1. Introduction

White LEDs have the advantages of high brightness, low energy consumption, long life, small size, no radiation, no pollution, etc. It is considered the new generation of green light sources. The two commonly used methods for implementing white LEDs are: blue-ray chip and YAG:Ce³⁺ yellow phosphor combination, and near-ultraviolet LED chip combined with the trichromatic phosphor. However, the former lacks the red portion, resulting in a lower color rendering index (less than 80) and a higher color temperature (greater than 40), while the latter is less commercially available and lacks suitable red light materials. Therefore, finding a suitable red luminescent material and improving the color rendering index has become an important issue in the development of trichromatic white LEDs. In the rare earth family, Eu³⁺ ions are widely used in various fields of luminescent materials because they have good luminescence properties and can emit red fluorescence with good monochromaticity.⁷⁻⁹ The luminescence of Eu³⁺ derived from the ⁴f⁶ transition consists of sharp peaks of the Eu³⁺-doped inorganic compound in the red region.¹⁰⁻¹²

Rare earth ion-doped borate luminescent materials have high UV transparency, nonlinear characteristics, good stability and optical properties, and they are expected to become a promising fluorescent material, attracting more and more research worldwide.¹³⁻¹⁵ Among the nonlinear optical crystal materials that have been found, ultraviolet and deep ultraviolet nonlinear optical crystals that have excellent performance are almost all borate compounds. Ca₅(BO₃)₃F was first reported by Lei et al. in 1989. The crystal was also a new type of nonlinear optical crystal. The powder doubling effect was measured to be 2–3 KDP, and the transmission range was 190–3600 nm.¹⁶,¹⁷ There are many published papers focusing on energy transfer and color-tunability of rare earth (e.g., Bi³⁺, Ce³⁺, Tb³⁺)-doped Ca₅(BO₃)₃F.¹⁸⁻²⁰ There are three kinds of octahedrons surrounding the Ca ions that could be substituted by Eu³⁺. They have different covalence, average bond lengths, central ion coordination numbers, and charges of ligands in chemical bonds. These result in Eu³⁺ ions with different photoluminescence properties. For the above reasons, Ca₅(BO₃)₃F compound with Ca³⁺ and B³⁺ cationic sites can be selected as a host lattice, and Eu³⁺ ions are used as a good activator. However, studies on the effects of Eu³⁺ on the CT properties and...
the local crystal sites occupied by Eu\(^{3+}\) in Ca\(_5\)(BO\(_3\))\(_3\)F:1% Eu\(^{3+}\) phosphor are rarely reported.

The environmental factor \(h_e\) was used to investigate the sites of Eu\(^{3+}\) based on the relationship between the CT bands of Eu\(^{3+}\) and the crystal structure of the host lattice. \(h_e\) can be calculated using the complex crystal chemical bond theory. The smaller the \(h_e\), the larger the charge transfer energy from O\(^2-\) to Eu\(^{3+}\). Through the literature, we know that the PL intensity ratio between the \(^{5}D_0 \rightarrow ^{7}F_2\) and \(^{5}D_0 \rightarrow ^{7}F_1\) transition of Eu\(^{3+}\) increases as the crystal distortion increases. The degree of distortion was calculated by the environmental factor standard deviation (EFSD) \(\sigma(h_e)\). This can provide information on the Eu ion sites. At the same time, the bond energy theory can be used to discuss the site occupancy of dopants into the host. In previous papers, this method has been proven; for example, the site preferential occupancy for Eu in \(\mathrm{Sr}_2\mathrm{V}_2\mathrm{O}_7\), \(\mathrm{Sr}_9\mathrm{Gd}(\mathrm{VO}_4)_7\), \(\mathrm{CaAl}_2\mathrm{Si}_2\mathrm{O}_8\) phosphors,\(^{26}\) as well as Bi\(^{3+}\) in \(\beta\)-Ca\(_3\)P\(_2\)O\(_7\) crystals,\(^{27}\) have been solved though the bond energy method. Furthermore, this method was also used in study of bond energy and preferential occupancy of Eu\(^{3+}\) doped in the \(\mathrm{Ca}_5\)(BO\(_3\))\(_3\)F crystal is a planar BO\(_3\) group. Both Ca and the surrounding anions form a CaO\(_4\)X\(_2\) (X = F or O) octahedral structure, in which Ca(1) forms a CaO\(_4\)F octahedron with six O atoms and one F atom, and Ca(2) forms a distorted octahedral structure with six O atoms. Ca(3) is coordinated with three Ca ion coordination environments in this structure, namely, Ca1, Ca2 and Ca3. The anionic structural group of the\(^{21}\)

