Synthesis and luminescence properties of novel Eu\(^{2+}/3^+\), Ce\(^{3+}\) ion single- and co-doped BaZn\(_2\)(PO\(_4\))\(_2\) phosphors for white-light applications

Yuhan Zhu, Wenjun Wang, Zefeng Xu, Qi Luo, Ling Li* and Xiaoguang Liu*

A series of novel Eu\(^{2+}/3^+\), Ce\(^{3+}\) ion single- and co-doped BaZn\(_2\)(PO\(_4\))\(_2\) samples were prepared via a high-temperature solid-state reaction. XRD powder diffraction results indicated that all of the products were pure phases. The photoluminescence properties of BaZn\(_2\)(PO\(_4\))\(_2\):Eu showed that Eu\(^{2+}\) and Eu\(^{3+}\) coexist in the system and Eu\(^{3+}\) can be self-reduced to Eu\(^{2+}\) in an air atmosphere. In addition, the strongest emission peak of Eu\(^{3+}\) ions at 593 nm implied that Eu\(^{3+}\) ions occupy the inversion symmetry lattice and also the site of Zn in BaZn\(_2\)(PO\(_4\)). We used the theoretical method of bond energy to explain why the self-reduction of Eu\(^{3+}\) to Eu\(^{2+}\) can occur in the BaZn\(_2\)(PO\(_4\)) system. The calculation results indicated that the bond energy change value \(\Delta E_{\text{Eu}^{3+}\rightarrow\text{Eu}^{2+}}\) is smaller than \(\Delta E_{\text{Eu}^{3+}\rightarrow\text{O}^{2-}}\), indicating that Eu\(^{2+}\) ions are more likely to occupy the Zn site and more stable than Eu\(^{3+}\) ions in BaZn\(_2\)(PO\(_4\)). Furthermore, the energy transfer process between Ce\(^{3+}\) and Eu\(^{2+}\) ions in the photoluminescence spectrum and the decay lifetime were observed, and the energy transfer mechanism was determined to be a dipole–dipole interaction. In this work, by adjusting the ratio of Ce and Eu ions, the emission color can be changed from blue to white, implying that the phosphor can be used as a promising candidate in the manufacture of white LEDs.
MZn$_2$(PO$_4$)$_2$ (M = Mg, Ca, Sr, Ba) is an important host with the advantages of low cost, high luminescence efficiency, low synthesis temperature and good thermal stability. Based on these characteristics, BaZn$_2$(PO$_4$)$_2$ has also become one of the hot topics of discussion. In the previous reports, the properties of BaZn$_2$(PO$_4$)$_2$ phosphors have been studied. For example, the photoluminescence properties of BaZn$_2$(PO$_4$)$_2$:Ce$^{3+}$, Tb$^{3+}$/Dy$^{3+}$ (ref. 27 and 28) and red phosphor BaZn$_2$(PO$_4$)$_2$:Sm$^{3+}$ (ref. 29) have been studied. However, the lattice occupancy and the self-reduction phenomenon of Eu$^{3+}$ doping in BaZn$_2$(PO$_4$)$_2$ and the energy transfer behavior of Ce$^{3+}$, Eu$^{2+}$ co-doping in BaZn$_2$(PO$_4$)$_2$ have not been discussed.

In this work, a series of Eu$^{2+}$/3+ and Ce$^{3+}$ single- and co-doped BaZn$_2$(PO$_4$)$_2$ products were synthesized via a high-temperature solid-state reaction. First, the self-reduction phenomenon was found from Eu$^{3+}$ to Eu$^{2+}$ in the BaZn$_2$(PO$_4$)$_2$ system. Next, we use the bond energy method to analyze the self-reduction reaction from Eu$^{3+}$ to Eu$^{2+}$ in the lattice position of Zn in BaZn$_2$(PO$_4$)$_2$. At the same time, we use this method to explain why Eu$^{3+}$ can be self-reduced to Eu$^{2+}$. Finally, the photoluminescence characteristics and energy transfer mechanisms of Ce$^{3+}$—Eu$^{2+}$ co-doped BaZn$_2$(PO$_4$)$_2$ are studied in detail. In addition, based on the energy transfer, the emission color can be adjusted from blue to white by adjusting the relative proportions of Ce and Eu ions.

