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Photoluminescence Tuning via Energy Transfer in the Eu-doped Ba$_2$(Gd,Tb)$_2$Si$_4$O$_{13}$ Solid-Solution Phosphors

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Abstract: We report on the phase formation of Ba$_2$(Gd,Tb)$_2$Si$_4$O$_{13}$ solid-solution, and the coexistence of Eu$^{2+}$/Eu$^{3+}$ was identified after Eu ions doping although the samples were prepared in a reducing atmosphere. Under 377 nm near-ultraviolet (UV) light excitation, Ba$_2$Tb$_2$Si$_4$O$_{13}$ exhibits the characteristic emission originating from Tb$^{3+}$ corresponding to $^5$D$_{4}$$^7$F$_{6,5,4,3}$ transitions; whereas Ba$_2$Tb$_2$Si$_4$O$_{13}$:Eu emits bright red emission from Eu$^{3+}$ with peaks around 594, 613 and 623 nm. Accordingly, photoluminescence tuning of the Eu-doped Ba$_2$(Gd,Tb)$_2$Si$_4$O$_{13}$ phosphors has been realized from the green, yellow, orange, to red emission light. Decay time and time-resolved luminescence results revealed that the tunable luminescence behavior should be ascribed to the existence of energy migration in the terbium subset, and successive energy transfer process Eu$^{2+}$-Eu$^{3+}$(Tb$^{3+}$) and Tb$^{3+}$-Eu$^{3+}$ appear to occur in the Ba$_2$Tb$_{2-y}$Si$_4$O$_{13}$:yEu ($y = 0-0.12$) solid-solution phosphors under investigation.
1. Introduction

Lanthanide-doped inorganic phosphor materials have attracted much attention in recent years owing to their potential applications in display technology, solid state lighting, and other fields. Amongst them, Eu ions have been widely used as activators because both Eu$^{3+}$ and Eu$^{2+}$ can function as emission centers in the host lattices. Comparing with the 4f-5d transition of Eu$^{2+}$, the emission of the 4f-4f transition of Eu$^{3+}$ is relatively insensitive to the host and temperature because the 4f shell is shielded by the outer filled 5s and 5p shells. However, the 4f-5d transition of Eu$^{2+}$ is parity allowed and therefore intense emission bands can be achieved. In addition, for Eu$^{2+}$ the absorption and emission wavelengths of can be tuned by the host lattice because of the strong interaction between the 5d electron and the ligand anions through covalency and crystal field. Eu$^{3+}$ ions are employed in luminescent devices such as fluorescent lamps and cathode ray tubes, and phosphors containing Eu$^{3+}$ ions as activators can emit red light; their excitation bands usually consist of host lattice excitation bands, charge-transfer bands, and direct excitation bands of Eu$^{3+}$ ions. However, the low oscillator strength and narrow line width of Eu$^{3+}$ 4f-4f absorption transitions leads to a weak absorption in the near-UV and blue region. As a comparison, Eu$^{2+}$ emits in the UV- to visible region and the emission wavelength strongly depends on the nature of the host lattice due to the participation of d orbitals. Therefore, as the characteristic broad-band transition excitation and emission of Eu$^{2+}$ have been well recognized, and it might be very exciting and interesting if an efficient Eu$^{2+}$-Eu$^{3+}$ energy transfer can occur in a single-phase
valence-varied Eu-doped phosphor, which can provide an opportunity to tailor the absorption of red-emitting phosphors containing Eu\(^{3+}\) ions. However, the existence of metal–metal charge transfer (MMCT) effect will quench the luminescence of the sensitizer for the designed Eu\(^{2+}\)-Eu\(^{3+}\) energy transfer. Therefore, Setlur firstly proposed that energy migration in the terbium subset can be used as an intermediate to alleviate the MMCT effect. After that, such a strategy has been realized in Ba\(_3\)Ln(PO\(_4\))\(_3\):Ce\(^{3+}\), Tb\(^{3+}\), Eu\(^{3+}\), LnPO\(_4\):Ce\(^{3+}\), Tb\(^{3+}\), Eu\(^{3+}\), and Ba\(_2\)(Ln\(_{1-x}\)Tb\(_x\))(BO\(_3\))\(_2\):Cl:Eu phosphors systems, and some interesting luminescence properties have been observed. In the present work, Eu-doped Ba\(_2\)(Gd,Tb)\(_2\)Si\(_4\)O\(_{13}\) solid-solution phosphors have been designed, the coexistence of Eu\(^{2+}\)/Eu\(^{3+}\) has been evidenced and energy transfer of Eu\(^{2+}\)-Eu\(^{3+}\)(Tb\(^{3+}\)) and Tb\(^{3+}\)-Eu\(^{3+}\) has been observed.

