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journal homepage: www.journals.elsevier.com/results-in-physicsSynthesis and tunable luminescent properties of Eu-doped $\text{Ca}_2\text{NaSiO}_4\text{F}$ – Coexistence of the Eu^{2+} and Eu^{3+} centersMubiao Xie ^{a,*}, Dongyu Li ^b, Guoxian Zhu ^a, Rongkai Pan ^a, Xionghui Fu ^c^a Institute of Physical Chemistry, School of Chemistry and Chemical Engineering, Lingnan Normal University, Zhanjiang 524048, China^b School of Physics Science and Technology, Lingnan Normal University, Zhanjiang 524048, China^c Department of Chemistry, Jinan University, Guangzhou 510632, China

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ABSTRACT

Novel phosphors $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{Eu}$ 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 $\text{Ca}_2\text{NaSiO}_4\text{F}$. 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 $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{Eu}$ phosphors have potential applications as a n-UV convertible phosphor for light-emitting diodes.

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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 $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ 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 $\text{Eu}^{2+}/\text{Eu}^{3+}$ co-doped phosphors have been reported, such as in CaO [12], $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ [13], SrB_4O_7 [14], $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$ [16], LiMgPO_4 [17], LiBaBO_3 [18], $\text{Sr}_{1.5}\text{Ca}_{0.5}\text{SiO}_4$ [19], and $\text{Ba}_2\text{Lu}(\text{BO}_3)_2\text{Cl}$ [20].

The detail structure of $\text{Ca}_2\text{NaSiO}_4\text{F}$ 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 $\text{Ca}_2\text{NaSiO}_4\text{F}$ as host were reported. Recently, You et al reported the structure and photoluminescence properties of phosphors $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{Re}$ (Re = Eu^{2+} , Ce^{3+} , Tb^{3+}) for wLEDs, and energy transfer mechanisms for $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ were studied systematically [23]. In this work, we report the preparation and luminescent properties of $\text{Eu}^{2+}/\text{Eu}^{3+}$ co-doped phosphors $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{Eu}^{2+}/\text{Eu}^{3+}$. White light emission can be realized in this case by adjusting the Eu overall concentration. It is believed that this phosphor $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{Eu}$ can act as a promising candidate for application in n-UV w-LEDs.

Experimental

The $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{xEu}$ ($x = 0.01, 0.02, 0.04, 0.06, 0.08, 0.10$) 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 K α radiation ($\lambda = 1.5405 \text{ \AA}$, 40 kV, 30 mA) on a PANalytical 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 $\text{Ca}_2\text{NaSiO}_4\text{F}:0.01\text{Eu}^{2+}/\text{Eu}^{3+}$ (a), $\text{Ca}_2\text{NaSiO}_4\text{F}:0.06\text{Eu}^{2+}/\text{Eu}^{3+}$ (b), $\text{Ca}_2\text{NaSiO}_4\text{F}:0.10\text{Eu}^{2+}/\text{Eu}^{3+}$ (c) and the standard data. The diffraction patterns of the samples agree well with the standard data for $\text{Ca}_2\text{NaSiO}_4\text{F}$ (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 $\text{Ca}_2\text{NaSiO}_4\text{F}:0.01\text{Eu}$ 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 $4f \rightarrow 5d$ 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 $4f^65d-4f^7$ tran-

