

Synthesis and luminescent properties of blue-emitting phosphors $\text{Ca}_2\text{SiO}_2\text{F}_2:\text{Ce}^{3+}$ for solid state lighting

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Novel blue-emitting phosphors $\text{Ca}_2\text{SiO}_2\text{F}_2:x\text{Ce}^{3+}$ were synthesized by a solid state reaction technique at high temperature, and the luminescence properties were investigated in detail. The $\text{Ca}_2\text{SiO}_2\text{F}_2:x\text{Ce}^{3+}$ phosphors show intense absorption at UV region and exhibit blue emission at ~ 455 nm under 365 nm excitation. The quenching concentration of Ce^{3+} in $\text{Ca}_2\text{SiO}_2\text{F}_2:x\text{Ce}^{3+}$ phosphors is about 1 mol%. The results indicate that the $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ phosphor has a potential application in white light emitting diodes (w-LEDs).

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1. Introduction

Nowadays, white light emitting diodes (w-LEDs) have been considered as the fourth-generation lighting source, which will take the place of conventional fluorescent lamps in the near future [1-5]. For phosphors converted w-LEDs, white light can be generated mainly in two ways: 1) Fabricate a blue LED chip with the yellow-emitting phosphor $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$; 2) Fabricate an ultraviolet (UV) or near-UV (350–420 nm) LED chip with tri-color (red, green and blue) phosphors. In consideration of the advantages in color-rendering index and color temperature, the UV or n-UV based w-LEDs are more favored recently [6-8]. Therefore, it is necessary to develop new tri-color emitting phosphors with good stabilities and highly efficient under excitation wavelength in the range of 350-420 nm.

As an efficient activator with intense absorption and emission broadband due to $4f^1-5d^1$ transitions, many Ce^{3+} ion doped phosphors for w-LEDs application have been developed, such as $\text{YAG}:\text{Ce}$ [9], $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+}$ [10], $(\text{Ca},\text{Sr},\text{Ba})\text{Si}_2\text{O}_2\text{N}_2$ [11], $\text{Ca}_2\text{NaSiO}_4\text{F}:\text{Ce}^{3+}$ [12], $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2:\text{Ce}^{3+}$ [13], $\text{Li}_2\text{SrSiO}_4:\text{Ce}^{3+}$ [14], $\text{Ca}_2\text{Gd}_8(\text{SiO}_4)_6\text{O}_2:\text{Ce}^{3+}$ [15], $\text{Sr}_3\text{AlO}_4\text{F}:\text{Ce}^{3+}$ [16], and so on. Recently, much attention has been paid for phosphors containing fluoride ions for low phonon energy in F anions and the efficient emission due to the minor quenching process from multi-phonon relaxation [13]. In this work, we report the preparation and luminescent properties of novel F-containing phosphors $\text{Ca}_2\text{SiO}_2\text{F}_2:x\text{Ce}^{3+}$. It is believed that the blue-emitting

phosphor $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ can act as a promising candidate for application in white light emitting diodes (w-LEDs).

2. Experimental

The $\text{Ca}_2\text{SiO}_2\text{F}_2:x\text{Ce}^{3+}$ ($x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.03$) phosphors were synthesized by a high-temperature solid-state reaction. The raw materials were CaCO_3 [analytical reagent (AR)], SiO_2 (AR), NH_4F (A.R), and CeO_2 (99.99%). The raw materials were carefully weighed stoichiometrically and ground in an agate mortar. After mixing and thorough grinding, the mixtures were preheated at 600 °C for 3 h in CO reducing atmosphere, then the temperature was increased to 850 °C, and kept at 850 °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 $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$, 40 kV, 30 mA) on a Rigaku D/max 2200 vpc 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. All the measurements were performed at room temperature (RT). The external quantum efficiency (QE) of the samples was measured by QY-2000 equipped with 365 nm LED lamp.

3. 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 sample $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ and the standard data. The diffraction patterns of the samples agree well with the standard data $\text{Ca}_2\text{SiO}_2\text{F}_2$ (JCPDS 19-1131). Hence, it can be concluded that the dopant Ce^{3+} ions are completely incorporated into the host lattice by substituting for Ca^{2+} ions without making significant changes to the crystal structure. So the chemical formulas of Ce^{3+} -doped phosphors $\text{Ca}_{2-x}\text{Ce}_x\text{SiO}_2\text{F}_2$ are written as $\text{Ca}_2\text{SiO}_2\text{F}_2:x\text{Ce}^{3+}$ for convenience in the latter discussion.

