


Cite this: *RSC Adv.*, 2023, 13, 12375

# Boron doping effect on the structural, spectral properties and charge transfer mechanism of orthorhombic tungsten bronze $\beta$ - $\text{SrTa}_2\text{O}_6\text{:Eu}^{3+}$ phosphor

Mustafa İlhan <sup>\*a</sup> and Lütüfe Feray Güleriyüz <sup>b</sup>

In the study, the effect of boron doping on spectral properties and CTB mechanism was investigated by using  $\text{Eu}^{3+}$  doped orthorhombic  $\beta$ - $\text{SrTa}_2\text{O}_6$ . A phosphor series of  $\text{Eu}^{3+}$  doped  $\text{SrTa}_2\text{O}_6$ , and  $\text{Eu}^{3+}$  and  $\text{B}^{3+}$  co-doped  $\text{SrTa}_2\text{O}_6$  polycrystals were fabricated by solid-state reaction at 1400 °C for 20 h in an air atmosphere. The X-ray diffractions of the main phase structure for all the ceramics maintained up to 10 mol%  $\text{Eu}^{3+}$  concentration, while the increase of XRD intensity for  $\text{Eu}^{3+}$  and  $\text{B}^{3+}$  co-doped samples was attributed to somewhat improvement of crystallization. SEM morphologies of grains showed that the presence of boron promotes agglomeration and grain growth. The doping of boron up to 20 mol% led to an increase in PL intensity, CTB energy slightly shifted to low energy, and also an increase occurred in the asymmetry ratio of the phosphor. Therefore, the low crystal field symmetry of the  $\text{Eu}^{3+}$  sites and some improvement in crystal structure properties for  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped samples supported the PL increase. The trend of Judd–Ofelt parameters ( $Q_2$ ,  $Q_4$ ) is  $\text{SrTa}_2\text{O}_6\text{:xEu}^{3+}$ ,  $0.1\text{B}^{3+} > \text{SrTa}_2\text{O}_6\text{:xEu}^{3+}$ . The high  $Q_2$  parameter for boron co-doped samples showed a covalent Eu–O bond character with low symmetry of  $\text{Eu}^{3+}$  environment, while the high  $Q_4$  value indicated the reduction in electron density of the ligands. Some increase in the short decays of  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped samples is probably due to the surface effect and low crystal field symmetry. The quantum efficiency of  $0.05\text{Eu}^{3+}$ ,  $0.1\text{B}^{3+}$  co-doped phosphor with the highest PL intensity increased by about 21% compared to that without boron.

Received 29th January 2023

Accepted 12th April 2023

DOI: 10.1039/d3ra00618b

rsc.li/rsc-advances

## 1. Introduction

The trivalent europium ion ( $\text{Eu}^{3+}$ ) is known for its strong luminescence in the red spectral region which exhibits interesting theoretical properties. The  $\text{Eu}^{3+}$  has a great advantage over other RE ions due to the initial levels of transitions in both the absorption and luminescence spectrum not degenerate ( $J = 0$ ).<sup>1,2</sup> The charge transfer (CT) transitions of  $\text{Eu}^{3+}$  luminescence exhibit broad absorption bands called charge transfer (CT) bands or ligand-to-metal charge transfer (LMCT) bands in the ultraviolet region of electromagnetic spectrum. CT bands occur due to electron transfer where an electron is transferred from one or more neighboring atoms to the  $\text{Eu}^{3+}$  ion, and  $\text{Eu}^{3+}$  is formally reduced to  $\text{Eu}^{2+}$ . The trivalent europium is the most oxidizing of the trivalent rare-earth ions, because  $\text{Eu}^{3+}$  lacks only one electron to reach a stable half-filled shell.<sup>1</sup> The CT bands are very intense compared to the f–f transitions due to the transitions are allowed by the Laporte selection rule, and the

position of the CT bands strongly depends on the nature of the ligands. CT bands can be useful for sensitization of  $\text{Eu}^{3+}$  luminescence, because they can act as an antenna to absorb light and to transfer the excitation energy to  $\text{Eu}^{3+}$  ion.<sup>1</sup>

Tungsten bronze (TB) crystal structures are good host matrix candidates for many luminescent applications due to their crystal structure with different coordinated cationic tunnels that allow doping of  $\text{RE}^{3+}$  ions.<sup>3–7</sup>  $\text{SrTa}_2\text{O}_6$  occurs as three different polymorphs in  $\text{SrO-Ta}_2\text{O}_5$  system.<sup>6–9</sup> Two polymorphs of  $\text{SrTa}_2\text{O}_6$  are related to TB symmetry and occur at high temperatures. The  $\beta$ - $\text{SrTa}_2\text{O}_6$  crystallizes at temperatures between 1300–1500 °C, while the  $\beta'$ - $\text{SrTa}_2\text{O}_6$  forms at temperatures over 1500 °C.<sup>6–9</sup> The other polymorph is orthorhombic  $\alpha$ - $\text{SrTa}_2\text{O}_6$  occurs at about 1100 °C and below. However, the synthesis of  $\alpha$ - $\text{SrTa}_2\text{O}_6$  is difficult with the solid state reaction, so it can be produced by the flux method using strontium borate.<sup>10</sup> Tungsten bronze polymorphs have similar lattice sizes but their crystal symmetries are different. This difference affects its physical properties, that  $\beta'$ - $\text{SrTa}_2\text{O}_6$  polymorph has better dielectric properties compared to  $\beta$ - $\text{SrTa}_2\text{O}_6$ .<sup>8,9</sup> The  $\beta$ - $\text{SrTa}_2\text{O}_6$  is orthorhombic with space group  $Pnam$  and lattice parameters  $a = 12.37 \text{ \AA}$ ,  $b = 12.43 \text{ \AA}$ ,  $c = 7.72 \text{ \AA}$ ,  $V = 1187.70 \text{ \AA}^3$ ,  $Z = 10$ .<sup>8,9</sup> The  $\beta'$ - $\text{SrTa}_2\text{O}_6$  is tetragonal with space group  $P4/mbm$  and lattice

<sup>a</sup>Department of Environmental Engineering, Faculty of Engineering, Marmara University, Kadıköy, 34722, İstanbul, Turkey. E-mail: mustafa.ilhan@marmara.edu.tr

<sup>b</sup>Department of Mechanical Engineering, Faculty of Engineering, Ege University, Bornova, 35040, İzmir, Turkey



parameters  $a = 12.47 \text{ \AA}$ ,  $c = 3.90 \text{ \AA}$ ,  $V = 606.27 \text{ \AA}^3$ ,  $Z = 5$ .<sup>8,9</sup> The comparison of the two tungsten bronze polymorphs shows that the orthorhombic distortion of  $\beta\text{-SrTa}_2\text{O}_6$  to  $\beta'\text{-SrTa}_2\text{O}_6$  is accompanied by an expansion of the  $\text{TaO}_6$  octahedral with narrowing of the  $(\text{Sr}_2)\text{O}_{13}$  tricapped pentagonal prisms. Although the crystal lattice of  $\beta\text{-SrTa}_2\text{O}_6$  is about 2.5% smaller than  $\beta'\text{-SrTa}_2\text{O}_6$ , Ta–O bond distances and corresponding octahedral volumes of  $\beta\text{-SrTa}_2\text{O}_6$  are large, and it has a relaxed anion sublattice where electrostatic interactions are optimized *via* octahedral tilting distortions.<sup>8</sup>