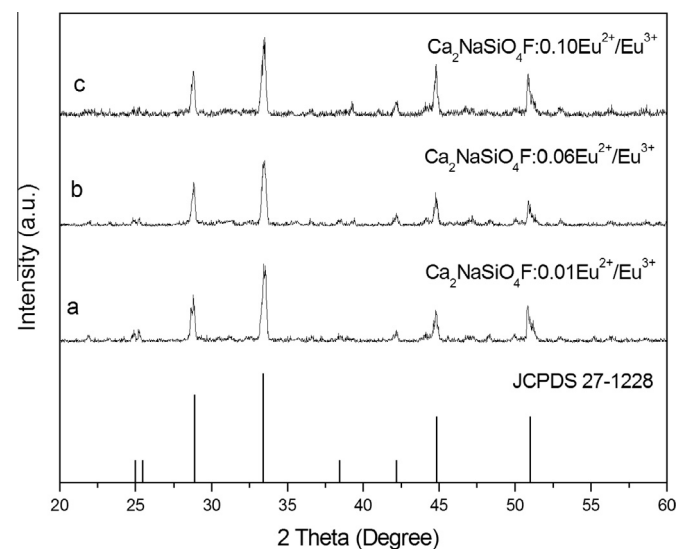


Fig. 1. XRD patterns of samples $\text{Ca}_2\text{NaSiO}_4\text{F}:x\text{Eu}^{2+}/\text{Eu}^{3+}$ (a: $x = 0.01$; b: $x = 0.06$; c: $x = 0.10$).

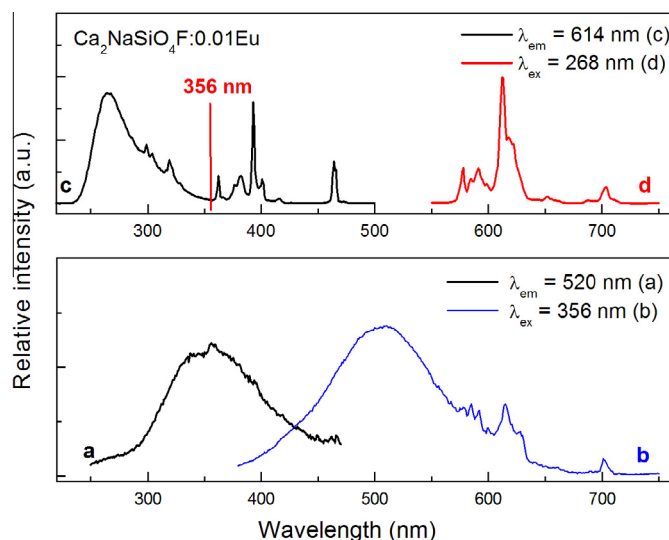


Fig. 2. PLE (a: $\lambda_{\text{em}} = 520 \text{ nm}$; c: $\lambda_{\text{em}} = 614 \text{ nm}$) and PL (b: $\lambda_{\text{ex}} = 356 \text{ nm}$; d: $\lambda_{\text{ex}} = 268 \text{ nm}$) spectra of sample $\text{Ca}_2\text{NaSiO}_4\text{F}:0.01\text{Eu}$.

sition 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 , $\sim 700 \text{ nm}$ exist in curve b, which correspond to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ 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 $\text{Ca}_2\text{NaSiO}_4\text{F}$ 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 $\sim 268 \text{ nm}$ 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 $\text{Ca}_2\text{NaSiO}_4\text{F}$ 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 re-absorption. 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.

Luminescence spectra of samples $\text{Ca}_2\text{NaSiO}_4\text{F}:x\text{Eu}$ 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 ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ 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+} (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ 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

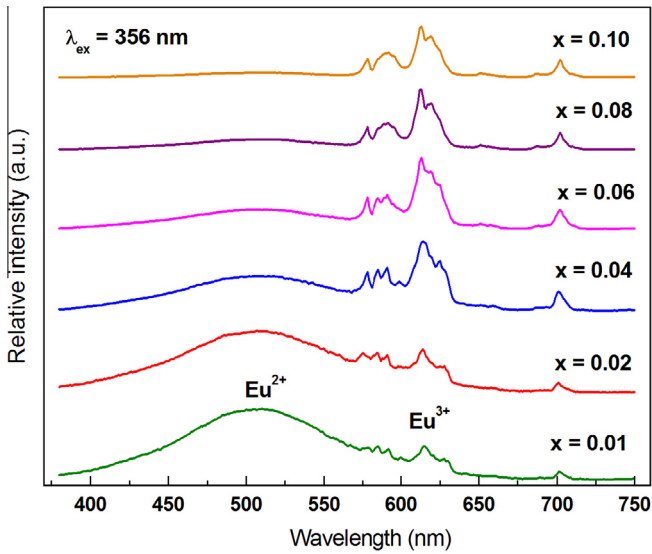


Fig. 3. PL spectra of samples $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{xEu}$ ($x = 0.01, 0.02, 0.04, 0.06, 0.08, 0.10$) under 356 nm excitation.

