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A blue-emitting Sc silicate phosphor for ultraviolet excited light-emitting diodes

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A blue-emitting phosphor BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ was synthesized by the conventional solid state reaction. The crystallographic occupancy of Eu$^{2+}$ in the BaSc$_2$Si$_3$O$_{10}$ matrix was studied based on the Rietveld refinements results and the photoluminescence properties. BaSc$_2$Si$_3$O$_{10}$ exhibit blue emission ascribed to $T_2$-A$_2$ and $T_1$-A$_2$ charge transfer of SiO$_4^2-$ excited by 360 nm. All the phosphors of BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ exhibit strong broad absorption bands in the near ultraviolet range, and give abnormal blue emission upon 330 nm excitation. The abnormal phenomenon was explored in detail through many experimental evidences. The concentration of Eu$^{2+}$ is optimized to be 3 mol% according to emission intensity and the quenching mechanism is verified to be the quadrupole-quadrupole interaction. The CIE coordinates of BaSc$_2$Si$_3$O$_{10}$: 0.03Eu$^{2+}$ are calculated to be (0.15, 0.05) and BaSc$_2$Si$_3$O$_{10}$: 0.03Eu$^{2+}$ shows similar thermal stability to commercial BaMgAl$_{10}$O$_{17}$: Eu$^{2+}$.

1. Introduction

Recently, phosphor conversion white light-emitting diodes (w-LEDs) have been attracted much attention owing to the merits of long operation time, high energy efficiency, low thermal radiation. At present, the combination of the ultraviolet (UV)/near-UV (n-UV) LED chips with tri-color phosphors (red/green/blue) are employed to realize the practical white light emission. The present commercial blue phosphor BaMgAl$_{10}$O$_{17}$: Eu$^{2+}$ and (Sr, Ba, Ca)MgSiO$_3$: Eu$^{2+}$ have high efficiency but poor thermal stability. Hence, the research on new blue phosphors with excellent thermal stability for n-UV pumped LEDs is necessary. Eu$^{2+}$ and Ce$^{3+}$ are the most commonly used activator for blue emitting phosphors. The emission of Eu$^{2+}$ originating from the 4f$^5$5d – 4f electronic transition is sensitive to the crystal field and covalency, exhibits broad emission bands from blue to red. Eu$^{2+}$-doped phosphors usually reveal strong absorption band in the region of 250-400 nm, which matches well with the emission of UV and n-UV LED chips. Meanwhile, the small Stokes shift and short decay time of Eu$^{2+}$ have attracted a lot of interesting, such as Ba$_2$Ca$_4$(PO$_4$)$_3$: Eu$^{2+}$, Ca$_2$(PO$_4$)$_2$: Eu$^{2+}$, CaAl$_2$Si$_2$O$_8$: Eu$^{2+}$, and Na$_3$(Y, Sc)Si$_2$O$_8$: Eu$^{2+}$. Among a lot of possible matrices, silicates compounds are considered to be good candidates as the host structure due to several virtues of excellent chemical and thermal stability, resistance to moisture and their abundance in nature. In silicates matrices, Sc silicates display the excellent photoluminescence properties on account of the stable physical and chemical properties and the rich crystal chemistry environment for the doped rare earth ions, such as Ca$_3$Sc$_2$Si$_3$O$_{12}$: Ce$^{3+}$, NaBaScSi$_3$O$_{10}$: Eu$^{2+}$. This proves Sc silicates can serve as the suitable phosphor hosts for LED application. A family of trisilicates BaRe$_3$Si$_3$O$_{10}$ (Re = Gd, Er, Yb, Sc) was firstly reported by M. Wierzbicka-Wieczorek et al. in 2010. Their topology is characterised by horseshoe-shaped trisilicate (Si$_3$O$_9$) groups and zigzag chains of edge-sharing distorted ReO$_6$ octahedra (Re = Gd, Er, Yb, Sc). In this paper, the structure and luminescence properties of BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ are explored. There are two coordination environments of cations: Ba$^{2+}$ and Sc$^{3+}$ in BaSc$_2$Si$_3$O$_{10}$. In our work, the radius percentage difference between the Eu$^{2+}$ and Ba$^{2+}$, Sc$^{3+}$ are calculated to be 11.9 % and 57 %, respectively. However, the radius percentage difference less than 30% is the necessary factor for the formation of solid solution. Moreover, the rare earth take place the sites of Na, Ca and Na, not Sc, in Na$_3$(Y, Sc)Si$_2$O$_8$: Eu$^{2+}$, Ca$_3$Sc$_2$Si$_3$O$_{12}$: Ce$^{3+}$ and NaBaScSi$_3$O$_{10}$: Eu$^{2+}$ respectively. Thus, there is only one suitable cationic site (Ba$^{2+}$) for Eu$^{2+}$ in BaSc$_2$Si$_3$O$_{10}$, then a symmetry emission should be expected. However, the emission of BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ is composed by two emission band. We think it is an abnormal phenomenon and carefully analyse crystallographic occupancy of Eu$^{2+}$ by the Rietveld analysis and the photoluminescence properties. In this study, based on the basic research and application for LEDs, we measured the luminescence efficiency, thermal quenching property and color chromaticity of the new blue phosphor BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$.

