Correlation among photoluminescence and the electronic and atomic structures of \( \text{Sr}_2\text{SiO}_4:x\text{Eu}^{3+} \) phosphors: X-ray absorption and emission studies

Shi-Yan Zheng\(^1\), Jau-Wern Chiou\(^3,4\), Yueh-Han Li\(^3\), Cheng-Fu Yang\(^4\), Sekhar Chandra Ray\(^5\), Kuan-Hung Chen\(^3\), Chun-Yu Chang\(^1\), Abhijeeet R. Shelke\(^1\), Hsiao-Tsu Wang\(^6\), Ping-Hung Yeh\(^3\), Chun-Yen Lai\(^7\), Shang-Hsien Hsieh\(^7\), Chih-Wen Pao\(^7\), Jeng-Lung Chen\(^7\), Jyh-Fu Lee\(^7\), Huang-Ming Tsai\(^7\), Huang-Wen Fu\(^7\), Chih-Yu Hua\(^7\), Hong-Ji Lin\(^7\), Chien-Te Chen\(^7\)& Way-Faung Pong\(^1\)

A series of \( \text{Eu}^{3+} \)-activated strontium silicate phosphors, \( \text{Sr}_2\text{SiO}_4:x\text{Eu}^{3+} \) (SSO:xEu\(^3+\), \( x = 1.0, 2.0 \) and 5.0%), were synthesized by a sol–gel method, and their crystalline structures, photoluminescence (PL) behaviors, electronic/atomic structures and bandgap properties were studied. The correlation among these characteristics was further established. X-ray powder diffraction analysis revealed the formation of mixed orthorhombic \( \alpha' \)-SSO and monoclinic \( \beta \)-SSO phases of the SSO:xEu\(^3+\) phosphors. When SSO:xEu\(^3+\) phosphors are excited under ultraviolet (UV) light (\( \lambda = 250 \text{ nm}, \sim 4.96 \text{ eV} \)), they emit yellow (\( \sim 590 \text{ nm} \)), orange (\( \sim 613 \text{ nm} \)) and red (\( \sim 652 \) and 703 nm) PL bands. These PL emissions typically correspond to \( 4f \rightarrow 4f \) electronic transitions that involve the multiple excited \( 5D_0 \rightarrow 7F_J \) levels (\( J = 1, 2, 3 \) and 4) of \( \text{Eu}^{3+} \) activators in the host matrix. This mechanism of PL in the SSO:xEu\(^3+\) phosphors is strongly related to the local electronic/atomic structures of the \( \text{Eu}^{3+}–\text{O}^{2-} \) associations and the bandgap of the host lattice, as verified by \( \text{Sr} \) K-edge and \( \text{Eu} \) L\(_3\)-edge X-ray absorption near-edge structure (XANES)/extended X-ray absorption fine structure, \( \text{O} \) K-edge XANES and \( \text{K} \alpha \) X-ray emission spectroscopy. In the synthesis of SSO:xEu\(^3+\) phosphors, interstitial \( \text{Eu}_2\text{O}_3 \)-like structures are observed in the host matrix that act as donors, providing electrons that are nonradiatively transferred from the \( \text{Eu} 5d \) and/or \( \text{O} 2p–\text{Eu} 4f/5d \) states (mostly the \( \text{O} 2p–\text{Eu} 5d \) states) to the \( 5D_0 \) levels, facilitating the recombination of electrons that have transitioned from the \( 5D_0 \) level to the \( 7F_J \) level in the bandgap. This mechanism is primarily responsible for the enhancement of PL emissions in the SSO:xEu\(^3+\) phosphors. This PL-related behavior indicates that SSO:xEu\(^3+\) phosphors are good light-conversion phosphor candidates for use in near-UV chips and can be very effective in UV-based light-emitting diodes.

---

\(^1\)Department of Physics, Tamkang University, Tamsui 251, Taiwan, ROC. \(^2\)College of Physics and Information Engineering, Quanzhou Normal University, Quanzhou 362000, Fujian, People's Republic of China. \(^3\)Department of Applied Physics, National University of Kaohsiung, Kaohsiung 811, Taiwan, ROC. \(^4\)Department of Chemical and Material Engineering, National University of Kaohsiung, Kaohsiung 811, Taiwan, ROC. \(^5\)Department of Physics, CSET, University of South Africa, Johannesburg 1710, South Africa. \(^6\)Department of Material Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, ROC. \(^7\)National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan, ROC. \(^*\)email: jwchiou@nuk.edu.tw; Raysc@unisa.ac.za; wfpong@mail.tku.edu.tw
Rare-earth ion-doped inorganic phosphors are luminescent materials with practical applications in many devices, including white light-emitting diodes (LEDs), multicolor sensors, high-density optical storage devices and devices for detecting high-energy radiation. Among the rare-earth elements, europium (Eu) is of special interest as a dopant because it exhibits valence fluctuation between divalent (Eu²⁺) and trivalent (Eu³⁺) states, remarkably efficient phosphors and narrow-band emission properties that cause it to function as an emission center in a host lattice. The coordination environment and the type of crystals determine the valence state of activators and affect the photoluminescence (PL) properties of phosphors in which they are incorporated. These materials, when excited by light of a suitable wavelength/energy, provide a high PL yield and favorable chromaticity owing to the intra-4f–4f parity-forbidden transitions of the Eu³⁺ activators or the 4f–5d transitions of the Eu²⁺ rare-earth ions, whose intensity depends on the site symmetry and the nature of the host matrix. Eu³⁺ dopants typically exhibit orange-red (5D0 → 7F2), green (5D1 → 7F2) or blue (5D2 → 7F2) luminescence as a result of intra 4f–4f transitions. Furthermore, the emission of the Eu³⁺ dopant originates from the 4f–5d transition, the color of which varies from ultraviolet (UV) to red, depending on the crystal symmetry and the effect of the crystal field on the excited 5d states. Notably, in Eu³⁺ emission, the resonant excitation cross-section of 4f–4f transitions is normally small, so emission occurs upon transition to the ground 7F state from 5D states, presumably involving the O²⁻ → Eu³⁺ charge-transfer (CT) band. The replacement of divalent ions in the host lattice with trivalent ions requires charge compensation to maintain electrical neutrality and plays a critical role in the excitation of Eu³⁺–activators in which nonradiative relaxation to 5D states is followed by radiative emission. Among various host oxides for phosphors, strontium silicate, Sr₂SiO₄ (SSO), is an excellent host material owing to its stable crystal structure, high mechanical strength and thermal stability, which is provided by the tetrahedral silicate (SiO₄)⁴⁻ host matrix, and it has potential application in the development of white LEDs. The sites of Sr²⁺ ions are of two types: (i) highly symmetric ten-coordinate sites (Sr₁ sites) and (ii) less symmetric nine-coordinate sites (Sr₂ sites). When this silicate host matrix is doped with europium ions, the local environments and control the Eu valence states (Eu²⁺ and Eu³⁺) when excited by light of a suitable wavelength/energy, providing high PL yield and favorable chromaticity.