2. Experimental

2.1 Synthesis of material

Ca\(_5\)(BO\(_3\))\(_3\)F:1% Eu\(^{3+}\) phosphor was prepared by high-temperature solid-state reaction in air. The desired Ca\(_2\)F\(_2\) (A.R., Macklin), H\(_3\)BO\(_3\) (A.R., Sinopharm), CaCO\(_3\) (99.99%, Aladdin), and Eu\(_2\)O\(_3\) (99.99%, Aladdin) were weighed according to the stoichiometric ratio of Ca\(_5\)(BO\(_3\))\(_3\)F:1% Eu\(^{3+}\), and the raw materials were placed in an agate mortar and ground for half an hour. The uniformly mixed raw materials were transferred to an alumina crucible, heated in a crucible calciner to 1150 °C, and then kept for 4 h. After the sample was cooled to room temperature, it was ground into a powder to obtain the desired sample.

2.2 Material characterization

In this experiment, we used a Bruker D8 Advance X-ray diffractometer to analyze the crystal structure of the prepared phosphor with Cu K\(\alpha\) (\(\lambda = 1.54056 \ \text{Å}\)) radiation and acceleration voltage of 30 kV. The scanning range was 5 to 80 degrees. The sample was detected by FLS980 fluorescence spectrometer to obtain the excitation spectrum and emission spectrum. The excitation source was a 450 W Xe lamp with a slit width of 2 nm and a measured spectral range of 200 nm to 750 nm, with a resolution of 0.2 nm. The sample was tested at room temperature. The Rietveld structure refinement was performed using the General Structure Analysis System (GSAS)\(^{23}\) software in order to determine the change of crystal structure.

3. Results and discussion

3.1 Phase characterization and crystal analysis

Fig. 1 is an XRD pattern of Ca\(_5\)(BO\(_3\))\(_3\)F:1% Eu\(^{3+}\) sample. Comparing the sample diffraction pattern with the standard card, it was found that the diffraction peak data were basically consistent with the Ca\(_5\)(BO\(_3\))\(_3\)F (ICSD-65763) card data, with a \(C1m\) space group and a monoclinic crystal system. There is an impurity phase, namely, Ca\(_3\)B\(_2\)O\(_6\). Fortunately, a very small amount of Ca\(_3\)B\(_2\)O\(_6\) has no effect on our system. Therefore, the substitution of Eu\(^{3+}\) for Ca\(^{2+}\) into Ca\(_5\)(BO\(_3\))\(_3\)F did not change the structure of the crystal.

Fig. 2 shows the crystal structure of Ca\(_5\)(BO\(_3\))\(_3\)F. There are three Ca ion coordination environments in this structure, namely, Ca1, Ca2 and Ca3. The anionic structural group of the Ca\(_5\)(BO\(_3\))\(_3\)F crystal is a planar BO\(_3\) group. Both Ca and the surrounding anions form a CaO\(_4\)X\(_2\) octahedral structure, in which Ca(1) forms a CaO\(_4\)F octahedron with five O atoms and one F atom, and Ca(2) forms a distorted octahedral structure with six O atoms. Ca(3) is coordinated with two F atoms and four O atoms. These polyhedrons are connected to the BO\(_3\) group by sharing O atoms to form a three-dimensional space structure.