The crystal structures of the Ba\(_2\)Gd\(_{2-x}\)Tb\(_x\)Si\(_4\)O\(_{13}\) phase under investigation were derived from the Ba\(_2\)Gd\(_2\)Si\(_4\)O\(_{13}\) phase via Gd/Tb substitution. Ba\(_2\)Gd\(_2\)Si\(_4\)O\(_{13}\) possesses a monoclinic structure and a space group C\(_2\)/c with lattice parameters \(a = 12.896(3)\) Å, \(b = 5.212(1)\) Å, \(c = 17.549(4)\) Å, \(\beta = 104.08(3)\) Å. Up to now, several studies regarding the luminescence properties of rare earth doped Ba\(_2\)Gd\(_2\)Si\(_4\)O\(_{13}\) have been reported. Guo et al. investigated the tunable photoluminescence properties of Ba\(_2\)Gd\(_2\)Si\(_4\)O\(_{13}\):Ce\(^{3+}\), Tb\(^{3+}\), and the spectroscopic properties of Ba\(_2\)Gd\(_2\)Si\(_4\)O\(_{13}\):Eu\(^{3+}\). Zhang et al. studied the vacuum UV spectroscopic properties of Ba\(_2\)Gd\(_2\)Si\(_4\)O\(_{13}\):Ln\(^{3+}\) (Ln\(^{3+}\) = Ce\(^{3+}\), Tb\(^{3+}\), Dy\(^{3+}\), Eu\(^{3+}\), Sm\(^{3+}\)). In 2015, Zhou et al. studied the green emitting phosphor BaGd\(_2\)Si\(_4\)O\(_{13}\):Eu\(^{2+}\). Herein, we have investigated the phase formation of Ba\(_2\)(Gd,Tb)\(_2\)Si\(_4\)O\(_{13}\), and the coexistence of Eu\(^{2+}\)/Eu\(^{3+}\); the energy
transfer processes $\text{Eu}^{2+}$-$\text{Eu}^{3+}(\text{Tb}^{3+})$ and $\text{Tb}^{3+}$-$\text{Eu}^{3+}$ in $\text{Ba}_2\text{Tb}_2\text{Si}_4\text{O}_{13}$ were investigated in detail.

2. Experimental section

2.1 Sample preparation

$\text{Ba}_2\text{Gd}_{2-x}\text{Si}_4\text{O}_{13}\cdot x\text{Tb}$ and $\text{Ba}_2\text{Tb}_{2-y}\text{Si}_4\text{O}_{13}\cdot y\text{Eu}$ phosphors were synthesized by high temperature solid-state reaction, starting from a mixture containing commercially-available $\text{BaCO}_3$ (99.9%), $\text{Gd}_2\text{O}_3$ (99.995%), $\text{SiO}_2$ (99.95%), $\text{Tb}_4\text{O}_7$ (99.995%) and $\text{Eu}_2\text{O}_3$ (99.995%) in the given stoichiometric proportions. After mixing and grinding, the mixtures were placed into an alumina crucible and then fired in air at 1360 °C for 5 h under a 5%H$_2$/N$_2$ gas mixture. After this, the samples were furnace-cooled to room temperature, and ground again into powder for the following measurement.

2.2 Characterization methods

The powder X-ray diffraction (XRD) measurements were conducted on a D8 Advance diffractometer (Bruker Corporation, Germany) operating at 40 kV and 40 mA with Cu Kα radiation ($\lambda = 0.15406$ Å), and the scanning rate was fixed at 4°/min. Diffuse reflectance spectra were measured on a UV-Vis-NIR spectrophotometer (SHIMADZU UV-3600) attached with an integrating sphere. $\text{BaSO}_4$ was used as a reference standard. Room temperature photoluminescence (PL) excitation and emission spectra were measured on a fluorescence spectrophotometer (F-4600, HITACHI, Japan) with a photomultiplier tube operating at 400 V, and a 150 W Xe
lamp used as the excitation lamp. The time-resolved PL spectra were measured by the Edinburgh FLS920 spectrofluorometer with the monitoring wavelength of 377 nm, and the room-temperature decay curves were recorded on the same spectrofluorometer and the corresponding wavelengths (365 nm for Eu\textsuperscript{2+} emission, 377 for Tb\textsuperscript{3+} emission and 393 nm for Eu\textsuperscript{3+} emission) were used to monitor the decay.

The temperature-dependence luminescence properties were measured on the same spectrophotometer, which was combined with a self-made heating attachment and a computer-controlled electric furnace. Quantum efficiency was measured using the integrating sphere on the FLS920 fluorescence spectrophotometer (Edinburgh Instruments Ltd., UK).

3. Results and discussion

Fig. 1(a) and Fig. 1(b) show the typical XRD patterns of the as-prepared Ba\textsubscript{2}Gd\textsubscript{2-x}Si\textsubscript{4}O\textsubscript{13}:xTb (x = 0, 0.5, 1.0, 1.5, 2.0) and Ba\textsubscript{2}Tb\textsubscript{2-y}Si\textsubscript{4}O\textsubscript{13}:yEu (y = 0, 0.01, 0.03, 0.06, 0.15, 2.0) samples, respectively. It can be found that all the diffraction peaks of these two series of samples can be exactly assigned to the corresponding standard data for the hexagonal phase of Ba\textsubscript{2}Gd\textsubscript{2}Si\textsubscript{4}O\textsubscript{13} (ICSD card no. 260737), indicating that this series of Ba\textsubscript{2}Gd\textsubscript{2-x}Si\textsubscript{4}O\textsubscript{13}:xTb (x = 0, 0.5, 1.0, 1.5, 2.0) solid solution samples with different Tb/Gd ratios can form a single phase, and a small amount of Eu also will not change the crystal structure. We find that the characteristic diffraction peak (1 1 4) shifts to higher diffraction angles from 29.28° to 29.40° for Ba\textsubscript{2}Gd\textsubscript{2-x}Si\textsubscript{4}O\textsubscript{13}:xTb, while it shifts to lower diffraction angles from 29.40° to 29.22° for Ba\textsubscript{2}Tb\textsubscript{2-y}Si\textsubscript{4}O\textsubscript{13}:yEu. This variation could be due to the different ionic radii for Gd\textsuperscript{3+}, Tb\textsuperscript{3+} and Eu\textsuperscript{3+}, further suggesting that continuous solid solution of
Ba$_2$Gd$_{2-x}$Si$_4$O$_{13}$:xTb and Ba$_2$Tb$_{2-y}$Si$_4$O$_{13}$:yEu have formed in the crystal structure.

