The concentration quenching and crystallographic sites of Eu^{2+} in Ca_2BO_3Cl*

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A yellow phosphor, Ca_2BO_3Cl:Eu^{2+}, is prepared by the high-temperature solid-state method. Under the condition of excitation sources ranging from ultraviolet to visible light, efficient yellow emission can be observed. The emission spectrum shows an asymmetrical single intensive band centred at 573 nm, which corresponds to the $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+}. Eu^{2+} ions occupy two types of Ca^{2+} sites in the Ca_2BO_3Cl lattice and form two corresponding emission centres, respectively, which lead to the asymmetrical emission of Eu^{2+} in Ca_2BO_3Cl. The emission intensity of Eu^{2+} in Ca_2BO_3Cl is influenced by the Eu^{2+} doping concentration. Concentration quenching is discovered, and its mechanism is verified to be a dipole–dipole interaction. The value of the critical transfer distance is calculated to be 2.166 nm, which is in good agreement with the 2.120 nm value derived from the experimental data.

Keywords: luminescence, Ca_2BO_3Cl:Eu^{2+}, concentration quenching, crystallographic sites

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1. Introduction

Nowadays, increasing interest has been focused on GaN/InGaN-based white light emitting diodes (LEDs).[1] There are several ways to obtain phosphor-converted white LEDs. One scheme is the combination of the blue LED chip and the yellow emitting phosphor, and the other is the combination of the near-ultraviolet (n-UV) LED chip and the red, green, and blue emission phosphors, or a single phase white emitting phosphor.[2−4] In order to fulfill the corresponding requirements, many research papers on developing new phosphor systems in which light-conversion phosphors are used for white LEDs have been reported. Among them, they contain chloro-based materials, such as chlorophosphate,[5−7] chlorosilicate,[8−10] chloroaluminate,[11−13] and chloroborate,[14−16] and these have become a hot issue in exploring new phosphor materials. In the process of the exploration of chloroborate-based light-conversion phosphors for white LEDs, they have been proved to be efficient in the application of white light-conversion phosphors. For instance, the luminescence characteristics of Eu^{2+}, Eu^{2+}/Ce^{3+} or Ce^{3+} in Ca_2BO_3Cl have been investigated, respectively, in Refs. [17]–[20]. In order to further study the interaction between the host lattice and the luminescent properties of Ca_2BO_3Cl:Eu^{2+} phosphors, the relationship between the Eu^{2+} luminescence and the lattice positions occupied by Eu^{2+} and the Eu^{2+} critical concentration must be examined.

In order to develop white LEDs, Eu^{2+} activated Ca_2BO_3Cl phosphors are prepared by the solid-state temperature method, and the concentration quenching and crystallographic sites of Eu^{2+} in Ca_2BO_3Cl are measured.

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2. Experiment

The yellow phosphor, $Ca_2BO_3Cl:Eu^{2+}$, was synthesized by the high temperature solid-state reaction method. $CaCO_3$, $CaCl_2$, H_3BO_3, and Eu_2O_3 were used as starting materials. After the individual materials were ground thoroughly in an agate mortar, the homogeneous mixture was heated at 900 °C for 2.5 h in a reducing atmosphere (a mixture of 5% H_2 and 95% N_2), and then these phosphors were obtained.

The crystal structure of the samples was characterized by X-ray powder diffraction using a D/max–rA X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.15406 nm) operated at 40 kV and 100 mA. The spectral characteristics were measured using a Shimadzu RF–540 fluorescence spectrophotometer equipped with a xenon discharge lamp as an excitation source. All the characteristics of the phosphors were studied at room temperature.

3. Results and discussion

3.1. Crystal structure

The XRD patterns of the $Ca_2BO_3Cl:xEu^{2+}$ (x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.04, 0.05 mol) samples are shown in Fig. 1. There are no observable differences between these diffraction patterns, indicating that a small number of doped rare-earth ions have almost no effect on the Ca_2BO_3Cl crystalline structure. The diffraction peak is well matched with the standard JCPDS card of the Ca_2BO_3Cl phase (No. 29-0302). Ca_2BO_3Cl has a monoclinic crystal structure with a space group of $P2_{1/c}$ (14), and the lattice parameter values are a = 0.3948 nm, b = 0.8692 nm, and c = 1.2402 nm.