The crystal structure of Ca\(_5\)(BO\(_3\))\(_3\)F (ICSD-65763) was used as the starting model for structure refinement. The Rietveld method refers to the point-by-point comparison of the calculated and measured values of the diffraction intensity of a crystal using a computer program, and the least squares method is used to adjust the parameters of the structural atoms and of the peak shape, so that the calculated peak shape is consistent with the measured peak shape. In the structural
refinement of this paper, based on the XRD peak of the existing Ca$_5$(BO$_3$)$_3$F:1% Eu$^{3+}$ crystal and Ca$_5$(BO$_3$)$_3$F standard card as the background, the set function is type 4, and about 30 terms were refined. Fig. 1 shows the observed, calculated and difference results for the Rietveld refinement of Ca$_5$(BO$_3$)$_3$F:1% Eu$^{3+}$ phosphor. The peak intensities and positions exhibited few differences between the experimental and calculated patterns. Crystallographic and refinement parameters are summarized in Table 1. The results show that almost all diffraction peaks can be directed to Ca$_5$(BO$_3$)$_3$F with a monoclinic unit cell (C1m1).

The cell parameters $a$, $b$, $c$, and $\beta$, etc., are close to those of Ca$_5$(BO$_3$)$_3$F (ICSD-65763). The atomic coordinates and isotropic displacement parameters of Ca$_5$(BO$_3$)$_3$F:1% Eu$^{3+}$ phosphor are listed in Table 2. The above results show that the crystal structure data of Ca$_5$(BO$_3$)$_3$F:1% Eu$^{3+}$ simulated by refinement can be well matched with its experimental data.

### 3.2 Photoluminescence properties

Fig. 3(b) is an excitation spectrum of the Ca$_5$(BO$_3$)$_3$F:1% Eu$^{3+}$ sample at a monitoring wavelength of 633 nm, which is composed of a broad excitation band of 225–350 nm, derived from the charge transfer transition of O$^{2-}$ to Eu$^{3+}$, where the strongest absorption peak is at 266 nm. The emission spectrum at an excitation wavelength of 266 nm is shown in Fig. 3(d), consisting of emission peaks at around 576, 612, 652 and 708 nm, corresponding to 5D$_0$ → 7F$_6$, 5D$_0$ → 7F$_5$, 5D$_0$ → 7F$_4$, 5D$_0$ → 7F$_3$, and 5D$_0$ → 7F$_2$ transitions of Eu$^{3+}$ ions, respectively.

We can clearly see that the charge transfer transition peaks of samples O to Eu have a significant shift when the monitoring wavelengths are 576, 612, 619 and 633 nm, as shown in Fig. 3(a) and (b). The two broadband peaks (O$^{2-}$ → Eu$^{3+}$) are located at 266 and 283 nm, respectively, which means that the Eu$^{3+}$ ions exhibit two lattice environments in the Ca$_5$(BO$_3$)$_3$F matrix. However, the excitation and emission spectra of Eu-doped Ca$_5$B$_2$O$_6$ are completely different from our luminescence properties of Eu-doped Ca$_5$(BO$_3$)$_3$F. The former shows an emission band peaking at 422 nm and excitation peaks at 362, 380 and 394 nm ($\lambda_{cm} = 616$ nm). These prove that the different luminescence of Eu is due to Eu occupying the different sites in the Ca$_5$(BO$_3$)$_3$F matrix.
spectrum peak will be around 580 nm. A $^5\text{D}_0 \rightarrow \ ^7\text{F}_0$ transition peak appears in each site. Therefore, based on the number of the peaks, the number of occupied sites of the Eu$^{3+}$ ion crystals can be judged. Fig. 3(c) and (d) show the emission spectra of Ca$_5$(BO$_3$)$_3$F:1% Eu$^{3+}$ upon excitation at 266 nm and 283 nm, respectively. Their peaks locate at 576 nm, which is due to $^5\text{D}_0 \rightarrow \ ^7\text{F}_0$ transition of Eu$^{3+}$ ions. Each $^5\text{D}_0 \rightarrow \ ^7\text{F}_0$ transition peak corresponds to a lattice. Two $^5\text{D}_0 \rightarrow \ ^7\text{F}_0$ peaks, $A_1$ and $A_2$, were found in Fig. 3(c) and (d), which indicate that Eu$^{3+}$ doping in Ca$_5$(BO$_3$)$_3$F has two sites. The data are shown in Table 3 for the luminescent levels of Ca$_5$(BO$_3$)$_3$F:1% Eu$^{3+}$ upon 266 and 283 nm excitation.