2. Experimental

The polycrystalline samples with nominal chemical formula Ba$_{1-x}$Eu$_x$Sc$_2$Si$_3$O$_{10}$ (x = 0.005-0.11) were prepared by the conventional solid-state reaction in one step. BaCO$_3$ (99.9%), Sc$_2$O$_3$ (99.9%), H$_2$SiO$_3$ (99.8%) and Eu$_2$O$_3$ (99.99%) were used as raw materials.
The raw materials were weighed out according to the stoichiometric ratio of the desired compositions and thoroughly mixed by grinding evenly in an agate mortar. Afterward, the obtained product was annealed at 1350 °C for 8 h under a reducing 5% H2/95% N2 atmosphere. Finally, the sample cooled down to room temperature and some white polycrystalline powder was obtained.

The crystalline phases of samples were recorded by using a Rigaku D/Max-2400 X-ray diffractometer (XRD) with Ni-filtered Cu Ka radiation, operating at 40 kV, 60 mA. The photoluminescence excitation (PLE) and emission (PL) spectra, quantum efficiency and decay curves of the samples were measured using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. The emission spectra and decay curves at low temperature (from 77 K to 298 K) were obtained by using FLS6920T fluorescence spectrophotometer and a heating apparatus equipped with a 450 W Xe light source. The emission spectra and decay curves at low temperature (from 77 K to 298 K) were measured using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. The emission spectra and decay curves at low temperature (from 77 K to 298 K) were measured using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. The emission spectra and decay curves at low temperature (from 77 K to 298 K) were measured using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. The emission spectra and decay curves at low temperature (from 77 K to 298 K) were measured using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. The emission spectra and decay curves at low temperature (from 77 K to 298 K) were measured using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. The emission spectra and decay curves at low temperature (from 77 K to 298 K) were measured using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. The emission spectra and decay curves at low temperature (from 77 K to 298 K) were measured using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. The emission spectra and decay curves at low temperature (from 77 K to 298 K) were measured using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. The emission spectra and decay curves at low temperature (from 77 K to 298 K) were measured using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source.

**3. Results and discussion**

**3.1 Phase identification and crystal structure**

![Graph](https://via.placeholder.com/150)

**Fig.1** (a) XRD refinement results of BaSc2Si10O30: 0.01Eu2+ using the MS program. (b) Structure view of BaSc2Si10O30 along [100] direction.