**Results and discussion**

Figure 1a,b shows the atomic structures of the (orthorhombic) α’ and (monoclinic) β phases of the SSO matrix, respectively. As the Eu³⁺ doping concentration increases, β-phase SSO is likely converted into α’-phase SSO. The structure of SSO is similar to the non-close-packed structure of K₂SiO₄. As displayed in Fig. 1a,b, one unit cell of SSO comprises 26 atoms that share four formula units. Its structure can be best described as comprising corner-sharing SiO₄ tetrahedra in parallel chains. The oxygen ions are located at three types of nonequivalent lattice sites, and the Si ions are located at the center of the oxygen tetrahedron. When Eu³⁺ is doped into the SSO matrix, the Eu³⁺ ions replace Sr²⁺ ions in the SSO lattice can be readily dissolved because the ionic radii of nine-coordinate Eu³⁺ (~ 1.3 Å) and ten-coordinate Eu²⁺ (~ 1.35 Å) are very close to those of nine-coordinate Sr²⁺ (~ 1.31 Å) and ten-coordinate Sr²⁺ (~ 1.36 Å), respectively. Additionally, SSO is a unique lattice in which the O²⁻ charge-compensating agent occupies the sites of defects, so the local environment of Eu³⁺ in the crystal field becomes more symmetrical, thus increasing the intensity of the PL. Yellow emission (5D0 → 7F₁) dominates when the site of the Eu³⁺ ions exhibits high symmetry, while orange-red emission (between 5D0 → 7F₂ and 5D0 → 7F₃) dominates when the site does not exhibit symmetry. An earlier study reported unusual luminescence spectra of Eu-doped SSO with a strong 5D₁ → 7F₂ line at ~ 575 nm, although whether the 575 nm emission arises from the 5D₁ → 7F₂ transition is ambiguous. This transition normally occurs when the site symmetry is very low. The anomalously high energy of emission in that study was postulated to result from the presence of extra interstitial O²⁻ ligands that were not bound to silicon but formed an association (Eu³⁺–O²⁻)₁,₃,₁₈. An O²⁻ → Eu³⁺ CT band at such long wavelengths in oxides is peculiar and is still debated. Eu typically yields very intense and wide visible emissions, which can be attributed to electric-dipole-allowed transitions from the Eu 5d to 4f energy in phosphors and related materials. Changes in the local environments and control the Eu valence states (Eu³⁺ and Eu²⁺) in phosphor materials to tune their activation have been extensively investigated with the aim of improving the materials’ PL properties. The PL mechanism of the Eu-doped SSO matrix is still debated despite the numerous studies mentioned above. However, the local environments of the Eu activators in the SSO host matrix have not been comprehensively investigated, and in particular, no direct experimental observation of the correlation among PL behavior, the electronic/atomic structures of Eu ions, and the bandgap of the host matrix has been reported. In this study, an alkaline earth silicate host doped with Eu ions (SSO:xEu³⁺ phosphors, x = 1.0, 2.0 and 5.0%) in the α’-phase and the β-phase at various Eu³⁺ concentrations is synthesized using the sol–gel process. The effect of Eu³⁺ activators on the PL properties, particularly the correlation among the PL emission, the local electronic/atomic structures and the energy bandgap of the SSO:xEu³⁺ phosphors, is studied using synchrotron-based X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS) and X-ray emission spectroscopy (XES) techniques. The aim of this work is to elucidate the PL emissions that originate from interstitial EuO₃-like structures in the host matrix. These structures are primarily responsible for the nonradiative electron transfer from Eu 5d states and/or O 2p–Eu 4f/5d states (mostly O 2p–Eu 5d states) to D₀ levels, facilitating the 4f–4f electronic transitions from the excited D₀ → 7F₂ levels in the band gap of the host matrix. Therefore, the overall PL intensity increases with Eu concentration in the SSO:xEu³⁺ phosphors.
matrix, the Eu\(^{3+}\) ions may affect the SSO host lattice by changing the lattice constants and/or causing structural distortion, varying the ratio of the α’ phase to the β phase in the SSO matrix\(^{16}\). However, this modification of the SSO matrix and/or site occupancy can only be observed by X-ray diffraction (XRD) at a rather high Eu\(^{3+}\)-dopant concentration (≥ 5%) in the host matrix\(^{18}\). Figure 1c presents XRD patterns of both the as-synthesized SSO:Eu\(^{3+}\) phosphors with various concentrations of Eu\(^{3+}\) ions and SSO, SrCO\(_3\) (SCO), SiO\(_2\) and Eu\(_2\)O\(_3\) for reference. The diffraction peak at (112) typically corresponds to the α’-SSO:xEu\(^{3+}\) phase, and the (211) and (301) peaks typically correspond to the β-SSO:xEu\(^{3+}\) phase. This result clearly shows that the crystal structures of the SSO:Eu\(^{3+}\) phosphors and the SSO host were mixed phases of both the α’ and β-SSO:Eu\(^{3+}\) phases. Prominent (211) and (301) diffraction peaks were observed at an Eu\(^{3+}\) ion concentration of 1.0%, whereas the (112) peak became more prominent as the concentration of Eu\(^{3+}\) ion increased above 1.0%, as was particularly evident for x = 5.0% and pure SSO. Apparently, as the Eu\(^{3+}\) doping concentration increased, the SSO matrix became increasingly α’-rich SSO:xEu\(^{3+}\) phase from β-rich SSO:xEu\(^{3+}\)\(^{28}\). Figure 1c also shows a characteristic (222) diffraction peak at ~28.2° that arises from the Eu\(_2\)O\(_3\) phase. This peak is identified as the cubic phase of Eu\(_2\)O\(_3\) and confirmed by comparison with the JCPDS pattern (card No. 34-0392). Apparently, XRD results show that doping with Eu\(^{3+}\) ions does not significantly change the structure of the lattice. The peaks that are marked with ‘♦’ in the XRD spectra indicate the presence of a tiny amount of SCO in the SSO:xEu\(^{3+}\) phosphors. The variation in the weight ratio of α’-SSO/β-SSO phases with the concentration of Eu\(^{3+}\) ion was analyzed. Table 1 indicates that the ratio of α’-SSO/β-SSO phase ratio was 0.70 at a Eu\(^{3+}\) ion concentration of x = 1.0% and increased to 8.65 and 16.93 at Eu\(^{3+}\) ion concentrations of x = 2.0 and 5.0%, respectively. However, the SSO host matrix had the highest (26.86) α’-SSO/β-SSO phase ratio. These results further confirm the formation of α’-rich SSO:Eu\(^{3+}\) phosphor at higher Eu\(^{3+}\)-doping concentrations in the SSO:Eu\(^{3+}\) phosphor, which are associated with a more
symmetry. The relative intensity $I_{\text{EDT}}/I_{\text{MDT}}$ strongly depends on the local symmetry around the Eu$^{3+}$ activators. The observed 5D0 $\rightarrow$ 7FJ transitions at ~ 590 (652) nm and 5D0 $\rightarrow$ 7FJ ($F_{J}$) transitions at ~ 613 (703) nm are similar to those of Eu$^{3+}$ ions in cubic Eu$^{3+}$/Eu$^{2+}$ structures in SSO:Eu$^{3+}$ phosphors. The parameters in Table 2 do not vary significantly with Eu$^{3+}$ doping in the SSO:Eu$^{3+}$ phosphors, suggesting that the Eu$^{3+}$ ions may/may not substitute at Sr sites in the SSO host matrix.

The results differ because SSO:xEu$^{3+}$ phosphors were not a straight mixture of SSO and Eu$_2$O$_3$, although in both cases, the synthesis process and temperatures remain the same. Table 2 shows the lattice constants (a, b and c) of the α′-SSO and β-SSO phases, the crystal angle θ in the β-SSO phase and volumes for both the β- and α′-SSO:xEu$^{3+}$ phases.