Since CT energy is susceptible to the central ionic environment, it can be quantitatively expressed by using environmental factors ($h_e$). $h_e$ consists of four chemical bond parameters: the bond volume polarization ($\alpha_B^\mu$), the covalency ($\xi^\mu$), the coordination number (C. N.) and the presented charge of the ligand ($Q_B^\mu$). Its calculation formula is as follows:

$$h_e = \left(\sum \xi^\mu \alpha_B^\mu Q_B^\mu\right)^{1/2} \quad (1)$$

where $\xi^\mu$ represents the covalent value of $\mu$ type bond, $Q_B^\mu$ is the charge exhibited by the nearest anion and $\alpha_B^\mu$ stands for the polarizability of the $\mu$-type chemical bond volume.

The four chemical bond parameters, with any change, will cause a shift in the CT bands. As $h_e$ increases, the CT energy decreases, which means that the CT bands will produce a red shift. In Table 4, we can see that the $h_e$ values of Ca1, Ca2, and Ca3 are 0.6397, 0.7439, and 0.3514, respectively. Therefore, it can be known that Eu will occupy the Ca1 and Ca2 sites, and at the same time, the O–Eu1 CT band at the Ca1 site corresponds to the peak at 266 nm and the O–Eu2 CT band at Ca2 corresponds to the position at 283 nm.

Table 3  The data for the luminescent levels of Ca$_5$(BO$_3$)$_3$F:1% Eu$^{3+}$ upon 266 and 283 nm excitation

| Energy level transition | The location of the peak (nm) ($\lambda_{ex} = 266$ nm) | Intensity | The location of the peak (nm) ($\lambda_{ex} = 283$ nm) | Intensity |
|-------------------------|-------------------------------------|-----------|-------------------------------------|-----------|
| $^5\text{D}_0 \rightarrow \ ^7\text{F}_0$ | 576 | 576 | 583 | 581 |
| $^3\text{D}_0 \rightarrow \ ^7\text{F}_1$ | 592 | 233 668.172 | 592 | 149 367.984 |
| $^3\text{D}_0 \rightarrow \ ^7\text{F}_2$ | 612 | 685 254.813 | 618 | 1 102 500 |
| $^3\text{D}_0 \rightarrow \ ^7\text{F}_3$ | 652 | 651 | 708 |
| $^3\text{D}_0 \rightarrow \ ^7\text{F}_4$ | 708 | 2.933 | 7.381 |
| $^3\text{D}_0 \rightarrow \ ^7\text{F}_2$ | 708 | 2.933 | 7.381 |