To detect the phase purity, Figure 1(a) shows Rietveld structural refinements of the powder diffraction patterns of BaSc2Si10O30: 0.01Eu2+. The black crosses and pink solid lines are calculated patterns and experimental patterns, respectively. The green short vertical lines show the position of the Bragg reflections of the calculated pattern. The difference between the experimental and calculated patterns is plotted by the black line at the bottom. The refined unit cell parameters and residual factors are summarized in Table 1. BaSc2Si10O30 has a monoclinic structure with space group P21/m, as shown in Fig. 1(b). The asymmetric unit of BaSc2Si10O30 contains one Ba, one Sc, two Si and six O atoms. The structure of BaSc2Si10O30 composed of three SiO4 tetrahedra, forms a horseshoe-shaped trisilicate Si2O6 group, Ba2+ octahedra and BaO6 polyhedron. The Ba, Si1, O1 and O2 atoms are located on mirror planes (y = 1/4), while all remaining atoms are in general positions. It is noteworthy that the Si10 group, composed of a central SiO4 tetrahedron corner-linked to two symmetry-equivalent terminal SiO4 tetrahedra, is located on mirror planes parallel to (010) at y = 1/4 and 3/4. In BaSc2Si10O30, Ba2+ are located in voids consisted of ScO6 octahedron and SiO4 tetrahedron. The structure of BaSc2Si10O30 offers two types of cation sites for occupancy by guest cations: type I with divalent Ba sites having 8-fold coordination and type II with trivalent Sc3+ sites in ScO6 polyhedra. The effective ionic radii of Ba2+ and Sc3+ are 1.42 and 0.745 Å, and the ionic radii for eight- and six-coordinated Eu2+ are 1.25 and 1.17 Å, respectively. Therefore, based on the comparison of the effective ionic radii of cations, Eu2+ is likely to enter into the Ba2+ sites in this series of samples. Furthermore, an acceptable percentage difference in ion radii between doped and substituted ions must not exceed 30 %. The radius percentage difference between the doped Eu2+ and the possible substituted ions (Ba2+, Sc3+) can be calculated based on the following equation:

\[ D_T = 100 \times \left[ R_m(CN) - R_d(CN) \right] / R_m(CN) \]

where \( D_T \) is the radius percentage difference; CN is the coordination number; \( R_m(CN) \) is the radius of the host cation; and \( R_d(CN) \) is the radius of the doped ion. The values of \( D_T \) for Eu2+ in Ba2+ and Sc3+ are determined to be 11.9 % and 57 %, respectively. Hence, it is reasonable that Eu2+ enters into the Ba2+ sites.
between them is 107.7°. All the composing elements of the sample have been detected, and no other impure elements are found. The EDX analysis spectrum of BaSc$_2$Si$_3$O$_{10}$ particle, as shown in Fig. 2(b), clearly displays the lattice fringes. The lattice spacing is 0.434 nm, corresponding to the (021) planes of BaSc$_2$Si$_3$O$_{10}$. The inset of Fig. 2(b) shows the SAED patterns confirming the single phase of BaSc$_2$Si$_3$O$_{10}$. Eu$^{2+}$ is given in Fig. 2(c). The corresponding high-magnification TEM image of a single BaSc$_2$Si$_3$O$_{10}$ particle thus obtained is shown in Fig. 2(a).

Table 1 Crystallographic Data and Reliability Factor of BaSc$_2$Si$_3$O$_{10}$. Eu$^{2+}$ (x = 0–0.05) Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>x = 0</th>
<th>x = 0.005</th>
<th>x = 0.01</th>
<th>x = 0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.27162</td>
<td>5.27516</td>
<td>5.2817</td>
<td>5.27851</td>
</tr>
<tr>
<td>b (Å)</td>
<td>11.91488</td>
<td>11.92276</td>
<td>11.9374</td>
<td>11.93607</td>
</tr>
<tr>
<td>c (Å)</td>
<td>6.58826</td>
<td>6.59290</td>
<td>6.6061</td>
<td>6.60343</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>395.61</td>
<td>396.45</td>
<td>398.19</td>
<td>397.88</td>
</tr>
<tr>
<td>$R_p$</td>
<td>9.56 %</td>
<td>9.56 %</td>
<td>8.45 %</td>
<td>9.87 %</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>12.91 %</td>
<td>12.55 %</td>
<td>11.07 %</td>
<td>13.20 %</td>
</tr>
</tbody>
</table>

### 3.2 Photoluminescence properties of BaSc$_2$Si$_3$O$_{10}$ and BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$