Boron is widely used as a dopant in glasses to improve its optical and mechanical properties which could promote vitrification of oxide.<sup>11</sup> However, the doping effect of boron has been studied in detail for certain structures such as  $\text{TiO}_2$ . In boron-doped  $\text{TiO}_2$ , interstitial B has the more stable form under high calcination temperature compared to substitutional B. An increase and decrease occurred in the lattice parameters are associated with interstitial B and substitutional B, respectively.<sup>12,13</sup> Boron types can take at least two different major positions in  $\text{TiO}_2$  which are the oxygen–boron substitution (paramagnetic state), and the interstitial boron (diamagnetic state). In the paramagnetic B arrangement, electrons can be easily captured from other defect states, whereas in the diamagnetic B arrangement, the centers do not transfer charge to other defects in the system. In any case, the driving force for boron to occupy interstitial positions is the formation of very strong bonds with oxygen.<sup>14</sup> The doping of boron to  $\text{SrAl}_2\text{O}_4$ – $\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  phosphor improves the performance of trapping centers and afterglow times at the low temperature.<sup>15</sup> The powders of  $\text{Eu}^{3+}$  doped  $\text{CdNb}_2\text{O}_6$  and  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped  $\text{CdNb}_2\text{O}_6$  are prepared by molten salt synthesis method and the presence of orthorhombic single phase without any other interphase showed that boron is incorporated in the host structure and a significant increase occurred in PL.<sup>16</sup>

In the study, the effect of boron doping on the photoluminescence, charge transfer transition, and structural properties of the  $\text{Eu}^{3+}$  doped  $\beta\text{-SrTa}_2\text{O}_6$  and  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped  $\beta\text{-SrTa}_2\text{O}_6$  phosphors were investigated. The structural and spectroscopic characterizations were carried out by XRD, SEM, XPS, PL, decay time analyses, and also the spectral properties were examined comparatively within the scope of Judd–Ofelt theory.

## 2. Experimental

$\text{SrTa}_2\text{O}_6$ : $x\text{Eu}^{3+}$ ,  $y\text{B}^{3+}$  ceramic samples were fabricated in three groups by solid-state reaction. First group contains  $\text{Eu}^{3+}$  doped samples with  $x = 0.5, 1.5, 3, 5, 7, 10 \text{ mol\%}$  concentrations, second group has  $x = 5 \text{ mol\%}$   $\text{Eu}^{3+}$  and  $y = 0, 5, 10, 20 \text{ mol\%}$   $\text{B}^{3+}$  co-doped samples while the third group represents the  $y = 10 \text{ mol\%}$   $\text{B}^{3+}$  and  $x = 0.5, 1.5, 3, 5, 7, 10 \text{ mol\%}$   $\text{Eu}^{3+}$  doped samples. Each 1 mol% of  $x$  represents two atomic% values of the  $\text{Eu}_2\text{O}_3$  compound. Strontium carbonate ( $\text{SrCO}_3$ : Sigma-Aldrich, 99%), and tantalum oxide ( $\text{Ta}_2\text{O}_5$ : Alpha Aesar, 99.9%) powders were used as starting materials in calculated stoichiometric amounts. Europium oxide ( $\text{Eu}_2\text{O}_3$ : Alpha Aesar, 99.9%) and boric acid ( $\text{H}_3\text{BO}_3$ : Kimyalab, %99.9) were used as dopant materials. The  $\text{SrCO}_3$  and  $\text{Ta}_2\text{O}_5$  were weighed according

to the stoichiometry of  $\text{SrTa}_2\text{O}_6$ . For  $\text{CO}_2$  extraction,  $\text{SrCO}_3$  was kept in a furnace at  $1200^\circ\text{C}$  for 1 h to obtain  $\text{SrO}$ . Then  $\text{SrO}$  and  $\text{Ta}_2\text{O}_5$  powders were homogenized by mixing well with the addition of acetone in an agate mortar. The powder mixture of  $\text{SrO}$  and  $\text{Ta}_2\text{O}_5$  was doped by the 0.5, 1.5, 3, 5, 7, 10 mol%  $\text{Eu}_2\text{O}_3$  (for the 1st group), 5 mol%  $\text{Eu}_2\text{O}_3$  and 0, 5, 10, 20 mol%  $\text{H}_3\text{BO}_3$  (for the 2nd group), 0.5, 1.5, 3, 5, 7, 10 mol%  $\text{Eu}_2\text{O}_3$  and 10 mol%  $\text{H}_3\text{BO}_3$  (for the 3rd group), respectively. The final powder mixtures were mixed by acetone for further homogenization. The prepared powders were sintered in an electric furnace at  $1400^\circ\text{C}$  for 20 h after pelleting.

The phase structure of the ceramic samples were examined by XRD (X-ray diffractometer; Bruker D-8 Advance, Bruker Corp., Germany) between  $2\theta = 20\text{--}65^\circ$  using  $\text{Cu-K}\alpha$  ( $1.5406 \text{ \AA}$ ) radiation and scan speed  $2^\circ \text{ min}^{-1}$ . The grain morphology of the ceramic samples was investigated by SEM (scanning electron microscopy; FEG-SEM; XL 30S, Philips Corp., Netherlands). Elemental analysis was performed by the Thermo-Scientific Al-K $\alpha$  model XPS device. Photoluminescence (PL) results were taken by a fluorescence spectrometer (FLS920, Edinburgh Instruments, UK) equipped with a 450 W ozone-free Xe lamp. Lifetime data were also obtained by fluorescence spectrometer (FLS920) using the time-correlated single-photon counting (TCSPC) system. PL analysis was performed at room temperature.

