Near-ultraviolet excitable pseudo-wollastonite α-$CaSiO_3$: Eu^{2+} blue phosphor for white light-emitting diodes

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Pseudo-wollastonite α-$CaSiO_3$ doped with Eu^{2+} was obtained through one-step calcination of precursors prepared by chemical co-precipitation method. This phosphor emits a strong blue band peaking at 449 nm with full width at half maximum of about 35 nm under the excitation at 365 nm. The blue luminescence originates from the allowed f-d transition of Eu^{2+} ions on Ca^{2+} sites. The energy transfer of Eu^{2+} in pseudo-wollastonite α-$CaSiO_3$:Eu^{2+} phosphor has been demonstrated to be a resonant type via a dipole-dipole mechanism. α-$CaSiO_3$:Eu^{2+} phosphor shows higher thermally stable luminescence which was found to be better than commercially available $Y_3Al_5O_{12}$:Ce^{3+} phosphor.

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1. Introduction

Recently, more and more attention is focused on white light emitting diodes (LEDs) as potential applications in the fields of flat panel displays and lighting sources because of their high luminescent efficiency, excellent chemical and thermal stability, long lifetime, and environmental friendly characteristics [1-6]. In order to obtain higher color temperature and color rendering [7-10], the common way to produce white light is through matching tri-color phosphors excited by ultraviolet (UV) or near-UV LED chips as a replacement for YAG:Ce phosphor excited by blue LED chips. However, the emission efficiency of current phosphor ($BaMgAl_{10}O_{17}$:Eu^{2+}) [11,12], as a blue component, is poor in this tri-color system because of the low luminous efficiency and the strong re-absorption of the blue light by the red or green-emitting phosphors. Therefore, it is necessary to search a novel blue phosphor.

Pseudo-wollastonite α-$CaSiO_3$ is an important phase in experimental petrology and commonly occurs in slags, cements and ceramic materials [13,14]. α-$CaSiO_3$ (CS) has a triclinic structure with a space group of C-1(2). The structure is characterized by four layers, one of which is composed of ternary rings of three tetrahedral of Si_3O_9 and a seemingly octahedral layer. The ternary rings are elongated in the stacking direction, while the octahedral layers are contracted in the same direction. Accordingly, Ca atoms are coordinated with eight O atoms instead of six. In this letter, we investigated the luminescence properties and demonstrated that energy transfer (ET) in α-$CaSiO_3$:Eu^{2+} phosphor was through a resonant type via a dipole-dipole mechanism. Furthermore, the luminescence intensity and decay time measurements were performed as a function of temperature. This could be helpful in understanding the mechanisms responsible for the quenching of luminescence at high temperatures and in developing new materials that have potential application for white LEDs.

2. Experiments

A series of $Ca_{1-x}Eu_xSiO_3$ (x=0.06, 0.08, 0.10, 0.12, 0.14, 0.16) samples were prepared by chemical co-precipitation method. $Ca(NO_3)_2$•$4H_2O$ (analytical reagent (AR)), Na_2SiO_3(AR) and Eu_2O_3(99.99%) were used as raw materials. Firstly, Eu_2O_3 was added into dilute nitric acid and heated to obtain $Eu(NO_3)_3$. $Ca(NO_3)_2$•$4H_2O$ and Na_2SiO_3 were dissolved in deionized water respectively and mixed with the above solution. The mixture was stirred and heated at 353 K for 1h, and then an appropriate amount of precipitator was added. Finally, CS:Eu^{2+} phosphor was obtained after the precipitate was dried at 373 K for several hours and calcined at 1373 K for 2h in reducing atmosphere.

The phase structure was identified by X-Ray diffraction (XRD) analysis using X'Pert PRO advanced automatic diffractometer with Cu K_α radiation operated at 25 kV and 25 mA. Photoluminescence spectra and decay time curves were checked using a Hitachi F-4600 florescence spectrometer (scanning rate=1200 nm/min, slit width = 5 nm, and PMT voltage = 400 V). The chromaticity coordinates of the samples were measured on a photoelectric color integrated test system (HSP-6000, HongPu, China).