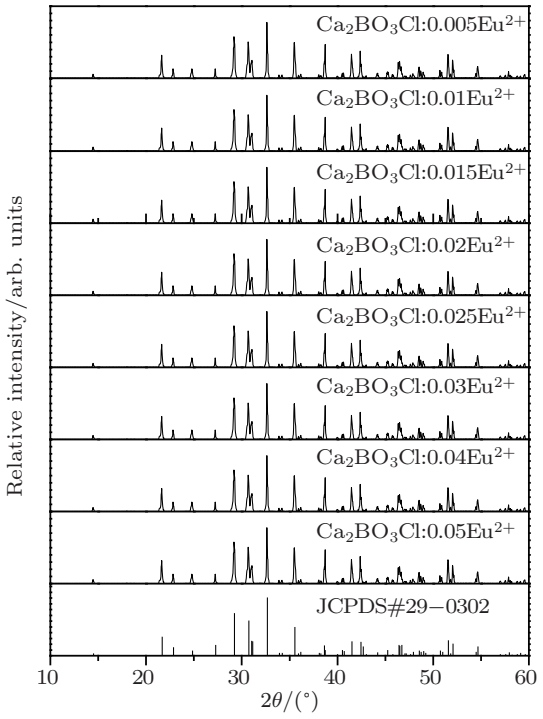


Fig. 1. The XRD patterns of $Ca_2BO_3Cl:xEu^{2+}$ phosphors (x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.04, 0.05 mol).

3.2. The photoluminescence characteristics of the $Ca_2BO_3Cl:Eu^{2+}$ phosphor

The emission and excitation spectra of $Ca_2BO_3Cl:xEu^{2+}$ phosphors with different Eu^{2+} concentrations (x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.04, 0.05 mol) are presented in Fig. 2.

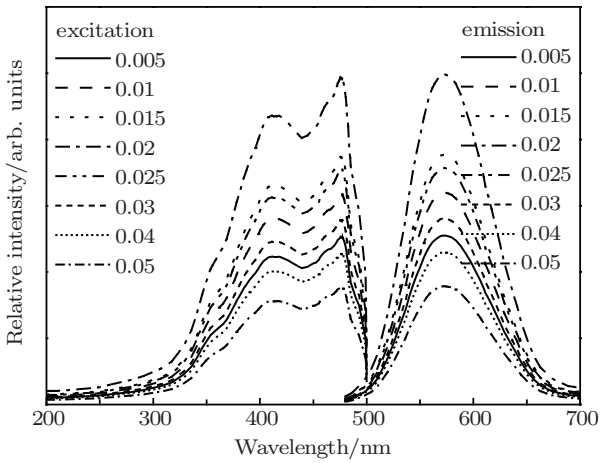


Fig. 2. (colour online) Excitation (λ_{em} = 573 nm) and emission (λ_{ex} = 460 nm) intensities of the $Ca_2BO_3Cl:xEu^{2+}$ phosphor for different Eu^{2+} concentrations (x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.04, 0.05 mol).

The results show that the positions of the excitation and emission bands have no obvious change for all the samples. All the phosphors exhibit a yellow emission band centred at 573 nm, which corresponds to the central position of the emission band from the f–d transition of Eu^{2+}. The 573 nm emission shows that the excitation spectrum is very broad, extends from 300 nm to 500 nm, and the peak values are located at 413 nm and 475 nm, respectively. The 5d energy level of Eu^{2+} and the lower level of the 4f state overlap, so the electrons of the 4f state can be excited to the 5d state. The broad luminescence of Eu^{2+} is due to the $4f^65d^1 \rightarrow 4f^7$ transition, which is an allowed electrostatic dipole transition. However, the 5d state is easily influenced by the crystal field, that is to say, different crystal fields can split the 5d state in different ways.[21] For Ca_2BO_3Cl, the Eu^{2+} ions enter into Ca^{2+} sites in

the crystal structure. Figure 2 shows that the emission intensities first increase and then reach their maxima at $x = 0.02$ mol with the increase in Eu^{2+} concentration. Concentration quenching occurs when the Eu^{2+} concentration is more than 0.02 mol.

Considering the mechanism of energy transfer in oxide phosphors, Blasse[22] pointed out that if the activator is introduced solely on Z ion sits, x_c is the critical concentration. Assuming that N is the number of Z ions in the unit cell and V is the volume of the unit cell, then the average volume of one activator ion will be V/x_cN. The critical transfer distance (R_c) is approximately equal to twice the radius of a sphere with the volume,[22] and given as

$$R_c \approx 2(3V/4\pi x_c N)^{1/3}. \quad (1)$$

By taking the appropriate values of V, N, and x_c (0.4256 nm^3, 4, and 0.02 mol, respectively), the critical transfer distance of Eu^{2+} in Ca_2BO_3Cl:Eu^{2+} is found to be 2.166 nm.