## 3. Results and discussions

### 3.1 Structural analyses

X-ray diffractions of  $\text{SrTa}_2\text{O}_6$ : $x\text{Eu}^{3+}$  samples for  $x = 0.5, 1.5, 3, 5, 7, 10 \text{ mol\%}$   $\text{Eu}^{3+}$  concentrations are shown in Fig. 1. The presence of single-phase continued from 0.5 to 10 mol%, and there was no impurity phase. The crystal symmetry of  $\beta\text{-SrTa}_2\text{O}_6$  is identified by the first report as *Pham* (no. 55) and JCPDS card no. 51-1683.<sup>17</sup> However, Lee *et al.*<sup>7</sup> reported that the crystal symmetry is suitable for the space group *Pham*. Accordingly, the crystal symmetry of the orthorhombic TB samples was indexed with space group *Pham* (no. 62).<sup>8,9</sup> Tetragonal tungsten bronze structure can be expressed by the  $\text{A}_4\text{B}_2\text{C}_4\text{M}_{10}\text{O}_{30}$  general formula where the pentagonal (A), square (B), and triangular (C) tunnels have 15 CN (large ions such as alkaline earth ions and alkali), 12 CN (such as rare earth ions), 9 CN (small ions such as  $\text{Li}^+$ ), respectively. Also, the octahedral Ta sites with small and highly charged ions have 6 CN.<sup>4–7</sup> The  $\text{Eu}^{3+}$  ions ( $r = 1.12 \text{ \AA}$ , for CN 9) will be suitable for the A and B sites with 15 and 12 CN, respectively. Tungsten bronze symmetry at high concentrations may persist despite of some change occurring in the lattice, which can be attributed to the superiority of TB for  $\text{RE}^{3+}$  doping.<sup>3–7</sup> In addition, although the  $\beta\text{-SrTa}_2\text{O}_6$  polymorph has preserved its single-phase structure, it is likely to suffer some increase in distortion due to its slightly longer Ta–O bond distances compared to  $\beta'\text{-SrTa}_2\text{O}_6$ . X-ray diffractions of  $\text{SrTa}_2\text{O}_6$ : $x\text{Eu}^{3+}$ ,  $y\text{B}^{3+}$  ( $x = 5 \text{ mol\%}$   $\text{Eu}^{3+}$ ,  $y = 0, 5, 10, 20 \text{ mol\%}$   $\text{B}^{3+}$ ), and  $\text{SrTa}_2\text{O}_6$ : $x\text{Eu}^{3+}$ ,  $y\text{B}^{3+}$  ( $x = 0.5, 1.5, 3, 5, 7, 10 \text{ mol\%}$   $\text{Eu}^{3+}$ ,  $y = 10 \text{ mol\%}$   $\text{B}^{3+}$ ) co-doped samples are shown in Fig. 2a, b and 3, respectively. As seen in the figures, the diffraction peaks of  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped samples exhibited a slight narrowing compared to



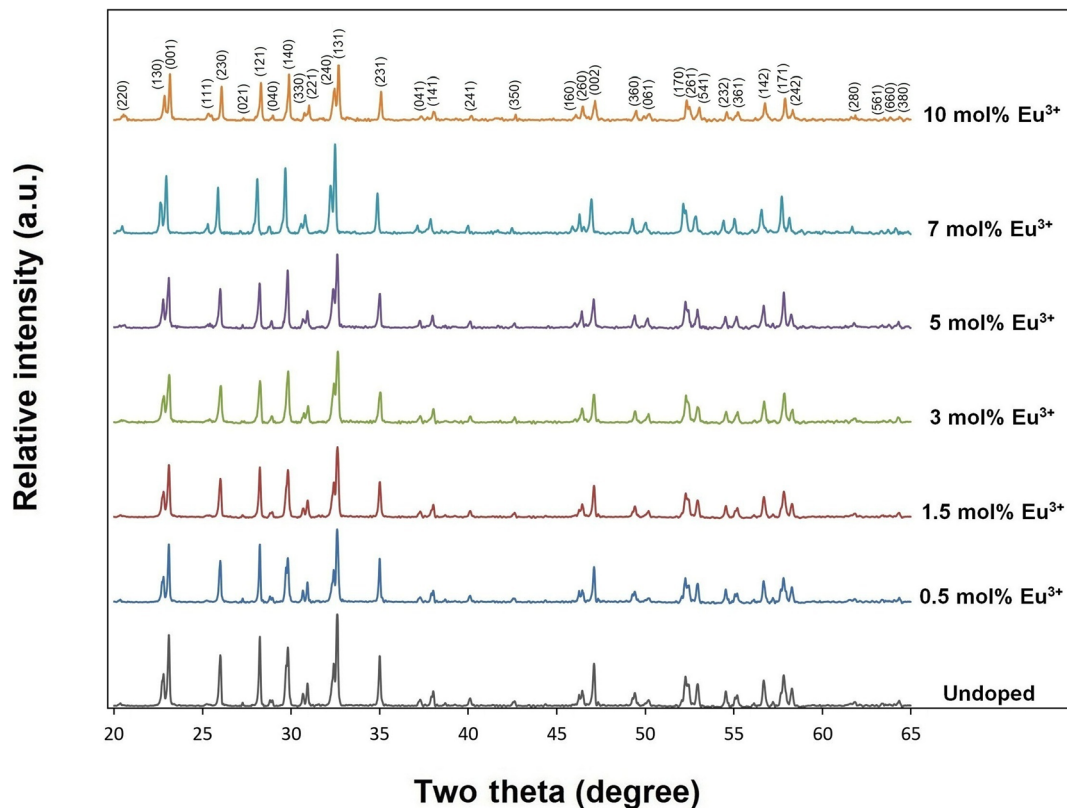


Fig. 1 XRD results of undoped, 0.5, 1.5, 3, 5, 7, and 10 mol%  $\text{Eu}^{3+}$  doped  $\text{SrTa}_2\text{O}_6$  samples.

the  $\text{Eu}^{3+}$  doped samples, indicating some improvement in crystallization. The absence of secondary phases in XRD patterns can be also associated with the boron's successful incorporation into the structure. In Fig. 2b, the reflection (131)

showed a slight shift towards the smaller two theta angles, which is likely related to the increase in  $\text{B}^{3+}$  concentration leading to the expansion of the lattice volume.

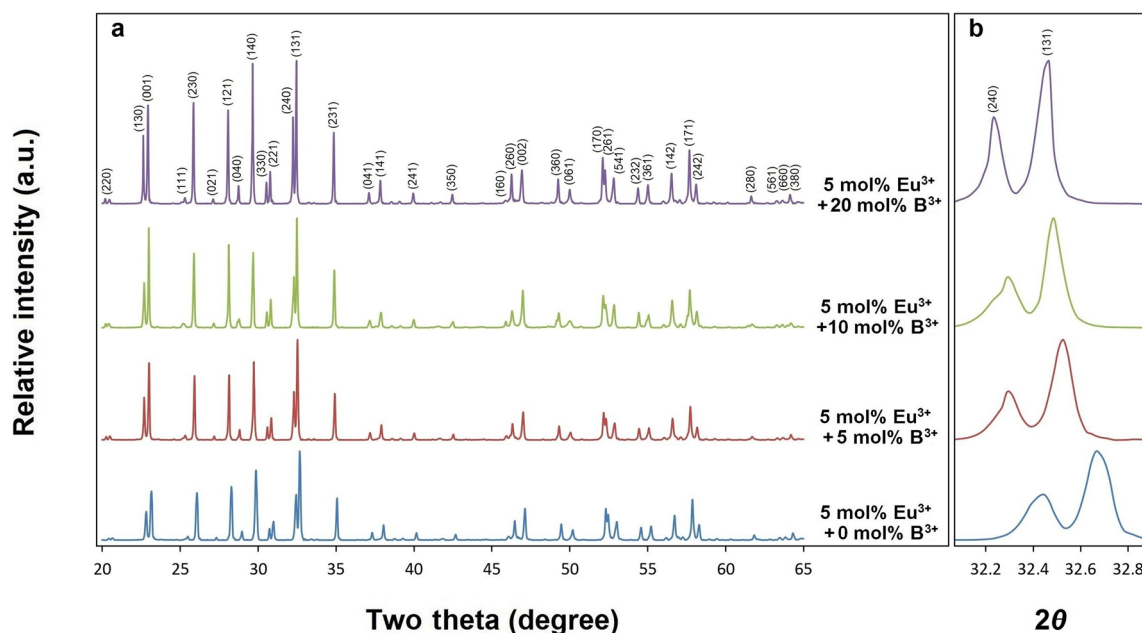


Fig. 2 XRD results of (a) 5 mol%  $\text{Eu}^{3+}$ , and 0, 5, 10, 20 mol%  $\text{B}^{3+}$  co-doped  $\text{SrTa}_2\text{O}_6$ , (b) the shift of the two theta angle peaks (240) and (131) to lower angles.