The evolution of the unit cell parameters $a$ and $V$ of Ba$_2$Gd$_{2-x}$Si$_4$O$_{13}$:xTb and Ba$_2$Tb$_{2-y}$Si$_4$O$_{13}$:yEu are given in Fig. 2(a) and Fig. 2(b), as a function of $x$ and $y$, respectively. The linear behavior of the cell parameters illustrate that these two series of compounds both belong to a continuous iso-structural solid solution. Fig. 2(c) presents the crystal structure of Ba$_2$(Gd,Tb)$_2$Si$_4$O$_{13}$. The structure is based on finite zigzag-shaped C$_2$-symmetric Si$_4$O$_{13}$ chains and Gd$_2$O$_{12}$ dimers built of edge-sharing GdO$_7$ polyhedra of C$_1$ symmetry. The [9+1]-coordinated Ba atoms are located in voids of the atomic arrangement, as highlighted in Fig. 2(d).

Room temperature photoluminescence excitation (PLE) and emission (PL) spectra of the Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu phosphors are shown in Fig. 3(a). Upon excitation at 365 nm, the PL spectra of Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu presents a broad band in the green region (350-600 nm) and several small peaks on the shoulders near 600 nm. It is well known that Eu$^{2+}$ ions provide a broad emission band corresponding to the $4f^5$d$^1$-4f$^7$ transition, while Eu$^{3+}$ ions emit discrete narrow lines belonging to the $^5D_0$-$^7F_J$ transitions ($J = 0$-6). Moreover, the two excitation spectra for Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu give the corresponding typical spectral profile for the two ions. Although the europium precursor was Eu$_2$O$_3$ containing the trivalent ion and the samples were prepared in a reducing atmosphere, it seems that the trivalent europium coexists with divalent europium in this compound. In order to prove it, a Eu$^{3+}$ singly doped Ba$_2$Gd$_2$Si$_4$O$_{13}$ phosphor was prepared in air and its PLE and PL spectra were comparatively investigated. As also shown in Fig. 3(a), there are three
narrow peaks centered at 594, 613 and 624 nm in the PL spectrum of 
Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu$^{3+}$ upon 393 nm excitation, which agrees with the position of 
Eu$^{3+}$ emission in Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu$^{2+}$/Eu$^{3+}$. Furthermore, the PLE spectral 
profile of Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu$^{3+}$ is similar to that of 
Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu$^{2+}$/Eu$^{3+}$ monitored at 613 nm; this confirms the consistence of 
Eu$^{2+}$ and Eu$^{3+}$ in the Ba$_2$Gd$_2$Si$_4$O$_{13}$ host when prepared in reducing atmosphere. Fig. 
3(b) shows the PLE (λ$_{em}$ = 543 nm) and PL (λ$_{em}$ = 377 nm) spectra of 
Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Tb$^{3+}$. The PLE spectrum observed in the range of 200-300 nm 
were attributed to the 4f$^8$-4f$^7$5d$^1$ ($^7$F$_6$-$^7$D) transition of Tb$^{3+}$ and those in the range of 
300-400 nm were come from the 4f-4f transition of Tb$^{3+}$. The Tb$^{3+}$ emission lines are 
located at 487 nm, 542 nm, 585 nm, and 624 nm, and are assigned to the $^5$D$_4$-$^7$F$_{6,5,4}$, 
transitions, respectively.$^{14}$

The decay curves and lifetime values of Eu$^{2+}$/Eu$^{3+}$ (excitation wavelength 365 
nm for Eu$^{2+}$ and 393 nm for Eu$^{3+}$) and Tb$^{3+}$ (excitation wavelength 377 nm) in 
Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu/Tb phosphor are shown in Fig. 4. Since there are several 
different cations with variable environments for the doped rare earth ions in this 
system, we have tried different exponential functions. It is found that, in order to get 
the best fitting (with the confidence coefficient of 99%) and evaluate the decay time, 
the experimental curves were fitted by the sum of two exponential decays using the 
formula:$^{15}$

\[ I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \]  

where $I$ is the luminescence intensity, $A_1$ and $A_2$ are constants, $\tau$ is the time, $\tau_1$ and $\tau_2$
are rapid and slow lifetimes for exponential components, respectively. On this basis, the effective lifetime constant ($\tau^*$) can be calculated as:

$$
\tau^* = \left( A_1\tau_1^2 + A_2\tau_2^2 \right) \left( A_1\tau_1 + A_2\tau_2 \right)
$$

The effective decay time ($\tau^*$) were calculated to be 2.01 µs, 1.96 ms, 1.89 ms and 2.21 ms for the $4f^5d-4f^7$ (Eu$^{2+}$ emission at 507 nm) in Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu, $5D_0-7F_2$ (Eu$^{3+}$ emission at 613 nm) in Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu, $5D_0-7F_2$ (Eu$^{3+}$ emission at 613 nm) in Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu, and $5D_0-7F_5$ (Tb$^{3+}$ emission at 543 nm) in Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Tb$^{3+}$, respectively. The decay profile of the $5D_4$ emission for the latter sample shows a clear rise at short times, due to the slow relaxation from $5D_3$ to $5D_4$, attributed to multiphonon relaxation in the silicate host containing high frequency vibrations. The non-exponential character of the decay profiles is presumably due to the presence of several slightly different sites for the dopants and, in the case of Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu, to possible Eu$^{2+}$-Eu$^{3+}$ energy transfer processes.