Table 1. Weight percentages of β-SSO and α′-SSO phases and α′-SSO/β-SSO phase ratio.

| Sample  | β-SSO | α′-SSO | α′-SSO/β-SSO |
|---------|-------|--------|-------------|
| 1.0%    | 58.89 ± 0.03 | 40.90 ± 0.02 | 0.70        |
| 2.0%    | 10.06 ± 0.03 | 87.02 ± 0.02 | 0.86       |
| 5.0%    | 5.39 ± 0.03 | 91.27 ± 0.02 | 16.93      |
| SSO     | 3.59 ± 0.03 | 96.41 ± 0.02 | 26.86      |

Table 2. Lattice constants (a, b and c) obtained by fitting with the β-SSO and α′-SSO phases, crystal angle θ in the β-SSO phase and volumes for both the β- and α′-SSO:xEu$^{3+}$ phases.

| Sample  | Fitting with β-SSO | Fitting with α′-SSO |
|---------|---------------------|---------------------|
|         | a (Å)   | b (Å)   | c (Å)   | θ (degree) | Volume (Å$^3$) | a (Å)   | b (Å)   | c (Å)   | θ (degree) | Volume (Å$^3$) |
| 1.0%    | 5.66 ± 0.002 | 7.08 ± 0.002 | 9.74 ± 0.002 | 92.61 ± 0.03 | 390.4 ± 0.2 | 5.66 ± 0.001 | 7.07 ± 0.001 | 9.73 ± 0.001 | 390.0 ± 0.2 |
| 2.0%    | 5.65 ± 0.002 | 7.06 ± 0.002 | 9.74 ± 0.002 | 92.57 ± 0.03 | 390.2 ± 0.2 | 5.66 ± 0.001 | 7.07 ± 0.001 | 9.73 ± 0.001 | 390.0 ± 0.2 |
| 5.0%    | 5.68 ± 0.002 | 7.09 ± 0.002 | 9.72 ± 0.002 | 92.45 ± 0.03 | 391.8 ± 0.2 | 5.65 ± 0.001 | 7.07 ± 0.001 | 9.72 ± 0.001 | 389.2 ± 0.2 |
| SSO     | 5.65 ± 0.002 | 7.08 ± 0.002 | 9.79 ± 0.002 | 92.60 ± 0.03 | 391.7 ± 0.2 | 5.66 ± 0.001 | 7.07 ± 0.001 | 9.74 ± 0.001 | 390.9 ± 0.2 |

symmetric structure in the more highly Eu$^{3+}$-doped samples. It is noted that the α′-SSO/β-SSO phase ratios of 1.0% Eu$^{3+}$-doped SSO and pure SSO are unlikely to close to each other. The results differ because SSO:Eu$^{3+}$ and pure SSO are synthesized separately in situ using the corresponding precursor; i.e., the SSO:Eu$^{3+}$ phosphors were not a straight mixture of SSO and Eu$_2$O$_3$, although in both cases, the synthesis process and temperatures remain the same. Table 2 shows the lattice constants (a, b and c) of the α′-SSO and β-SSO phases, the crystal angle θ in the β-SSO phase and volumes for both the α′- and β-SSO phases in the SSO:Eu$^{3+}$ phosphors. The parameters in Table 2 do not vary significantly with Eu$^{3+}$ doping in the SSO:Eu$^{3+}$ phosphors, suggesting that the Eu$^{3+}$ ions may/may not substitute at Sr sites in the SSO host matrix, as discussed above: not only do the nine-/ten-coordinate Eu$^{3+}$ ions have ionic radii comparable to those of the corresponding Sr in the host matrix, but also the atomic radii of Eu (2.56 Å) and Sr (2.45 Å) atoms are similar to each other. In particular, no clear XRD patterns of Eu$_2$O$_3$-like structures in SSO:Eu$^{3+}$ phosphors were observed, as shown in Fig. 1c, and this result can be explained by the fact that the Eu$^{3+}$ doping concentration in the SSO host matrix is too low to be detected by XRD. However, high-resolution transmission electron microscopy (HRTEM) clearly shows the cubic Eu$_2$O$_3$ phase in the SSO:Eu$^{3+}$ matrix, as presented in the lower inset of Fig. 4a, and will be discussed later.

Figure 2a displays the PL spectra of SSO:xEu$^{3+}$ phosphors recorded at room temperature upon excitation at a wavelength (λ) of 250 nm (~ 4.96 eV). The PL spectra include rather broad features that are centered at ~ 590, 613, 652 and 703 nm, consistent with previously reported results. The PL spectral features reveal emissions from Eu$^{3+}$ activators in the host matrix; the emission features are related to the intra-4$f$-4$f$ transitions at ~ 590 (652) nm and 5D0 $\rightarrow$ 7FJ ($F_{J}$) transitions at ~ 613 (703) nm are similar to those of Eu$^{3+}$ ions in cubic Eu$^{3+}$/Eu$^{2+}$ structures in SSO:Eu$^{3+}$ phosphors. Both are sensitive to the local environment and depend on the symmetry of the crystal field of the Eu$^{3+}$ activators in the host matrix. Typically, the most important parameter for understanding the symmetry is the asymmetric ratio or asymmetric factor (I$\text{MDT}$ = I$\text{EDT}$/I$\text{MDT}$), which is defined as the ratio of the integral intensity of EDT ($I(D_0 \rightarrow F_J)$) to that of MDT ($I(D_0 \rightarrow F_{J-1})$). At a crystal site with inversion symmetry, EDT is usually the most intense emission feature, whereas at a site without inversion symmetry, EDT is the strongest emission feature because transitions with $\Delta J = \pm 2$ are hypersensitive to small deviations from inversion symmetry. The relative intensity $I_{\text{EDT}}/I_{\text{MDT}}$ strongly depends on the local symmetry around the Eu$^{3+}$ activators and thus provides information about the degree of distortion from inversion symmetry of the local environment around the Eu$^{3+}$ activators in the host matrix. A lower symmetry around Eu$^{3+}$ activators results in higher asymmetric ratio or asymmetric factor. In this work, I$\text{MDT}$ = I$\text{MDT}$($D_0 \rightarrow F_{J}$)/I$\text{MDT}$($D_0 \rightarrow F_{J-1}$), which is the ratio of the integrated intensities in the regions 603 to 634 and 577 to 601 nm, changed from 1.29 (x = 1.0%) to 1.57 (x = 2.0%) to 1.61 (x = 5.0%) as the asymmetric field around the Eu$^{3+}$ activators increased, reflecting a small change in the lattice distortion, possibly caused by either substitution at the Sr sites or the formation of interstitial Eu–O–O associations in the SSO:Eu$^{3+}$ phosphors. Yin et al. observed the PL properties of a Eu$_2$O$_3$/Tb$_2$O$_3$ film that was deposited on a p$^+$/Si substrate with a small lattice mismatch using ITO and Ag as the negative and positive electrodes, respectively. These excitations ($I(D_0 \rightarrow F_{J}$ at 583 nm and $I(D_0 \rightarrow F_{J}$ at 611 nm) yielded relatively broad-band features and improved the I$\text{MDT}$, which can be associated with the CT band, owing to the injection of electrons and holes into the unoccupied Eu 5d and occupied O 2p states of the Eu$_2$O$_3$ layer from ITO and Tb$_2$O$_3$ films, respectively, thus enhancing the 4f–4f electronic transitions. The transition from $I(D_0 \rightarrow F_{J}$ (J = 0) is forbidden by both ED and MD, and only weak transitions are observed as a result of the crystal field-induced J-mixing effect of the Eu$^{3+}$ activators. However, this transition (4f$^0 \rightarrow F_{J}$) occurs because of the unique structural features of the orthorhombic polymorph of SSO. In the atomic structure of SSO, as shown in Fig. 1ab, the Si atoms in the SiO$_4$ tetrahedra form a parallel chain. The Sr sites form more symmetric linear chains of Si–O–Sr$\_1$–O–Sr$\_2$, but...
the Sr₂ sites form less symmetric zig-zag chains of Sr₁–O–Sr₂–O–Sr₁ along the b-axis.¹,³ In the present case, the ⁵D₀ → ⁷F₀ transition (~ 575 nm) is completely absent, suggesting that the Eu³⁺ activators have rather asymmetric environments in the SSO:xEu³⁺ phosphors. Notably, the total PL intensity in Fig. 2a is proportional to the ratio of α’-SSO/β-SSO phases, as presented in Table 1. Based on the above discussion, the enhanced PL emission is associated with not only the α’-SSO/β-SSO phase ratio (or the degree of symmetry of Eu³⁺ activators) but also the effect on the CT band of the Eu–O associations in the SSO:xEu³⁺ phosphors described here.

