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Luminescence characteristics of Eu^{2+} activated Ca_2SiO_4, Sr_2SiO_4 and Ba_2SiO_4 phosphors for white LEDs*

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This paper investigates the luminescence characteristics of Eu^{2+} activated Ca_2SiO_4, Sr_2SiO_4 and Ba_2SiO_4 phosphors. Two emission bands are assigned to the f–d transitions of Eu^{2+} ions doped into two different cation sites in host lattices, and show different emission colour variation caused by substituting M^{2+} cations for smaller cations. This behaviour is discussed in terms of two competing factors of the crystal field strength and covalence. These phosphors with maximum excitation of around 370 nm can be applied as a colour-tunable phosphor for light-emitting diodes (LEDs) based on ultraviolet chip/phosphor technology.

Keywords: luminescence, white LEDs, Eu^{2+}, silicate
PACC: 7855, 7630K

1. Introduction

Recently, remarkable progress has been made in the development of white light emitting diodes (LEDs) using InGaN chips.[1−4] For the method of phosphor conversion, white light can be obtained by combining blue LEDs and a yellow phosphor,[5] blue LEDs can also be combined with phosphors to convert part of the blue light to red and green light to produce white light.[6] Moreover, for ultraviolet (350–410 nm) white light, LED chip coated by red, green and blue light-emitting phosphors is a promising way of white light generation. Because the eyes are not sensitive to the range of 350–410 nm, therefore, the colour of this mechanism depends completely on phosphor. The kinds of phosphors and the mixture ratio can be varied to adjust the chromaticity of the illuminating source according to different needs. For this approach, silicate-based phosphors activated with Eu^{2+} are very suitable. These phosphors show broad emission colours through 4f–5d transition of Eu^{2+} activators strongly coupled to the host lattice. The absorption and emission bands of activators are also controlled by changing the crystal field or the covalence depending on site size, site symmetry and coordination number of the activator ion.[7,8]

This paper investigates the luminescent characteristics of alkaline earth orthosilicates Ca_2SiO_4, Sr_2SiO_4 and Ba_2SiO_4 doped with Eu^{2+} ions. The different emission variation of two emission bands is presented, and their origins are revealed through crystal field strength and covalence.

2. Experimental

Ca_2SiO_4:Eu^{2+}, Sr_2SiO_4:Eu^{2+} and Ba_2SiO_4:Eu^{2+} phosphors were synthesized by solid state reaction. The starting materials were $CaCO_3$, $SrCO_3$, $BaCO_3$, SiO_2 and Eu_2O_3. The synthesis was performed at 1300° for 6 h under the ambience of 5% H_2 in N_2 to reduce Eu^{3+} to Eu^{2+}. The excitation and emission spectra were measured by a SHIMADZU RF-540 ultraviolet spectrophotometer. All the characteristics of these phosphors were conducted at room temperature.

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3. Results and discussion

3.1. Excitation and emission spectra of Ca_2SiO_4:Eu^{2+}, Sr_2SiO_4:Eu^{2+} and Ba_2SiO_4:Eu^{2+} phosphors

Figure 1 illuminates the excitation and emission spectra of Ca_2SiO_4:Eu^{2+}, Sr_2SiO_4:Eu^{2+} and Ba_2SiO_4:Eu^{2+} phosphors with 1 mol% Eu^{2+}. The emission spectra of these three phosphors consist of two bands: Eu(I) of a shorter wavelength emission and Eu(II) of a longer wavelength emission. In the case of Sr_2SiO_4:Eu^{2+}, one band is located around 480 nm, and the other band is positioned at 547 nm. In the case of Ba_2SiO_4:Eu^{2+} and Ca_2SiO_4:Eu^{2+}, two peaks merge at 503 nm and 501 nm, respectively, and they overlap as a single band. The emission band of the shorter wavelength originates from the Eu^{2+} ion on the large-sized M(I) site with a weak crystal field. The Eu^{2+} ions on the small-sized M(II) site with a strong crystal field results in the other emission band of the longer wavelength. The intense broad peaks of Ca_2SiO_4:Eu^{2+}, Sr_2SiO_4:Eu^{2+} and Ba_2SiO_4:Eu^{2+} originate from 5d→4f transition of Eu^{2+} ions due to the strong coupling of the 5d electron with host lattice.