The possibility of the Eu$^{2+}$/Eu$^{3+}$ coexistence can be verified by the luminescence behavior. Fig. 5(a) shows the PLE and PL spectra of Ba$_2$Tb$_2$Si$_4$O$_{13}$. It can be seen that the PLE spectrum of Tb$^{3+}$ exhibits two obvious broad bands from 200 to 300 nm with two peaks at 252 and 279 nm and some weak transitions from 300 to 400 nm. Fig. 5(b) represents the PLE and PL spectra of Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu obtained at different experimental conditions. When Eu ions with a low concentration ($y = 0.03$) were introduced into this matrix, the PLE spectrum of Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu phosphor prepared in reducing atmosphere has been obviously broadened and the intensity of the sharp lines corresponding to the emission of Tb$^{3+}$ has obviously increased.
Moreover, the excitation band edge has shifted to 450 nm, showing a broad-band character. By comparing the two excitation bands of Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu phosphor obtained at different experimental conditions, there is an obvious difference in the excitation band owing to the appearance of a broad excitation band, which supports the existence of Eu$^{2+}$. Upon excitation at 377 nm, the Tb$^{3+}$ emission intensity decreases accompanied by a remarkable increase of the emission intensities at 594, 613, and 624 nm for Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu phosphor, which are the characteristic red emission peaks of Eu$^{3+}$ ions corresponding to the transitions from $^5$D$_0$ to $^7$F$_J$ ($J = 1$ and 2).\textsuperscript{17} Generally, we can propose that the enhancement of the red-emitting luminescence can be ascribed to the energy transfer from Tb$^{3+}$ to Eu$^{3+}$.\textsuperscript{18-19} Furthermore, it is notable that the emission intensity of the Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu phosphor prepared in reducing atmosphere is relatively higher than the one of the Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu fired in air, indicating that the efficient energy transfer between Eu$^{2+}$-Eu$^{3+}$ (Tb$^{3+}$) and the Eu$^{2+}$ absorption.

The diffuse reflectance spectra of Ba$_2$Gd$_{2x}$Si$_4$O$_{13}$:$x$Tb ($x = 0, 0.5, 1.0, 1.5, 2.0$) phosphors are shown in Fig. 6(a). The spectrum of the Ba$_2$Gd$_2$Si$_4$O$_{13}$ host shows a high reflectance in the visible range, and the band gap estimation in the Ba$_2$Gd$_2$Si$_4$O$_{13}$ host is shown by the inset in Fig. 6(a). The band gap of the Ba$_2$Gd$_2$Si$_4$O$_{13}$ host can be estimated according to eq 3\textsuperscript{20}

\[ [F(R_{\infty})hv]^n = A(hv - E_g) \]  

where $hv$ is the photon energy; $A$ is a proportional constant; $E_g$ is the value of the band gap; $n = 2$ for a direct transition or 1/2 for an indirect transition; and $F(R_{\infty})$ is
the Kubelka-Munk function defined as

$$ F(R_a) = \frac{(1 - R)^2}{2R} = \frac{K}{S} $$

(4)

where $R$, $K$, and $S$ are the reflection, absorption, and scattering coefficient, respectively. From the linear extrapolation of $[F(R_a)h\nu]^2 = 0$ in the inset of Figure 6a, the $E_g$ value was estimated to be about 4.20 eV. As Tb$^{3+}$ ions were doped into the Ba$_2$Gd$_2$Si$_4$O$_{13}$ host, a strong absorption in the range of 200-350 nm assigned to the f-d transition of Tb$^{3+}$ was observed, as found in the excitation spectrum. The $E_g$ value gradually increases, and the absorption intensity is enhanced at higher Tb$^{3+}$ ion concentrations. As a comparison, Ba$_2$Tb$_{2-x}$Si$_4$O$_{13}$:Eu phosphors show an obvious broad absorption band near 400 nm (Fig. 6(b)), which should be caused by the 4f$^2$-4f$^6$5d$^1$ transition of Eu$^{2+}$. The reflectance spectrum and PLE spectrum indicate that the absorption of Ba$_2$Tb$_2$Si$_4$O$_{13}$:Eu phosphor matches well with near-UV chips for applications in near-UV LEDs.

Fig. 7(a) illustrates the emission spectra of Ba$_2$Tb$_{2-y}$Si$_4$O$_{13}$:Eu ($y = 0$-0.12) samples upon excitation at 377 nm. With increasing Eu concentration, one can see that the relative emission intensities of Tb$^{3+}$ becomes weak, whereas the emission intensities of Eu$^{3+}$ firstly increase until they reach saturation at $y = 0.03$, reflecting the result of energy transfer from Tb$^{3+}$ to Eu$^{3+}$. In addition, it is surprising to find the appearance of a broad band centered around 507 nm with increasing $y$, which can be assigned to the 4f$^6$5d$^1$-4f$^7$ transition of Eu$^{2+}$, further supporting the coexistence of Eu$^{2+}$ and Eu$^{3+}$. Because of the Eu$^{2+}$-(Tb$^{3+})_n$-Eu$^{3+}$ energy transfer process, the CIE coordinates upon 377 nm excitation of Ba$_2$Tb$_{2-y}$Si$_4$O$_{13}$:Eu ($y = 0$, 0.01, 0.03, 0.09)
progressively shifted from green (0.2966, 0.5798) to red (0.5048, 0.3955) with increasing \( y \) as displayed in Fig. 7(b). As also given in the photographs of the emitting phosphors, the as-observed emitting color is obvious, which means that the tunable luminescence can be realized in the novel \( \text{Ba}_2\text{Nb}_{2}\text{Si}_4\text{O}_{13}:y\text{Eu} \) phosphors via \( \text{Eu}^{2+}\text{-(Tb}^{3+})_n\text{-Eu}^{3+} \) energy transfer processes.