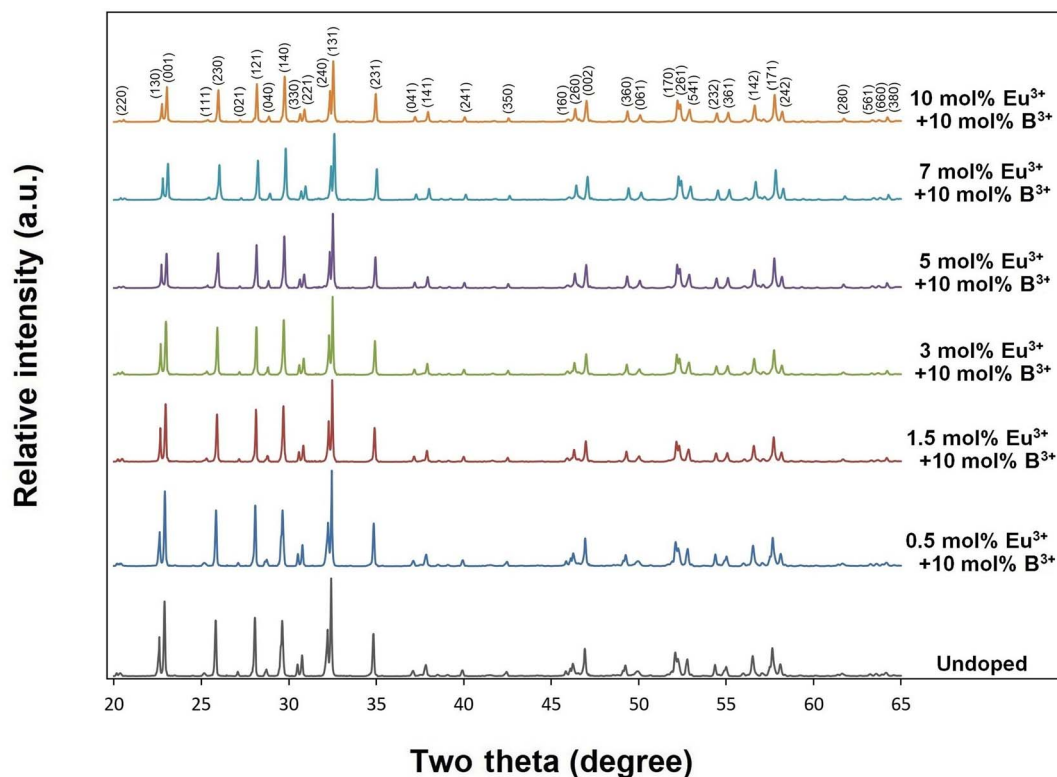


Fig. 3 XRD results of 10 mol%  $B^{3+}$ , and undoped, 0.5, 1.5, 3, 5, 7, 10 mol%  $Eu^{3+}$  co-doped  $SrTa_2O_6$  samples.

SEM micrographs of  $SrTa_2O_6:xEu^{3+}, yB^{3+}$  samples for  $x = 5$  mol%  $Eu^{3+}$ ,  $y = 0, 5, 10, 20$  mol%  $B^{3+}$  co-doped concentrations at  $2000\times$  and  $10\,000\times$  magnifications under 15 kV accelerating voltage are shown in Fig. 4a–h, respectively. In SEM micrographs, it is seen that boron doping promotes agglomeration and growth, where grain boundaries are reduced or disappeared. In addition, grain size and agglomeration increase with increasing boron, as reported in the supporting study.<sup>15</sup> The increase in grain size can be seen in Fig. 4a, c, e and g at  $2000\times$  magnifications. More detail is shown in Fig. 4b, d, f and h at  $10\,000\times$  magnifications, which are shown in the inset figures of Fig. 4a, c, e and g as yellow windows. Fig. 5a and b shows the XPS analysis of the 5 mol%  $Eu^{3+}$ , 20 mol%  $B^{3+}$  co-doped sample. In Fig. 5a, the binding energies of O1s, Sr3d, and Ta4f were identified at 529.26, 133.44, and 26.23 eV which belong to tantalum oxide structure, respectively. Also, the 1133 eV peak defines the europium dopant with Eu3d. In Fig. 5b, the binding energy of B1s is 189.59 eV. The broad spectrum in the range of about 187–192 eV shows that boron was incorporated into the structure. The binding energies of boron for the elemental and fully oxidized form ( $B_2O_3$ ) are 187.2 eV (ref. 18) and 193.0 eV,<sup>19,20</sup> respectively. Accordingly, the broad B1s spectrum shows that interstitial B atoms can exist in different stoichiometric forms with oxygen in the structure.

### 3.2 Photoluminescence of $SrTa_2O_6:xEu^{3+}$ and $SrTa_2O_6:xEu^{3+}, yB^{3+}$ phosphors

Fig. 6a–c and 7a–c show PL excitations and emissions of orthorhombic tungsten bronze  $\beta$ - $SrTa_2O_6$  phosphors

corresponding to the  $SrTa_2O_6:xEu^{3+}$  ( $x = 0.5, 1.5, 3, 5, 7, 10$  mol% “without boron”),  $SrTa_2O_6:xEu^{3+}, yB^{3+}$  ( $x = 5$  mol% “ $Eu^{3+}$  fixed”,  $y = 0, 5, 10, 20$  mol%), and  $SrTa_2O_6:xEu^{3+}, yB^{3+}$  ( $x = 0.5, 1.5, 3, 5, 7, 10$  mol%,  $y = 10$  mol% “boron fixed”), respectively. In Fig. 6a–c, PL excitations under 618 nm were assigned with  ${}^7F_0 \rightarrow {}^5D_4$ ,  ${}^7F_0 \rightarrow {}^5G_7$ ,  ${}^7F_0 \rightarrow {}^5L_6$ ,  ${}^7F_0 \rightarrow {}^5D_3$ , and  ${}^7F_0 \rightarrow {}^5D_2$  transitions, respectively. In Fig. 7a–c, PL emissions with 465 nm excitation were observed at  ${}^5D_0 \rightarrow {}^7F_J$  ( $J = 0, 1, 2, 3, 4, 5$ ) corresponding to the  $Eu^{3+}$  transitions. Fig. 7a shows the PL spectra of  $SrTa_2O_6:xEu^{3+}$  ( $x = 0.5, 1.5, 3, 5, 7, 10$ ) phosphors. The PL intensity reached its maximum value at 5 mol%, while the concentration quenching occurred at 7 and 10 mol%. Therefore, the concentration of the 5 mol%  $Eu^{3+}$  doped phosphor with the highest PL intensity was used to investigate the effect of different  $B^{3+}$  concentrations. The PL emissions of  $SrTa_2O_6:xEu^{3+}, yB^{3+}$  ( $x = 5, y = 0, 5, 10, 20$  mol%) phosphors are given in Fig. 7b. The PL emission intensity increased up to 20 mol%  $B^{3+}$  concentration, while the intensity increase slightly slowed down over 10 mol%. By choosing 10 mol%  $B^{3+}$  doping ratio,  $SrTa_2O_6:xEu^{3+}, yB^{3+}$  ( $x = 0.5, 1.5, 3, 5, 7, 10$  mol%,  $y = 10$  mol%) phosphors were fabricated to compare with the  $SrTa_2O_6:xEu^{3+}$  ( $x = 0.5, 1.5, 3, 5, 7, 10$  mol%) series. The PL emissions of  $SrTa_2O_6:xEu^{3+}, 0.1B^{3+}$  phosphors are presented in Fig. 7c, respectively. The PL emission intensity of  $SrTa_2O_6:xEu^{3+}, 0.1B^{3+}$  phosphors showed a nearly threefold increase compared to the  $SrTa_2O_6:xEu^{3+}$  series, which is compatible with the luminescence increase reported in the literature due to boron effect.