2 Experimental

2.1 Preparation of phosphors

A series of Eu$^{2+}$/3+ and Ce$^{3+}$ ion single- and co-doped BaZn$_2$(PO$_4$)$_2$ phosphors were synthesized by a traditional high-temperature solid-state method in an air atmosphere. The raw materials selected include BaCO$_3$, (NH$_4$)$_2$HPO$_4$, ZnO, CeO$_2$ and Eu$_2$O$_3$. The exact amount of raw materials of each component was calculated, and the analytical balance was accurately and effectively weighed. The raw materials were thoroughly ground and mixed evenly in an agate mortar, and transferred to an alumina crucible of appropriate size. Then the mixtures were pre-sintered at 850 °C for 4 h, and further calcined at 1000 °C for 4 h. Finally, all the as-synthesized products were naturally cooled to room temperature and ground to a powder.

2.2 Characterization methods

The phase purity characterization of the phosphors was performed using an X-ray diffractometer. Excitation source information: 40 kV, 40 mA on a Bruker D8 Advance X-ray diffractometer with Cu Kα ($\lambda = 1.5418$ Å) radiation. The scanning mode is continuous, the scanning speed is 2° per minute, and the test range is 5–80°. The morphologies of the samples were characterized by scanning electron microscopy (SEM) on an instrument of JSM 6510 LV Electronics, Japan; the resolution is 3 nm. The spectrometer FLS980 was used to test the emission and excitation as well as decay curves of the samples. A 450 W xenon lamp was used as a steady-state light source in the test and a 60 W μF flash lamp was used as the decay curve test source.

3 Results and discussion

3.1 Phase analysis and crystal structure

Fig. 1 depicts the XRD patterns of Eu$^{2+}$/3+, Ce$^{3+}$ ion single- and co-doped BaZn$_2$(PO$_4$)$_2$ phosphors. Compared with the standard card JCPDS#16-0554, it can be seen that the diffraction peaks of the synthesized samples corresponded well to the standard card, and no other diffraction peaks appeared. Therefore, the prepared samples were all pure phases and no impurities were formed. This indicates that rare-earth ions enter the BaZn$_2$(PO$_4$)$_2$ lattice, and no other impurity phases are formed; hence, the doping of these ions does not cause any change in the lattice structure of BaZn$_2$(PO$_4$)$_2$. However, the XRD patterns of Eu$^{2+}$/3+, Ce$^{3+}$ ion single- and co-doped BaZn$_2$(PO$_4$)$_2$ phosphors are light-shifted compared with the pure BaZn$_2$(PO$_4$)$_2$ compound. This result could be attributed to the larger ionic radii of Eu$^{3+}$ ($\text{CN} = 7, \text{r} = 1.09$ Å and $1.101$ Å for CN = 4 and 7, respectively) and Ce$^{3+}$ ($\text{CN} = 7, \text{r} = 1.07$ Å for CN = 7, respectively) and Zn$^{2+}$ ($\text{CN} = 4, \text{r} = 0.60$ Å for CN = 4, respectively). Moreover, as the radius of the dopant ions increase, the lattice gets distorted, and hence, the position of the diffraction peak shifts slightly.

The unit cell of BaZn$_2$(PO$_4$)$_2$ is exhibited in Fig. 2. BaZn$_2$(PO$_4$)$_2$ belongs to a monoclinic crystal structure of space group P2$_1$/c. The unit cell contains five kinds of cation coordination environments, namely Ba$^{2+}$, Zn$^{1+}$, Zn$^{2+}$, P$_1$ and P$_2$. Ba$^{2+}$ form isolated BaO polyhedra, which has seven coordination sites with an asymmetric polyhedron surrounded by oxygen atoms. Both Zn$^{1+}$ and Zn$^{2+}$ are tetrahedrons connected to oxygen. At the same time, there are two environments of tetrahedrons, one with vertices connected to a polyhedron centered on Ba and the other with a co-edge. P$_1$ and P$_2$ are also two four-coordinated sites. The parameters of the unit cell are $a = 8.598$ Å, $b = 9.761$ Å, $c = 9.159$ Å, and $V = 768.45$ Å$^3$, respectively.

The SEM micrograph, EDS mapping images and elemental distribution of Eu/Ce doped in BaZn$_2$(PO$_4$)$_2$ synthesized under...
ambient conditions are displayed in Fig. 3. According to the SEM image of the two samples, we can see that all the samples have a block structure with inconsistent size. According to the EDS scanning structure and elemental distribution image, the atomic distribution patterns of Ba, O, P, Zn, Eu or Ce can be obtained very clearly in the Eu- or Ce-doped BaZn2(PO4)2 samples. These indicate that the Ce and Eu elements are indeed present in the BaZn2(PO4)2 sample.