The PL of selected rare-earth ions that are doped into host matrices is well known to be able to be used as a spectral probe of crystal structure, which is closely related to the crystal field of the activators and is determined by the valence-band maximum (VBM) and conduction-band minimum (CBM) of the matrix, as well as the partial electronic density of states (DOS) of the luminescent centers and intrinsic/extrinsic defects, which function as trap centers in the matrix.⁹ The Eu³⁺ ion has six electrons in the ⁴f shell, which is not an entirely filled f orbital. Figure 2b presents a typical energy diagram of Eu ⁴f–⁴f electronic transitions, and the Eu³⁺ activators usually comprise emission features in the red spectral region, where the emission transition is caused by the crystal field splitting of the ⁷F_J levels. In addition to these emission features, emissions from higher ⁵D levels, viz. ⁵D₁ (green), ⁵D₂ (blue) and even ⁵D₃, are commonly observed. However, their presence or absence depends principally on the host lattice.⁹ Nevertheless, in this study of the origin of the Eu³⁺ luminescence of SSO:xEu³⁺ phosphors, the emission features mostly correspond to transitions from the excited ⁵D₀ level to the ⁷F_J levels in the Eu ⁴f⁶ configuration and are affected strongly by the CT band and/or the local electronic/atomic structures of the Eu³⁺ ions in the formation of the Eu³⁺–O₂⁻ associations and the host lattice. Principally, the PL is a three-step process: (1) absorption of a UV photon, (2) transfer of the excitation energy (or electrons) to the luminescent centers, and (3) radiative emission from the luminescent centers. To illustrate the effects of the luminescent centers of Eu³⁺ activators that are involved in the correlation between the CT band and the Eu³⁺–O₂⁻ associations and of the bandgap of the host lattice on the absorption/excitation and emission processes, Fig. 2b schematically depicts the excitation of electrons from the valence band (VB) to the conduction band (CB) of the host matrix upon excitation by UV light (λ = 250 nm, ~ 4.96 eV); the excitation by UV light presumably exceeds the energy gap (the energy separation between the VBM and the CBM), Eₓ, of the SSO:Eu³⁺ phosphors because the bandgap of the α’-phase/β-phase SSO is close to 4.49/4.11 eV¹⁹, and that of the mixed α’- and β-phases of SSO is close to 4.12 eV³², yielding free electrons and holes in the CB and VB, respectively. This process also involves the relative energy levels of Eu³⁺–O₂⁻ associations, since the valence electrons of the activators/Eu³⁺–O₂⁻ associations can also be excited directly by UV or by energy that is transferred from the host lattice, resulting in nonradiative transfer to lower ⁵D₀ levels.

Figure 2. (a) PL spectra of SSO:xEu³⁺ phosphors with sharp lines centered at ~ 590, 613, 652 and 703 nm. (b) Energy level scheme of the Eu³⁺-activator and a sketch of the excitation of electrons from VB/VBM to CB/CBM upon excitation by UV light (λ = 250 nm, ~ 4.96 eV) with energies that exceed the energy gap in the SSO:xEu³⁺ phosphors. The process also involves transfer of electrons from the Eu³⁺–O₂⁻ associations to the ⁵D₀ level (dashed line), corresponding to PL spectra of the ⁵D₀ → ⁷Fᵢ transitions (ᵢ = 1, 2, 3 and 4), as observed in (a).
Figure 3. (a) Normalized Sr K-edge XANES spectra of SSO:xEu³⁺ phosphors (x = 1.0, 2.0 and 5.0%) and reference SSO. The inset shows a magnification of the near-edge feature from 16,080 to 16,140 eV after subtracting the Gaussian background from the near-edge feature. (b) FT of EXAFS in R-space of SSO:xEu³⁺ phosphors and SSO. The solid profile was obtained from raw data, whereas the circular marks represent the best fit for the first coordination shell. The upper and lower insets present Sr K-edge EXAFS $k^3\chi$ data and magnifications of the first main FT spectra of SSO:xEu³⁺ phosphors and SSO, respectively.

| Sample  | N₁/N₂ | R₁/R₂(Å)   | $\sigma_1^2/\sigma_2^2 \times 10^{-5}$Å² |
|---------|-------|------------|----------------------------------------|
| 1.0%    | 10/9  | 2.92 ± 0.03/2.68 ± 0.03 | 2.5 ± 0.1/2.6 ± 0.1                   |
| 2.0%    | 10/9  | 2.92 ± 0.03/2.69 ± 0.03 | 2.6 ± 0.1/2.7 ± 0.1                   |
| 5.0%    | 10/9  | 2.90 ± 0.03/2.66 ± 0.03 | 2.5 ± 0.1/2.7 ± 0.1                   |
| SSO     | 10/9  | 2.89 ± 0.03/2.66 ± 0.03 | 2.6 ± 0.1/2.8 ± 0.1                   |

Table 3. Parameters obtained by best-fitting of the Sr K-edge EXAFS data in R-space mode from ~1.5 to 3.0 Å: nearest-neighbor (NN) coordination number (N₁/N₂), Sr₁–O/Sr₂–O bond length (R₁/R₂), and mean square fluctuation of the Debye–Waller factor (DWF, $\sigma_1^2/\sigma_2^2$) at Sr₁/Sr₂ sites in the SSO:xEu³⁺ phosphors and SSO.

Figure 3a displays the normalized Sr K-edge XANES spectra of SSO:xEu³⁺ phosphors (x = 1.0, 2.0 and 5.0%) and the reference SSO obtained in bulk-sensitive transmission mode. The inset shows a magnification of the near-edge feature from 16,080 to 16,140 eV after subtracting the Gaussian background from the main near-edge feature, as represented by the dashed line in Fig. 3a. By the dipole-transition selection law, the main absorption near-edge feature of SSO:xEu³⁺ phosphors at the Sr K-edge represents the transition of electrons from Sr 1s to 5p unoccupied states and is slightly more (x = 1.0 and 5.0%) or less (x = 2.0%) intense than that of the reference SSO, suggesting no significant change in the electronic unoccupied Sr 5p states of Eu-doped SSO:xEu³⁺ phosphors relative to that of SSO. Figure 3b shows the magnitudes of the Fourier transformed (FT) Sr K-edge EXAFS of the SSO:xEu³⁺ phosphors and SSO. The upper inset shows the corresponding $k^3\chi$ oscillating spectra. The selected k-range for the FT spectra was ~2.9–10.7 Å⁻¹. To provide more comprehensive insight into the local atomic structures at the Sr₁ and Sr₂ sites as the Eu concentration in the SSO:xEu³⁺ phosphors increases, the nearest-neighbor (NN) coordination number (N₁/N₂), Sr₁–O/Sr₂–O bond length (R₁/R₂), and mean square fluctuation of the Debye–Waller factor (DWF, $\sigma_1^2/\sigma_2^2$) at the Sr₁/Sr₂ sites were obtained by fitting Sr K-edge EXAFS spectra. All spectra were analyzed by standard procedures using the Athena program package33,34 to extract quantitative local information about the local atomic structures at the Sr₁/Sr₂ sites in the SSO:xEu³⁺ phosphors and SSO. Table 3 presents the fitting results for the first shell (mixing NN Sr₁–O and Sr₂–O bond lengths) of the SSO:xEu³⁺ phosphors and SSO. The results of the analysis in Table 3 clearly indicate that...
the local atomic structures (N1/N2, R1/R2 and σ1/σ2) at the Sr1/Sr2 sites in the matrix with various Eu3+ doping concentrations remain nearly unchanged, revealing that the SSO:xEu3+ phosphors easily tolerate Eu incorporation without significant distortion of the host lattice. Clearly, the coordination number of N1/N2, the NN Sr–O/Sr–O bond length and the corresponding DWF σ1/σ2 in the SSO:xEu3+ phosphors and SSO are also very similar, although the former have slightly longer bond lengths and a smaller DWF than the latter [the slight shift in the magnified scale of the over plotting first main FT features is easily observed in the lower inset of Fig. 3b]. With reference to Fig. 3a, b, the similarity of the general line shapes in the XANES/the first main FT spectral feature at the Sr K-edge of the SSO:xEu3+ phosphors relative to those of the SSO host reveals that Eu3+-doping in the SSO:xEu3+ phosphors does not significantly distort the local electronic and atomic structures at the Sr sites in the matrix. Since Eu3+ does not replace the Sr site and exists in the host lattice, the host lattice provides space to accommodate Eu3+ ions in the SSO:xEu3+ matrix. Importantly, these results suggest that the Eu3+ activators may not substitute at both/either the Sr1 and Sr2 sites, so the CT band of O2−→Eu3+ does not initially undergo electron transfer by polyhedral SrO10/SrO9 (Sr–O/Sr–O→Eu) in the SSO:xEu3+ phosphors1,3,16. Furthermore, as shown in the lower inset of Fig. 3b, the intensities of the first main feature (NN Sr–O bond length) in the FT spectra of the SSO:xEu3+ phosphors overall exceed that of SSO, primarily because the former contains fewer defects/oxygen vacancies, resulting in less structural disorder and/or DWF than in the SSO host matrix.35 This phenomenon follows from the fact that the NN Sr–O shell around Sr sites in the SSO: xEu3+ phosphors has fewer defects/oxygen vacancies, so the DWF is smaller than that of SSO (Table 3). As stated above, the defects or oxygen vacancies that act as trap centers are primarily attributed to the presence of the luminescent activators13–15, but as shown in the lower inset in Fig. 3b, the maximum intensity of the feature associated with the NN Sr–O bond length in the FT spectra of the SSO:xEu3+ phosphors is slightly greater than that of SSO. Apparently, the Sr K-edge EXAFS studies do not support the claim that defects or oxygen vacancies are formed by doping with luminescent Eu activators, which critically determine the PL property in SSO:xEu3+ phosphors13–15.