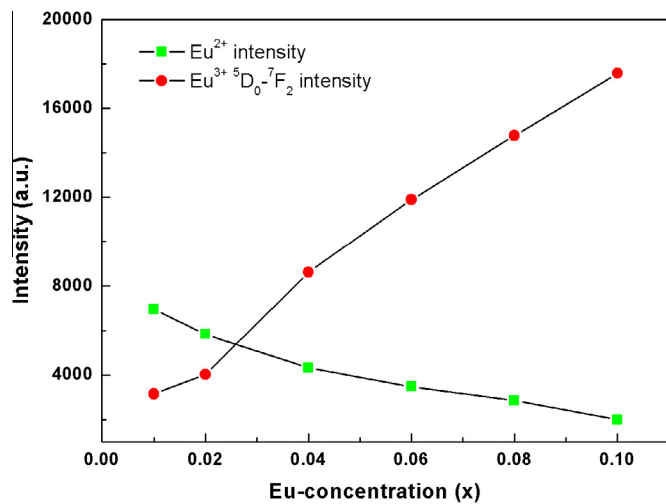


Fig. 4. Emission intensities of Eu^{2+} and Eu^{3+} (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) as a function of the overall Eu content (x value).

Eu^{3+} increase distinctly. There should be three reasons for this intensity variation [15]: (a) concentration quenching of Eu^{2+} ions; (b) the increasing difficulty of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reduction with increasing content of the Eu; (c) energy transfer from Eu^{2+} to Eu^{3+} occurs. However, it still needs to be pointed out that the reason for why the difficulty increases in the reduction process is not clear in the present experiment. Further work should be done to reveal it.

In general, if the radiative energy transfer works, the decay time of the sensitizer remains constant with increasing concentrations of the activator [24]. Fig. 5 presents the decay curves of the Eu^{2+} emission in $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{xEu}$ ($x = 0.01, 0.10$) upon excitation at 356 nm. We find that the two decay curves for different Eu concentration samples overlap each other, with a similar decay time about 235 ns, which further proves that the mechanism of $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ energy transfer is considered to be the radiation and re-absorption, but not the resonance non-radiative energy transfer.

The CIE chromaticity diagram and CIE chromaticity coordinates for the $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{xEu}$ ($x = 0.01, 0.02, 0.04, 0.06, 0.08, 0.10$) phosphors upon excitation at 356 nm were calculated through emission spectra, and shown in Table 1 and Fig. 6, respectively. It appears

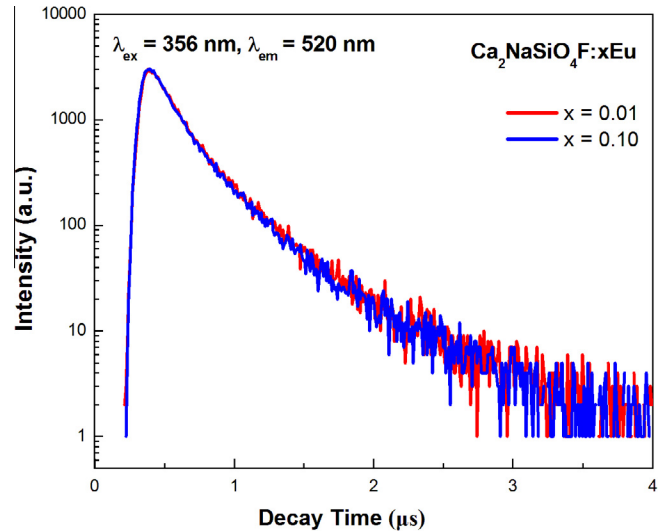


Fig. 5. Decay curves for Eu^{2+} emission in $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{xEu}$ samples ($\lambda_{\text{ex}} = 356$ nm, $\lambda_{\text{em}} = 520$ nm).