Fig. 3  (a) and (b) Excitation spectra under different monitoring wavelengths of Ca$_5$(BO$_3$)$_3$F:1% Eu$^{3+}$; (c) and (d) emission spectra of Ca$_5$(BO$_3$)$_3$F:1% Eu$^{3+}$ under 266 and 283 nm excitation.
the f–f transition relative intensity is mainly affected by the Ca$^{2+}$ symmetry. The different $^5D_0 \rightarrow ^7F_j$ transition intensities of Eu$^{3+}$ depend on the local symmetry of the Eu$^{3+}$ ion crystal field. The $^5D_0 \rightarrow ^7F_2$ transition is sensitive, while the $^5D_0 \rightarrow ^7F_1$ transition is stable to the crystal field environment. For example, when the Eu$^{3+}$ ion is in a site with a strict inversion center, it will be dominated by the allowable $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition, and the emission spectrum is around 590 nm, which is orange light. When the Eu$^{3+}$ ion is in the site away from the inversion center, the parity selection in the crystal is relaxed, and a $^5D_0 \rightarrow ^7F_2$ electric dipole transition will occur; the emission spectrum is around 610 nm, emitting red light. If the intensity of the $^5D_0 \rightarrow ^7F_2$ transition is much higher than the intensity of $^5D_0 \rightarrow ^7F_1$, the Eu$^{3+}$ ion mainly occupies the non-inversion symmetry of the lattice. It is known that the PL intensity ratio between $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transition of Eu$^{3+}$ increases as the crystal distortion increases. The degree of distortion can be calculated by using the standard deviation of

| Central ion | Bond type | Distance (Å) | $f_v$ | $o_v$ | $Q_v$ | C.N. | $h_e$ | $(h_e)$ | $\sigma(h_e)$ | O–Eu charge transfer peak |
|------------|-----------|-------------|------|------|-------|------|-------|--------|-------------|--------------------------|
| Ca1/Eu     | Ca1–O1    | 2.3556      | 0.1160| 0.4491| 1.3333| 1    | 0.6397| 0.3043  | 0.1607      | 266 nm                   |
| Ca1–O1     | 2.3960    | 0.1151      | 0.4819| 1.3333| 1    |       | 0.3140|         |            |                          |
| Ca1–O2     | 2.2283    | 0.1191      | 0.3569| 1.3333| 1    |       | 0.2748|         |            |                          |
| Ca1–O2     | 2.4020    | 0.1150      | 0.4870| 1.3333| 1    |       | 0.3155|         |            |                          |
| Ca1–O4     | 2.2428    | 0.1187      | 0.3666| 1.3333| 1    |       | 0.2781|         |            |                          |
| Ca1–F      | 2.3810    | 0.0258      | 0.2053| 1.3333| 1    |       | 0.0970|         |            |                          |
| Ca2/Eu     | Ca2–O1    | 2.3237      | 0.1167| 0.4244| 1.3333| 1    | 0.7439| 0.2967  | 0.0184      | 283 nm                   |
| Ca2–O2    | 2.4795    | 0.1135      | 0.5557| 1.3333| 1    |       | 0.3348|         |            |                          |
| Ca2–O4     | 2.4653    | 0.1137      | 0.5426| 1.3333| 1    |       | 0.3312|         |            |                          |
| Ca2–O4     | 2.5136    | 0.1129      | 0.5882| 1.3333| 1    |       | 0.3436|         |            |                          |
| Ca2–O5     | 2.3311    | 0.1165      | 0.4300| 1.3333| 1    |       | 0.2984|         |            |                          |
| Ca2–O5     | 2.3726    | 0.1156      | 0.4627| 1.3333| 1    |       | 0.3083|         |            |                          |
| Ca3/Eu     | Ca3–O3    | 2.2691      | 0.1050| 0.3493| 1.0000| 1    | 0.3514| 0.1915  | 0.0520      |                          |
| Ca3–O3     | 2.3551    | 0.1031      | 0.4080| 1.0000| 1    |       | 0.2051|         |            |                          |
| Ca3–O5     | 2.3363    | 0.1056      | 0.2512| 0.6667| 1    |       | 0.1086|         |            |                          |
| Ca3–O5     | 2.3371    | 0.1056      | 0.2515| 1.0000| 1    |       | 0.1630|         |            |                          |
| Ca3–F      | 2.4366    | 0.0257      | 0.2289| 1.0000| 1    |       | 0.0767|         |            |                          |
| Ca3–F      | 2.4497    | 0.0257      | 0.2347| 1.0000| 1    |       | 0.0777|         |            |                          |