Figure 4a displays XANES spectra at the Eu L3-edge of the SSO:xEu3+ phosphors (x = 1.0, 2.0 and 5.0%) and reference Eu2O3. The upper inset shows a magnification of the near-edge features from ~6,960 to 7,000 eV after subtracting the arctan background from the near-edge feature. The lower inset shows the HRTEM image of the cubic Eu2O3 phase with the presence of d-spacing (222) in the SSO:xEu3+ (x = 5.0%) matrix, and its inset shows the corresponding selective area electron diffraction pattern. (b) FT spectra of k3χ data of SSO:xEu3+ phosphors at the Eu L3-edge from k = 2.7 to 9.5 Å−1. The solid profile was obtained from raw data, whereas the circular marks represent the best fit for the first coordination shell. The inset presents Eu L3-edge EXAFS k3χ data of the SSO:xEu3+ phosphors and Eu2O3.
matrix, we conducted HRTEM measurements and observed the cubic EuO$_3$ phase with the presence of $d$-spacing (222) in the SSO:Eu$^{3+}$ ($x = 5.0\%$) matrix, as presented in the lower inset of Fig. 4a, further supports the result of the Eu $L_{3}$-edge XANES spectra of the SSO:Eu$^{3+}$ phosphors. Nevertheless, previous studies have established according to the dipole-transition selection law that the two resolvable main features of Eu $L_{3}$-edge XANES at ~6,975 and 6,983 eV are attributable to the 2$p_{3/2}$→5$d$ electron transitions of Eu$^{2+}$ and Eu$^{3+}$ ions, respectively, in aqueous solution$^{38}$ and in milled SrAl$_2$O$_4$:Eu$^{3+}$. Evidently, as shown in Fig. 4a, the single sharp and strong feature at ~6,982 eV corresponds to the transition of electrons from the 2$p_{3/2}$ to 5$d$ unoccupied states of Eu$^{3+}$ ions in the SSO:Eu$^{3+}$ phosphors, and this feature is much more intense than that in Eu$_2$O$_3$, particularly at the highest Eu concentration ($x = 5.0\%$) in the SSO:Eu$^{3+}$ phosphors. The strong intensity of the near-edge feature (many more unoccupied Eu 5$d$ states) is caused by the transfer of electrons from the Eu 5$d$ orbitals in the EuO$_3$-like structures (or Eu$^{3+}$–O$^{2-}$ associations) to O$^{2-}$ levels in the SSO:Eu$^{3+}$ phosphors, consistent with the model presented in Fig. 2b. The integrated intensity of the Eu $L_{3}$ near-edge feature of the SSO:Eu$^{3+}$ phosphors was obtained from the area in the range of 6,960 to 7,000 eV, as shown in the upper inset of Fig. 4a. Importantly, the integrated intensity of the Eu $L_{3}$ near-edge feature (19.32 → 19.52 → 20.19) varies in proportion to the Eu-doping concentration in a manner similar to the variation with the PL intensity ratio, $I_{EDT}/I_{MDT}$ (1.29 → 1.57 → 1.61), as discussed above. A higher Eu$^{3+}$ activator content yields more Eu$_2$O$_3$-like structures in the SSO:Eu$^{3+}$ phosphors and thereby more hypersensitive EDT, thus facilitating the transfer of electrons from Eu$^{3+}$ 5$d$ states to the $D_0^-$ level and yielding higher PL emissions in the SSO:Eu$^{3+}$ phosphors, as obtained/proposed in Fig. 2a,b.

To conclusively elucidate the formation by Eu$^{3+}$ ions of interstitial Eu$_2$O$_3$-like structures, rather than the substitution of these ions at Sr sites in the SSO:Eu$^{3+}$ phosphors, Fig. 4b shows the FT spectra of $k^3\chi$ data of the SSO:Eu$^{3+}$ phosphors ($x = 1.0, 2.0$ and $5.0\%$) and Eu$_2$O$_3$ from $k = 2.7$ to 9.5 Å$^{-1}$ at the Eu $L_{3}$-edge. The inset presents the Eu $L_{3}$-edge EXAFS $k^3\chi$ data for the SSO:Eu$^{3+}$ phosphors and Eu$_2$O$_3$. The feature in the FT spectra at ~2.4 Å corresponds to the NN Eu–O bond length, and the second main feature at ~3.2–3.3 Å corresponds to the Eu–Eu bond length. The first (second) main FT feature of SSO:Eu$^{3+}$ reflects a slightly longer (shorter) Eu–O (Eu–Eu) bond length in the SSO:Eu$^{3+}$ phosphors than in Eu$_2$O$_3$. The general FT spectra at the Eu $L_{3}$-edge of SSO:Eu$^{3+}$ phosphors and Eu$_2$O$_3$ exhibit similar line shapes of FT features in Fig. 4b, confirming that the local atomic structures of Eu$^{3+}$ ions in the SSO:Eu$^{3+}$ phosphors are comparable to that of the cubic phase of Eu$_2$O$_3$. To quantitatively elucidate the local atomic structures around Eu$^{3+}$ ions in SSO:Eu$^{3+}$ phosphors and Eu$_2$O$_3$, the fitting results concerning the NN coordination number (N), Eu–O bond length (R) and corresponding DWF ($\sigma^2$) were also obtained using the Athena program package$^{33,34}$ and are presented in Table 4. Although the amount of Eu$_2$O$_3$-like structures in the host matrix is very small and not detectable by long-range sensitive XRD measurements, as presented in Fig. 1c, they were indeed incorporated as interstitial Eu$_2$O$_3$-like structures (cubic, monoclinic and hexagonal phases) under ambient pressure. The novel correlation property of Eu$_2$O$_3$ is presenting the Eu$^{3+}$–O$^{2-}$ associations to 5$D_0$ levels in the SSO:Eu$^{3+}$ phosphors, consistent with the model presented in Fig. 2b.