Table 1

CIE chromaticity coordinates for $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{xEu}$ upon excitation at 356 nm.

Samples Number	Eu concentration (x)	Chromaticity coordinates
1	0.01	(0.259, 0.384)
2	0.02	(0.283, 0.284)
3	0.04	(0.356, 0.381)
4	0.06	(0.415, 0.377)
5	0.08	(0.461, 0.377)
6	0.10	(0.527, 0.377)

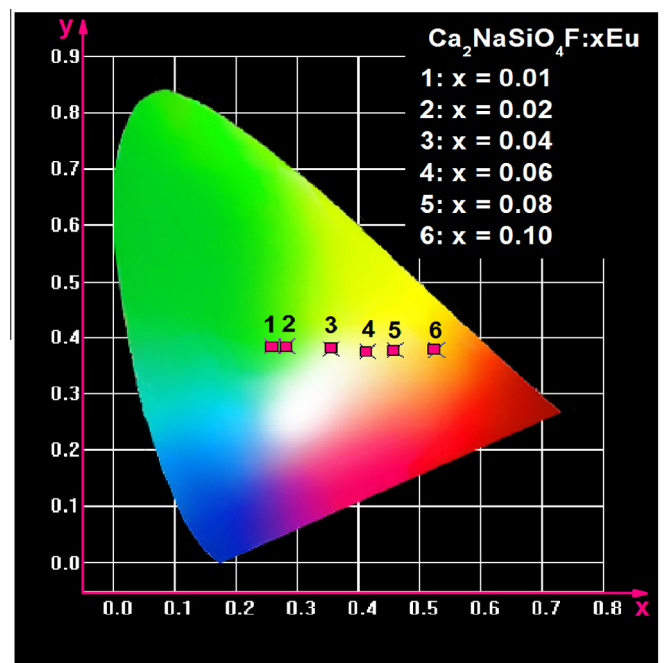


Fig. 6. CIE chromaticity diagram for samples $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{xEu}$ under 356 nm excitation: 1: $x = 0.01$; 2: $x = 0.02$; 3: $x = 0.04$; 4: $x = 0.06$; 5: $x = 0.08$; 6: $x = 0.10$.

that the emission color can be tunable by controlling the Eu overall concentration. As the x value increases from 0.01 to 0.10, the corresponding emission color of the phosphors shifts from bluish-green to white and eventually to orange-red. In particular,

by controlling Eu overall concentration at $x=0.10$, a white light emission with CIE coordinates of (0.356, 0.381) is realized as shown in points 3 in Fig. 6. Even though the white light point in this case deviates from the regular white light point (0.333, 0.333) a little, it is still a fact that the phosphors $\text{Ca}_2\text{NaSiO}_4\text{F:Eu}$ may be a potential single-component white-light phosphor for n-UV LEDs, because CIE coordinates can be further improved by making fine adjustments of Eu overall concentration.

Conclusions

In summary, bivalent Eu^{2+} and trivalent Eu^{3+} ions were detected together in a novel phosphors $\text{Ca}_2\text{NaSiO}_4\text{F:Eu}$ by UV–vis luminescence spectroscopy. The blue emission of Eu^{2+} at around 520 nm and red emission of Eu^{3+} appears simultaneously upon excitation at 356 nm due to radiative energy transfer from Eu^{2+} to Eu^{3+} . The relative intensity of Eu^{3+} versus Eu^{2+} luminescence gets higher and higher. Hence, the emission color of $\text{Ca}_2\text{NaSiO}_4\text{F:xEu}$ changes continuously from bluish-green to white and eventually to orange-red as the concentration of the Eu increases. The present results show that the $\text{Ca}_2\text{NaSiO}_4\text{F:Eu}$ phosphor can act as a single-component white-light phosphor for wLEDs.

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