In order to demonstrate the energy transfer from \( \text{Tb}^{3+} \) to \( \text{Eu}^{3+} \), the decay curves of \( \text{Tb}^{3+} \) emission at 542 nm and \( \text{Eu}^{3+} \) emission at 613 nm of \( \text{Ba}_2\text{Nb}_{2}\text{Si}_4\text{O}_{13} \) and \( \text{Ba}_2\text{Nb}_{1.995}\text{Si}_4\text{O}_{13}:0.005\text{Eu} \) phosphors are shown in Fig. 8(a) (Excitation at 377 nm). Using Eq 1 and Eq 2, the values of the effective decay time were found to be 2.59, 0.96 and 1.83 ms for the \( ^5\text{D}_4\rightarrow^7\text{F}_5 \) (\( \text{Tb}^{3+} \) emission at 543 nm) in \( \text{Ba}_2\text{Nb}_{2}\text{Si}_4\text{O}_{13} \), \( ^5\text{D}_4\rightarrow^7\text{F}_5 \) (\( \text{Tb}^{3+} \) emission at 543 nm) in \( \text{Ba}_2\text{Nb}_{1.995}\text{Si}_4\text{O}_{13}:0.005\text{Eu} \), and \( ^5\text{D}_0\rightarrow^7\text{F}_2 \) (\( \text{Eu}^{3+} \) emission at 613 nm) in \( \text{Ba}_2\text{Nb}_{1.995}\text{Si}_4\text{O}_{13}:0.005\text{Eu} \), respectively. Accordingly, the energy transfer efficiency (\( \eta_T \)) can be calculated using the following expression:

\[
\eta_T = 1 - \frac{\tau_x}{\tau_0}
\]

here \( \tau_0 \) and \( \tau_x \) are the corresponding lifetime values of donor \( \text{Tb}^{3+} \) in the absence and the presence of the acceptor \( \text{Eu}^{3+} \), and \( \eta_T \) is the energy transfer efficiency. As shown in the inset of Fig. 8(a), the total \( \eta_T \) is found to be 62.9% from \( \text{Tb}^{3+} \) to \( \text{Eu}^{3+} \) in the \( \text{Ba}_2\text{Nb}_{1.995}\text{Si}_4\text{O}_{13}:0.005\text{Eu} \) phosphor. We also measured the decay curves of the \( \text{Ba}_2\text{Nb}_{2}\text{Si}_4\text{O}_{13}:y\text{Eu} \) phosphors excited at 377 nm, as given in Fig. 8(b). It was found that the lifetimes for \( \text{Tb}^{3+} \) decreased with increasing Eu concentration, which offers clear evidence for the presence of energy transfer from \( \text{Tb}^{3+} \) to \( \text{Eu}^{3+} \), and the energy transfer efficiencies are 62.9%, 68.7%, 73.7%, 81.5% and 89.2% depending on
different Eu concentration, 0.005, 0.01, 0.02, 0.03 and 0.06, respectively. Fig. 8(c) shows the decay curves of the $^5D_4-^7F_5$ transition of Tb$^{3+}$ upon excitation at 273, 365, and 377 nm. Based on the decay curves in Fig. 8(c), Eq 1 and Eq 2, the value of decay time were calculated to be practically independent of the excitation wavelength, with values 0.49, 0.45 and 0.48 ms for excitation of 273, 365, and 377 nm, respectively.

To study the energy transfer process from Tb$^{3+}$ to Eu$^{3+}$ in Ba$_2$TbSi$_4$O$_{13}$:Eu phosphor in more detail, time-resolved emission spectra of Ba$_2$Tb$_{1.995}$Si$_4$O$_{13}$:0.005Eu were measured upon excitation into the Tb$^{3+}$ band with a delay time ranging from 0 to 3.12 ms (Fig. 9). At $t = 0$ ms, only the characteristic emission Tb$^{3+}$ is observed; no Eu$^{3+}$ emission is present because the excitation energy Tb$^{3+}$ has not been transferred yet to Eu$^{3+}$. As also shown in Fig. 9, when $t = 0.78$ ms, the emission of Tb$^{3+}$ starts to decrease accompanied by the presence of Eu$^{3+}$ emissions due to the efficient energy transfer of Tb$^{3+}$ to Eu$^{3+}$. The emission of Tb$^{3+}$ decreases gradually with further increase of the decay time, whereas that of Eu$^{3+}$ begins to increase due to transfer of more excitation energy from Tb$^{3+}$ to Eu$^{3+}$. Therefore, the Eu$^{3+}$ ion acts as the terminal of the thermal of the energy transfer processes in the Ba$_2$TbSi$_4$O$_{13}$:Eu phosphor. Thus, we can obtain bright red luminescence in the Ba$_2$TbSi$_4$O$_{13}$:Eu phosphor upon near UV excitation.