The PLE and PL spectra of BaSc$_2$Si$_3$O$_{10}$ are shown in Fig. 3. The red and black lines denote the excitation and emission spectra of BaSc$_2$Si$_3$O$_{10}$ in air and reducing atmosphere, respectively. The excitation band monitored by 426 nm is made up of a strong band centered at 360 nm and a weak one peaked at 257 nm. The two excitation bands centered at 360 nm and 257 nm can be associated with the $^1$A$_1$-$^3$T$_2$ and $^1$A$_1$-$^3$T$_1$ charge transfer of SiO$_4$$^{2-}$, respectively. Under the excitation of 360 nm, the emission spectrum exhibits a broad charge transfer band range from 380 to 550 nm located at 420 nm, as shown in Fig. 3. The broad emission band can be fitted into two Gaussian components, presented as the dotted line in Fig. 3. The higher-energy component (line a) centered at 415 nm and the lower-energy component (line b) centered at 445 nm are attributed to the $^3$T$_2$-$^1$A$_1$ and $^3$T$_1$-$^1$A$_1$ charge transfer of SiO$_4$$^{2-}$, respectively. The photoluminescence properties of the BaSc$_2$Si$_3$O$_{10}$ samples calcined in a reducing atmosphere and that of air-calcined samples are compared to show that the calcined atmosphere also affects the photoluminescence properties of phosphors. Both the spectra are similar except for the peak intensity. The photoluminescence intensity is enhanced by 191 % while calcined in a reducing atmosphere compared with the air-calcined phosphor. In fact, the calcining in air atmosphere induces the diffusion of oxygen ions into the BaSc$_2$Si$_3$O$_{10}$ particle thus lowering the oxygen vacancy concentration. Calcining in a reducing atmosphere induces the oxygen diffusion out of the sample, increases of oxygen vacancy. Here, the oxygen vacancy deficiency is considered to be responsible for the enhancement of photoluminescence intensity.
multipole–multipole interaction. It was reported that three values of $0$ stands for the energy transfer among the nearest neighbor ions as $0 = 6, 8, \text{and } 10$ represent the dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The inset of Fig. 5 plots the dependence of $\log(I/x)$ on $\log(x)$ and with a slop of $(-0.3)$ is obtained to be $-3.37$. Then the value of $0$ can be determined to be $10.11$ which is close to $10$, meaning that the quenching is quadrupole–quadrupole interactions in present BaSc$_2$Si$_3$O$_{10}$:xEu$^{2+}$ phosphors. 

$$I/x = K \left[ 1 + \beta(x)^{\theta} \right]^{-1}$$

Where $x$ is the activator concentration, which is higher than the critical concentration; $I/x$ is the emission intensity $(I)$ per activator concentration $(x)$; $K$ and $\beta$ are constants for the same excitation condition for a given host crystal; and $\theta$ is a function of multipole–multipole interaction. It was reported that three values

5 The PLE spectrum of the selected BaSc$_2$Si$_3$O$_{10}$:0.03Eu$^{2+}$ and variations PL spectra of BaSc$_2$Si$_3$O$_{10}$:xEu$^{2+}$ (0.005 $\leq x \leq 0.11$) are revealed in Fig. 4. The PLE spectrum of the phosphor monitored by 445 nm shows characteristic excitation broad band of Eu$^{2+}$ in the range from 250 to 420 nm according with the emission light from UV–LED chips. Besides, the PLE spectrum contains three distinct bands originating from the $4f^6$ ground state to different excited states of Eu$^{2+}$. Upon the excitation of 330 nm, the PL spectra show broad band extending from 420 to 520 nm centered at 445 nm attributed to the transition from lower $4f^5 5d^1$ excited states to the quasi-degenerate $^8S_{7/2}$ ground state of Eu$^{2+}$. The lowest energy zero phonon line of BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ is estimated at about 409 nm, which is empirically determined as the intersection point of the excitation and emission spectra. The degree of the non-radiative relaxation of rare earth ions and the rigid of host lattice can be measured by the value of Stokes shift. The Stokes shift of BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ is calculated to be 0.491 eV, which can be roughly estimated as twice of the energy difference between the peak energy of the emission band and lowest energy zero phonon line.$^{25}$ The Eu$^{2+}$ content dependent PL intensities are drawn in Fig. 4. Obviously, the optimum Eu$^{2+}$ concentration is 0.03 and then the PL intensities decrease with increasing Eu$^{2+}$ concentration due to the concentration quenching effect. The CIE coordinates of BaSc$_2$Si$_3$O$_{10}$:0.03Eu$^{2+}$ are calculated to be $(0.15, 0.05)$ indicating good blue emitting light. According to the Dexter’s theory, concentration quenching is mainly caused by the non-radiative energy migration among the activators due to the exchange interaction or multipole–multipole interaction.$^{27}$ It is well-known that the interaction type between activators can be calculated by the following equation:$^{28}$

