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Concentration quenching of Eu^{2+} in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor

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In $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor, blue Eu^{2+} luminescence is observed from Eu^{2+} on the strontium site present in the lattice. The concentration quenching process between Eu^{2+} ions is determined and the corresponding concentration quenching mechanism is verified as dipole-dipole interaction. The value of the critical transfer distance is calculated as 25 Å and its reliability is confirmed by using Dexter's theory on energy transfer.

1. Introduction

$SrO \cdot 6Al_2O_3 : Eu^{2+}$ is well known as a high-efficiency phosphor with good stability. It has been widely studied and reported [1–4]. The crystal structure of the aluminate with the formula $SrAl_{12}O_{19}$ is known as the magnetoplumbite structure, from the mineral magnetoplumbite $PbFe_{12}O_{19}$, in which this structure was first found. Eu^{2+}, incorporated as an activator in the phosphor, may be built into the intermediate layers of the aluminate lattice on the sites of the large cations. In order to study further the interaction between the host lattice micro-structure and the luminescent properties of the phosphors, the relationship between Eu^{2+} luminescence and the lattice positions occupied by Eu^{2+} are examined and the Eu^{2+} critical concentration at which appreciable quenching occurs is determined. The value of the critical distance of energy transfer in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ and the transfer mechanism in Eu^{2+} are found and verified from the Eu^{2+} critical concentration and Dexter's theory for energy transfer [5].

2. Experimental

According to the nominal composition $(Sr_{1-x}Eu_x)O \cdot 6Al_2O_3$ ($x = 0.01 \sim 0.08$), appropriate amounts of the starting materials $SrCO_3$(AR), $Al(OH)_3$(AR), Eu_2O_3 (99.99%) and a little flux H_3BO_3 (AR) were thoroughly mixed and ground in an agate ball mill for 4 h. Subsequently, the mixture was prefired at 1000°C for 5 h. After milling for a second time, the samples were calcined at 1300°C for 4 h in a reducing atmosphere.

All measurements were performed on powder samples. The emission and excitation spectra were recorded on a Hitach 850 fluorescence spectrometer. A Rigaku D/Max ∼ 3B X-ray diffractometer (Cu K_α, 40 kV × 35 mA), used in a step-scan mode ($0.022°/2\theta$), was used to collect the power diffraction data for Rietveld analysis.

3. Results and discussion

3.1. Concentration quenching law of Eu^{2+} in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor

The two sites available for incorporating Eu^{2+} in the $SrO \cdot 6Al_2O_3$ lattice are either the Al^{3+} sites or the Sr^{2+} sites. In $SrO \cdot 6Al_2O_3$, there are six different sites for Al^{3+} and only one site for Sr^{2+}. Al^{3+} is small (0.50 Å) but Sr^{2+} is almost equal in size to Eu^{2+}(1.13 Å vs 1.12 Å). The crystal structure of $(Sr_{0.96}Eu_{0.04})O \cdot 6Al_2O_3$ phosphor is refined by Rietveld analysis [6] and the analyzed results are shown in Table I (where, R_p and R_{wp} are the pattern R-factor and weighted pattern R-factor respectively. When the values of them are less than 10%, the implication is that the refinement results are good and reasonable [7]; x/a y/b z/c are the fraction coordinates of the different atoms in the cell, which define crystal axes as coordinate axes and the length of cell edges as unit length. N_{total} represents the sum of equivalent atoms in the cell). As shown in Table I, it is found that the incorporation of Eu^{2+} ions into the $SrO \cdot 6Al_2O_3$ crystal lattice does not cause any significant lattice distortions. Eu^{2+} ions occupy the Sr^{2+} sites and substitute for 3.96% of the Sr^{2+} ions. The occupation ratio of Eu^{2+} in the lattice is approximately equal to the nominal doping amount (4%), which indicates that Eu^{2+} ions only replace Sr^{2+} ions. The excitation and emission spectra of $(Sr_{1-x}Eu_x)O \cdot 6Al_2O_3$ (x varies from 0.01 to 0.106) phosphors are presented in Fig. 1. From Fig. 1 it can be seen that only an asymmetrical emission band is observed at 398 nm in the emission spectra of $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor. With an increase

TABLE I The structure of $(Sr_{0.96}Eu_{0.04})O \cdot 6Al_2O_3$ phosphor from Rietveld refinement

Composition phase	System and space group	Crystal cell parameters a (Å)	b (Å)	c (Å)	V(Å^3)	R-factor R_p	R_{wp}
$SrO \cdot 6Al_2O_3$	Hexagonal, P6$_3$/mmc	5.5637	5.5637	22.0134	590.12	6.16%	8.55%