Fig. 4 The coordination environment mechanism of Ca1 (or Eu1), Ca2 (or Eu2), and Ca3 (or Eu3) in Ca$_5$(BO$_3$)$_3$:F:1% Eu.
Environmental factor (EFS) \( \sigma(h_0) \), which can be calculated as below:

\[
\sigma(h_0) = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (h_i - \bar{h})^2}
\]

where

\[
h_i = \left( f_i^s a^s \right) ^{1/2} Q_i^u
\]

and

\[
\delta = \frac{1}{N} \sum_{i=1}^{N} h_i
\]

The related chemical parameters of the covalency \( f^s \), the present charge of the ligand in the binary crystals, and the polarizability of the chemical bond volume \( a^s \) are shown in Table 4. On the basis of the eqn (2)-(4), their standard deviation for the six Ca–O environmental factors (\( \sigma(h_0) \)) of Ca1O5F, Ca2O4F2, and Ca3O6 polyhedrons in Ca5(BO3)3F:1% Eu can be calculated to be 0.1607, 0.0184 and 0.052, respectively. Generally, the \( \ln C_{D_{0}}^h / C_{D_{0}}^w \) value of Eu3+ increases with increasing \( \sigma(h_0) \). The \( \sigma(h_0) \) value of Ca1O5F in Ca5(BO3)3F:1% Eu is larger than that of Ca2O4F2. By comparison, the intensity ratio of \( 5D_0 \rightarrow 7F_2 \) transition at Ca2 (7.381) is 2.5 times stronger than that of Eu3+ at Ca1 site (2.933). Therefore, the \( \ln C_{D_{0}}^h / C_{D_{0}}^w \) value of Eu3+ in the Ca1O5F site is stronger than that in the Ca2O4F2 site. Ca1 and Ca2 correspond to excitations at 283 nm and 266 nm, respectively. However, this is contrary to the conclusion drawn in Table 4. In ideal state, the order of \( \sigma(h_0) \) is in Fig. 4. When Eu3+ is doped into Ca5(BO3)3F, part of the Ca2+ ions must be occupied by Eu3+, so the local environment of Eu3+ must be changed in order to keep the conservation of charge in Fig. 4(a) and (b). At this time, one F of the sub-stationary \([\text{Eu1]}_{\text{O5}}\text{F}\) and \([\text{Eu3]}_{\text{O4}}\text{F}_2\) will be replaced by an O to maintain their own stability; \([\text{Eu2]}_{\text{O5}}\text{F}\) will receive an F, and it will eventually become a 7-coordinated environment in Fig. 4(c). In summary, we can conclude that the Ca2 distortion degree should be greater than that of Ca1. Therefore, Ca1 and Ca2 correspond to excitations at 266 nm and 283 nm, respectively, consistent with the results obtained in Table 4.

### 3.3 Chemical bond energy calculation

From the point of view of matched valence, the bond energy of Eu3+ into the Ca5(BO3)3F phosphor can be estimated by the following equation,

\[
\Delta E_{\text{Eu}^{3+} \rightarrow \text{O}^{-}} = E_{\text{M}} - E_{\text{M} + \text{O}^{-}}
\]

Table 6 The bond parameters of the central atom and values of bond energy when Eu3+ locates at Ca and B sites in Ca5(BO3)3F. All of the bond energy units are kcal mol\(^{-1}\).