The charge transfer bands (CTB) under 618 nm wavelength of  ${}^5D_0 \rightarrow {}^7F_2$  transition are shown in Fig. 6a–c. As seen in the





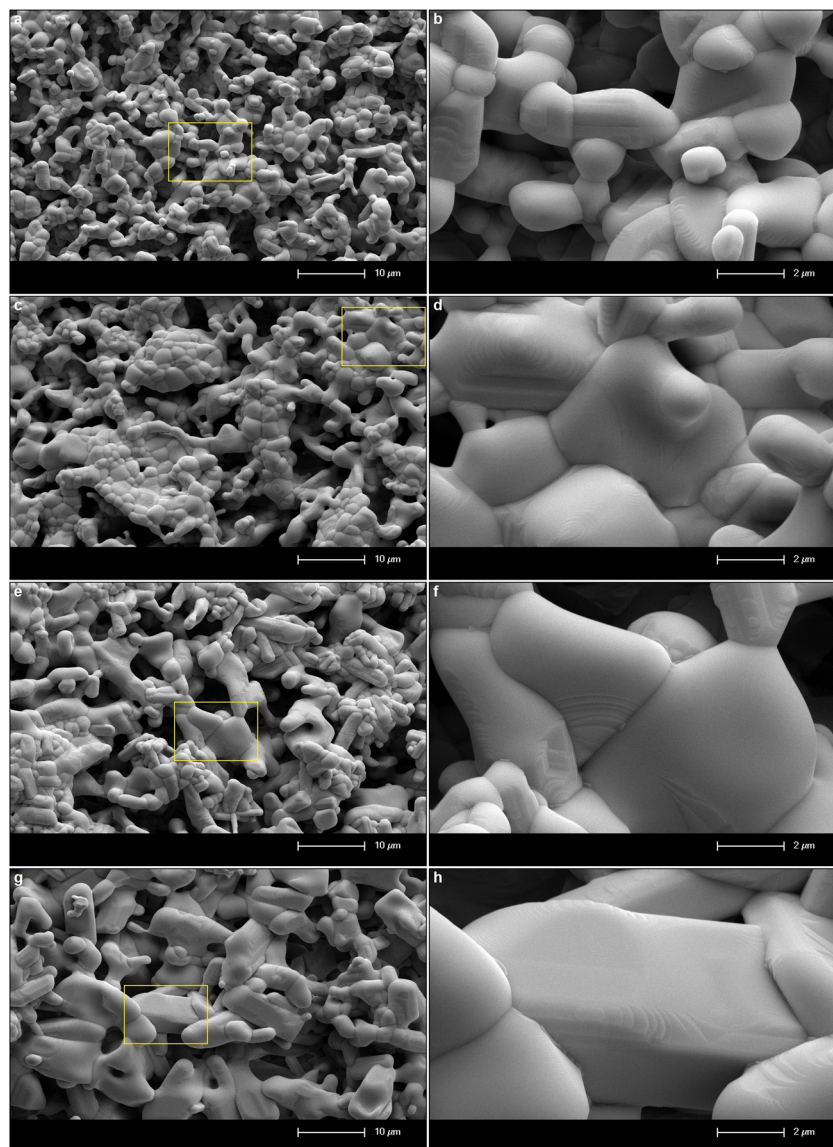


Fig. 4 SEM micrographs of 5 mol%  $\text{Eu}^{3+}$ , and different concentrations  $\text{B}^{3+}$  co-doped  $\text{SrTa}_2\text{O}_6$  samples: (a and b) without  $\text{B}^{3+}$ , (c and d) 5 mol%  $\text{B}^{3+}$ , (e and f) 10 mol%  $\text{B}^{3+}$ , (g and h) 20 mol%  $\text{B}^{3+}$ , under 15 kV accelerating voltage at 2000 $\times$  and 10 000 $\times$  magnifications, respectively.

figures, the CTB peaks are over 300 nm, which is related to the ligand nature of the host structure.<sup>21,22</sup> It has been reported by many studies that the CTB energy is found at low energies or over 300 nm due to the ligand environment with highly coordinated A and B tunnels of the tungsten bronze structure.<sup>6</sup> Fig. 6b shows CT band position slightly affected with the increase in boron concentration, where the CTB peaks are at the wavelengths of 308.6, 310.4, 312.7, 314.2 nm for 0, 5, 10, 20 mol%  $\text{B}^{3+}$  concentrations, respectively. A shift to the lower energy in CTB position is also evident for the  $\text{SrTa}_2\text{O}_6:x\text{Eu}^{3+}$ , 0.1 $\text{B}^{3+}$  phosphors (Fig. 6c) compared to  $\text{SrTa}_2\text{O}_6:x\text{Eu}^{3+}$  series (Fig. 6a), where CTB positions are by average about 313 and 309 nm, respectively. The shift in CTB energy is related to the binding strength of valence electrons and the site of rare earth.<sup>22</sup> An atom with higher electronegativity will bind the oxygen 2p

electron more strongly than an atom with lower electronegativity, where CT band will shift to a higher energy. The CTB energy will rise to a higher level, while the  $\text{Eu}^{3+}$  sites tend to be smaller. So, the CTB energy shift to the lower energy despite the high electronegativity of boron may be ascribed to the fact that the  $\text{Eu}^{3+}$  sites become larger. Another phenomenon is the relationship between CTB and hypersensitive transition. The inverse relationship between  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition and CTB is highlighted, where the more intensity of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition indicates the lower energy of CTB.<sup>22,23</sup> In Fig. 7b, the asymmetry ratios for 0, 5, 10, and 20 mol%  $\text{B}^{3+}$  concentrations are 1.97, 2.34, 2.48, and 2.49, respectively. In Fig. 7a and c, the asymmetry values for  $\text{Eu}^{3+}$  doped and  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped phosphors varied in the range of 1.83–2.07, and 2.21–2.58, respectively. The results show that boron doping causes a decrease in CTB energy