3.2 Photoluminescence properties of BaZn2(PO4)2:Eu

The excitation and emission spectra of the undoped BaZn2(PO4)2 sample are shown in Fig. 4. At an excitation wavelength of 240 nm, the emission spectrum consists of a broad peak at a maximum wavelength position of 345 nm in the wavelength range of 300–425 nm (Fig. 4a). In the excitation spectrum (Fig. 4b), the maximum wavelength position of the excitation spectrum is at 240 nm.

Fig. 5 displays the photoluminescence spectra of BaZn2(PO4)2:Eu phosphors. It can be found that a series of sharp peaks with an emission spectrum between 550–750 nm are due to the 5D0–7FJ (J = 0, 1, 2, 3, 4) transition of Eu3+ upon the 258 nm excitation, whose maximum wavelength position belongs to the 5D0–7F1 transition at 593 nm. By monitoring the emission at 593 nm, it was found that the excitation spectrum in the range of 200–550 nm consists of a broadband excitation with a central wavelength at 258 nm, which is attributable to the charge transition of O2−–Eu3+ and some sharp peaks can be ascribed to the characteristic excitation of Eu3+ in Fig. 5(a). We know that when the Eu3+ ion is in a position with a strict inversion center, it will be dominated by the allowable 5D0–7F1 magnetic dipole transition, and the emission peak is around 590 nm. Therefore, it can be judged that in the BaZn2(PO4)2:Eu sample we prepared, the Eu3+ ion occupies the inversion symmetry position. According to the asymmetrical structure centered on the Ba atom, it is presumed that the Eu3+ ion enters a symmetric tetrahedral structure centered on the Zn atom.

The spectrum of the phosphor BaZn2(PO4)2:Eu at different excitation and monitoring wavelengths is shown in Fig. 5(b).
Upon monitoring the wavelength at 532 nm, it was found that the excitation spectrum of BaZn$_2$(PO$_4$)$_2$:Eu consists of a narrow band absorption ranging from 200 to 450 nm with the dominant absorption peak at 374 nm, which comes from the 4f \( \rightarrow \) 5d transition of Eu$^{2+}$ ions. Under the excitation of 283 and 375 nm, BaZn$_2$(PO$_4$)$_2$:Eu phosphors exhibited broad emission bands in the range of 350–750 nm with a maximum at 532 nm, which originates from the 5d \( \rightarrow \) 4f transitions of Eu$^{2+}$ ions. At the same time, the emission sharp peaks belonging to the 5D$_0$ \( \rightarrow \) 7F$_1$ transition of Eu$^{3+}$ at 593 nm can also be clearly observed. Therefore, the existence of Eu$^{2+}$ was proved. From Fig. 5(a), it can be observed that Eu$^{2+}$ and Eu$^{3+}$ coexist in the system, indicating that the self-reduction process from Eu$^{3+}$ to Eu$^{2+}$ occurred in the BaZn$_2$(PO$_4$)$_2$ crystal. We also made a Gaussian fitting to the excitation spectrum monitored at 532 nm wavelength and the emission spectrum at 365 nm wavelength, as shown in Fig. 5(c and d). The center positions of the three sub-excitation peaks obtained by Gaussian fitting are at 282, 344, and 375 nm, respectively. This is due to the splitting of the excitation peak broadband. Similarly, two sub-emission peaks of the emission spectrum are obtained with center positions at 500 and 544 nm. From this, we conclude that Eu$^{2+}$ ions occupy two sites in the BaZn$_2$(PO$_4$)$_2$ lattice.

