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Synthesis and tunable luminescent properties of Eu-doped Ca_2NaSiO_4F – Coexistence of the Eu^{2+} and Eu^{3+} centers

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ABSTRACT

Novel phosphors Ca_2NaSiO_4F:Eu were synthesized successfully by the conventional solid-state method in CO atmosphere, and their spectroscopic properties in UV–vis region were investigated. The photoluminescence properties show that Eu^{3+} ions were partially reduced to Eu^{2+} in Ca_2NaSiO_4F. As a result of radiation and re-absorption energy transfer from Eu^{2+} to Eu^{3+}, both Eu^{2+} bluish-green emission at around 520 nm and Eu^{3+} red emission are observed in the emission spectra under the n-UV light excitation. Furthermore, the ratio between Eu^{2+} and Eu^{3+} emissions varies with increasing content of overall Eu. Because relative intensity of the red component from Eu^{3+} became systematically stronger, white light emission can be realized by combining the emission of Eu^{2+} and Eu^{3+} in a single host lattice under n-UV light excitation. These results indicate that the Ca_2NaSiO_4F:Eu phosphors have potential applications as a n-UV convertible phosphor for light-emitting diodes.

Introduction

Phosphor-converted white light-emitting diodes (pc-WLED) have attracted much attention in recent years for their high efficiency, reasonable cost, long lifetime and environmental friendliness [1]. As is known to all, the pc-WLED by fabricating a blue LED chip with the yellow-emitting phosphor $Y_3Al_5O_{12}:Ce^{3+}$ has some important drawbacks. Consequently, w-LEDs with a near-UV (350–420 nm) LED chip and tri-color (red, green and blue) or two complementary wavelength phosphors being fabricated were studied widely [2–4]. In consideration of the merits and drawbacks in compatibility and cost for tri-color phosphors with different hosts, it is better to develop a single-component white-light phosphor for fabricating white LED devices. Generally, single-component white-light phosphor can be obtained by two means as follows: (a) co-doping two or more activators into the same host; (2) different luminescence center from the same ion in the host, for example, different Ce^{3+} emission in one host [5–11]. This gives us an idea that it would be better if white light can be realized by two activators from the same element in different valence states. Hence, we consider exploring a single-component white-light phosphor doped with Eu^{2+} ions with bluish-green emission and Eu^{3+} ions with red emission. Recently, some Eu^{2+}/Eu^{3+} co-doped phosphors have been reported, such as in CaO [12], $Sr_2B_5O_9Cl$ [13], SrB_4O_7 [14], $Ca_3Y_2Si_3O_{12}$ [16], $LiMgPO_4$ [17], $LiBaBO_3$ [18], $Sr_{1.5}Ca_{0.5}SiO_4$ [19], and $Ba_2Lu(BO_3)_2Cl$ [20].

The detail structure of Ca_2NaSiO_4F was first reported by Andac with the orthorhombic structure, and Krüger and Kahlenberg reported another monoclinic structure [21,22]. To the best of our knowledge, until now, very few phosphors with Ca_2NaSiO_4F as host were reported. Recently, You et at reported the structure and photoluminescence properties of phosphors Ca_2NaSiO_4F:Re (Re = Eu^{2+}, Ce^{3+}, Tb^{3+}) for wLEDs, and energy transfer mechanisms for $Ce^{3+} \rightarrow Tb^{3+}$ were studied systematically [23]. In this work, we report the preparation and luminescent properties of Eu^{2+}/Eu^{3+} co-doped phosphors $Ca_2NaSiO_4F:Eu^{2+}/Eu^{3+}$. White light emission can be realized in this case by adjusting the Eu overall concentrating. It is believed that this phosphor Ca_2NaSiO_4F:Eu can act as a promising candidate for application in n-UV w-LEDs.

Experimental

The $Ca_2NaSiO_4F:x$Eu ($x = 0.01, 0.02, 0.04, 0.06, 0.08, 0.10$) phosphors were synthesized by a high-temperature solid-state reaction. The raw materials were $CaCO_3$ [analytical reagent (AR)], SiO_2 (AR), NaF (AR), and Eu_2O_3 (99.99%). The raw materials were carefully weighed stoichiometrically and ground in an agate mortar. After

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mixing and thorough grinding, the mixtures were preheated at 600 °C for 3 h in CO reducing atmosphere, then the temperature was increased to 950 °C, and kept at 950 °C for 4 h. The final products were cooled to room temperature by switching off the muffle furnace and ground again into white powder.