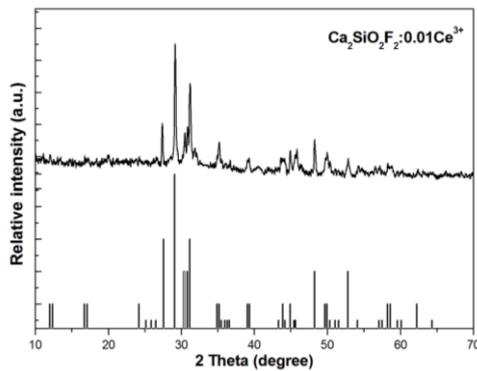


Fig. 1. XRD patterns of sample $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ and the standard pattern of ICSD-19-1131

Fig. 2 presents the UV excitation and emission spectra of $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ phosphor. As shown in curve a of Fig. 2, the excitation spectrum monitored at 450 nm consists of two distinct bands at ~ 365 nm (marked as A), ~ 330 nm (marked as B) and a weak band at ~ 270 nm (marked as C) from 250 to 430 nm wavelength region. These three broad bands are attributed to the transition of Ce^{3+} ions from the ground states to different 5d excited state. In addition, a tail at the spectrum edge (~ 250 nm) may be the result of the instrumental response. More interestingly, the strongest absorption band A shows maximum peak at about 368 nm, which matches well with the n-UV LED chips.

As shown in curve b of Fig. 2, the emission spectrum of $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ under excitation at 365 nm exhibits a blue emission with a maximum peak at ~ 456 nm within the wavelength range 390-600 nm. The broad band is due to 5d \rightarrow 4f transition of the Ce^{3+} ions. Usually, the emission of Ce^{3+} ions in a specific lattice site occurs as doublet bands relating to the transitions from the lowest 5d excited state to the $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ spin-orbit split 4f ground states. The energy separation of the two bands corresponds to the usual spin-orbit splitting of 2000 cm^{-1} [17]. The Gaussian fit curves of the emission spectrum are shown in Fig. 2. Clearly, the emission curve can be fitted well by a sum of two Gaussian functions

with maxima at 453 nm and 501 nm. So, the energy difference is 2115 cm^{-1} for the doublet emissions of Ce^{3+} ions. At the same time, the Stokes shift, which is defined as the difference between the maximum of the lowest excitation band and that of the highest emission band, can be calculated to $5.10 \times 10^3\text{ cm}^{-1}$ in this case.

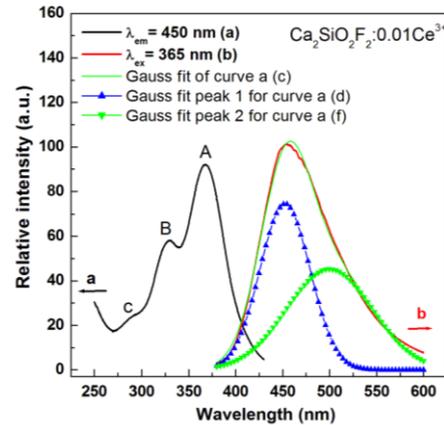


Fig. 2. UV excitation spectrum (a: $\lambda_{em} = 450$ nm) and emission spectrum (b: $\lambda_{ex} = 365$ nm) of $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ phosphors

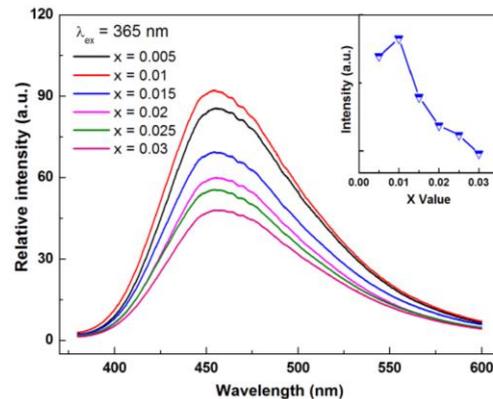


Fig. 3. Emission spectra of $\text{Ca}_2\text{SiO}_2\text{F}_2:x\text{Ce}^{3+}$ phosphors under 365 nm excitation. The right inset shows the dependence of PL intensity on the Ce^{3+} doping concentration (x value)