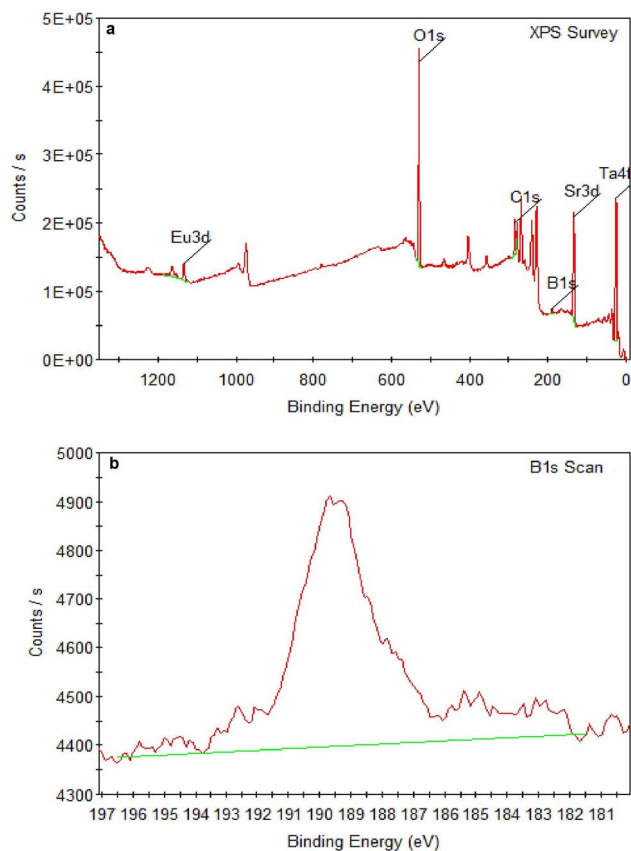


Fig. 5 XPS spectra of (a) 5 mol%  $\text{Eu}^{3+}$ , 20 mol%  $\text{B}^{3+}$  co-doped  $\text{SrTa}_2\text{O}_6$  sample, (b) B1s.

and an increase in the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition intensity. On the other hand, the inverse correlation between CTB intensity and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition is previously observed in  $\text{TTB-MTa}_2\text{O}_6\text{:Eu}^{3+}$  (Sr, Ba, Pb) phosphors. The trend of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition is  $\text{BaTa}_2\text{O}_6\text{:Eu}^{3+} > \text{SrTa}_2\text{O}_6\text{:Eu}^{3+} > \text{PbTa}_2\text{O}_6\text{:Eu}^{3+}$  while trend of intensity of CTB and  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition is reverse.<sup>6</sup> Hua *et al.*<sup>24</sup> compared the  $\text{CINO:Eu}^{3+}$ ,  $\text{SINO:Eu}^{3+}$ , and  $\text{BINO:Eu}^{3+}$  phosphors. The  $\text{CINO:Eu}^{3+}$  phosphor has strong  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition and weak CTB intensity, while there is an opposite effect for  $\text{SINO:Eu}^{3+}$ ,  $\text{BINO:Eu}^{3+}$ . A similar phenomenon was also observed in this study. In Fig. 6c,  $\text{SrTa}_2\text{O}_6\text{:xEu}^{3+}$ ,  $0.1\text{B}^{3+}$  phosphors have a low CTB transition intensity and high asymmetry compared to  $\text{SrTa}_2\text{O}_6\text{:xEu}^{3+}$  phosphors (Fig. 6a). Since the formation of charge transfer bands or reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  is largely dependent on the nature of the ligands, the decrease in CTB density for the  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped phosphors may be associated with the decreased electron transfer from neighboring atoms to  $\text{Eu}^{3+}$  ions in the tungsten bronze host. It has been reported in many studies that the addition of boron contributes to the improvement of crystallization and increases luminescence. Besides, it is generally believed that improved crystallinity properties and low crystal field symmetry are advantageous for the luminescence of rare earth activators.<sup>25</sup> Consequently, the increase in asymmetry associated with the low crystal field symmetry of the  $\text{Eu}^{3+}$  sites as well as some

enhancement crystallinity in  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped samples support the PL increase.

UV lamp photographs of the phosphors under 365 nm are given in Fig. 8a–c. As seen from the pictures, the  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped phosphors in Fig. 8c are brighter than  $\text{Eu}^{3+}$  doped samples in Fig. 8a. The increase in brightness with the increasing  $\text{B}^{3+}$  concentration is more evident after 10 mol%, which is given in Fig. 8b.

### 3.3 Judd–Ofelt analysis of $\text{SrTa}_2\text{O}_6\text{:xEu}^{3+}$ and $\text{SrTa}_2\text{O}_6\text{:xEu}^{3+}$ , $0.1\text{B}^{3+}$ phosphors

Judd–Ofelt (JO) theory explains the intensity of electron transitions in 4f shell of rare-earth ions using three parameters and describes their spectral properties.<sup>26,27</sup> The JO intensity parameters  $\Omega_J$  ( $J = 2, 4, 6$ ) from emission spectrum for  $\text{Eu}^{3+}$  can be determined by eqn (1):<sup>28,29</sup>

$$\Omega_J = \frac{S_{\text{MD}}(V_1^3)}{e^2(V_J^3)} \frac{9n^3}{n(n^2 + 2)^2} \frac{\int I_1(V_1)}{|\langle J \| U^J \| J' \rangle|^2 \int I_J(V_J)} \quad (1)$$

where  $V$  is the transition frequency,  $I_1$  and  $I_J$  for  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  transitions are the integrated intensities, respectively,  $S_{\text{MD}} = 9.6 \times 10^{-42}$  ( $\text{esu}^2 \text{ cm}^2$ ) is the magnetic dipole line strength,<sup>6</sup>  $n$  is the refractive index,  $e = 4.803 \times 10^{-10}$  ( $\text{esu}$ ) is the elementary charge,  $J$  and  $J'$  for the initial state and final state are the total angular momentum, respectively,  $|\langle J \| U^J \| J' \rangle|^2$  is the symbol of double reduced matrix elements for unit tensor operators. For all electric dipole (ED) transitions originating from the  $^5\text{D}_0$  level, the reduced matrix elements are zero except for the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  ( $U^2 = 0.0032$ ),  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  ( $U^4 = 0.0023$ ) and  $^5\text{D}_0 \rightarrow ^7\text{F}_6$  ( $U^6 = 0.0002$ ) transitions.<sup>28,29</sup> The  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  ( $J = 1, 2, 4, 6$ ) transitions are used for the determination of the radiative transition probabilities while  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  ( $J = 0, 3, 5$ ) transitions are prohibited, and are not included JO calculation. The  $^5\text{D}_0 \rightarrow ^7\text{F}_6$  transition related to  $\Omega_6$  parameter was not included in the calculation because it could not be detected by PL in infrared region. However, the effect of this transition on the calculation is negligible, which has been reported in some studies.<sup>28,29</sup> The spontaneous transition probability ( $A$ ) is related to its dipole strength which can be expressed as eqn (2):

$$A(J, J') = \frac{64\pi^4 V^3}{3h(2J + 1)} [\chi_{\text{ED}} S_{\text{ED}} + \chi_{\text{MD}} S_{\text{MD}}] \quad (2)$$

where  $S_{\text{ED}}$  (electric dipole) and  $S_{\text{MD}}$  (magnetic dipole) are line strengths (in  $\text{esu}^2 \text{ cm}^2$ ),  $h$  is Planck constant. The electric dipole line strengths ( $S_{\text{ED}}$ ) from the JO parameters can be calculated by eqn (3):

$$S_{\text{ED}}(J, J') = e^2 \sum_{J=2,4,6} \Omega_J |\langle J \| U^J \| J' \rangle|^2 \quad (3)$$