| Sample | N    | R (Å)         | $\sigma^2 (10^{-4} \text{Å}^2)$ |
|--------|------|---------------|-------------------------------|
| 1.0%   | 6.0 ± 0.1 | 2.39 ± 0.01  | 1.0 ± 0.1                     |
| 2.0%   | 6.0 ± 0.1 | 2.38 ± 0.01  | 0.8 ± 0.1                     |
| 5.0%   | 6.0 ± 0.1 | 2.39 ± 0.01  | 1.0 ± 0.1                     |
| Eu$_2$O$_3$ | 6.0 | 2.33 ± 0.01  | 1.3 ± 0.1                     |

Table 4. Parameters obtained by best-fitting the Eu $L_{3}$-edge EXAFS data in $R$-space mode from ~1.7 to 3.0 Å: NN coordination number (N), Eu–O bond length (R) and corresponding DWF ($\sigma^2$) at the Eu ions in the SSO:Eu$^{3+}$ phosphors and Eu$_2$O$_3$. |
approximation have shown that the electronic structures of Eu$_2$O$_3$ in its three phases are similar, but the positions of occupied/unoccupied Eu 4$f$ and 5$d$ states near the VBM/CBM of Eu$_2$O$_3$ vary among the phases because the Eu 4$f$/5$d$ states have different orbital symmetries. Nonetheless, as shown in Fig. 5, the O K-edge XANES absorption features (between features A$_1$ and A$_2$) of Eu$_2$O$_3$ at ~531.8 and 533.5 eV are attributed to unoccupied O 2$p$–Eu 4$f$ and O 2$p$–Eu 5$d$ hybridized states, respectively, above/at the CBM. The Eu 4$f$ and 5$d$ states strongly overlap with each other, and the Eu 4$f$ state is below the energy level of the 5$d$ states. The O K$_\alpha$ XES features (between features B$_1$ and B$_2$) at ~526.5 and 524.8 eV are attributed to occupied O 2$p$–Eu 4$f$ hybridized states, and the B$_1$ feature is predominately occupied by Eu 4$f$ states below/at the VBM of Eu$_2$O$_3$. The A$_1$ and B$_1$ features of Eu$_2$O$_3$ appear to be shifted to higher energy than those of SSO:xEu$^{3+}$ phosphors and SSO, as clearly indicated by the dashed line shown in Fig. 5. The general line shapes of the emission and absorption features, especially of the A$_1$ and A$_2$ absorption features in the SSO:xEu$^{3+}$ phosphors, differ from those of the SSO host due to the incorporation of Eu$_2$O$_3$-like structures in the host matrix. Clearly, the two main absorption features, A$_1$ and A$_2$, of the SSO:xEu$^{3+}$ phosphors herein are associated with the O 2$p$, Si 3$p$ and O 2$p$–Eu 4$f$/5$d$ hybridized states, whereas the B$_1$ and B$_2$ emission features are primarily associated with occupied O 2$p$, Si 3$p$ and O 2$p$–Eu 4$f$/5$d$ hybridized states. The inset in Fig. 5 represents a well-defined bandgap of $E_g$ by the solid lines that are obtained by extrapolating the leading edges in the O K-edge XANES and O K$_\alpha$ XES spectra to the baseline (guided by eye). The lower panel shows the different spectra of O K-edge XANES and K$_\alpha$ XES between SSO:xEu$^{3+}$ phosphors and SSO.

Figure 5. Normalized O K-edge XANES and K$_\alpha$ XES spectra of SSO:xEu$^{3+}$ phosphors (x = 1.0, 2.0 and 5.0%), SSO and Eu$_2$O$_3$. The inset shows the CBM and VBM, as indicated by the solid lines and obtained by extrapolating the leading edges in the XANES and XES spectra to the baseline (guided by eye). The lower panel shows the different spectra of O K-edge XANES and K$_\alpha$ XES between SSO:xEu$^{3+}$ phosphors and SSO.
To reveal the enhancement of DOFs within the band gap of SSO:Eu$^{3+}$ phosphors that is caused by doping of the SSO host matrix with Eu, the lower panel in Fig. 5 displays the difference between unoccupied/occupied states of the CB/VB of SSO:Eu$^{3+}$ phosphors and those of the SSO. As revealed by the XRD data in Fig. 1c, the minor/imurity SCO phase may also contribute to the O K-edge XANES and K$_{α}$ XES spectra of the SSO:Eu$^{3+}$ phosphors and the SSO, but its intensity can be treated as an equal quantity, canceling out in the different XANES and XES spectra, as shown in the lower panel. A large difference in the O K-edge XANES and K$_{α}$ XES spectra around the A$_{1}$ (B$_{1}$) and A$_{2}$ (B$_{2}$) features was clearly observed between the spectra near/at the CBM (VBM) of the SSO:Eu$^{3+}$ phosphors and the SSO. The enhanced features near/at the CBM (VBM) in the right (left) lower panel arise from the increased density of the unoccupied O 2p–Eu 4f/5d states (occupied O 2p–Eu 4f states). In particular, the large enhancement of the A$_{1}$ feature (O 2p–Eu 5d states) reveals an increase in the DOSs in the band gap of SSO:Eu$^{3+}$ phosphors upon doping with Eu. The electron excitation from the VB to the CB by excitation by UV light (λ = 250 nm, ~ 4.96 eV) exceeds the energy gap E$_{g}$ (~ 3.7 eV) of SSO:Eu$^{3+}$ phosphors, yielding extra free electrons and holes at the CB and VB, respectively, owing to incorporation of Eu$_{2}$O$_{3}$–like structures in the host matrix. The increase in the intensities of the features in the O K-edge XANES and K$_{α}$ XES spectra demonstrate the contribution of O 2p–Eu 4f/5d hybridized states (mostly from unoccupied Eu 5d states at the CB and occupied O 2p–Eu 4f states at the VB, respectively) in the band gap of the host matrix. As shown in Fig. 2b, the O 2p–Eu 4f/5d (major of Eu 5d states, Eu$^{3+}$$^{–}$$^{–}$O$^{2−}$ associations) above/at CBM likely act as donor levels for the nonradiative transfer of electrons to d$_{5/2}$ levels, generating unoccupied Eu$^{3+}$-doped states, as consistently observed at the O K-edge and Eu L$_{3}$-edge XANES (Figs. 4a, 5), and yielding intra 4f–4f electronic transitions followed by excited 3D$_{0}$$^{→}$$^{→}$F$_{J}$ ($J = 1, 2, 3$ and $4$) transitions, which allow the PL of SSO:Eu$^{3+}$ phosphors upon Eu$^{3+}$–doping. Again, based on the above results, the CT band plays a critical role in the radiative emission of Eu$^{3+}$–activators because Eu$_{2}$O$_{3}$–like structures formed interstitially in the SSO:Eu$^{3+}$ matrix rather than at polyhedral SrO$_{10}$/SrO$_{9}$ sites in the SSO:Eu$^{3+}$ matrix$^{1,3,18}$. Additionally, due to the slightly varied crystal field splitting of Eu activators in the matrix, the PL property of SSO:Eu$^{3+}$ phosphors is caused by the Eu$_{2}$O$_{3}$–like structures, yielding all of the PL emission features (~ 590, 613, 652$^{$ and $703$ nm) at slightly higher wavelengths than those of Eu$_{2}$O$_{3}$ thin films (~ 583, 611, 648$^{$ and $694$ nm) and at lower wavelengths than those of Sr$_{1.9}$SiO$_{4}$:0.1Eu powder (~ 592, 620, 654$^{$ and $704$ nm). Since Eu$_{2}$O$_{3}$–like structures act as interstitial sites in the SSO:Eu$^{3+}$ phosphors, SSO is a host material with a large band gap and stable lattice, making it a suitable host for accommodating Eu$^{3+}$–activator phosphors.