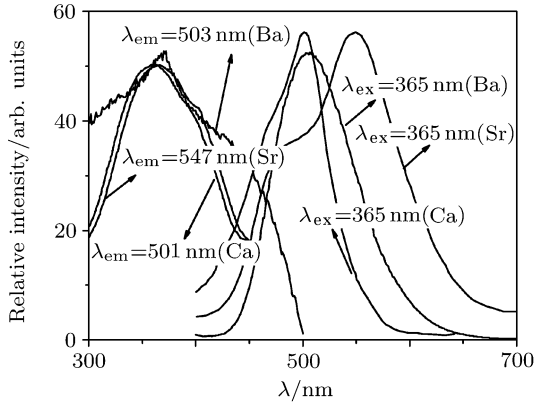


Fig.1. Excitation and emission spectra of Ca_2SiO_4:Eu^{2+}, Sr_2SiO_4:Eu^{2+} and Ba_2SiO_4:Eu^{2+} phosphors.

Figure 2 shows the emission bands of nine different sets of samples with 1 mol% Eu^{2+}. They are as follows: (1) Ba_2SiO_4: Eu^{2+}, (2) $(Ba_{1-0.25}Sr_{0.25})_2SiO_4$: Eu^{2+}, (3) $(Ba_{1-0.5}Sr_{0.5})_2SiO_4$: Eu^{2+}, (4) $(Ba_{1-0.75}Sr_{0.75})_2SiO_4$: Eu^{2+}, (5) Sr_2SiO_4 : Eu^{2+}, (6) $(Sr_{1-0.25}Ca_{0.25})_2SiO_4$: Eu^{2+}, (7) $(Sr_{1-0.5}Ca_{0.5})_2SiO_4$: Eu^{2+}, (8) $(Sr_{1-0.75}Ca_{0.75})_2SiO_4$: Eu^{2+} and (9) Ca_2SiO_4 : Eu^{2+}. The positions of two emission bands extracted through Gaussion fitting are depicted in Fig.3. From Ba_2SiO_4:Eu^{2+} to Sr_2SiO_4:Eu^{2+}, the emission bands of longer wavelength show redshift behaviour whereas these of shorter wavelength are slightly blueshifted. On the other hand, in the case from Sr_2SiO_4:Eu^{2+} to Ca_2SiO_4:Eu^{2+}, the emission bands of longer wavelength show blueshift whereas these of shorter wavelength show redshift. This phenomenon can be explained in terms of two competing factors: the crystal field and the covalence.[7]

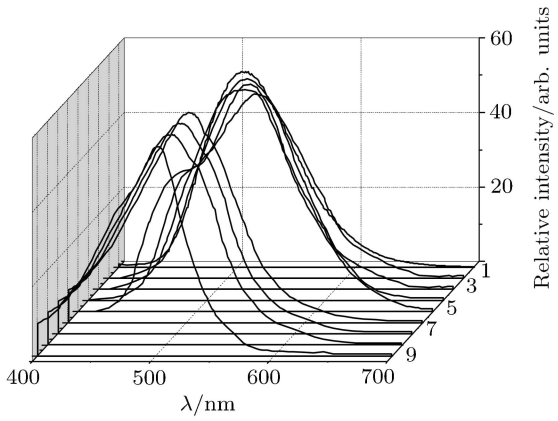


Fig.2. Emission spectra of different sets of samples.

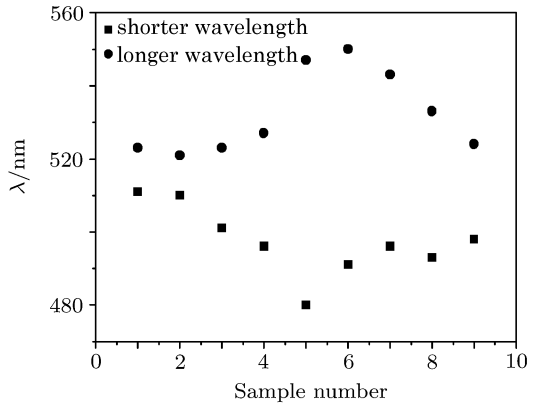


Fig.3. Emission peaks of different sets of samples.

The crystal field strength is increased with a decrease in bond length by replacing with smaller M cations; $D_q = \dfrac{3Ze^2r^4}{5R^5}$, where D_q is the crystal field, R is the bond length between the centre ion and ligand ions.[9] Therefore, the increase in the crystal field can result in a redshift for the 5d→4f transition of Eu^{2+}. In addition, the blueshift can be explained in terms of the decreasing Nephelanxetic effect.[10] With the decrease in the degree of covalence of Eu–O bonds in order of Ba, Sr and Ca, less negative charge transfer occurs to Eu^{2+} ions, thus increasing the difference between the 4f and the 5d levels. So the degree of covalence in the Eu–O bonds is decreased with the

substitution of M ions for smaller M cations, and consequently can result in blueshift of the Eu^{2+} emission band.