$$I/x = K \left[ 1 + \beta(x)^{\theta} \right]^{-1}$$

In addition, the reabsorption begin to reduce the high-energy wing of Eu$^{2+}$ emission band with increasing Eu$^{2+}$ concentration, which also cause the red shift of the emission band. Furthermore, the Eu$^{2+}$ ionic radius is smaller than Ba$^{2+}$, then the crystal field may become stronger, which results in a larger split of 5d levels

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**Fig. 4** PLE ($\lambda_{ex} = 445$ nm) and PL ($\lambda_{em} = 330$ nm) spectra for BaSc$_2$Si$_3$O$_{10}$:xEu$^{2+}$ (0.005 $\leq x \leq 0.11$) phosphors. The inset shows the normalized emission spectra.

**Fig. 5** PL intensities of BaSc$_2$Si$_3$O$_{10}$:Eu$^{2+}$ as a function of Eu$^{2+}$ content. The inset shows the relationships of $\log(x)$ versus $\log(I/x)$.

**Fig. 6** (a) Gaussian curves of BaSc$_2$Si$_3$O$_{10}$:0.03Eu$^{2+}$ and (b) XRD patterns of BaSc$_2$Si$_3$O$_{10}$:xEu$^{2+}$ ($x = 0, 0.005, 0.01, 0.03, 0.05$ and $0.07$) phosphors.
and exhibits a red shift in the spectra. However, these reasons could not explain the further blue shift. Accordingly, the partial Eu\(^{2+}\) entry into Sc\(^{3+}\) site is speculated to be the possible reason for this abnormal asymmetry emission band. Fig. 6(b) depicts the XRD patterns of BaSc\(_2\)Si\(_3\)O\(_{10}\) and Eu\(^{2+}\) activated BaSc\(_2\)Si\(_3\)O\(_{10}\) with different Eu\(^{2+}\) contents. Compared with the XRD pattern of host, when the Eu\(^{2+}\) content is low, the diffraction peaks are shifted a little to lower angles implies Eu\(^{2+}\) replace smaller ions according to the Bragg equation. Then the diffraction peaks of samples are shifted to higher angles as the increase of Eu\(^{2+}\) concentration, originating from Eu\(^{2+}\) replacing bigger ions. In BaSc\(_2\)Si\(_3\)O\(_{10}\), the ionic radius of Sc\(^{3+}\) is smaller than Eu\(^{2+}\) and Ba\(^{2+}\) is bigger than Eu\(^{2+}\). Moreover, it is obvious that the unit cell parameters increased firstly and then slightly reduced with the increase of Eu\(^{2+}\), shown in Table 1. These results indicate Eu\(^{2+}\) likely occupy Sc\(^{3+}\) site at low concentration of Eu\(^{2+}\), and then occupy Ba\(^{2+}\) site with the increase of Eu\(^{2+}\) content.

![Schematic diagrams of Sc\(^{3+}\) and Y\(^{3+}\) in BaSc\(_2\)Si\(_3\)O\(_{10}\) and BaY\(_2\)Si\(_3\)O\(_{10}\).](image)

Fig. 7. Schematic diagrams of Sc\(^{3+}\) in BaSc\(_2\)Si\(_3\)O\(_{10}\) and Y\(^{3+}\) in BaY\(_2\)Si\(_3\)O\(_{10}\).