3. Results and discussions

The photoluminescence excitation (PLE) and photoluminescence (PL) spectra of the CS:Eu^{2+} (8 at%) are represented in Fig. 1. The PLE spectrum monitored at 449 nm shows a broad band ranging from 240 to 410 nm, which can be attributed to the 4f5d multiplet excited states of the Eu^{2+} ions. It suggests that the CS:Eu^{2+} phosphor can be effectively excited by UV or near-UV LED. The PL spectrum exhibits a strong blue emission band centered at about 449 nm with full width at half maximum about 35nm under the excitation at 365 nm, which corresponds to the typical $4f^65d^1 \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+} ions substituted for Ca^{2+} sites. The characteristic emission peaks of Eu^{3+} ions are not observed in Fig. 1, which exhibits sharp lines between 580 and 650 nm. This suggests that the Eu ion in the α-$CaSiO_3$ host exists as the divalent state. Generally, the Stokes shift of the Eu^{2+} emission is defined as the difference between the energy of the $4f^7(^8S_{7/2})$-$4f^6(^7F_0)5d^1$ transition and the emission energy [15]. The Stokes shift is calculated to be 0.6355 eV for CS:Eu^{2+} phosphor. Moreover, the energy of the zero-phonon line E_0 at the intersection of the emission and excitation spectra was estimated to 2.90 eV (427 nm) [16]. The zero-line corresponds to a transition between purely electronic states.

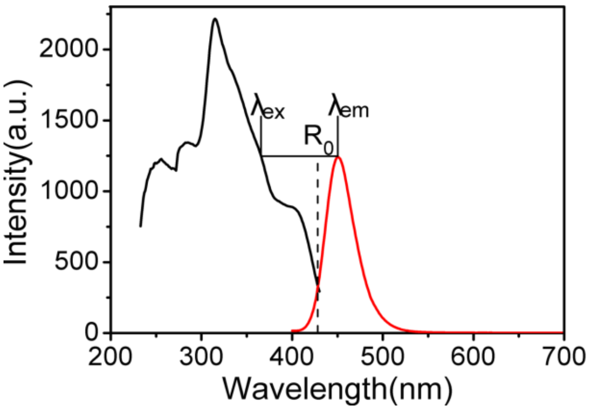

Fig. 1. Excitation and emission spectra of the CS:Eu^{2+} (8 at%) (color online)

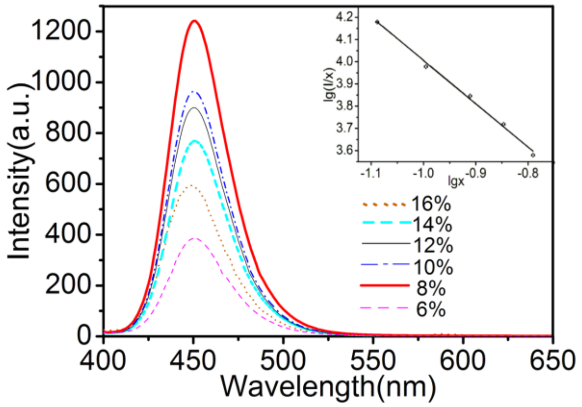

Fig. 2. Emission spectra of α-$Ca_{1-x}SiO_3$:xEu^{2+} using 365 nm excitation at room temperature; the inset plots lg(I/x)-lgx of α-$Ca_{1-x}SiO_3$:xEu^{2+} phosphors (color online)

Fig. 2 represents the PL spectra of CS:Eu^{2+} phosphors with different Eu^{2+} doping concentrations. As the content of Eu^{2+} increases from 0.06 to 0.16 mol, the emission intensity increases sharply at first, then gets to a maximum with the doped concentration of 0.08 mol Eu^{2+} and decreases gradually thereafter because of concentration quenching effect. According to Dexter's theory [17], if the energy transfer (ET) occurs between the same sorts of activators, the intensity of multipolar interaction can be determined from the change of the emission intensity from the emitting level which has the multipolar interaction. The emission intensity (I) per activator ion follows the equation [18],

$$\frac{I}{x} = K[1+\beta(x)^{Q/3}]^{-1} \tag{1}$$

where x is the activator concentration; Q = 6, 8 or 10 for dipole-dipole, dipole-quadrupole or quadrupole -quadrupole interactions, respectively; and K and β are constant at the same excitation conditions for a given host crystal. When x is larger than the critical quenching concentration, Eq. (1) can approximately be reduced to Eq. (2) for $\beta(x)^{Q/3} >> 1$, where C is a constant [19],

$$\lg(I/x) = C - (Q/3)\lg x \tag{2}$$

The *lg(I/x)-lgx* plots are shown in the inset of Fig. 2. It can be seen that the concentration dependence curve is linear and the slope is -1.96. The value of Q can be calculated as 5.88, which is approximately 6. It can be conducted that dipole-dipole interaction is dominant in the energy transfer mechanism of Eu^{2+} in α-$CaSiO_3$:Eu^{2+} phosphor.