The phase purity and structure of the final products were characterized by a powder X-ray diffraction (XRD) analysis using Cu Kα radiation (λ = 1.5405 Å, 40 kV, 30 mA) on a PANalytilal X'pert Powder X-ray Diffractometer at room temperature (RT). The Photoluminescence properties were measured on a HITACHI F7000 fluorescence spectrometer equipped with a 450 W Xenon lamp as the excitation source. The luminescence decay spectra were measured by a FLS 920 steady-state spectrometer equipped with a fluorescence lifetime spectrometer, and a 150 W nF900 ns flash lamp was used as the flash-light source, respectively. All the measurements were performed at room temperature (RT).

Results and discussion

The phase purities of the as-prepared samples were examined by X-ray diffraction (XRD) at RT. Fig. 1 shows the XRD patterns of typical samples $Ca_2NaSiO_4F:0.01Eu^{2+}/Eu^{3+}$ (a), $Ca_2NaSiO_4F:0.06Eu^{2+}/Eu^{3+}$ (b), $Ca_2NaSiO_4F:0.10Eu^{2+}/Eu^{3+}$ (c) and the standard data. The diffraction patterns of the samples agree well with the standard data for Ca_2NaSiO_4F (JCPDS 27-1228). Hence, it can be concluded that the dopant Eu ions are completely incorporated into the host lattice by substituting for Ca^{2+} ions without making significant changes to the crystal structure.

It has been reported that Eu^{3+} ions can be partially reduced into Eu^{2+} in air or weak reduction atmosphere [12–20]. That is to say, Eu^{3+} and Eu^{2+} can coexist stably in a single host lattice. It is a good way to design white light emitting phosphors with Eu^{3+} (red emission) and Eu^{2+} (bluish–green emission) ions in a single host lattice for solid state lighting application. The photoluminescence excitation (PLE) and photoluminescence emission (PL) spectra of Ca_2NaSiO_4F:0.01Eu phosphor are presented in Fig. 2. By monitoring 520 nm emission (curve a), it can be seen that the excitation spectrum exhibits a broad band with a peak at around 356 nm, which corresponds to the 4f → 5d allowed transition of Eu^{2+}. The emission spectrum (curve b) under 356 nm excitation shows a broad band and some weak lines ranged from 570 to 700 nm. This observed broad-band emission is attributed to the $4f^65d$–$4f^7$ transition of the Eu^{2+} ions, which dovetail with the work reported by You [23]. Besides, three small narrow emission lines with peaks centered at ∼577, ∼65, ∼700 nm exist in curve b, which correspond to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+}. It indicates that Eu^{3+} ions are not reduced into Eu^{2+} ions completely. In order to prove the existence of Eu^{3+} ions in the Ca_2NaSiO_4F host, 614 nm emission line is chosen as monitoring wavelength to measure the excitation spectrum, as shown in curve c. A broad band with a maximum at ∼268 nm and several sharp lines can be seen in curve c. The broad band should be assigned to the charge transfer transition between oxygen ligand and Eu^{3+}. The sharp peaks in the range of 300–500 nm are attributed to the $4f^6$–$4f^6$ intraconfiguration transitions of Eu^{3+} ions. Therefore, it can be confirmed that both Eu^{2+} and Eu^{3+} ions exist in the Ca_2NaSiO_4F host. Fig. 2(d) shows the emission under the excitation of 268 nm which is corresponds to the Eu^{3+} charge transfer band. The Eu^{3+} characteristic emissions can be observed clearly in the emission spectrum (curve d). It should be noted that the excitation spectrum (Fig. 2c) shows no absorption at 356 nm wavelength. It means that 356 nm light can hardly excite Eu^{3+} ions directly. So why Eu^{3+} emissions can be detected upon 356 nm excitation in Fig. 2b? We believe that the energy transfer from Eu^{2+} to Eu^{3+} could be the only reason. However, we should be also aware that Eu^{2+} excitation band cannot be detected by monitoring Eu^{3+} 614 nm emission as shown in Fig. 2c. So it is concluded that the energy transfer of Eu^{2+} to Eu^{3+} is by means of radiation and reabsorption. This is not surprising, because overlap between the excitation spectrum of Eu^{2+} and emission spectrum of Eu^{3+} can be clearly seen at around 465 nm in this case.

