A novel Eu$^{3+}$/Eu$^{2+}$ co-doped MgSrLa$_8$(SiO$_4$)$_6$O$_2$ single-phase white light phosphor for white LEDs

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A novel MgSrLa$_{8-x}$(SiO$_4$)$_6$O$_2$:xEu (MLSO:xEu) phosphor was synthesized through a high-temperature solid-state reaction. The crystal structures, luminescent properties, fluorescence decay time, and oxygen vacancies were investigated systematically. XRD analysis shows a typical oxyapatite structure with the space group $P6_3/m$. Europium can enter crystal matrices simultaneously in the form of Eu$^{3+}$ and Eu$^{2+}$ and occupy nonequivalent crystallographic positions in a lattice, thus forming various optical centers. Under ultraviolet light excitation, the phosphors simultaneously show the blue-green emission of Eu$^{2+}$ and the green-yellow-red emission of Eu$^{3+}$. The optimal doping content of Eu is 7.5 mol% ($x = 0.075$).

White light can be realized with a CIE coordinate of (0.3664, 0.3260) by adjusting the concentration of Eu. The lifetimes of Eu$^{3+}$ and Eu$^{2+}$ in this study are considerably longer than those in other references. The results suggest that the MLSO:Eu$^{2+}$/Eu$^{3+}$ (0.075) phosphor is a promising candidate for white LEDs.

In general, the introduction of a variety of activated ions can compensate for the lack of spectrum, whereas this method may reduce the luminous intensity and the efficiency of energy transfer among the doped ions to a certain extent. Therefore, we focus on how to improve the loss of the doping system in the spectral distribution and how to obtain white phosphors to meet the requirements of different applications.

Among the various RE element species, europium has traditionally occupied a dominant role. Luminescence of the Eu$^{3+}$ ion originates from its 4f$^{6} \rightarrow 4f^{7}$ transition consisting of sharp lines in the red region. The positions of its emission lines are independent of the host materials. Eu$^{2+}$ presents broad emission from the parity-allowed transitions 4f$^{5}5d^{1} \rightarrow 4f^{6}$, which presents wide-emission range changing in the blue-green-yellow or red band. The emission band position can be tuned by selecting different host materials.

Nevertheless, only a few studies have been considered this topic, thus inspiring us to explore the luminescence properties of Eu$^{2+}$/Eu$^{3+}$ co-doped single-phase white-light-emitting phosphors.

In this study, in Eu$^{3+}$-doped material, part of Eu$^{3+}$ is reduced to Eu$^{2+}$. The crystal structures, luminescent properties, fluorescence decay time, and oxygen vacancies were investigated systematically. Finally, the phosphors simultaneously show blue emission of the Eu$^{2+}$ ion and green-yellow-red emission of the Eu$^{3+}$ ion under UV light excitation. Surprisingly, high energy level emission peaks of Eu$^{2+}$ can be observed, i.e., $^5D_{4} \rightarrow ^7F_J (J = 0, 1, 2)$ and $^5D_{3} \rightarrow ^7F_J (J = 0, 1, 2, 3)$, which are our biggest innovation. White light can be realized by adjusting the concentration of Eu. Results show that MLSO:Eu$^{2+}$/Eu$^{3+}$ is a promising white-emitting phosphor for WLEDs.
Experimental

Sample preparation

MSLSO doped with Eu was synthesized with a high-temperature solid phase method by calcining a mixture of La2O3 (99.9%), MgCO3, 3H2O (99.99%), SrCO3, Eu2O3 (99.99%), SiO2 (99.9%), and H2BO3, where H2BO3 acted as flux. All calculations were performed assuming that Eu replaces La3+ exclusively and formally yielding MSLSO:xEu (x = 0.05, 0.075, 0.09, 0.10, and 0.125). That is to say, n(Mg) : n(Sr) : n(La) : n(Si) : n(Eu) = 1 : 1 : (8 - x) : 6 : x. Subsequently, the mixture was preheated at 1000 °C for 3 h in a weak reducing atmosphere with using carbon powder. Then, the products were cooled to room temperature naturally. After grinding for second time, and the samples were calcined at 1100 °C for 4 h under the same conditions.

Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu Kα1 radiation (λ = 1.5406 Å) in the range of 2θ = 10–90° with the step of Δ2θ = 0.02° operating at 40 mA and 40 kV. The fluorescent properties of the as-obtained samples were recorded by FluoroMax-4 (HORIBA Jobin Yvon) fluorescence spectrometer with a Xe-arc lamp of 150 W power, and the lifetime was measured with a phosphorimeter attached to the main system with a Xe-flash lamp (25 W power).

Results and discussion

X-ray phase analysis

The solid solutions MSLSO:xEu (x = 0, 0.05, 0.075, 0.09, 0.10, and 0.125) belong to the oxypatite structure type. According to ref. 36 the site-symmetry of atoms in Sr2La8(SiO4)6O2 crystals (space group P63/m, z = 1) is La1-4f, Sr-4f, La2-6h, Si-6h, O-6h, O-6h, O-12i, O-2a; z = 1. The structure contains isolated SiO4 tetrahedra. Oxygen O(4) in the 2a position does not enter into the composition of the tetrahedra and forms chains that are parallel to the hexagonal crystal axis.37 On this basis, we assumed that the Mg atoms also occupy the 4f position. Europium replacing the La atoms in Sr2La8(SiO4)6O2 can also be located in these two positions. In the unit cell, the six 6h sites are occupied exclusively by 6La3+, whereas the four 4f sites are randomly shared by 1Sr2+, 1Mg2+, and 2La3+.38

Photoluminescence

Fig. 2(a) illustrates that, in the PLE spectrum of 614.5 nm luminescence for the unreduced sample, two bands are centered at about 284 and 304 nm by using Gaussian fitting corresponding to the allowed G2−−→ Eu3+ charge transfer state (CTS1 and CTS2) of Eu3+ ion. The sharp excitation peaks between 350 and 600 nm are attributed to the intra-4f transitions from the Eu3+ ground state 7F0. Meanwhile, for the reduced samples, three bands are centered at about 267, 304, and 330 nm by using Gaussian fitting corresponding to the allowed G2−−→ Eu3+ charge transfer state (CTS1 and CTS2) of Eu3+ ion and the 4f7→ 4f55d1 from Eu2+, respectively, as shown in Fig. 2(c). CTS1 and CTS2 correspond to the 6h sites and the 4f sites, as is consistent with the reported literature.39 Weak sharp excitation peaks are found between 350 and 600 nm, meaning that for the emission of the Eu3+ ions when Eu2+ is excited and the CTS majorly contribute, and the contribution of f-f transition is smaller. An inflection around 290 nm of the band is centered at 330 nm, suggesting that Eu3+ in this site can exchange the excitation energy with Eu2+ probably located at the same site-type. For the reduced samples, by comparing the intensity of the peaks of the excitation spectrum, x = 0.075 is a more favorable condition. Next, in Fig. 2(b), we will research the emission spectra of the reduced and unreduced samples about MSLSO:0.075Eu excited at 267 and 290 nm, respectively. Compared with the unreduced sample, the reduced sample possess several sharp peaks, the intense emission peaks from transitions 5D0−−→ FJ (J = 0, 1, 2) and weak peaks from 3D2−−→ FJ (J = 0, 1, 2, 3) of Eu3+ appear to the emission spectra besides the peaks from 3D0−−→ FJ (J = 0, 1, 2, 3, 4) of Eu2+. According to our previous experimental results, given the energy transfer from Eu3+ ions to the Eu2+ ions, high-energy level emission of Eu3+. The emission spectra of the unreduced sample excited at 290 nm, where high energy level emission lines are not observed. The levels with J = 0 are normally not degenerated, so the 5D0−−→ F0 transition shows no more than one band at the spectrum. Two lines for the transition 3D0−−→ F0 indicate that the Eu3+ ions occupies the 4f and 6h positions.40 According to G. Blasse,41 for the unreduced sample, the Eu3+ 3D0−−→ F0 transition is observed as the strongest peak at 577 nm and the 3D0−−→ F0 emission of Eu3+ is rather intense, indicating a strong linear