In the structure of BaRe\(_2\)Si\(_3\)O\(_{10}\), the space size of Re is tunable because it can replaced by different trivalent ions, such as Gd\(^{3+}\), Yb\(^{3+}\), Er\(^{3+}\) and Y\(^{3+}\), which show bigger size than Sc\(^{3+}\). The radius and values of \(D_r\) between Eu\(^{2+}\) and these rare earth ions are shown in Table 2. Figure 7 shows the Schematic diagram for the tunable space size of Re in BaRe\(_2\)Si\(_3\)O\(_{10}\) (Re = Sc, Y). Therefore, even though the value of \(D_r\) is much higher than 30% when Eu\(^{2+}\) enters Sc\(^{3+}\) site, there are still enough space for Eu\(^{2+}\) in BaSc\(_2\)Si\(_3\)O\(_{10}\). Therefore, it is possible for Eu\(^{2+}\) to enter into Sc\(^{3+}\) site.

<table>
<thead>
<tr>
<th>Rare earth</th>
<th>Sc(^{3+})</th>
<th>Gd(^{3+})</th>
<th>Yb(^{3+})</th>
<th>Er(^{3+})</th>
<th>Y(^{3+})</th>
<th>Eu(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (Å)</td>
<td>0.745</td>
<td>0.93</td>
<td>0.868</td>
<td>0.89</td>
<td>0.90</td>
<td>1.17</td>
</tr>
<tr>
<td>(D_r) (%)</td>
<td>57</td>
<td>25</td>
<td>34</td>
<td>31</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

![Time-resolved photoluminescence (TRPL) emission spectra of BaSc\(_2\)Si\(_3\)O\(_{10}\): 0.05Eu\(^{2+}\).](image)

Fig. 9 Time-resolved photoluminescence (TRPL) emission spectra of BaSc\(_2\)Si\(_3\)O\(_{10}\): 0.05Eu\(^{2+}\).

In order to confirm that the broad band emission originates from two luminescent centers, a series of lifetime decay curves were recorded by monitoring the BaSc\(_2\)Si\(_3\)O\(_{10}\): 0.05Eu\(^{2+}\) sample at

![Decay curves of BaSc\(_2\)Si\(_3\)O\(_{10}\): Eu\(^{2+}\) phosphors with different Eu\(^{2+}\) contents.](image)

Fig. 8 Decay curves of BaSc\(_2\)Si\(_3\)O\(_{10}\): Eu\(^{2+}\) phosphors with different Eu\(^{2+}\) contents.

The decay curves of BaSc\(_2\)Si\(_3\)O\(_{10}\): Eu\(^{2+}\) were performed and shown in Fig. 8. All the decay curves could be well fitted with not a single exponential but second-order exponential decay mode, demonstrating that there are two light luminescent centers in the phosphor. The average decay times (\(\tau\)) can be determined by the formula given in the following:

\[
\tau = \left(\frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}\right)
\]

where \(A_1\) and \(A_2\) are constants, and \(\tau_1\) and \(\tau_2\) are rapid and slow lifetimes for the exponential components, respectively. As can be seen from Fig. 8, the values of decay time decrease from 655.78 to 454.76 ns when the doped Eu\(^{2+}\) concentration increased from 0.01 to 0.07 mol%, which is a typical sign of energy transfer and eventually causes concentration quenching. The values of energy transfer rate (\(k_{ET} = 1/\tau - 1/\tau_0\)) and efficiency (\(\eta = 100(1 - \tau/\tau_0)\)) have been calculated and shown in Fig. 8. The maximum energy transfer rate (\(k_{ET}\)) and efficiency (\(\eta\)) are calculated to be 0.674 \(\mu\)s\(^{-1}\) and 30.7%, respectively.
different wavelengths from 400 to 550 nm at 5 nm intervals. The TRPL spectra shown in Fig. 9 were obtained by slicing them. Obviously, the TRPL spectra are clearly constituted by two emission peaks centered at 440 and 460 nm, which has not been found from the emission spectra shown in Fig. 4. Simultaneously, with the time interval prolonging, it was interesting to observe that the intensity ratio of 440 to 460 nm descended significantly, confirming that there are two light luminescent centers. The occurrence of the two emission peaks further demonstrates Eu$^{2+}$ occupying the two different cationic lattice sites: Ba$^{2+}$ and Sc$^{3+}$ sites. In order to assign the emission from the two luminescent centers, the following equation has been used to build up the relationship between the coordination environment and emission peaks, which is proposed by Van Uitert and successfully used to explain many structure–property relationship studies in Eu$^{2+}$ or Ce$^{3+}$ doped systems.\(^{31}\)