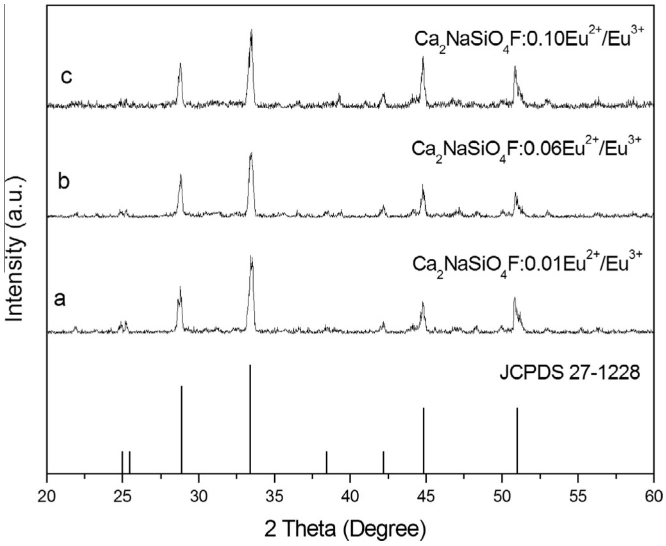

Fig. 1. XRD patterns of samples $Ca_2NaSiO_4F:xEu^{2+}/Eu^{3+}$ (a: x = 0.01; b: x = 0.06; c: x = 0.10).

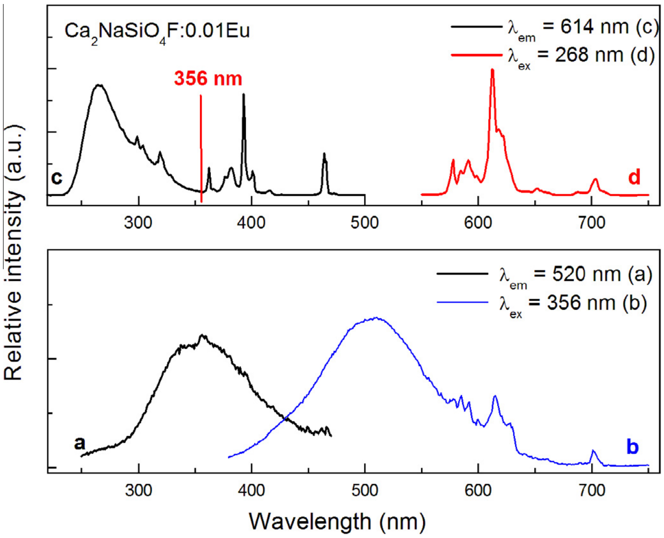

Fig. 2. PLE (a: λ_{em} = 520 nm; c: λ_{em} = 614 nm) and PL (b: λ_{ex} = 356 nm; d: λ_{ex} = 268 nm) spectra of sample Ca_2NaSiO_4F:0.01Eu.

Luminescence spectra of samples $Ca_2NaSiO_4F:x$Eu under 356 nm excitations are presented in Fig. 3. As mentioned above, the short-wavelength part of the spectra, bluish-green broad band emission with a maximum about 510 nm is attributed to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}, while the series of sharp peaks located in the long-wavelength range is ascribed to the $^5D_0 \rightarrow {}^7F_J$ transitions of Eu^{3+}. Furthermore, the relative intensity of Eu^{3+} versus Eu^{2+} luminescence vary with the doping content of overall Eu. To observe directly the relative emission intensity variation, the intensities of Eu^{2+} and Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$ transition) as a function of the overall Eu content are given in Fig. 4. With the overall Eu concentration increasing, it can be seen that the relative emission intensities of Eu^{2+} ions decrease systematically, while those of