Conclusion

In conclusion, PL measurements show that the wavelengths of the emission spectra do not significantly vary with Eu$^{3+}$ doping concentration in SSO:Eu$^{3+}$ phosphors. However, the PL intensity increases with increasing Eu$^{3+}$ doping concentration. The PL intensity is associated with the α–SSO/β–SSO phase weight ratio in the SSO:Eu$^{3+}$ phosphors. At higher Eu$^{3+}$ contents, the luminescence is stronger because more Eu$_{2}$O$_{3}$–like structures are present in the host matrix, favoring the nonradiative transfer of electrons from Eu 5d states above/at the CBM to the d$_{5/2}$ level, which observably increases the absorption intensity at Eu L$_{3}$-edge XANES spectra of SSO:Eu$^{3+}$ phosphors. Furthermore, the results of the O K-edge XANES and K$_{α}$ XES spectra clearly demonstrate that the unoccupied O 2p–Eu 4f/5d and occupied O 2p–Eu 4f states within the band gap (or near/at the CBM and the VBM) of the SSO:Eu$^{3+}$ phosphors with increased Eu$^{3+}$–doping in the matrix. Significantly, this study demonstrates that the Eu activators (or Eu$^{3+}$$^{–}$$^{–}$O$^{2−}$ associations) interact weakly with the host matrix, which provides sufficient room to accommodate the Eu$^{3+}$ dopants as luminescence centers without substitution at the Sr sites in SSO:Eu$^{3+}$ phosphors.

Experimental methods and characterizations

The SSO:Eu$^{3+}$ phosphors in the α phase and the β phase with various Eu$^{3+}$ concentrations (x = 1.0, 2.0, and 5.0%) were synthesized using a sol–gel process, stoichiometric ratios of SCO, SiO$_{2}$ and Eu$_{2}$O$_{3}$ were taken in the solvent into an aqueous solution based on the above results, the CT band plays a critical role in the radiative emission of Eu$^{3+}$–activators because Eu$_{2}$O$_{3}$–like structures formed interstitially in the SSO:Eu$^{3+}$ matrix rather than at polyhedral SrO$_{10}$/SrO$_{9}$ sites in the SSO:Eu$^{3+}$ matrix$^{1,3,18}$. Additionally, due to the slightly varied crystal field splitting of Eu activators in the matrix, the PL property of SSO:Eu$^{3+}$ phosphors is caused by the Eu$_{2}$O$_{3}$–like structures, yielding all of the PL emission features (~ 590, 613, 652 and 703 nm) at slightly higher wavelengths than those of Eu$_{2}$O$_{3}$ thin films (~ 583, 611, 648 and 694 nm) and at lower wavelengths than those of Sr$_{1.9}$SiO$_{4}$:0.1Eu powder (~ 592, 620, 654 and 704 nm). Since Eu$_{2}$O$_{3}$–like structures act as interstitial sites in the SSO:Eu$^{3+}$ phosphors, SSO is a host material with a large band gap and stable lattice, making it a suitable host for accommodating Eu$^{3+}$–activator phosphors.

Conclusion

In conclusion, PL measurements show that the wavelengths of the emission spectra do not significantly vary with Eu$^{3+}$ doping concentration in SSO:Eu$^{3+}$ phosphors. However, the PL intensity increases with increasing Eu$^{3+}$ doping concentration. The PL intensity is associated with the α–SSO/β–SSO phase weight ratio in the SSO:Eu$^{3+}$ phosphors. At higher Eu$^{3+}$ contents, the luminescence is stronger because more Eu$_{2}$O$_{3}$–like structures are present in the host matrix, favoring the nonradiative transfer of electrons from Eu 5d states above/at the CBM to the d$_{5/2}$ level, which observably increases the absorption intensity at Eu L$_{3}$-edge XANES spectra of SSO:Eu$^{3+}$ phosphors. Furthermore, the results of the O K-edge XANES and K$_{α}$ XES spectra clearly demonstrate that the unoccupied O 2p–Eu 4f/5d and occupied O 2p–Eu 4f states within the band gap (or near/at the CBM and the VBM) of the SSO:Eu$^{3+}$ phosphors with increased Eu$^{3+}$–doping in the matrix. Significantly, this study demonstrates that the Eu activators (or Eu$^{3+}$$^{–}$$^{–}$O$^{2−}$ associations) interact weakly with the host matrix, which provides sufficient room to accommodate the Eu$^{3+}$ dopants as luminescence centers without substitution at the Sr sites in SSO:Eu$^{3+}$ phosphors.
energy range between ~550 and 555 eV fixed. The energy resolutions of Eu L$_{3}$- and Sr K-edge XANES were set to ~0.5 and 1 eV, respectively.