In BaZn$_2$(PO$_4$)$_2$ crystals, there are five kinds of cationic sites that can be occupied by the dopant, namely Ba1, Zn1, Zn2, P1 and P2. From the photoluminescence spectrum, we know that the strongest position of the emission peak of Eu$^{3+}$ ions is at 593 nm, indicating that Eu$^{3+}$ ions are in the inversion symmetry position and occupy the position of Zn. We use the theoretical method of bond energy to explain the reduction of Eu$^{3+}$ to Eu$^{2+}$ in the air and the priority of Eu$^{2+}$ and Eu$^{3+}$ ions in the lattice position of Zn in the system. It can be used by the following expression:

$$E_{Zn^{2+} \rightarrow O_2^-} = J \exp \left( \frac{d_0 - d_{M-O}}{0.37} \right) \left( \frac{V_N}{V_M} \right)$$  \hspace{1cm} (1)$$

where $V_N$ is the valence state of Zn$^{2+}$ cations in the system and $V_M$ is the number of valence states of Eu$^{2+}$ and Eu$^{3+}$. For Eu$^{3+}$ ions taken as an example, if Eu$^{3+}$ occupies the Zn site, then $V_N/V_M = 2/3$; if the doping ion Eu$^{2+}$ is at the Zn site, then $V_N/V_M = 1/1$. This indicates that the valence state has some effect on the bond energy of the crystal. $J$ represents the intrinsic standard atomization energy and $d_0$ is equal to a constant for a given pair of atoms. The $J$ and $d_0$ of the compounds involved are listed in Table 1. $E_{M-O}$ is the bond energy value. According to formula (1), the bond energy values $E_{Zn^{2+} \rightarrow O^-}$, $E_{Eu^{3+} \rightarrow O^-}$ and $E_{Eu^{2+} \rightarrow O^-}$ are

<table>
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<th>Ions</th>
<th>$J$ (kcal mol$^{-1}$)</th>
<th>$d_0$ (Å)</th>
</tr>
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<tr>
<td>Zn$^{2+}$−O$^{-}$</td>
<td>86.900</td>
<td>1.704</td>
</tr>
<tr>
<td>Eu$^{3+}$−O$^{-}$</td>
<td>109.400</td>
<td>2.074</td>
</tr>
<tr>
<td>Eu$^{2+}$−O$^{-}$</td>
<td>56.180</td>
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Fig. 5  (a and b) Excitation ($\lambda_{em}$ = 593, 532 nm) and emission spectra ($\lambda_{ex}$ = 258, 283 and 375 nm) of the BaZn$_2$(PO$_4$)$_2$:Eu sample. (c and d) Gaussian fitting excitation ($\lambda_{em}$ = 532 nm) and emission band ($\lambda_{ex}$ = 365 nm) of BaZn$_2$(PO$_4$)$_2$:Eu.
calculated and shown in Table 2. The variation of bond energy reflects the preferential occupancy of the dopant ions. Its calculation method is as follows:

\[
\Delta E_{\text{Eu}^{2+/3+}} = |E_{\text{Zn}^{2+/3+}} - E_{\text{Eu}^{2+/3+}}|
\]

where \(\Delta E_{\text{Eu}^{2+/3+}}\) is the variation of bond energy, that is, a change of bond energy caused when \(\text{Eu}^{2+}\) and \(\text{Eu}^{3+}\) ions enter the lattice to replace the \(\text{Zn}1\) and \(\text{Zn}2\) sites. The smaller the change in bond energy, the easier it is to be occupied by dopant ions. Here, if the bond energy change value \(\Delta E_{\text{Eu}^{2+/3+}}\) is smaller than \(\Delta E_{\text{Eu}^{2+/3+}}\), then the \(\text{Eu}^{2+}\) ion is more likely to occupy the position of \(\text{Zn}\), and vice versa. From eqn (2), we calculated the variation in bond energy when \(\text{Eu}^{2+/3+}\) ions occupy the \(\text{Zn}1\) and \(\text{Zn}2\) sites in the \(\text{BaZn}_2(\text{PO}_4)_2\) system. The results are shown in Table 2. For \(\text{Eu}^{2+/3+}\) ions, we can see that the bond energy variation values of \(\Delta E_{\text{Eu}^{2+/3+}}\) at the \(\text{Zn}\) site is smaller than that of \(\Delta E_{\text{Eu}^{2+/3+}}\), so \(\text{Eu}^{2+}\) is more likely to occupy this site than the \(\text{Eu}^{3+}\) ion. At the same time, this also implies that \(\text{Eu}^{2+}\) is more stable in the \(\text{Zn}\) site and it provides conditions that \(\text{Eu}^{2+}\) can be reduced to \(\text{Eu}^{2+}\) under non-reducing condition.