According to Dexter's theory on non-radiative energy transfer, the critical transfer of Eu^{2+} can also be calculated from the spectral experimental data. The value of the critical transfer distance (R_c) can be found from[23]

$$R_c^6 = 0.63 \times 10^{28}(4.8 \times 10^{-16}P/E^4)\mathrm{SO}, \quad (2)$$

where P is the oscillator strength of the absorption transition of the Eu^{2+} ion, E is the energy of the maximum spectral overlap, and SO is the spectral overlap integral. For P, a value of 0.01 for the broad $4f^7 \rightarrow 4f^6 5d^1$ absorption band is taken. E and SO, which are derived from the spectral experimental data, are 2.01 eV and 0.049 eV^{-1}. According to these data, a value of $R_c = 2.120$ nm is obtained. Thus, the R_c value based on the calculated crystal structure data is in good agreement with that obtained from the experimental spectral data.

3.3. The energy transfer mechanism in the Ca_2BO_3Cl:Eu^{2+} phosphor

Non-radiative energy transfer from one Eu^{2+} ion to another Eu^{2+} ion may occur by exchange interaction, radiation reabsorption or multiple–multiple interaction, and Eu^{2+} is an isolated emission centre in Ca_2BO_3Cl:Eu^{2+} phosphors. The $4f^7 \rightarrow 4f^6 5d^1$ transition of Eu^{2+} is allowed, while exchange interaction is responsible for the energy for forbidden transitions, and typical critical distances are then about 0.5 nm.[23] This indicates that the mechanism of exchange interaction plays no role in energy transfer between Eu^{2+} ions in Ca_2BO_3Cl:Eu^{2+} phosphors. The mechanism of radiation reabsorption comes into effect only in the presence of the broad overlap of the fluorescent spectra of the sensitizer and activator, and in view of the emission and excitation spectra of the Ca_2BO_3Cl:Eu^{2+} phosphor, it is unlikely to occur in this case since the fluorescent mechanism of Eu^{2+} in the Ca_2BO_3Cl:Eu^{2+} phosphor is due to the 4f→5d allowed electric multiple–multiple interaction, according to Dexter's theory. If the energy transfer occurs between activators of the same kind, the intensity of the multipolar interaction can be at a determinable level, which has multipolar interaction. The emission intensity per activator ion follows the following equation[24,25]

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

where x is the activator concentration; $Q = 6$, 8, and 10 for the dipole–dipole (d–d), dipole–quadrupole (d–p), and quadrupole–quadrupole (q–q) interactions, respectively; and K and β are constants under the same excitation conditions for a given host crystal.

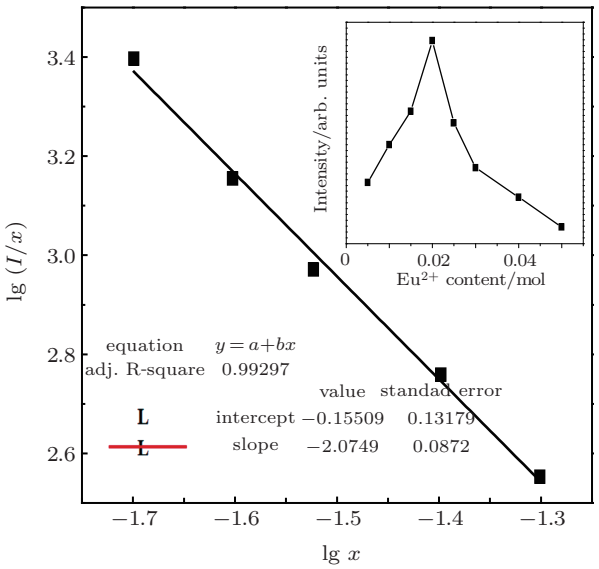


Fig. 3. (colour online) Plot of $\lg(I/x_{Eu}^{2+})$ versus $\lg x_{Eu}^{2+}$ in Ca_2BO_3Cl:xEu^{2+} phosphors ($\lambda_{ex} = 460$ nm). The inset shows the emission intensity of the Ca_2BO_3Cl:Eu^{2+} phosphors as a function of Eu^{2+} concentration.