The  $\chi_{\text{ED}}$  and  $\chi_{\text{MD}}$  are the local field corrections for the ED and MD transitions which can be found by eqn (4) and (5) respectively:

$$\chi_{\text{ED}} = \frac{n(n^2 + 2)^2}{9} \quad (4)$$



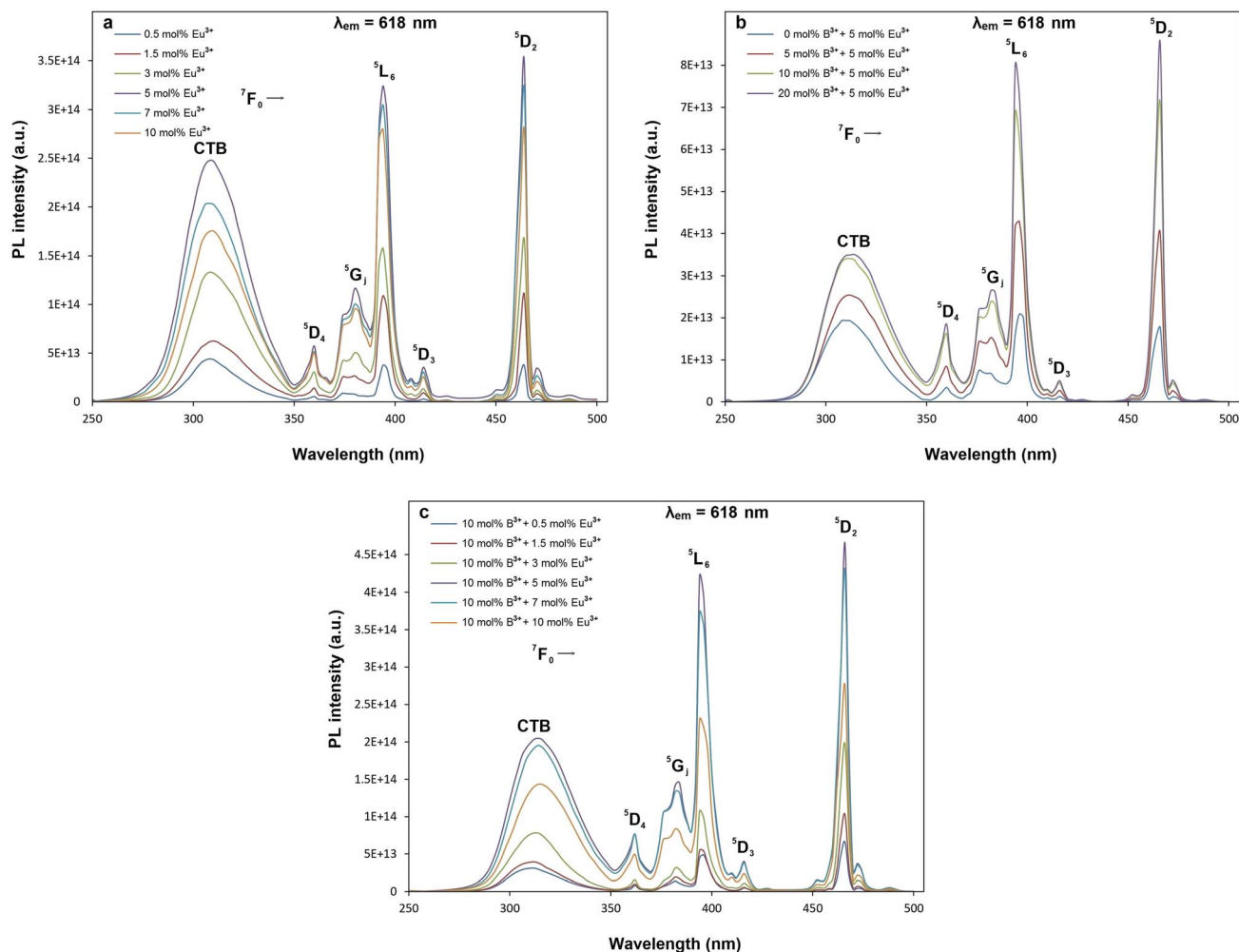


Fig. 6 PL excitation spectra and CT bands of (a)  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$ , (b)  $\text{SrTa}_2\text{O}_6:0.05\text{Eu}^{3+}, \text{yB}^{3+}$  (c)  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+}$  phosphors corresponding to 618 nm emission.

$$\chi_{\text{MD}} = n^3 \quad (5)$$

where  $n$  is the refractive index of  $\text{SrTa}_2\text{O}_6$  which was taken as 1.828 from ref. 6 and 7. The Judd–Ofelt intensity parameters ( $\Omega_2, \Omega_4$ ) are given in Table 1. The parameter  $\Omega_2$ , which is closely related to the hypersensitive electric dipole transition ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ), indicates the covalency of the Eu–O bond character and the environmental changes of the  $\text{Eu}^{3+}$  ion.<sup>6,7</sup> The trend of the  $\Omega_2$  parameter is  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+} > \text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$ , where the slightly higher  $\Omega_2$  parameters of the boron doped phosphors indicate relatively high covalency of Eu–O and low local symmetry of  $\text{Eu}^{3+}$  sites. The parameter  $\Omega_4$  is related to the electron density of the surrounding ligands, where an increase in  $\Omega_4$  parameter indicates a decreased electron density.<sup>28,29</sup> The trend of the  $\Omega_4$  parameter is  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+} > \text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$  wherein  $\text{B}^{3+}$  co-doped phosphors have relatively weak ligand density. The relatively high value of the  $\Omega_4$  parameter may be ascribed to the reduced charge transfer from the ligand ions to the  $\text{Eu}^{3+}$  ion, which supports the effect of boron to

decrease the formation of CTB or the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  and increase the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition intensity.

Fig. 9a–c shows the decay curves of  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$ ,  $\text{SrTa}_2\text{O}_6:0.05\text{Eu}^{3+}, \text{yB}^{3+}$ , and  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+}$  phosphors, respectively. The decay curves for  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition were detected by the emission of 618 nm and excitation of 465 nm. Fluorescence bi-exponential decay curves can be produced using eqn (6):<sup>27,28</sup>

$$I_t = I_0 + I_1 \exp\left(-\frac{t}{\tau_1}\right) + I_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (6)$$

where  $I_t$  is PL intensity,  $t$  is the time after excitation,  $I_0$  is the background,  $I_1$  and  $I_2$  are luminescence intensities corresponding to  $\tau_1$  (long) and  $\tau_2$  (short) lifetimes, respectively. Accordingly, the average lifetime ( $\tau$ ) can be calculated through eqn (7):<sup>28,30</sup>