| Central atom | Coordination atom | Count | \( d (\text{Å}) \) | \( E_{\text{M}} \) | \( E_{\text{M} + \text{O}^{-}} \) | \( \Delta E_{\text{Eu}^{3+} \rightarrow \text{O}^{-}} \) |
|--------------|------------------|-------|----------------|----------------|----------------|------------------|
| Ca1          | O2               | 1×    | 2.2283         | 62.4781        | 48.0633        | 11.0351          |
|              | O4               | 1×    | 2.2428         | 60.7770        | 46.2162        |                   |
|              | O1               | 1×    | 2.3556         | 44.2901        | 34.0716        |                   |
|              | O1               | 1×    | 2.3960         | 39.7088        | 30.5473        |                   |
|              | O2               | 1×    | 2.4020         | 39.0701        | 30.5599        |                   |
|              | F1               | 1×    | 2.3810         | 41.3517        | 31.8111        |                   |
| Ca2          | O1               | 1×    | 2.3237         | 48.2781        | 48.0632        | 1.7744           |
|              | O2               | 1×    | 2.4795         | 31.6867        | 46.2162        |                   |
|              | O4               | 1×    | 2.4653         | 32.9264        | 34.0716        |                   |
|              | O4               | 1×    | 2.5136         | 28.8969        | 30.5473        |                   |
|              | O5               | 1×    | 2.3311         | 47.3221        | 30.5599        |                   |
|              | O5               | 1×    | 2.3726         | 42.3012        | 31.8111        |                   |
| Ca3          | O3               | 1×    | 2.2691         | 55.9549        | 37.1394        | 14.2398          |
|              | O3               | 1×    | 2.3551         | 44.3500        | 24.3760        |                   |
|              | O5               | 1×    | 2.3363         | 46.6617        | 25.3297        |                   |
|              | O5               | 1×    | 2.3731         | 46.3609        | 22.2999        |                   |
|              | F1               | 1×    | 2.4366         | 35.5821        | 36.4041        |                   |
|              | F1               | 1×    | 2.4497         | 34.3444        | 32.5416        |                   |
| B1           | O2               | 1×    | 1.4296         | 107.8004       | 73.209         | 551.7228         |
|              | O5               | 1×    | 1.5032         | 88.35499       | 70.712         |                   |
|              | O2               | 1×    | 1.2091         | 149.2999       | 687.725        |                   |
| B2           | O1               | 1×    | 1.4297         | 107.7712       | 624.1322       | 636.8898         |
|              | O1               | 1×    | 1.4304         | 107.5676       | 622.9525       |                   |
|              | O3               | 1×    | 1.2329         | 183.4429       | 1062.3664      |                   |
where $V_M$ presents the dopant valence and $V_N$ stands for the valence state of N. When the pure Ca$_5$(BO$_3$)$_3$F phosphor does not have any dopant, the value of $V_N/V_M$ is 1. This indicates that the valence state has no effect on the bond energy. If $V_N/V_M$ is not equal to 1, it implies that the valence state effectively affects the crystal bond energy. Consequently, the effect of different valence states of the dopant on the Ca$^{2+}$ site bond energy can be quantitatively described through eqn (5). The $J$ and $d_0$ values are given in the report of Li et al.$^{20}$ $d_{M-O}$ represents the bond length between atoms M and O. Required $d_0$ and $J$ value tables are in Table 5. When Eu enters Ca$_5$(BO$_3$)$_3$F, the bond energy difference is calculated by the following equation:

$$\Delta E_{Eu} = |E_{Eu} - E_{Eu-0}|$$

Here, $\Delta E_{Eu}^M$ is the bond energy difference when the Eu ion locates at the site of Ca$^{2+}$. As previously reported, we can know that the dopants preferentially occupy a site where the bond energy difference is small ($\Delta E_{Eu}^M$), that is, a site having a smaller absolute value of $\Delta E_{Eu}^M$. According to the detailed crystallographic data from a pure Ca$_5$(BO$_3$)$_3$F phosphor (longer Ca–O bonds of 1.967 Å; shorter B–O bonds of 1.371 Å; longer Ca–F bonds of 1.842 Å), all calculated $E_{Eu}$ and $\Delta E_{Eu}$ values of Eu$^{3+}$ on both Ca$^{2+}$ and B$^{3+}$ sites are shown in Table 6. The corresponding occupancies of Eu$^{3+}$ are summarized, according to the calculated $\Delta E_{Eu}$ values. Dopants preferentially occupy the sites where the bond energy difference ($\Delta E_{Eu}$) is smaller; that is, Eu$^{3+}$ ions preferentially occupy Ca$^{2+}$ sites if $|\Delta E_{Eu}^{Ca}| < |\Delta E_{Eu}^{Eu-0}|$; they preferentially occupy B$^{3+}$ sites if $|\Delta E_{Eu}^{Ca}| > |\Delta E_{Eu}^{Eu-0}|$, otherwise.

There are three Ca$^{2+}$ sites and two B$^{3+}$ sites in the structure of Ca$_5$(BO$_3$)$_3$F. On the basis of the bond energy method, the values of $\Delta E_{Eu}$ and $\Delta E_{Eu}$ have been listed in Table 6. The order of difference of bond energy that Ca$^{2+}$ and B$^{3+}$ ions are replaced by Eu$^{3+}$ is $\Delta E_{Eu}^{Ca} < \Delta E_{Eu}^{Eu-0} < \Delta E_{Eu}^{Ca} \ll \Delta E_{Eu}^{Eu} < \Delta E_{Eu}^{Eu-0}$, which means that Eu$^{3+}$ preferentially replaces Ca2 and Ca1. According to our calculation, Eu$^{3+}$ preferentially occupies Ca2 and Ca1 sites, which is consistent with the environmental factor, the $\sigma(h_e)$ analysis and PL spectrum.

4. Conclusions

The photoluminescence of Ca$_5$(BO$_3$)$_3$F: Eu$^{3+}$ shows that the excitation spectrum consists of some broadband from the $O^{2-}$ to Eu$^{3+}$ charge transfer (CT) band and some sharp emission peaks derived from the f-f transition of Eu$^{3+}$. Two different $O^{2-}$ to Eu$^{3+}$ CT broad bands with the peaks at 266 and 283 nm in Ca$_5$(BO$_3$)$_3$F: Eu$^{3+}$ can be assigned to the Eu$^{3+}$ sites occupying Ca1 and Ca2, respectively. Two $^5D_0 \rightarrow ^7F_0$ peaks, $A_1$ and $A_2$, were found, which implies that Eu$^{3+}$ doped in Ca$_5$(BO$_3$)$_3$F has two sites. According to the dielectric theory of the crystal, the important chemical bonds such as the polarizability, the covalency and the environmental factor were quantitatively calculated. When Eu$^{3+}$ ions occupy the Ca1, Ca2 and Ca3 sites of Ca$_5$(BO$_3$)$_3$F, their environmental factors are 0.6397, 0.7439 and 0.3514, respectively. The intensity ratio of $^5D_0 \rightarrow ^7F_1$ transition to the $^5D_0 \rightarrow ^7F_0$ transition of Eu$^{3+}$ at Ca2 (7.381) is 2.5 times stronger than that of Eu$^{3+}$ at Ca1 site (2.933). The calculated ideal $\sigma(h_e)$ showed that the $I[^5D_0/[^7F_1]]/I[^5D_0/[^7F_0]]$ value at Eu1 is larger than that at Eu2 site. The local nonequivalence substitution distortion model was proposed to explain the result. The smaller deviation value of the bond energy method of $\Delta E_{Eu}^{Ca}$ and $\Delta E_{Eu}^{Eu}$ showed that the preferential sites of Eu$^{3+}$ ion occupancy in Ca$_5$(BO$_3$)$_3$F are Ca2 and Ca1. All of results are consistent with each other. The three theoretical methods provide us a new strategy to study the occupancy of Eu$^{3+}$ in Eu$^{3+}$-doped inorganic compounds.

**Conflicts of interest**

There are no conflicts to declare.

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