For electric dipole-dipole mechanism, the critical transfer distance (Rc) of ET between two Eu^{2+} ions is approximately equal to twice the radius of a sphere with this volume [20, 21],

$$R_c \approx 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3} \tag{3}$$

where x_c is the critical concentration, N is the number of cations in the unit cell and V is the volume of the unit cell. The unit cell volume was 1603.68 $Å^3$ in Ref. [14]. The quenching concentration is used as the critical concentration x_c. The number of formula units per unit cell is 22. Therefore, the R_c of ET in α-$CaSiO_3$ phosphor was calculated to be about 12.03 Å.

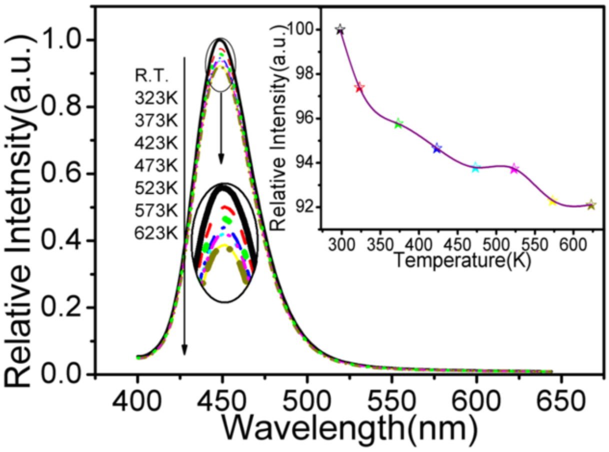

Fig. 3. The emission spectra of CS:Eu^{2+} at various temperatures. The inset is the temperature dependence of the emission intensity (color online)

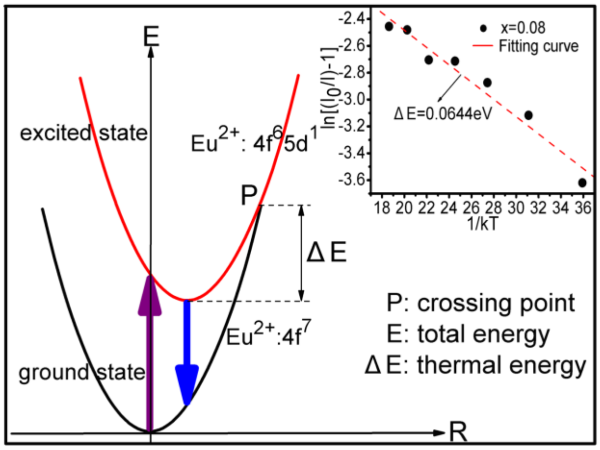

Fig. 4. Configuration coordinate diagram of Eu^{2+} in α-CaSiO$_3$-based phosphors. Inset: Plot of activation energy for thermal quenching of CS:Eu^{2+} (color online)

Fig. 3 shows the thermal quenching of luminescence spectra of CS:Eu^{2+} (8 at%) at different temperatures from room temperature (R.T.) to 623 K. With the temperature increasing, the emission intensity decreases gradually. When the temperature is up to 423 K and 623 K, the normalized emission intensity of CS:Eu^{2+} is decreased to 94.65% and 92.10% of the initial value (R.T.) respectively, as illustrated in the inset of Fig. 3. Liu et al. [22] reported that the normalized emission intensity of LiSr$_{0.95}$PO$_4$:Eu$_{0.05}$$^{2+}$ is decreased to 77.5% of the initial value (273 K) with increasing temperature up to 450 K, whereas it is decreased to 82.0% for commercially available Y$_3$Al$_5$O$_{12}$:Ce^{3+} phosphor. Tang et al. [23] reported that the relative emission intensity of KSr$_{0.995}$PO$_4$:Eu$_{0.005}$ dropped to 10% of the initial value at 423 K. The results in this experiment indicate that this quenching effect is better than the reported results in Eu^{2+} doped phosphors as mentioned above. It can be seen that the optimized CS:Eu^{2+} (8 at%) phosphor has comparatively low thermal quenching effect. This quenching mechanism can be explained through the configuration coordinate diagram as depicted in Fig. 4. In the simple oscillator model, the ground and excited states of the activator can be presented by two parabolas in the configuration coordinate diagram. The electrons in the excited states of Eu^{2+} can cross the intersection point (P) between the ground state and the excited state in a configuration coordinate diagram. After crossing P from the excited state, the electrons return to the ground state through heat dissipation rather than light emission. The probability of nonradiative transition via thermal activation strongly depends on temperatures, and the probability of nonradiative transition per unit time (*f*) is expressed as the following equation [24],