Atom	Fraction coordinate and Total number of equivalent atom in unit cell x/a	y/b	z/c	N_{Total}
Sr 1	0.6667	0.3333	0.2500	1.9208
Eu 1	0.6667	0.3333	0.2500	0.0792
Al 1	0.0000	0.0000	0.0000	2.0000
Al 2	0.0000	0.0000	0.2500	2.0000
Al 3	0.3333	0.6667	0.0283	4.0000
Al 4	0.1689	0.3378	−0.1083	12.000
Al 5	0.3333	0.6666	0.1906	4.0000
O 1	0.0000	0.0000	0.1479	4.0000
O 2	0.3333	0.6667	−0.0539	4.0000
O 3	0.1824	0.3649	0.2500	6.0000
O 4	0.1564	0.3128	0.0520	12.000
O 5	0.5016	0.0032	0.1474	12.000

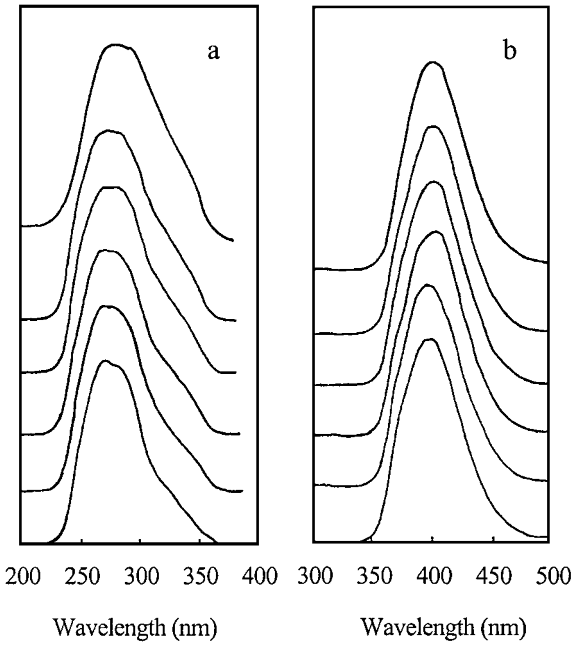

Figure 1 The excitation spectra[a] (emission 397.9 nm) and emission spectra[b] (excitation 268.2 nm) of $(Sr_{1-x}Eu_x)O \cdot 6Al_2O_3$ ($x = 0.01$, 0.018, 0.024, 0.034, 0.04, 0.072 from bottom to top) phosphors.

in the Eu^{2+} concentration, the shapes and positions of emission and excitation bands have no obvious changes. The dependence of the emission intensity on the Eu^{2+} concentration under 254 nm excitation for the $(Sr_{1-x}Eu_x)O \cdot 6Al_2O_3$ (x varies from 0.01 to 0.08) is shown in Fig. 2.

From the results of Table I and Fig. 2, it can be seen that Eu^{2+} ions only occupy Sr^{2+} sites in the $SrO \cdot 6Al_2O_3 : Eu^{2+}$ lattice and form the corresponding emission center, which peaks at about 400 nm. With an increase in the Eu^{2+} concentration, the emission intensity of $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor increases gradually.

The critical quenching concentration of Eu^{2+} (x_c) is defined as the concentration at which the emission intensity begins to decrease and the critical distance corresponding to the critical quenching concentration is defined as the average distance between the nearest Eu^{2+} ions between which energy transfer occurs. From Fig. 2 it can be seen that the critical concentration of Eu^{2+} in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor is about 3.6%.

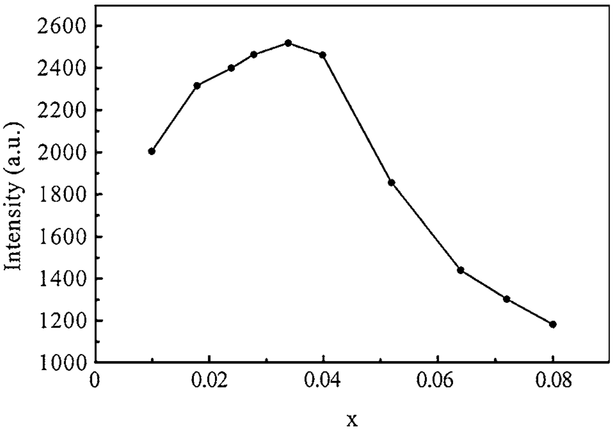

Figure 2 Emission intensity as a function of Eu^{2+} concentration (x) for $(Sr_{1-x}Eu_x)O \cdot 6Al_2O_3$ ($x = 0.01$, 0.018, 0.024, 0.028, 0.034, 0.04, 0.052, 0.064, 0.072, 0.08) phosphors ($\lambda_{ex} = 268.2$ nm).

3.2. Critical transfer distance (R_c) in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor

When considering the mechanism of energy transfer in oxide phosphors, Blasse [8] has pointed out that if the activator is introduced solely on Z ion sites, x_c is the critical concentration, N the number of Z ions in the unit cell and V is the volume of the unit cell, then there is on the average one activator ion per V/x_cN. The critical transfer distance (R_c) is approximately equal to twice the radius of a sphere with this volume:

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

By taking the appropriate values of V, N and x_c (590.12 Å^3, 2, 0.036, which are shown in Table I and Fig. 2), the critical transfer distance of Eu^{2+} in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor is found to be 25 Å.