Fig. 10 illustrates the energy level model for the energy transfer processes of and Eu$^{2+}$-Tb$^{3+}$-Eu$^{3+}$ in the Ba$_2$Tb$_2$Si$_4$O$_{13}$ host. As can be seen from Fig. 10, the excitation lines of Ba$_2$Tb$_2$Si$_4$O$_{13}$:Eu phosphors in the n-UV region come from the
absorption of the combined effect of Tb$^{3+}$, Eu$^{3+}$, and Eu$^{2+}$, so that a broad and strong
absorption band can be observed in the PLE spectrum (Figure 3b). The energy
absorbed by Eu$^{2+}$ can also be efficiently transferred from the 4f$^6$5d$^1$ band to the
excited levels of Eu$^{3+}$ and Tb$^{3+}$; accordingly, the energy absorbed by Tb$^{3+}$ can be
transferred from the $^5D_4$ level of Tb$^{3+}$ to the $^5D_0$ ($^5D_1$) level of Eu$^{3+}$.25-26

The thermal stability of phosphor is one of the important parameters for
possible applications. For this reason, the emission spectra of the selected
Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu phosphor at various temperatures are shown in Fig. 11(a).
The variations of the relative emission intensities as a function of temperature are
plotted in Fig. 11(b). When the temperature is increased to 150 °C, the PL intensities
of Tb$^{3+}$ and Eu$^{3+}$ ions decrease to 94.9% and 88.2% of the corresponding initial value
(25 °C). In Fig. 11(b), we have also given the temperature dependent PL intensities
variation of the commercial BaMgAl$_{10}$O$_{19}$:Eu$^{2+}$ (BAM) blue phosphor, and the
comparable thermal stability can be found. The small intensity decrease indicates
that Ba$_2$Tb$_2$Si$_4$O$_{13}$:Eu could be used for high-power LED application. In general, the
thermal quenching of emission intensity can be explained by several mechanisms. A
widely accepted mechanism is the electronic transition through the intersection
between the ground and excited states. In other words this mechanism is described as
a large displacement between the potential energy curves of the ground and excited
state in the configuration coordinate diagram.27 In the present case, this mechanism
would be valid in the case of excitation in the absorption profile of Eu$^{2+}$. To better
understand the thermal quenching phenomena, the activation energy for the thermal
quenching was fitted using the equation describing the crossover between Franck-Condon displaced potential energy curves:

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

(6)

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, \(\Delta E\) is the activation energy for thermal quenching, and \(k\) is Boltzmann constant (8.62 \(\times\) 10\(^{-5}\) eV). According to the equation, the activation energy \(\Delta E\) can be calculated from a plotting of \(\ln[(I_0/I) - 1]\) against \(1/kT\), where a straight slope equals \(-\Delta E\). As shown in Fig. 11(b), \(\Delta E\) were found to be 0.351 and 0.296 eV for \(\text{Tb}^{3+}\) and \(\text{Eu}^{3+}\), respectively. The relatively high activation energy results in a good thermal stability for this phosphor. The quantum efficiency of the phosphor is another important parameter to be considered for practical application, and we have also measured the internal quantum efficiency (QE) of \(\text{Ba}_2\text{Tb}_{2-x}\text{Si}_4\text{O}_{13}:x\text{Eu}\) (\(x = 0, 0.005, 0.03\), and 0.09) phosphors. The measured internal QE values are 30.06\%, 31.66\%, 39.35\% and 23.39\%, respectively, for \(x = 0, 0.005, 0.03, 0.09\) under 377 nm excitation.

4. Conclusion

In summary, color-tunable \(\text{Ba}_2\text{Gd}_{2-x}\text{Tb}_x\text{Si}_4\text{O}_{13}:y\text{Eu}\) solid-solution phosphors were prepared by the high-temperature solid-state reaction in reducing atmosphere. The terbium ions in the host can not only form the iso-structural phase originated from the \(\text{Ba}_2\text{Gd}_2\text{Si}_4\text{O}_{13}\), but they can be also used to realize the \(\text{Eu}^{2+}\)\(\text{-Tb}^{3+}\)\(\text{-Eu}^{3+}\) energy transfer channel between broad-band absorption of \(\text{Eu}^{2+}\) and the narrow-line emission of \(\text{Eu}^{3+}\). On the basis of this process, the emission color of the obtained
phosphors can be varied from green to yellow and finally to red by adjusting the
concentration of Eu. Moreover, the temperature dependence of the luminescence
intensity shows that this phosphor has an excellent thermal stability against
temperature quenching.

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References

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11525.


The figure captions are as follows,

**Fig. 1** XRD patterns of as-prepared (a) Ba$_2$Gd$_{2-x}$Si$_4$O$_{13}$:xTb ($x = 0, 0.5, 1.0, 1.5, 2.0$) and (b) Ba$_2$Tb$_{2-y}$Si$_4$O$_{13}$:yEu ($y = 0, 0.01, 0.03, 0.06, 0.15, 2.0$) samples. The standard data for Ba$_2$Gd$_2$Si$_4$O$_{13}$ (ICSD card no. 260737) is shown as a reference.

**Fig. 2** Unit cell parameters $a$, $V$ of (a) Ba$_2$Gd$_{2-x}$Si$_4$O$_{13}$:xTb ($x = 0, 0.5, 1.0, 1.5, 2.0$) and (b) Ba$_2$Tb$_{2-y}$Si$_4$O$_{13}$:yEu ($y = 0, 0.01, 0.03, 0.06, 0.15$) are plotted. (c) Crystal structure of Ba$_2$Gd$_2$Si$_4$O$_{13}$ viewed along the $b$ axis. The SiO$_4$ tetrahedra and GdO$_7$ polyhedra are highlighted in the unit cell, and Ba$_2$Tb$_2$Si$_4$O$_{13}$ is isostructural with Ba$_2$Gd$_2$Si$_4$O$_{13}$. (d) The bonding of O$^{2-}$ anions with Ba$^{2+}$, Si$^{4+}$ and Gd$^{3+}$ cations in the independent part of the Ba$_2$(Gd,Tb)$_2$Si$_4$O$_{13}$ unit cell.