The critical concentration of Eu^{2+} is determined to be 0.02 mol. The dependence of the emission intensity of the Ca_2BO_3Cl:Eu^{2+} phosphor excited at 460 nm on the corresponding concentration of Eu^{2+} for a concentration greater than the critical concentration is determined. The plot of $\lg I/x_{Eu}^{2+}$ versus

$\lg x_{\mathrm{Eu}}^{2+}$ in the $Ca_2BO_3Cl:Eu^{2+}$ phosphor is shown in Fig. 3. From the figure it follows that the dependence of $\lg I/x_{\mathrm{Eu}}^{2+}$ on $\lg x_{\mathrm{Eu}}^{2+}$ is linear and the slope is -2.07. The value of Q can be calculated to be 6.21, which is approximately 6. This indicates that the d–d interaction is the concentration quenching mechanism of the Eu^{2+} emission in the $Ca_2BO_3Cl:Eu^{2+}$ phosphor.

3.4. Crystallographic sites of Eu^{2+} in Ca_2BO_3Cl

The inset of Fig. 4 shows the structure of Ca_2BO_3Cl, and in the crystal lattice there are two types of seven-fold coordination Ca polyhedra: $CaCl_3O_4$ and $CaCl_2O_4$, and each O atom is surrounded by three Ca atoms. One B atom is in the form of a distorted tetrahedral and the Cl atoms are always situated at the corners of the trigonal base.[26] When the Eu^{2+} ion is incorporated into the Ca_2BO_3Cl, it substitutes for Ca^{2+} and can form two Eu^{2+} emission centres. Therefore, we can predict that the $Ca_2BO_3Cl:Eu^{2+}$ phosphor presents two emission bands or a dissymmetrical emission band. Figure 4 shows the emission spectrum of the $Ca_2BO_3Cl:Eu^{2+}$ phosphor under 460 nm excitation, and it can be seen that an asymmetrical single intensive band is centred at 573 nm. This means that two Eu^{2+} sites exist in the Ca_2BO_3Cl. According to Ref. [27], the energy distribution of the fluorescence emission band accords with Gaussian distribution via the following equation

$$E_\nu = E_{\nu 0} \exp[-2.772(\nu - \nu_0)^2/(\Delta\lambda)^2], \qquad (4)$$

where ν is the frequency, ν_0 is the frequency of the peak value, $E_{\nu 0}$ is the peak value, $\Delta\lambda$ is the full width at half maximum, and E_ν is the luminescence energy at ν. According to the formula and the structure of the Ca_2BO_3Cl, two emission bands can be obtained by fitting the two Gaussian peaks, as shown in Fig. 4. One emission band is located at 556 nm, the other is located at 593 nm, and the two emissions are both from the Eu^{2+} centres of the seven-fold coordination Ca polyhedra. However, the emission intensities of the two emission centres are different. In other words, Eu^{2+} occupies two types of Ca^{2+} sites in the Ca_2BO_3Cl lattice separately and forms two corresponding emission centres, but their Eu^{2+} emission centres have a difference in number.

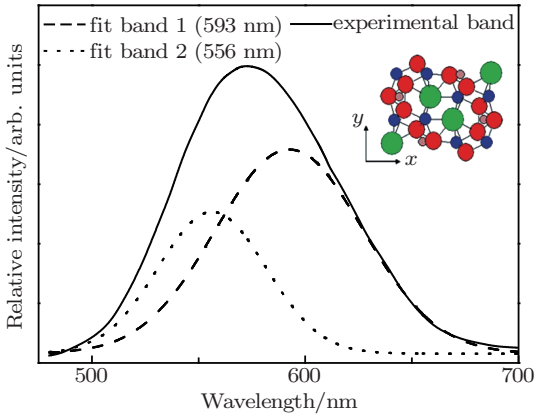


Fig. 4. (colour online) The emission spectra of $Ca_2BO_3Cl:xEu^{2+}$ phosphors (λ_{ex} = 460 nm). The inset shows the structure of Ca_2BO_3Cl.

4. Conclusions

$Ca_2BO_3Cl:Eu^{2+}$ shows an asymmetrical single intensive band centred at 573 nm under 460 nm excitation. The asymmetrical emission means that the Eu^{2+} ions occupy two types of Ca^{2+} sites in the Ca_2BO_3Cl lattice, separately, and form two corresponding emission centres, and the two emission centres of Eu^{2+} have a difference in number, leading to the emission intensity of the band at 556 nm, differing from that of 593 nm. Moreover, the emission intensities are influenced by the Eu^{2+} concentration, and the critical quenching concentration of Eu^{2+} in the $Ca_2BO_3Cl:Eu^{2+}$ phosphor is about 0.02 mol. The corresponding concentration quenching mechanism is verified to be due to a dipole–dipole interaction, and the value of the critical transfer distance is calculated to be 2.166 nm, which is in good agreement with the 2.120 nm value derived from the experimental data.

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