$$E = Q \left[ 1 - \left( \frac{V}{A} \right)^2 \times 10^{\frac{near}{60}} \right]$$

where E is the position of the rare-earth ion emission peak (cm$^{-1}$), Q represents the position in energy for the lower d-band edge for the free Eu$^{2+}$ ion (Q = 34 000 cm$^{-1}$ for Eu$^{2+}$), V is the valence of the “active” cation (V = 2 for Eu$^{2+}$), n is the number of anions in the immediate shell around the “active” cation, and r is the radius of the host cation occupied by the Eu$^{2+}$ ion (Å), ea is the electron affinity of the atoms that form anions (eV). In BaSc$_2$Si$_3$O$_{10}$, the effective ionic radii for Ba$^{2+}$ and Sc$^{3+}$ are 1.42 Å (CN=8) and 0.745 Å (CN=6), respectively. From the equation, one can see that the larger value of $n \times r$ , the higher value of $E$. Therefore, it is obvious that Eu$^{2+}$ occupying the Ba$^{2+}$ position should exhibit a higher-energy (440 nm) emission peak and the Sc$^{3+}$ position reveal emission at 460 nm. Therefore, it can reasonable explained that the emission spectra shift to longer wavelength (red shift) and then to shorter wavelength (blue shift) with the increase of Eu$^{2+}$ concentration in Fig.4.

A series of PL spectra curves of BaSc$_2$Si$_3$O$_{10}$: 0.03Eu$^{2+}$ measured at different temperature is shown in Fig.10 (a). At low temperature, the emission spectra obviously split into two peaks, which are different from that at room temperature. This result further demonstrates Eu$^{2+}$ occupy Ba$^{2+}$ and Sc$^{3+}$ sites in BaSc$_2$Si$_3$O$_{10}$. As increasing the temperature, the emission intensity decrease. The decay curves was measured excited at 375 nm and monitored at 445 nm. The lifetimes at 77 K and 298 K were calculated to be 644.14 ns and 632.10 ns, respectively. The decreased decay times can be attributed to increase interaction between Eu$^{2+}$ when rising temperature.

### 3.4 Thermally stable luminescence properties
The thermal stability of phosphors is one of the important parameters for the application in high performance LEDs because it has a considerable influence on the light output and CRI. So the temperature dependent PL properties are investigated and exhibited in Fig. 11(a). Clearly, the emission intensity gradually decrease with increasing temperature, and the intensity decreases to 62% (at 250 °C) of the initial value. BaSc$_2$Si$_3$O$_{10}$: 0.03Eu$^{2+}$ shows similar thermal stability to commercial BAM (BAM: 1261) as can be seen from the insert of Fig. 11(a). Meanwhile, the emission shows a tiny blueshift with increasing temperature, which can be ascribed to the thermally active phonon-assisted tunneling from lower-energy excited states to higher-energy excited state of the configuration coordinate diagram. To better understand the thermal quenching phenomenon, the activation energy (ΔE) for the thermal quenching can be calculated using the Arrhenius equation:

$$ I_T = \frac{I_0}{1 + c \exp \left( \frac{-\Delta E}{kT} \right)} $$

where $I_0$ is the initial PL intensity of the phosphor at room temperature, $I_T$ is the PL intensity at different temperatures, c is a constant, ΔE is the activation energy for thermal quenching, and $k$ is the Boltzmann constant ($8.62 \times 10^{-5}$ eV). According to above equation, the ln$\left(I_0/I_T - 1\right)$ against 1/κT is plotted in Fig. 11(b) and the straight slope equals ΔE. The activation energies are calculated to be 0.19 and 0.17 eV for BaSc$_2$Si$_3$O$_{10}$: 0.03Eu$^{2+}$ and commercial reference blue phosphor, respectively. The results show that BaSc$_2$Si$_3$O$_{10}$: 0.03Eu$^{2+}$ has a similar thermal stability with commercial BAM.

With increasing temperature, the electron–phonon interaction in both the ground state and excited states of the luminescence center becomes dominant resulting in broadening of the emission spectra and decrease of the emission intensity. The thermal quenching temperature is defined as the temperature at which the PL intensity is 50% of its initial intensity. In our case, the quenching temperature is obvious above 250 °C. This high quenching temperature indicates the rigid lattice of BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ phosphor with weaker electron-phonon interaction. Figure 11(c) and (d) plot the dependence of the full width at half maximum (FWHM) of the emission spectra on various measurement temperatures and the margin of error which were

![Figure 11](image-url)
analyzed using MATLAB software. The FWHM ($T$) can be described by using the configuration coordinate model and the Boltzmann distribution and expressed by the following equation: 

$$\text{FWHM} (T) = \ln\left[8 \times \ln 2 \times S \times \coth\left(h\nu/2k_BT\right)\right]^{1/2}$$

where $h\nu$ is the phonon energy, $S$ is the Huang–Rhys parameter, and $k_B$ is the Boltzmann constant. For the 4f$^5$5d excited state of Eu$^{2+}$, $h\nu$ is assumed to be the same. According to the above equation, the best fit is obtained with $S = 5.3 \pm 0.4\ eV$ and $h\nu = 0.04 \pm 0.0033\ eV$. The Stokes shift ($\Delta S$) can be estimated from $\Delta S = h\nu \times (2.5 - 1)$ and $\Delta S$ is calculated to be 0.384 eV. The value of Huang–Rhys factor reveals weaker electron–phonon interaction in this phosphor and also provides an evidence for the good thermal photoluminescence property of BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$.

### 3.5 Luminescence quantum efficiency

The quantum efficiency ($\eta$) can be obtained by using the following formulas:

$$\phi = \frac{L_0(\lambda) - L_1(\lambda)}{L_0(\lambda)}$$

$$\eta = \frac{E_0(\lambda) - (1 - \phi)E_0(\lambda)}{E_0(\lambda)\phi}$$

where $L_0(\lambda)$ is the integrated excitation profile when sample is directly excited by the incident beam and $L_1(\lambda)$ are the integrated excitation profile obtained from the empty integrated sphere (without the sample present). $E_0(\lambda)$ and $E_1(\lambda)$ are the integrated luminescence of powder caused by direct excitation and by indirect illumination from the sphere, respectively. Upon excitation at 330 nm, the external quantum efficiency of this sample is 42.65%.

### 4. Conclusion

In conclusion, a series of BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ have been prepared by the solid state reaction. BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ phosphor shows broad absorption band ranging from 250 to 420 nm, which can match well with the UV-LEDs. The BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ exhibits blue broadband emission peaking at 446 nm with a tail on the long wavelength side and CIE coordinates (0.15, 0.05). The concentration quenching mechanism has been carefully investigated to be quadrupole–quadrupole interaction. The Rietveld refinements results and the time-resolved photoluminescence emission spectra are used to study the abnormal emission of Eu$^{2+}$ in BaSc$_2$Si$_3$O$_{10}$. The emission intensities of BaSc$_2$Si$_3$O$_{10}$: Eu$^{2+}$ dependence on different temperatures show similar thermal property compared with BAM. All results show that the obtained phosphors have potential application in UV excited w-LEDs as blue emitting components.

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### Footnotes

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