In the case of Ba_2SiO_4:Eu^{2+} to Sr_2SiO_4:Eu^{2+}, the difference between the size of the M(II) site and the diameter of the Eu^{2+} ions is smaller than that between the size of the M(I) site and the diameter of the Eu^{2+} ions. So Eu^{2+} ions doped into the M(II) site are effectively affected by crystal field resulting in the redshift of Eu^{2+}(II) emission of longer wavelength. On the other hand, Eu^{2+} ions doped into the large M(I) site experience low crystal field due to larger bond length, and are dominantly influenced by the Nephelanxetic effect. The decrease in covalence causes the slight blueshift of Eu^{2+}(I) emission of shorter wavelength.

In the case of Sr_2SiO_4:Eu^{2+} to Ca_2SiO_4:Eu^{2+}, the difference between the size of the M(II) site and the diameter of the Eu^{2+} ions is much larger than that between the size of the M(I) site and the diameter of the Eu^{2+} ions. The symmetry of the ligand ions surrounding the Eu^{2+} ions is slightly distorted and their crystal fields are relaxed. So the ligand ions do not effectively exert a crystal field on the Eu^{2+} ions doped into M(II) sites. Consequently, the covalence effect in the M(II) site is more dominant and the covalence is decreased in order of Sr and Ca ions so that the slight blueshift of Eu^{2+}(II) emission of longer wavelength is observed. On the other hand, the difference between the size of the M(I) site and the diameter of the Eu ions is smaller than that between the size of the M(II) site and the diameter of the Eu ions. The Eu ions doped into the larger M(I) site are dominantly influenced by the crystal field causing the slight redshift of Eu^{2+}(I) emission of shorter wavelength.

3.2. Effect of Eu^{2+} concentration on emission spectra of Ca_2SiO_4:Eu^{2+}, Sr_2SiO_4:Eu^{2+} and Ba_2SiO_4:Eu^{2+} phosphors

The emission spectra of Ca_2SiO_4:Eu^{2+}, Sr_2SiO_4:Eu^{2+} and Ba_2SiO_4:Eu^{2+} phosphors with different Eu^{2+} concentrations are shown in Figs.4, 5 and 6, respectively. The Eu^{2+} concentration is from 0.25 mol% to 3 mol%. As can be seen from these figures, the emission intensity initially increases with Eu^{2+} concentration and reaches a maximum at 1 mol% Eu^{2+}. A decrease in the emission intensity is observed as the Eu^{2+} concentration increases, and this shows the occurrence of energy migration between Eu^{2+} in different sites in the lattice, resulting in concentration quenching. A nonradiative energy transfer from one Eu^{2+} ion to another Eu^{2+} ion takes place. According to Ref.[11], the probability of energy transfer among Eu^{2+} ions increases when the Eu^{2+} concentration increases. Nonradiative energy transfer from one Eu^{2+} ion to another Eu^{2+} ion usually may occur by exchange interaction, radiation reabsorption

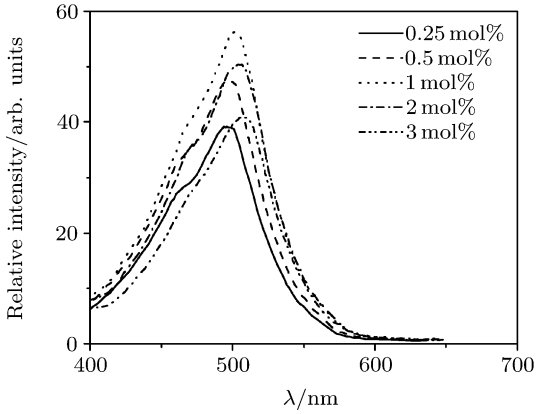


Fig.4. Emission spectra of Ca_2SiO_4:Eu^{2+} phosphor as a function of Eu^{2+} concentration.

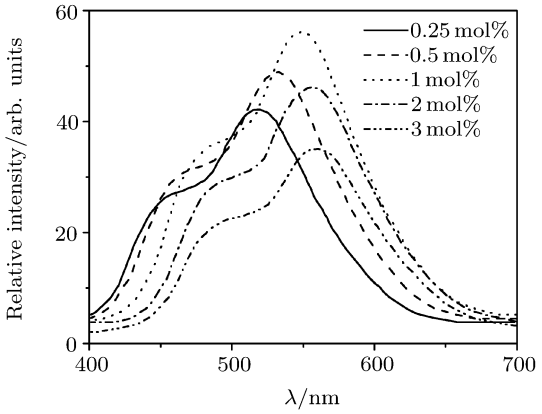


Fig.5. Emission spectra of Sr_2SiO_4:Eu^{2+} phosphor as a function of Eu^{2+} concentration.