Fig. 1 (a) Powder XRD patterns of Sr2La8Si6O26 (ICSD 15-5625) and MSLSO:xEu phosphors. (b) EDS spectrum.
crystal-field component at the Eu$^{3+}$ ion. This case is evident in the (6h) site. The site symmetry is $C_s$, with one free oxygen ion in the symmetry plane. For the reduced sample, we found two bands with peaks at 577 and 581 nm (see the Table 1) for the $5D_0 \rightarrow 7F_0$ transition, indicating that Eu$^{3+}$ occupies two sites (6h and 4f, respectively) confirming the occurrence of two optical centers generated by Eu$^{3+}$. The transitions of emission spectra were identified in Table 1.\textsuperscript{42-46}

Table 1  Transitions in the emission spectra of MSLSO:Eu$^{2+}$/Eu$^{3+}$

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Transition</th>
<th>Wavelength (nm)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>489</td>
<td>$^5D_2 \rightarrow ^7F_5$</td>
<td>585.5</td>
<td>$^3D_1 \rightarrow ^3F_3$</td>
</tr>
<tr>
<td>460</td>
<td>$^5D_2 \rightarrow ^7F_6$ (Eu$^{2+}$)</td>
<td>623</td>
<td>$^3D_2 \rightarrow ^3F_4$</td>
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<tr>
<td>466</td>
<td>$^5D_2 \rightarrow ^7F_0$</td>
<td>577, 581</td>
<td>$^3D_0 \rightarrow ^3F_0$</td>
</tr>
<tr>
<td>473.5</td>
<td>$^5D_2 \rightarrow ^7F_1$</td>
<td>587, 589.5, 594, 598</td>
<td>$^3D_2 \rightarrow ^3F_1$</td>
</tr>
<tr>
<td>494.5</td>
<td>$^5D_2 \rightarrow ^7F_2$</td>
<td>614.5, 619, 623</td>
<td>$^3D_2 \rightarrow ^3F_2$</td>
</tr>
<tr>
<td>511</td>
<td>$^5D_2 \rightarrow ^7F_3$</td>
<td>669</td>
<td>$^3D_2 \rightarrow ^3F_3$</td>
</tr>
<tr>
<td>527</td>
<td>$^5D_2 \rightarrow ^7F_4$</td>
<td>701.5, 704</td>
<td>$^3D_2 \rightarrow ^3F_4$</td>
</tr>
<tr>
<td>538</td>
<td>$^5D_2 \rightarrow ^7F_5$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>555, 561</td>
<td></td>
<td>—</td>
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</tr>
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</table>

The excitation spectra of MSLSO:Eu$^{2+}$/Eu$^{3+}$ ($x = 0.05, 0.075, 0.09, 0.10, 0.125$) are shown in Fig. 3(a) and 4(a) monitored at 460 nm, the excitation spectra consists of two distinct broad excitation bands peaking at 330 nm and 365 nm related to $4f^6 5d^1 (8S_{7/2}) \rightarrow 4f^5 d^1$ from Eu$^{2+}$. The emission spectra of MSLSO:Eu$^{2+}$/Eu$^{3+}$ ($x = 0.05, 0.075, 0.09, 0.10$ and 0.125) are shown in Fig. 3(b) and (c) and 4(b), in addition, the insert Fig. 3(c) is from Fig. 3(b) between 415 and 520 nm, the whole emission spectra consists of a broad emission band peaking at 460 nm related to $4f^5 5d^1 \rightarrow 4f^6 5d^1 (8S_{7/2})$ luminescence of Eu$^{2+}$ and several sharp lines between the 530 nm and 710 nm region, ascribed to the $^5D_I \rightarrow ^7F_J (I = 0, 1, 2; J = 0, 1, 2, 3, 4)$ transitions in Eu$^{3+}$. That is to say, part of the energy of Eu$^{2+}$ transfer to Eu$^{3+}$, another part for its own emission; in this case, it is possible to achieve white light emission. In the oxyapatite structure,\textsuperscript{44} Sr$^{2+}$ occupy the 4f sites, the ionic radii of Eu$^{2+}$ is very close to that of Sr$^{2+}$, moreover, the Eu$^{2+}$ ion match the Sr$^{2+}$ electrovalence, so it is reasonable that Eu$^{2+}$ will substitute for Sr$^{2+}$ to occupy the 4f sites. Thus, the energy transfer between Eu$^{2+}$ and Eu$^{3+}$ occurs to the 4f sites.