According to Dexter's theory on non-radiative energy transfer, the critical transfer distance of Eu^{2+} can also be calculated from the spectral experimental data, i.e. the value of the critical transfer distance (R_c) can be found from [5]

$$R_c = 0.36 \times 10^{28} \frac{4.8 \times 10^{-16} P}{E^4} S.O. \qquad (2)$$

Where P is the oscillator strength of the absorption transition of the Eu^{2+} ion, E the energy of maximum spectral overlap, and $S.O.$ the spectral overlap integral. For P a value of 10^{-2} for the broad $4f^7 \rightarrow 4f^6 5d^1$ absorption band is taken [9]. E and $S.O$, which are derived from the spectral experimental data, are 2.92 eV and 0.84 eV^{-1} respectively. This gives a calculated value of R_c for the energy transfer between inequivalent Eu^{2+} ions in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ of about 24 Å. Thus the calculated crystal structure data and the experimental spectral data give results for R_c which are in agreement.

3.3. Mechanism of energy transfer in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor

Non-radiative energy transfer from a Eu^{2+} ion to another Eu^{2+} ion may occur by exchange interaction, radiation reabsorption or multipole-multipole interaction. Eu^{2+} is an isolated emission center in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor. The $4f^7 \rightarrow 4f^6 5d^1$ transition of Eu^{2+} is allowed while exchange interaction is responsible for the energy transfer for forbidden transitions and typical critical distances are then about 5 Å [5]. This indicates that the mechanism of exchange interaction plays no role in energy transfer between Eu^{2+} ions in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor. The mechanism of radiation reabsorption comes into effect only when there is broad overlap of the fluorescent spectra of the sensitizer and activator and in the view of the emission and excitation spectra of $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor is unlikely to be occurring in this case. Since the fluorescent mechanism of Eu^{2+} in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor is the $4f \rightarrow 5d$ allowed electric-dipole transition, the process of energy transfer should be controlled by electric multipole-multipole interaction according to Dexter's theory [5]. If the energy transfer occurs between the same sort 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 [10, 11]:

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

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 for the same excitation conditions for a given host crystal.

Since the critical concentration of Eu^{2+} has been determined as 3.6%, the dependence of the emission intensity of the $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor excited at 268.2 nm as a function of the corresponding concentration of Eu^{2+} for concentrations greater than the critical concentration (3.6%) is determined (see Fig. 3). It can be seen from Fig. 3 that the dependence of $\lg I/x_{Eu^{2+}}$ on $\lg x_{Eu^{2+}}$ is linear and the gradient is −2.0729. The value of Q can be calculated as 6.2, which is approximately to 6. This indicates that dipole-dipole interaction is the concentration quenching mechanism of Eu^{2+} emission in the $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor.

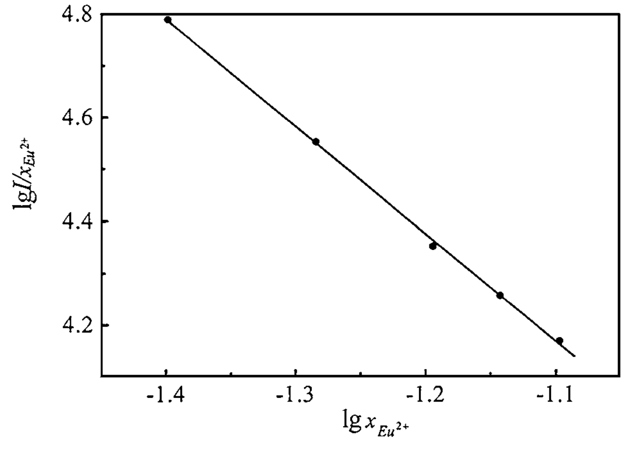

Figure 3 Log of the emission intensity per activator ion ($\lg I/x_{Eu^{2+}}$) as a function of log of the Eu^{2+} concentration ($\lg x_{Eu^{2+}}$) in $(Sr_{1-x}Eu_x)O \cdot 6Al_2O_3$ phosphors ($\lambda_{ex} = 268.2$ nm).

4. Conclusions

1. Eu^{2+} ions only occupy Sr^{2+} sites and form one emission center at about 400 nm. With an increase in the Eu^{2+} concentration, the excitation energy is quenched by lattice defects.

2. The critical quenching concentration of Eu^{2+} in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor is determined as 3.6%. From crystallographic data, the critical transfer distance is calculated as 25 Å which is in good agreement with the value derived from the spectral experimental data.

3. The mechanism of concentration quenching of Eu^{2+} in $SrO \cdot 6Al_2O_3 : Eu^{2+}$ phosphor is determined to be dipole-dipole interaction.

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