_3O_8$:$0.03Eu^{2+}$

The two excitation spectra (λ_{em}=440 nm and λ_{em}=480 nm, respectively) in Fig. 2 indicate that Eu^{2+} ions occupy more than one site in the lattice. The emission spectrum (λ_{ex}=310 nm) can be deconvoluted into at least two Gaussian components with peaks at 440 nm (referred to as Eu1) and 480 nm (referred to as Eu2). This indicates that two Eu^{2+} luminescence centers exist in $K_2MgSi_3O_8$ lattice.

Fig. 3 shows the luminescence decay curves of $K_2MgSi_3O_8$:$0.03Eu^{2+}$ phosphor under the excitation of 355 nm. It can be seen that the luminescence decay curves can be fitted by double exponential equation as follows:

$$I=I_1\exp[-t/\tau_1]+I_2\exp[-t/\tau_2] \quad (1)$$

where I_1 and I_2 are constant, τ_1 and τ_2 are luminescence lifetime. There are two kinds of decays in Fig. 3. One is slow decay and the luminescence lifetime is 1.75 μs at the peak of 480 nm, the other is fast decay and the luminescence lifetime is 1.44 μs at the peak of 440 nm. In view of the different luminescence lifetimes in Fig. 3 (1.44 μs for 440 nm and 1.75 μs for 480 nm), two different emission centers are also identified to exist in the lattice of $K_2MgSi_3O_8$.

The emission spectra of $K_2MgSi_3O_8$:xEu^{2+} phosphors with Eu^{2+} content are presented in Fig. 4. The emission spectra show that the emission intensity varies as the content of Eu^{2+} increased. As shown in the upper inset of Fig. 4, the emission intensity increases with increasing Eu^{2+} content up to a maximum value at x=0.03. Then the emission intensity decreases when the Eu^{2+} content further increases beyond x=0.03 because of the concentration quenching effect. Moreover, it can be observed that the peak center shifts to long wavelength with Eu^{2+} content increasing. This is caused by the $K_2MgSi_3O_8$ lattice distortion originated by bigger radius of Eu^{2+} ions.

As discussed above, there are two Eu^{2+} luminescence centers in $K_2MgSi_3O_8$ lattice. Fig. 5 shows the relation-

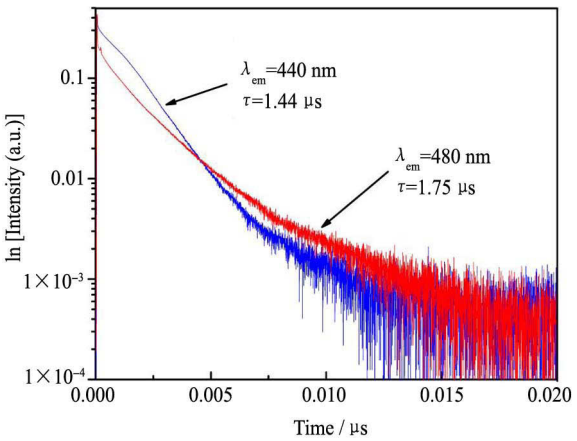

Fig. 3 Decay curves of emission bands at 440 and 480 nm in $K_2MgSi_3O_8$:$0.03Eu^{2+}$ under the excitation of 355 nm