**Fig. 3** PLE and PL spectra of (a) Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu$^{2+}$/Eu$^{3+}$ prepared in a reducing atmosphere, Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu$^{3+}$ prepared in air, and (b) Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Tb$^{3+}$ prepared in air.

**Fig. 4** (a) Decay time curves and the corresponding lifetime values of Eu$^{2+}$ in Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu phosphor. (b) Eu$^{3+}$ and Tb$^{3+}$ decay curves of Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu/Tb phosphor.

**Fig. 5** PLE and PL spectra of (a) Ba$_2$Tb$_2$Si$_4$O$_{13}$ and (b) Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu phosphor.

**Fig. 6** The diffuse reflectance spectra of (a) Ba$_2$Gd$_{2-x}$Si$_4$O$_{13}$:xTb ($x = 0, 0.5, 1.0, 1.5, 2.0$) and (b) Ba$_2$Tb$_{2-y}$Si$_4$O$_{13}$:yEu ($y = 0, 0.01, 0.04, 0.06$) phosphors. The extrapolation of the band gap energy for (inset of a) Ba$_2$Gd$_2$Si$_4$O$_{13}$, (inset of b) Ba$_2$Tb$_2$Si$_4$O$_{13}$, (c) Ba$_2$Gd$_{1.5}$Tb$_{0.5}$Si$_4$O$_{13}$, (d) Ba$_2$GdTbSi$_4$O$_{13}$, and (e) Ba$_2$Tb$_2$Si$_4$O$_{13}$.
\[ \text{Ba}_2\text{Gd}_{0.5}\text{Tb}_{1.5}\text{Si}_4\text{O}_{13}. \]

**Fig. 7** (a) PL spectra for the phosphors \( \text{Ba}_2\text{Tb}_{2-y}\text{Si}_4\text{O}_{13}:y\text{Eu} \) \((y = 0, 0.005, 0.01, 0.03, 0.04, 0.06, 0.09, 0.12)\) phosphors, and (b) the corresponding CIE coordinates and photographs.

**Fig. 8** (a) Decay time curves and lifetimes of \( \text{Eu}^{3+} \) in \( \text{Ba}_2\text{Tb}_{1.995}\text{Si}_4\text{O}_{13}:0.005\text{Eu} \) phosphor and \( \text{Tb}^{3+} \) in \( \text{Ba}_2\text{Tb}_2\text{Si}_4\text{O}_{13} \) and \( \text{Ba}_2\text{Tb}_{1.995}\text{Si}_4\text{O}_{13}:0.005\text{Eu} \) phosphor. (b) \( \text{Tb}^{3+} \) decay curves of \( \text{Ba}_2\text{Tb}_2\text{Si}_4\text{O}_{13}:y\text{Eu} \) phosphors monitoring 542 nm emission. (c) \( \text{Tb}^{3+} \) decay curves of \( \text{Ba}_2\text{Tb}_{1.97}\text{Si}_4\text{O}_{13}:0.03\text{Eu} \) phosphors monitoring 542 nm emission under 273, 365 and 377 nm excitation.

**Fig. 9** The time-resolved spectra of \( \text{Ba}_2\text{Tb}_{1.995}\text{Si}_4\text{O}_{13}:0.005\text{Eu} \) phosphor under 377 nm excitation.

**Fig. 10** Energy level diagram for the ET processes among \( \text{Eu}^{2+}, \text{Tb}^{3+}, \) and \( \text{Eu}^{3+} \) in \( \text{Ba}_2\text{Tb}_2\text{Si}_4\text{O}_{13} \) phosphor.