In summary, we calculated that when \(\text{Eu}^{2+}\) and \(\text{Eu}^{3+}\) ions are into the \(\text{BaZn}_2(\text{PO}_4)_2\) matrix, the bond energy change values of \(\text{Eu}^{2+}\) and \(\text{Eu}^{3+}\) ions at the \(\text{Zn}1\) and \(\text{Zn}2\) sites by using the theoretical method of bond energy. The bond energy change value \(\Delta E_{\text{Eu}^{2+/3+}}\) is smaller than \(\Delta E_{\text{Eu}^{2+/3+}}\), indicating that \(\text{Eu}^{2+}\) is more likely to occupy the \(\text{Zn}\) site than \(\text{Eu}^{3+}\), which also implies that \(\text{Eu}^{3+}\) can be self-reduced to \(\text{Eu}^{2+}\). All theoretical calculations are consistent with the PL spectrum phenomena.

Based on the principle of charge compensation mechanism, when \(\text{Eu}^{3+}\) replaces the site of \(\text{Zn}^{3+}\), the charge in the environment is unbalanced. In order to maintain the overall charge exhibiting electrical neutrality, the formation of the cationic vacancy defect \(\text{Zn}^{2+}\) will generate two negative electrons to compensate for the cation vacancy defects induced by \(\text{Eu}^{3+}\). Then form a dipole complex \(\text{Zn}^{2+}\), where \(\text{Eu}^{3+}\) represents an electron donor and \(\text{Eu}^{3+}\) an electron acceptor. When the negative charge generated on \(\text{Zn}^{2+}\) is transferred to \(\text{Eu}^{3+}\), \(\text{Eu}^{3+}\) will be reduced to \(\text{Eu}^{2+}\):

\[
2\text{Eu}^{2+} + 3\text{Zn}^{2+} \rightarrow \text{Zn}^{2+} + 2\text{Eu}^{3+}
\]

3.3 Photoluminescence properties of \(\text{BaZn}_2(\text{PO}_4)_2\):Ce, Eu

Fig. 6 depicts the excitation and emission spectra of different concentrations of \(\text{Ce}^{3+}\) doped in \(\text{BaZn}_2(\text{PO}_4)_2\). For Fig. 6(a), under the monitoring of 336 nm, the excitation spectrum is in the range of 230–310 nm, and the strongest absorption of these excitation bands is about 287 nm, which is due to the transition of the \(\text{Ce}^{3+}\) ion from the ground state to crystal field splitting level of the 5d state. In general, the emission spectrum of \(\text{Ce}^{3+}\) ion sample has a dual characteristic due to the ground state \(\text{F}_{5/2}\) and \(\text{F}_{7/2}\) spin orbital splitting, which indicates that \(\text{Ce}^{3+}\) is successfully doped into \(\text{BaZn}_2(\text{PO}_4)_2\). As shown in Fig. 6(b), the emission spectra have two broad bands centered at 334 and 410 nm in the range of 300–500 nm, which can be clearly observed under the excitation at 287 nm.

The excitation spectra of the \(\text{BaZn}_2(\text{PO}_4)_2\):x% Ce sample monitored at 336, 356 and 410 nm are shown in Fig. 6(c–e). We can see that the photoluminescence intensity reaches the maximum when the doping concentration of \(\text{Ce}^{3+}\) is 0.5%. At the same time, we normalized the excitation spectra under these different monitoring wavelengths, as shown in Fig. 6(f–h). At the monitoring wavelength of 336 nm, the broadband center of the excitation spectrum was located at 286 nm; it is worth noting that when the monitoring wavelength is 356 nm, the central position of the excitation spectrum changes with different concentrations of \(\text{Ce}^{3+}\) doping, that is, the central position of the broad excitation bands is 290 and 305 nm, respectively. In addition, the excitation spectrum exhibited a red shift phenomenon when monitored at 410 nm which is due to the influence of the crystal field. By comparing the excitation spectra at different monitoring wavelengths in Fig. 6, it can

Table 2  Bond energy of \(\text{Zn}^{n+}–\text{O}\) bonds in \(\text{BaZn}_2(\text{PO}_4)_2\) \((\text{Zn}^{n+}–\text{O}^-)\) and bond energy of \(\text{Eu}–\text{O}\) bond \((\text{Eu}–\text{O}^-)\) and variation in bond energy when \(\text{Eu}^{2+/3+}\) is at the sites of \(\text{Zn}1\) and \(\text{Zn}2\) in \(\text{BaZn}_2(\text{PO}_4)_2\) \((\Delta E_{\text{Eu}^{2+/3+}})\). The units are kcal mol\(^{-1}\)

<table>
<thead>
<tr>
<th>Central atom</th>
<th>Coordination atom</th>
<th>Count</th>
<th>(d_{\text{Zn}–\text{O}})</th>
<th>(E_{\text{M}–\text{O}})</th>
<th>(E_{\text{Eu}–\text{O}})</th>
<th>(E_{\text{Eu}^{2+/3+}})</th>
<th>(\Delta E_{\text{Eu}^{2+/3+}})</th>
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be seen that in addition to the difference in luminescence intensity, the peak shape and the dominated peak position also have significant differences.