$$f \approx \frac{\tau_0}{\tau_v}\exp\left(\frac{-\Delta E}{kT}\right) \tag{4}$$

where τ_0 is the attempt rate for thermal quenching, τ_v is the radiative decay rate of the 5d state of Eu^{2+}, τ_0/τ_v is the frequency factor, ΔE is the activation energy for thermal quenching, and k is Boltzmann's constant, T is Kelvin temperature. The attempt rate τ0 has similar magnitude as the maximum phonon frequency (typically 3×1013 Hz corresponding with phonon energies of 1000 cm^{-1}) in compounds. The radiative decay rate (τ_v) of the 5d-4f emission in Eu^{2+} is typically 1.1×106 Hz. Because τ_0/τ_v, k and ΔE are constant in this phosphor system, it is clear that higher temperatures lead to greater probability of nonradiative transition, thereby causing a decrease in the emission intensity of the phosphors. To investigate the activation energy for thermal quenching, the Arrhenius equation is frequently used to fit the thermal quenching data [25],

$$I \approx \frac{I_0}{1+f} \tag{5}$$

where I is the intensity at a given temperature, I_0 is the initial intensity, f is the frequency of nonradiative transition and its influencing factor is seen in Eq.(4). As shown in the inset of Fig. 4, the plot of ln[(I_0/I)-1] vs 1/(kT) indicates a linear relation, and the activation energy (ΔE) is evaluated to be 0.0644 eV for CS:Eu^{2+} (8 at%) phosphor.

The chromaticity diagram established by the Commission Internationale de l'Eclairage (CIE) in 1931 is a two-dimensional graphical representation of any color perceivable by the human eye on an x–y plot. Fig. 5 shows the CIE chromaticity coordinates of the samples excited at 365 nm at various temperatures (from R.T. to 623 K). The CIE coordinates shift slightly from (0.156, 0.058) to (0.156, 0.057). This change in CIE Chromaticity coordinates with the temperature increasing is hardly observed, which may be due to the excellent thermal stability on temperature quenching effects in CS:Eu^{2+} phosphors.

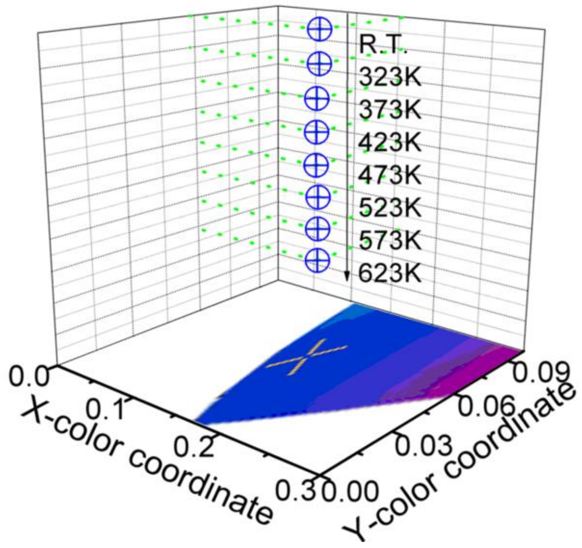

Fig. 5. CIE chromaticity coordinates of CS:Eu^{2+} phosphors at various temperature (color online)

4. Conclusions

The luminescence properties of α-$CaSiO_3$:Eu^{2+} blue emitting phosphors were investigated for applications to white LEDs. The energy transfer of Eu^{2+} is dominated by resonance-type dipole-dipole interaction. The phosphor showed excellent thermal luminescence stability better than commercially available YAG phosphor. The present letter indicates that the α-$CaSiO_3$:Eu^{2+} phosphor can be a promising candidate phosphor for white LEDs.

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