**Fig. 11** (a) Temperature-dependent PL spectra of \( \text{Ba}_2\text{Tb}_{1.97}\text{Si}_4\text{O}_{13}:0.03\text{Eu} \). (b) The variations of the relative emission intensities as a function of temperature of the \( \text{Ba}_2\text{Tb}_{1.97}\text{Si}_4\text{O}_{13}:0.03\text{Eu} \) phosphor and commercial BAM phosphor. The inset shows relative PL intensities of \( \text{Tb}^{3+}, \text{and Eu}^{3+} \) in \( \text{Ba}_2\text{Tb}_2\text{Si}_4\text{O}_{13} \) host with raised temperatures. The inset shows the activation energy \((\Delta E)\) of \( \text{Tb}^{3+} \) and \( \text{Eu}^{3+} \) in \( \text{Ba}_2\text{Tb}_{1.97}\text{Si}_4\text{O}_{13}:0.03\text{Eu} \) phosphor.
Fig. 1 XRD patterns of as-prepared (a) $\text{Ba}_2\text{Gd}_{2-x}\text{Tb}_x\text{Si}_4\text{O}_{13}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$) and (b) $\text{Ba}_2\text{Tb}_{2-y}\text{Si}_4\text{O}_{13}$($y = 0, 0.01, 0.03, 0.06, 0.15, 2.0$) samples. The standard data for $\text{Ba}_2\text{Gd}_2\text{Si}_4\text{O}_{13}$ (ICSD card no. 260737) is shown as a reference.
Fig. 2 Unit cell parameters $a$, $V$ of (a) $\text{Ba}_2\text{Gd}_{2-x}\text{Si}_4\text{O}_{13}:x\text{Tb}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$) and (b) $\text{Ba}_2\text{Tb}_{2-y}\text{Si}_4\text{O}_{13}:y\text{Eu}$ ($y = 0, 0.01, 0.03, 0.06, 0.15$) are plotted. (c) Crystal structure of $\text{Ba}_2\text{Gd}_2\text{Si}_4\text{O}_{13}$ viewed along the $b$ axis. The $\text{SiO}_4$ tetrahedra and $\text{GdO}_7$ polyhedra are highlighted in the unit cell, and $\text{Ba}_2\text{Tb}_2\text{Si}_4\text{O}_{13}$ is isostructural with $\text{Ba}_2\text{Gd}_2\text{Si}_4\text{O}_{13}$. (d) The bonding of $\text{O}^{2-}$ anions with $\text{Ba}^{2+}$, $\text{Si}^{4+}$ and $\text{Gd}^{3+}$ cations in the independent part of the $\text{Ba}_2(\text{Gd,Tb})_2\text{Si}_4\text{O}_{13}$ unit cell.
Fig. 3 PLE and PL spectra of (a) $\text{Ba}_2\text{Gd}_{1.99}\text{Si}_4\text{O}_{13}:0.01\text{Eu}^{2+}/\text{Eu}^{3+}$ prepared in a reducing atmosphere, $\text{Ba}_2\text{Gd}_{1.99}\text{Si}_4\text{O}_{13}:0.01\text{Eu}^{3+}$ prepared in air, and (b) $\text{Ba}_2\text{Gd}_{1.99}\text{Si}_4\text{O}_{13}:0.01\text{Tb}^{3+}$ prepared in air.
Fig. 4 (a) Decay time curves and the corresponding lifetime values of Eu$^{2+}$ in Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu phosphor. (b) Eu$^{3+}$ and Tb$^{3+}$ decay curves of Ba$_2$Gd$_{1.99}$Si$_4$O$_{13}$:0.01Eu/Tb phosphor.
Fig. 5 PLE and PL spectra of (a) Ba$_2$Tb$_2$Si$_4$O$_{13}$ and (b) Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu phosphor.
Fig. 6 The diffuse reflectance spectra of (a) Ba$_2$Gd$_{2-x}$Si$_4$O$_{13}$:Tb ($x = 0$, 0.5, 1.0, 1.5, 2.0) and (b) Ba$_2$Tb$_{2-y}$Si$_4$O$_{13}$:Eu ($y = 0$, 0.01, 0.04, 0.06) phosphors. The extrapolation of the band gap energy for (inset of a) Ba$_2$Gd$_2$Si$_4$O$_{13}$, (inset of b) Ba$_2$Tb$_2$Si$_4$O$_{13}$, (c) Ba$_2$Gd$_{1.5}$Tb$_{0.5}$Si$_4$O$_{13}$, (d) Ba$_2$GdTbSi$_4$O$_{13}$, and (e) Ba$_2$Gd$_{0.5}$Tb$_{1.5}$Si$_4$O$_{13}$.
Fig. 7 (a) PL spectra for the phosphors $\text{Ba}_2\text{Tb}_{2x}\text{Si}_4\text{O}_{13}:x\text{Eu} (x = 0, 0.005, 0.01, 0.03, 0.04, 0.06, 0.09, 0.12)$ phosphors, and (b) the corresponding CIE coordinates and photographs.
Fig. 8 (a) Decay time curves and lifetimes of Eu\(^{3+}\) in Ba\(_2\)Tb\(_{1.995}\)Si\(_4\)O\(_{13}\):0.005Eu phosphor and Tb\(^{3+}\) in Ba\(_2\)Tb\(_2\)Si\(_4\)O\(_{13}\) and Ba\(_2\)Tb\(_{1.995}\)Si\(_4\)O\(_{13}\):0.005Eu phosphor. (b) Tb\(^{3+}\) decay curves of Ba\(_2\)Tb\(_{2-y}\)Si\(_4\)O\(_{13}\):yEu phosphors monitoring 542 nm emission. (c) Tb\(^{3+}\) decay curves of Ba\(_2\)Tb\(_{1.9}\)Si\(_4\)O\(_{13}\):0.03Eu phosphors monitoring 542 nm emission under 273, 365 and 377 nm excitation.
**Fig. 9** The time-resolved spectra of Ba$_2$Tb$_{1.995}$Si$_4$O$_{13}$:0.005Eu phosphor under 377 nm excitation.
Fig. 10 Energy level model for the ET processes among Eu$^{2+}$, Tb$^{3+}$, and Eu$^{3+}$ in Ba$_2$Tb$_2$Si$_4$O$_{13}$ phosphor.
Fig. 11 (a) Temperature-dependent PL spectra of Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu. (b) The variations of the relative emission intensities as a function of temperature of the Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu phosphor and commercial BAM phosphor. The inset shows relative PL intensities of Tb$^{3+}$, and Eu$^{3+}$ in Ba$_2$Tb$_2$Si$_4$O$_{13}$ host with raised temperatures. The inset shows the activation energy ($\Delta E$) of Tb$^{3+}$ and Eu$^{3+}$ in Ba$_2$Tb$_{1.97}$Si$_4$O$_{13}$:0.03Eu phosphor.
Photoluminescence Tuning via Energy Transfer in the Eu-doped Ba$_2$(Gd,Tb)$_2$Si$_4$O$_{13}$ Solid-Solution Phosphors

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Successive energy transfer process Eu$^{2+}$-Eu$^{3+}$(Tb$^{3+}$) and Tb$^{3+}$-Eu$^{3+}$ appear to occur in the Ba$_2$Tb$_{2-x}$Si$_4$O$_{13}$:yEu ($y = 0-0.12$) solid-solution phosphors.