The emission spectrum of the BaZn₂(PO₄)₂:4% Ce, x% Eu series sample at an excitation wavelength of 304 nm for Ce³⁺ is shown in Fig. 7(a). There are two distinct broadband emission peaks in the range of 300–800 nm, which are the 5d–4f transitions corresponding to Ce³⁺ and Eu²⁺ at 428 and 609 nm, respectively. In the BaZn₂(PO₄)₂:4% Ce, x% Eu co-doped sample, not only the emission of Ce³⁺ but also the emission of Eu²⁺ was observed by the 304 nm characteristic excitation of Ce³⁺. At the same time, it can be clearly seen that as the concentration of Eu ions increases, the luminescence intensity of Ce³⁺ ions gradually decreases, and that of Eu²⁺ ions gradually increases. This strongly proves that energy transfer occurs between Ce³⁺ and Eu²⁺. Fig. 7(b) is the excitation spectrum obtained under the monitoring of 609 nm. It shows that there are three strong broad bands in the range of 225–550 nm, and their central positions at 248, 303 and 376 nm belong to the charge transition of O²⁻–Eu⁴⁺, the f-d energy level transition of Ce³⁺ and the 4f-5d transition of Eu³⁺, respectively. Therefore, we found that under the monitoring of Eu²⁺, the excitation spectrum exhibits the excitation peak of Ce³⁺, which further proves the phenomenon of Ce³⁺–Eu²⁺ energy transfer.

3.4 Energy transfer mechanism

In order to further study the energy transfer process, we tested the lifetime of Ce³⁺ ions under 320 nm excitation (λex = 302 nm, λem = 428 nm) and Eu²⁺ ions under the corresponding excitation and emission wavelengths, as shown in Fig. 7(c). The decay curves are better fitted by the second-order exponential decay. The formula is as follows:

\[
I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)
\]

where \(I(t)\) represents the luminescence intensity; \(A_1\) and \(A_2\) are the amplitude constants; \(t\) is the decay time; and \(\tau_1\) and \(\tau_2\) are the exponential components of fast and slow decay times, respectively. The average decay time \((\tau^*)\) is calculated using the following formula:

\[
\tau^* = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)
\]

According to eqn (3) and (4), the decay time of Ce³⁺ in BaZn₂(PO₄)₂:4% Ce, x% Eu samples are approximately 1.5, 1.47, 1.42, 1.31 and 1.30 µs corresponding to \(x = 3, 4, 6, 8, 10\) in Fig. 7(c). We can observe that as the concentration of Eu ions increases, the lifetime of Ce³⁺ ions decreases, whereas the lifetime of Eu²⁺ ions increases, which is in good agreement with the
spectral characteristics of BaZn₂(PO₄)₂:4% Ce, x% Eu. This also strongly indicates the energy transfer behavior between Ce³⁺ and Eu²⁺ ions.

Based on Dexter’s theory, the critical distance of energy transfer is defined as the distance at which the transition probability is equal to the probability of Ce³⁺ radiation emission. The critical distance $R_c$ for energy transfer between Ce³⁺ and Eu²⁺ in BaZn₂(PO₄)₂ is discussed by the following formula:

$$R_c = 2 \left[ \frac{3V}{4\pi X_c N} \right]^{\frac{1}{3}}$$

(5)

where $V$ represents the volume of the unit cell and $X_c$ stands for the critical concentration of the dopant, and $N$ is the number of available sites per unit cell. In the BaZn₂(PO₄)₂ crystal structure, the values of $V$, $X_c$ and $N$ are 768.45 Å³, 0.1 and 4, respectively. The critical distance $R_c$ is calculated to be 15.426 Å by eqn (5). We know that when the distance between two luminescence centers is less than the critical distance of 5 Å, the energy transfer between the two luminescence centers is carried out by the exchange interaction mechanism, otherwise it is through electric multipolar interactions. Therefore, it can be seen that energy transfer from Ce³⁺ to Eu²⁺ in BaZn₂(PO₄)₂ belongs to electrical multipole interaction. Based on Dexter’s multipole interaction energy transfer formula and Reisfeld’s approximation, the mechanism in the present system is applied through the following relationship:

$$\frac{I_{S0}}{I_S} = C^{n/3}$$

(6)

where $I_{S0}$ indicates the luminescence intensity of Ce³⁺ ions when Eu²⁺ ions are not doped; $I_S$ is equal to the luminescence intensity of Ce³⁺ ions with the presence of Eu²⁺ ions; and $C$ stands for the sum of the concentrations when Eu²⁺ and Ce³⁺ coexist. When the value of $n$ is 6, 8, or 10, it means dipole–dipole (d–d), dipole–quadrupole (d–q), and quadrupole–quadrupole (q–q) interactions, respectively. The $I_{S0}/I_S$–$C^{n/3}$ plots are exhibited in Fig. 8. Obviously, when $n = 6$, 8 and 10, the linear fitting $R^2$ values of $I_{S0}/I_S$–$C^{n/3}$ are 0.9920, 0.9826 and 0.9667, respectively, that is, when $n = 6$, linear behavior is the best. Therefore, the energy transfer of Ce³⁺–Eu²⁺ in this system follows the electric dipole–dipole interaction mechanism. The quantum efficiency was determined to be 24.58%, 29.12%,
The chromaticity calculation was performed based on the photoluminescence spectra of the BaZn2(PO4)2:4% Ce, x% Eu phosphor at 304 nm excitation, and the calculation results of the CIE coordinates are shown in Fig. 9. Detailed CIE chromaticity coordinates are listed in Table 3. In a series of samples of BaZn2(PO4)2:4% Ce, x% Eu, as the doping concentration of Eu ions is from 0.03 to 0.1, we can see that the CIE coordinates of the samples change from the blue region to the white region. It is worth noting that the CIE chromaticity coordinates of the BaZn2(PO4)2:4% Ce, 8% Eu sample in the white light region (0.3195, 0.2959) is very close to the ideal white luminescence (0.33, 0.33), indicating that the phosphor has potential applications in white LEDs.

4. Conclusions

A series of novel Eu2+/3+, Ce3+ ion single- and co-doped BaZn2(PO4)2 samples have been synthesized via a high-temperature solid-state reaction. It was confirmed by XRD powder diffraction that our target products are all pure phases. The self-reduction from Eu3+ to Eu2+ has been found in the BaZn2(PO4)2 system. The photoluminescence spectra show that Eu2+ and Eu3+ ions coexist in the BaZn2(PO4) crystal. At the same time, the strongest emission peak of Eu3+ ions belongs to the 5D0 \rightarrow 7F1 transition of Eu3+ at 593 nm, which indicates that Eu3+ ions occupy the inversion symmetry lattice and occupy the site of Zn in BaZn2(PO4). According to the bond energy method, the priority of Eu2+ and Eu3+ ions in the lattice position of Zn and the self-reduction of Eu3+ to Eu2+ were explained in BaZn2(PO4). The results indicate that the value \Delta E_{\text{Eu}^{2+} \rightarrow \text{O}^{2-}} is smaller than \Delta E_{\text{Eu}^{3+} \rightarrow \text{O}^{2-}}^0, indicating that Eu2+ is more likely to occupy the Zn site and is more stable than Eu3+ in BaZn2(PO4), which also explains why Eu3+ ion can reduce to Eu2+ ion. For BaZn2(PO4)2:4% Ce, x% Eu phosphors, the energy transfer from Ce3+ to Eu2+ was deduced by excitation and emission spectra, which was further confirmed by the decrease in the decay lifetime of Ce3+ as the concentration of Eu ions gradually increases. The energy transfer mechanism between Ce3+ and Eu2+ proved to be a dipole–dipole interaction. Moreover, the CIE chromaticity coordinates show that the emission color of BaZn2(PO4)2:4% Ce, x% Eu phosphors can be changed from blue to white. In particular, the chromaticity coordinates (0.3195, 0.2959) of BaZn2(PO4)2:4% Ce, 8% Eu are very close to the ideal white luminescence (0.33, 0.33), indicating that the phosphor has potential applications in white LEDs.

Conflicts of interest

There are no conflicts to declare.

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Notes and references