Received: 11 May 2020; Accepted: 7 July 2020
Published online: 29 July 2020

References
1. Nag, A. et al. The light induced valence change of europium in Sr$_2$SiO$_4$: Eu involving transient crystal structure. J. Mater. Chem. A 14, 1598–1604 (2004).
2. Wang, C. et al. Multicolor tunable luminescence based on Tb$^{3+}$/Eu$^{3+}$ doping through a facile hydrothermal route. ACS Appl. Mater. Interfaces 9, 26184–26190 (2017).
3. Huang, K. W. et al. Controlling the activator site to tune europium valence in oxyfluoride phosphors. Chem. Mat. 24, 2220–2227 (2012).
4. Gupta, S. K. et al. Structure and site selective luminescence of sol–gel derived Eu$_2$Si$_2$O$_6$: J. Lumin. 132, 1329–1338 (2012).
5. Bace, E. D. et al. Influence of Zn$^{2+}$ Co-doping on ion Eu$^{3+}$–O$^{2-}$ associate luminescence in Sr$_2$SiO$_4$: J. Alloys Compd. 344, 312–315 (2002).
6. Huang, W. L. et al. Determination of the microstructure of Eu-treated ZnO nanowires by X-ray absorption. Appl. Phys. Lett. 96(062112), 1–3 (2010).
7. Poort, S. H. M. et al. Optical properties of Eu$^{3+}$–activated orthosilicates and orthophosphates. J. Alloys Compd. 260, 93–97 (1997).
8. Nag, A. et al. Role of B$_2$O$_3$ on the phase stability and long phosphorescence of SrAl$_2$O$_4$:Eu:Dy. J. Alloys Compd. 354, 221–231 (2003).
9. Blasse, G. et al. Luminescent Materials (Springer, Berlin, 1994).
10. Kim, S. Y. et al. A strategy to enhance Eu$^{3+}$ emission from LiYF$_4$: Eu nanophosphors and green-to-orange multicolor tunable, transparent nanoporphos-polymer composites. Sci. Rep. 5(8766), 1–11 (2015).
11. Naka, Y. et al. Synthesis and luminescence investigation of RE$^{3+}$ (Eu$^{3+}$, Tb$^{3+}$ and Ce$^{3+}$)–doped lithium silicate (Li$_2$SiO$_3$). J. Lumin. 129, 1225–1229 (2009).
12. Gaeta, M. et al. Eu$^{3+}$ luminescence in high-symmetry sites of natural apatite. J. Lumin. 72–74, 572–574 (1997).
13. Kumar, V. et al. Monochromatic orange emission under blue and green excitation from Eu$^{3+}$ doped ZnO–Y$_2$O$_3$ luminescent micro composite. J. Lumin. 179, 100–106 (2016).
14. Gupta, S. K. et al. Origin of blue emission in TbO$_3$ nanorods: exploring it as a host for photoluminescence of Eu$^{3+}$, Tb$^{3+}$ and Dy$^{3+}$. RSC Adv. 4, 5124–51255 (2014).
15. Finley, E. et al. Intrinsic defects drive persistent luminescence in monoclinic SrAl$_2$O$_4$:Eu$^{3+}$. J. Phys. Chem. C 122, 16309–16314 (2018).
16. Rau, S. et al. Probing local environments in Eu$^{3+}$ doped SrSm$_2$O$_3$ nano-rods by luminescence and Sr K-edge EXAFS techniques. Chem. Phys. Lett. 561–562, 82–86 (2013).
17. Lu, L. C. et al. Modification of the coordination environment of Eu$^{3+}$ in Sr$_2$SiO$_4$:Eu$^{3+}$ phosphors to achieve full color emission. J. Mater. Chem. C 3, 1567–1575 (2015).
18. Gupta, S. K. et al. An insight into local environment of lanthanide ions in Sr$_2$SiO$_4$: Eu; Ln (Ln = Sm, Eu and Dy). New J. Chem. 39, 6531–6539 (2015).
19. Pan, H. et al. Crystal structure and luminescent properties of Sr$_2$SiO$_4$:Eu$^{3+}$ phosphor prepared by sol-gel method. J. Appl. Biomater. Funct. Mater. 14, 562–567 (2016).
20. Shannon, R. D. et al. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Cryst. Sec. A 32, 751–767 (1976).
21. Fiauciuk, K. et al. On peculiarities of Eu$^{3+}$ and Eu$^{2+}$ luminescence in SrGeO$_3$:host. RSC Adv. 6, 9186–9185 (2016).
22. Qin, R. et al. Mechanistic study of the persistent luminescence of CaAl$_2$O$_4$:Eu. Nd. Chem. Mater. 27, 2195–2200 (2015).
23. Wen, J. et al. Thermodynamic stabilities, electronic properties, and optical transitions of intrinsic defects and lanthanide ions (Ce$^{3+}$, Eu$^{3+}$, and Eu$^{2+}$) in Li$_2$SrSiO$_4$: Inorg. Chem. 57, 6124–6151 (2018).
24. Ding, B. et al. Effect of Dy$^{3+}$ and Eu$^{3+}$ 4f band gap states on luminescence and energy transfer in monoclinic lutetium tungstate. ACS Appl. Electron. Mater. 1, 772–782 (2019).
25. Li, G. et al. Controllable Eu valence for photoluminescence tuning in apatite-type phosphors by the cation co-substitution effect. Chem. Commun. 52, 7376–7379 (2016).
26. Hench, L. L. et al. The sol–gel process. Chem. Rev. 90, 33–72 (1990).
27. Yang, J. et al. Luminescence behaviour of Eu$^{3+}$ in Ca$_5$SiO$_4$:Eu$^{3+}$ (Bi$^{3+}$) and Sr$_3$Si$_2$O$_6$:Eu$^{3+}$ (Bi$^{3+}$). J. Alloys Compd. 454, 506–509 (2008).
28. Qiao, Y. M. et al. Photoluminescent properties of Sr$_2$SiO$_4$:Eu$^{3+}$ and Sr$_2$SiO$_4$:Eu$^{3+}$ luminescers prepared by solid-state reaction method. J. Rare Earths 27, 323–326 (2009).
29. Larson, A. C. et al. General structure analysis system (GSAS). Los Alamos National Laboratory Report LAUR, 86-748 (2004).
30. Table of Periodic Properties of the Elements, Sargent-Welch Scientific Company, Skokie, ILL.
31. Yin, X. et al. Observation of red electroluminescence from an Eu$_2$O$_3$/p–Si device and improved performance by introducing a Tb$_2$O$_3$ layer. J. Phys. D: Appl. Phys. 50(105103), 1–5 (2017).
32. Mishra, K. C. et al. First-principles investigation of the luminescence mechanism of Eu$^{3+}$ in M$_2$SiO$_4$:Eu$^{3+}$ (M = Ba, Sr). ECS J. Solid State Sci. Tech. 1, R87–R91 (2012).
33. Rehr, J. J. et al. Theoretical X-ray absorption fine structure standards. J. Am. Chem. Soc. 113, 5135 (1991).
34. Frenkel, A. I. et al. Multiple-scattering X-ray-absorption fine-structure analysis and thermal expansion of Alkali halides. Phys. Rev. B 48, 12449 (1993).
35. Wang, Y. F. et al. Origin of magnetic properties in implanted ZnO nanowires. Sci. Rept. 8, 7758 (2018).
36. Wei, Y. et al. Emitting tuneable Eu$^{3+}$–doped Ca$_{0.4}$La$_{1.6}$PO$_{4}$ (PO$_4$)$_2$ (SiO$_4$)$_2$apatite phosphor for n-UV WLEDs with high-color-rendering. RSC Adv. 7, 1899–1907 (2017).
37. Liang, H. B. et al. VUV and Eu-L$_{3}$ edge XANES spectra of europium–doped strontium tetraborate prepared in Air. J. Electron Spectrosc. Relat. Phenomena 124, 67–72 (2002).
38. Moreau, G. et al. Structural investigation of the aqueous Eu$^{3+}$ ion: comparison with Sr$^{2+}$ using the XAFS technique. J. Phys. Chem. A 106, 3034–3043 (2002).
39. Kandel, S. K. et al. Investigation of the emission mechanism in milled SrAl$_2$O$_4$:Eu, Dy using optical and synchrotron X-ray spectroscopy. ACS Appl. Mater. Interfaces 3, 3482–3486 (2011).
40. Jiang, H. et al. Electronic properties of lanthanide oxides from the GW perspective. Phys. Rev. B 86, 125115 (2012).
41. Meng, J. et al. Density functional characterization of the 4f relevant electronic transitions of lanthanide-doped In$_2$O$_3$ luminescence materials. ChemPhysChem 19, 1–8 (2018).
42. Chuang, C. H. et al. The effect of thermal reduction on the photoluminescence and electronic structures of graphene oxide. Sci. Rep. 4, 4525 (2014).
43. Wang, B. Y. et al. Nonlinear bandgap opening behavior of BN Co–doped graphene. Carbon 107, 857–864 (2016).
44. Gillen, R. et al. Nature of the electronic band gap in lanthanide oxides. Phys. Rev. B 87, 125116 (2013).
45. Chen, H. Y. et al. Preparation of Sr$_2$SiO$_4$:Eu$^{3+}$ phosphors by microwave-assisted sintering and their luminescent properties. *Ceram. Int.* **38**, 125–130 (2012).
46. Momma, K. et al. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Cryst.* **44**, 1272–1276 (2011).
47. Dong, C.-L. et al. Photon-in/photon-out soft X-ray spectroscopy at the TPS 45A beamline. *Synchrotron Radiation News* **30**(2), 24–29 (2017).

**Acknowledgements**

One of the authors (S.Y.Z.) would like to thank the Special Foundation for Young Scientists of Quanzhou Normal University for supporting this research under Grant No. 201604. The authors (J.W.C. and W.F.P.) would like to thank the Ministry of Science and Technology (MoST) of Taiwan for providing financial support for the research under the Projects MoST 108-2112-M-390-001, 108-2112-M-032-005 and 108-2112-M-032-006.

**Author contributions**

S.Y.Z., J.W.C., S.C.R. and W.F.P. designed the experiments after prior discussion with C.F.Y. The SSO:xEu$^{3+}$ samples were synthesized by J.W.C., Y.H.L. and C.F.Y. All measurements were performed by S.Y.Z., J.W.C., K.H.C., C.Y.C., A.R.S., H.T.W., P.H.Y., C.Y. L., S.H.H., C.W.P., J.L.C., J.F.L., H.M.T., H.W.F., C.Y.H., H.J.L. and C.T.C. The data analysis and manuscript writing were performed by S.Y.Z., J.W.C., S.C.R. and W.F.P. All authors discussed the results and contributed to finalization of the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

**Correspondence** and requests for materials should be addressed to J.-W.C., S.C.R. or W.-F.P.

**Reprints and permissions information** is available at www.nature.com/reprints.

**Publisher’s note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2020