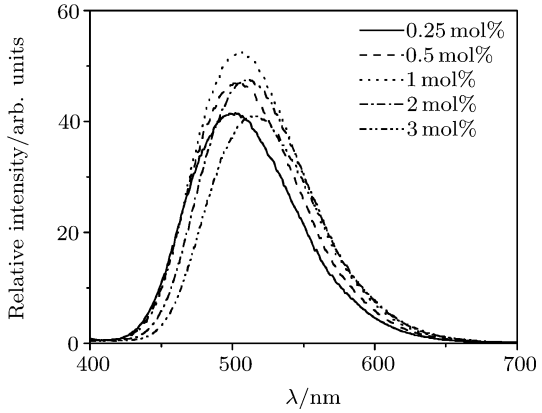


Fig.6. Emission spectra of Ba_2SiO_4:Eu^{2+} phosphor as a function of Eu^{2+} concentration.

or mutipole–multipole interaction. In the case of the Eu^{2+} ion, the $4f^7 \rightarrow 4f^6 5d^1$ transition is allowed, while exchange interaction is responsible for energy transfer for forbidden transitions with a typical critical distance, which is about 0.5 nm.[12]

We can select Sr_2SiO_4:Eu^{2+} to estimate roughly the critical distance of energy transfer (R_c), the distance at which the probability of transfer equals to the probability of radiative emission, can be made by using the relation suggested by Blasse[13] to calculate R_c between activator ions of the kind doped in a host lattice $R_c \approx 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3}$, where V is the volume of the unit cell, x_c is the critical concentration of the activator ion, and N is the number of host cations in the unit cell. The x-ray diffraction pattern of Sr_2SiO_4:Eu^{2+} was obtained in our previous research results, which are in good agreement with 39-1256 by JCPDS fingerprints,[14] and their lattice parameter values are $a = 0.7079$ nm, $b = 0.5672$ nm, $c = 0.9743$ nm, so the unit cell volume of Sr_2SiO_4 is 0.3912 nm^3. Since the emission spectra of Sr_2SiO_4 [$x = 0.0025 - 0.03$] show maximum intensity for $x = 0.01$, this value is used as the critical concentration x_c. The number of formula units per unit cell in Sr_2SiO_4 is 4, resulting in 8 Sr^{2+} ions in the unit cell. Using these values, we obtain that the value of R_c is ≈2.65 nm. This value is higher than 0.5 nm, and is similar to the values obtained for Eu^{2+} in several oxide host lattices.[15] Therefore, the energy transfer in the present case will occur only by electric multipolar interaction. It is reported[16] that the electric multipolar interaction is responsible for the energy transfer between Eu^{2+} ions in M_2SiO_4. The probability of energy transfer is inversely proportional to R^n, where R is the distance between the activators and n is an integer ($n = 6$, 8, 10 for electric dipole–dipole, dipole–quadripole and quadripole–quadripole, respectively). As the concentration of Eu^{2+} increases, the distance between Eu^{2+} ions becomes smaller, leading to the high probability of energy transfer. The high R_c value of 2.65 nm in Sr_2SiO_4:Eu^{2+} can be correlated to the rigid nature of the host lattice, which is made up of SiO_4 tetrahedral network. Also, with increase in concentration of Eu^{2+}, different sites are occupied in the lattice and the migration of excitation energy is rapid, resulting in concentration quenching.

4. Conclusions

In conclusion, Ca_2SiO_4:Eu^{2+}, Sr_2SiO_4:Eu^{2+} and Ba_2SiO_4:Eu^{2+} show two emission bands of Eu^{2+} ions doped into two different cation sites in host lattices. These phosphors with maximum excitation of around 370 nm can be applied as a colour-tunable phosphor for LED based on ultraviolet chip technology. In the cases of Ba_2SiO_4:Eu^{2+}, Sr_2SiO_4:Eu^{2+} and Ca_2SiO_4:Eu^{2+}, the reason for the shifting emission bands is discussed in terms of two competing factors of crystal field strength and covalence. A nonradiative energy transfer from one Eu^{2+} ion to another Eu^{2+} ion takes place when Eu^{2+} concentration increases.

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