The above results suggest that Eu$^{2+}$ ions play a sensitizing agent role in the emission process and also acts as an activator. To further understand the relationship plot between the intensity of $^5D_1$, we constructed $^5D_0$ emission and the Eu$^{3+}$ ion
increased with increasing Eu\textsuperscript{3+} ion concentration in the MSLSO yellow, white, and blue regions. Both spectra are calculated to be (0.5008, 0.4518), (0.3664, 0.3260), and (0.2300, 0.125). The coordinates are respectively displayed in the CIE chromaticity diagram as shown in Fig. 6(a), indicating that the emission hue is tunable from yellow to white and eventually to blue by adjusting the excitation wavelength. Moreover, according to the emission spectrum of the MSLSO:Eu\textsuperscript{2+}/Eu\textsuperscript{3+} (0.075) excited at 330 nm, containing the composition of the three primary colors of white light so that white light emission is exhibited.

Fig. 7 illustrates the fluorescence decay curves of MSLSO:Eu\textsuperscript{2+}/Eu\textsuperscript{3+} (0.075) phosphor at room temperature. The experimental decay curves of MSLSO:Eu\textsuperscript{2+}/Eu\textsuperscript{3+} (0.075) can be best fitted with a double exponential eqn (1):

\[
I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + y_0
\]

Suggesting the significance of the energy transfer between Eu\textsuperscript{3+} ions and Eu\textsuperscript{2+} ions, where \( I \) is the luminescence intensity, \( A_1 \) and \( A_2 \) are constants, \( t \) is the time, \( \tau_1 \) and \( \tau_2 \) are the decay times for the exponential components. The average decay times \( \tau \) can be estimated by the following eqn (2):

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

The fluorescence decay times of Eu\textsuperscript{2+} ions and Eu\textsuperscript{3+} ions are listed in Table 2. The lifetimes of \( ^5\text{D}_1 \) and \( ^5\text{D}_0 \) levels in the current study are considerably longer than those of the reports from ref. 48–51 and the lifetimes of \( ^5\text{D}_0 \) level are longer than those of the \( ^5\text{D}_1 \) level. We speculate that the energy transmission from \( ^5\text{D}_1 \) to \( ^5\text{D}_0 \) is interfered. As a result, the intense luminescence of \( ^5\text{D}_1 \) level is achieved due to the enhanced probability of radiation transition.

Reduction of Eu\textsuperscript{3+} → Eu\textsuperscript{2+} was considered, which may be due to vacancy formation in the 4\text{f} crystal lattice position and the negative charge transfer by this vacancy to two types of Eu\textsuperscript{3+} ions. \[\text{Fig. 8(a) displays three series of sharp peaks in the excitation spectra monitored at different wavelengths ranging from 474 nm to 655.5 nm, 382.5 nm to 523 nm, and 377.5 nm to 600 nm.}\]
438 nm, respectively. These peaks all describe a number of sharp peaks with decreasing intensity, which are brought about by absorption of radiation by oxygen vacancies. As the wavelength of detected signals increases, the luminescence maxima of the peaks are displaced to the long-wave region of the spectrum. A similar displacement of lines in the excitation spectra is described in work. This displacement reflects an inhomogeneous character of oxygen vacancy distribution in the silicate matrix. Fig. 8(b) shows the peaks of oxygen vacancies vary from monitor wavelengths, the linear relationship formulas are as follows:

\[
\lambda_{\text{vacancy-1}} = 0.91\lambda_{\text{moni}} + 1.10 \quad (3)
\]

\[
\lambda_{\text{vacancy-2}} = 0.72\lambda_{\text{moni}} + 9.76 \quad (4)
\]

\[
\lambda_{\text{vacancy-3}} = 0.61\lambda_{\text{moni}} - 0.99 \quad (5)
\]

Under normal circumstances, transfer of energy from the \( ^5D_1 \) level to \( ^5D_0 \) level rapidly occurs in phosphors; therefore, the lifetime of the \( ^5D_1 \) level is relatively short and the lines of the intense \( ^5D_1 \) emission cannot be observed. In this host, the transfer of energy from \( ^5D_1 \) to \( ^5D_0 \) was hindered by oxygen vacancies; thus, the energy cannot be transmitted from \( ^5D_1 \) to \( ^5D_0 \). Therefore, the lines of the intense \( ^5D_1 \) emission can be observed and \( ^5D_1 \) level lifetimes are extremely long.