The emission spectra of the phosphors $\text{Ca}_2\text{SiO}_2\text{F}_2:x\text{Ce}^{3+}$ ($x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.03$) under excitation at 365 nm are shown in Fig. 3. All the emission spectra have similar spectral shape except for the emission intensities. The right inset of Fig. 3 shows the dependence of PL intensity on the Ce^{3+} doping concentration. It is observed that the optimum doping concentration of Ce^{3+} is 1 mol% ($x = 0.01$). The emission intensity first increases and reaches a maximum at $x = 0.01$, and then decreases obviously as the concentration of Ce^{3+} is increased due to the concentration quenching effect of Ce^{3+} ions. The quenching mechanism of Ce^{3+} ions can be estimated by the following equation (1) [18, 19]:

$$I/x = k[1 + \beta(x)^{\theta/3}]^{-1} \quad (1)$$

Here, I is the emission intensity, x is the concentration of activator ions (Ce^{3+}), k and β are constants under the same excitation condition, and θ relates to the multipole–multipole interaction type. When the value of θ are 6, 8, or 10, the interaction type corresponds to dipole–dipole (d–d), dipole–quadrupole (d–q), or quadrupole–quadrupole (q–q), respectively. To get the θ value, the $\lg(I/x)$ and $\lg(x)$ are calculated and plotted in Fig. 4. Obviously, an approximate linear relation between $\lg(I/x)$ and $\lg(x)$ can be found. The slope of the straight line is calculated to be -1.33 which equals $-\theta/3$ according to equation (1). Thus, the value of θ is 4, which is closer to 6, suggesting that the quenching mechanism of Ce^{3+} ions in $\text{Ca}_2\text{SiO}_2\text{F}_2:x\text{Ce}^{3+}$ phosphors is dipole–dipole interactions.

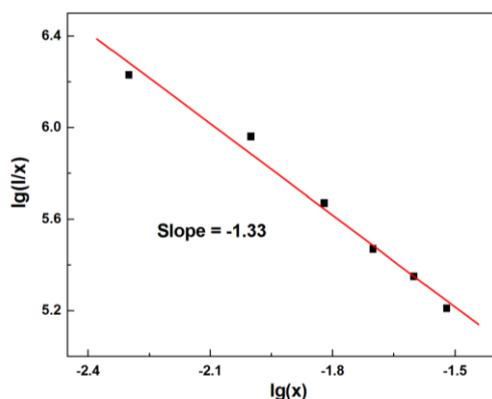


Fig. 4. The curve of $\lg(x)$ versus $\lg(I/x)$ of $\text{Ca}_2\text{SiO}_2\text{F}_2:x\text{Ce}^{3+}$ phosphors

The CIE chromaticity diagram for the sample $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ under 365 nm excitation is shown in Fig. 5. The color coordinate is calculated to be ($x = 0.164$, $y = 0.190$). The inset also shows the photograph of $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ phosphor taken under 365 nm excitation in a UV lamp, and its intense blue emission can be clearly observed, indicating that this phosphor can be used as a potential blue-emitting phosphor for w-LEDs application.

The external quantum efficiency of sample $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ was also measured to evaluate the phosphors. The external quantum efficiencies of $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ was measured to be 58.86%. The quantum efficiency may be improved by optimizing the particle size, size distribution, morphology and crystalline defects of the phosphors.

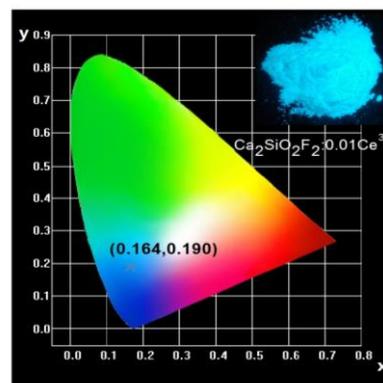


Fig. 5. Color coordinates of $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ in the CIE chromaticity diagram and the inset shows a photograph of the blue-emitting phosphor $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ taken under 365 nm excitation in a UV lamp

4. Conclusions

In summary, a new series of blue-emitting phosphors $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2:x\text{Ce}^{3+}$ were synthesized and their luminescent properties were studied. The phosphors $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2:x\text{Ce}^{3+}$ show strong broad absorption bands in the UV range, and show blue emissions upon 365 nm excitation. The optimal doping concentration of Ce^{3+} is 1 mol%, and the concentration quenching mechanism is determined to be dipole–dipole interaction. The CIE coordinates are ($x = 0.153$, $y = 0.169$). The external quantum efficiency of sample $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ was measured to be 58.86%. Hence, it is believed that the as-prepared phosphors $\text{Ca}_2\text{SiO}_2\text{F}_2:0.01\text{Ce}^{3+}$ can be considered as potential blue-emitting components for n-UV based LEDs.

Acknowledgments

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