We infer two possible routes to transmit the excitation energy: one route is direct transmission to levels of Eu\(^{3+}\), and another route is through the oxygen vacancies trapping the energy and then releasing the energy again. Direct transmission is fast, and the release process is slow. As the slow release process leading to the decay curves displayed double exponential form, we summarize these two processes as a slow process that determines \( ^5D_1 \) level with extraordinary long lifetime and superior strength.

**Conclusions**

MSLSO doped with Eu phosphors were synthesized via high-temperature solid phase method. XRD analysis shows a typical oxyapatite structure with the space group of \( P_{6_3}/m \). The broad excitation spectra ranging from 220 nm to 430 nm, matched well with UV LED chips. Luminescence measurements indicate that the emission spectrum of as-obtained phosphors contain both the characteristic emissions of Eu\(^{2+}\) and Eu\(^{3+}\) ions, in which the broad band luminescence of Eu\(^{2+}\) and narrower \( 4f \rightarrow 4f \) luminescent of Eu\(^{3+}\) can be observed upon 330 and 365 nm excitation. With increasing Eu contents, the relative intensity of the red component from Eu\(^{3+}\) become stronger gradually, whereas that of Eu\(^{2+}\) decreases, correspondingly. In addition, the optimal doping contents of Eu is confirmed to be 7.5 mol\% \( (x = 0.075) \). Moreover, in the silicate lattice, inhomogeneously distributed oxygen vacancies are responsible for

<table>
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<th>Monitored wavelength (nm)</th>
<th>( A_1 )</th>
<th>( A_2 )</th>
<th>( \tau_1 )</th>
<th>( \tau_2 )</th>
<th>( \tau ) [ms]</th>
<th>Fitted function</th>
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<tr>
<td>460</td>
<td>0.20</td>
<td>0.83</td>
<td>0.0008</td>
<td>0.00003</td>
<td>0.0007</td>
<td>Double exponential</td>
</tr>
<tr>
<td>538</td>
<td>0.92</td>
<td>0.15</td>
<td>0.18</td>
<td>7.96</td>
<td>7.01</td>
<td>Double exponential</td>
</tr>
<tr>
<td>555</td>
<td>1.09</td>
<td>0.12</td>
<td>0.15</td>
<td>8.10</td>
<td>6.95</td>
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<tr>
<td>586</td>
<td>0.89</td>
<td>0.16</td>
<td>0.19</td>
<td>7.51</td>
<td>6.60</td>
<td>Double exponential</td>
</tr>
<tr>
<td>614.5</td>
<td>0.97</td>
<td>0.08</td>
<td>0.41</td>
<td>8.34</td>
<td>5.50</td>
<td>Double exponential</td>
</tr>
<tr>
<td>623</td>
<td>0.90</td>
<td>0.11</td>
<td>0.45</td>
<td>11.02</td>
<td>8.34</td>
<td>Double exponential</td>
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</table>
nonradiative transfer of excitation energy. The oxygen vacancies trap and release the energy, and the release process is slow. The slow release process leads to the decay curves displayed double exponential form. The CIE chromaticity diagram for MSLSO:Eu$^{2+}$/Eu$^{3+}$ (0.075) phosphor excited at 330 nm is displayed in the white region. In other words, by adjusting the concentration of Eu, the white light can be realized with the CIE coordinate (0.3664, 0.3260). Therefore, MSLSO:Eu$^{2+}$/Eu$^{3+}$ (0.075) is predicted to be a promising candidate for WLEDs.

Acknowledgements

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References