$$\tau = \frac{I_1 \tau_1^2 + I_2 \tau_2^2}{I_1 \tau_1 + I_2 \tau_2} \quad (7)$$



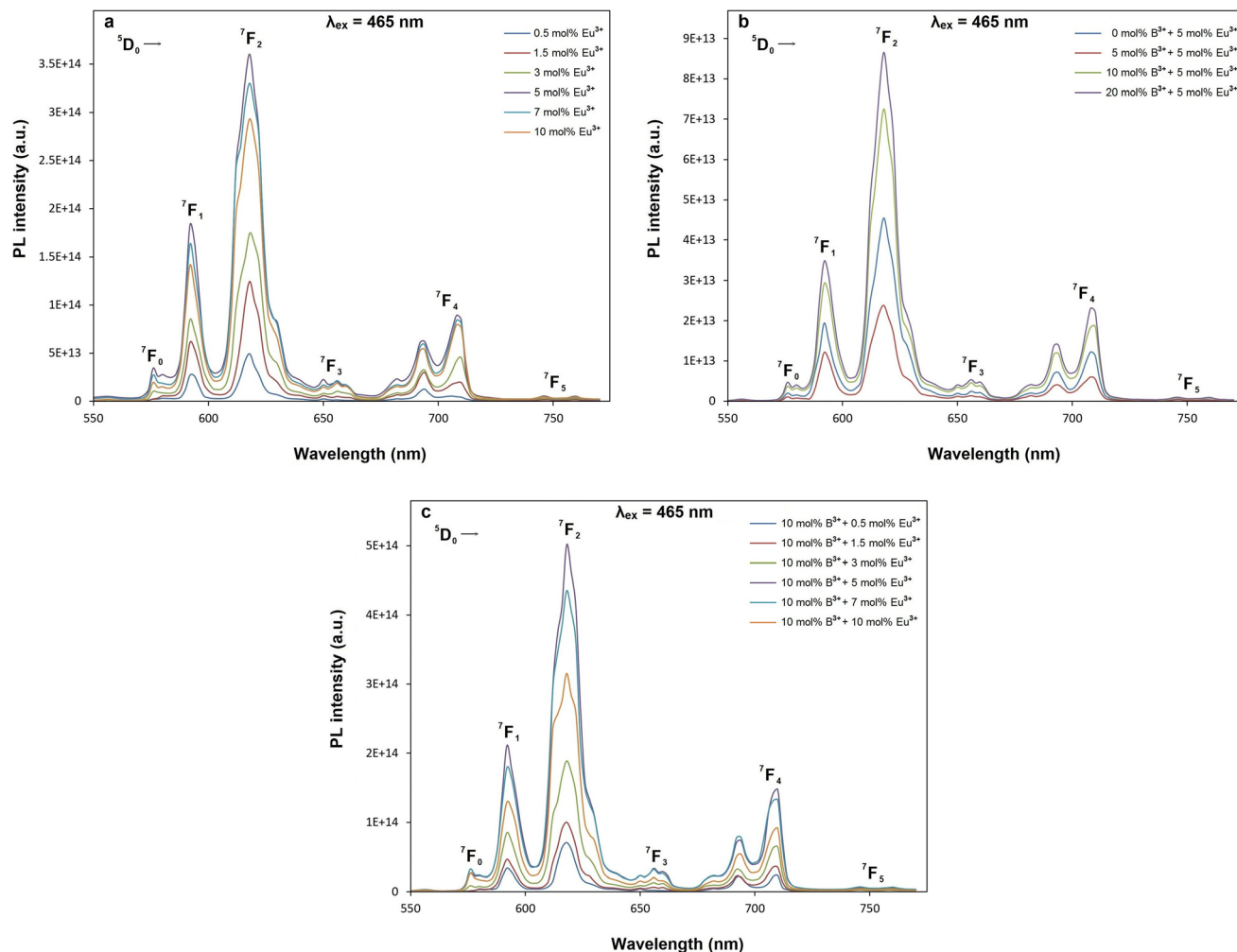


Fig. 7 PL emission spectra of (a)  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$ , (b)  $\text{SrTa}_2\text{O}_6:0.05\text{Eu}^{3+}, \text{yB}^{3+}$  (c)  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+}$  phosphors with excitation of 465 nm.

The fitting parameters of bi-exponential decays for  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$ ,  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+}$ , and  $\text{SrTa}_2\text{O}_6:0.05\text{Eu}^{3+}, \text{yB}^{3+}$  are tabulated in Tables 2 and 3, where the average lifetimes varied between 1.178–0.904, 1.162–0.892, and 0.979–0.958 ms, respectively. In Table 2, for both phosphor series, a somewhat decrease was observed in the decay times with the increase of the  $\text{Eu}^{3+}$  concentration, and slightly low decay times were found in  $\text{Eu}^{3+}, \text{B}^{3+}$  co-doped samples compared to  $\text{Eu}^{3+}$  doped samples. The increased asymmetry supports the relatively lower average lifetimes of  $\text{Eu}^{3+}, \text{B}^{3+}$  co-doped samples.<sup>31</sup> The  $\tau_1$  (long) and  $\tau_2$  (short) lifetimes of the phosphors are given in Tables 2 and 3. In the literature, the authors made definitions of the long ( $\tau_1$ ) and short ( $\tau_2$ ) lifetimes, where the short decay component is associated with  $\text{Eu}^{3+}$  ions close to the surfaces of the particles, while the long decay component is related to  $\text{Eu}^{3+}$  ions in inner part of the particles.<sup>32–35</sup> Padlyak *et al.*<sup>36</sup> emphasized that the long lifetimes are characteristic of luminescence centers and belong to isolated  $\text{Eu}^{3+}$  centers in oxide glasses and polycrystalline samples while the short components belong to the  $\text{Eu}^{3+}$ – $\text{Eu}^{3+}$  exchange-coupled pairs or small exchange-coupled  $\text{Eu}^{3+}$  clusters. On the other hand, Gupta

*et al.*<sup>37,38</sup> highlighted that the long component and the short component are associated with high symmetry and low symmetry of  $\text{Eu}^{3+}$  ions, respectively. In Tables 2 and 3, there is an increase in  $\tau_2$  lifetimes and slight decrease in  $\tau_1$  lifetimes of  $\text{Eu}^{3+}, \text{B}^{3+}$  co-doped samples compared to  $\text{Eu}^{3+}$  doped phosphors. Accordingly, the change in the  $\tau_1$  and  $\tau_2$  lifetimes may be originated from the activation of  $\text{Eu}^{3+}$  luminescence centers at the particle surface rather than in the particle core/isolated centers. The variation in  $\tau_2$  and  $\tau_1$  lifetimes can be explained by the lowering of local symmetry of  $\text{Eu}^{3+}$  due to the presence of boron, which was previously expressed as an increase in  $^5\text{D}_0 \rightarrow ^7\text{F}_2/^5\text{D}_0 \rightarrow ^7\text{F}_1$ . The asymmetry variation of the  $\text{Eu}^{3+}$  doped samples is associated with the A, and B site occupation, charge balance, or some degree of crystal distortion in the tungsten bronze structure.<sup>4,39</sup> On the other hand, although there is some improvement in the crystal properties, the increase in the ratio of  $^5\text{D}_0 \rightarrow ^7\text{F}_2/^5\text{D}_0 \rightarrow ^7\text{F}_1$  or the decrease in the local symmetry of  $\text{Eu}^{3+}$  ions is high in  $\text{Eu}^{3+}, \text{B}^{3+}$  co-doped samples. As mentioned in the XPS results, the fact that boron makes strong bonds with oxygen in the structure may be the reason for this difference (such as polarization). As another consequence,





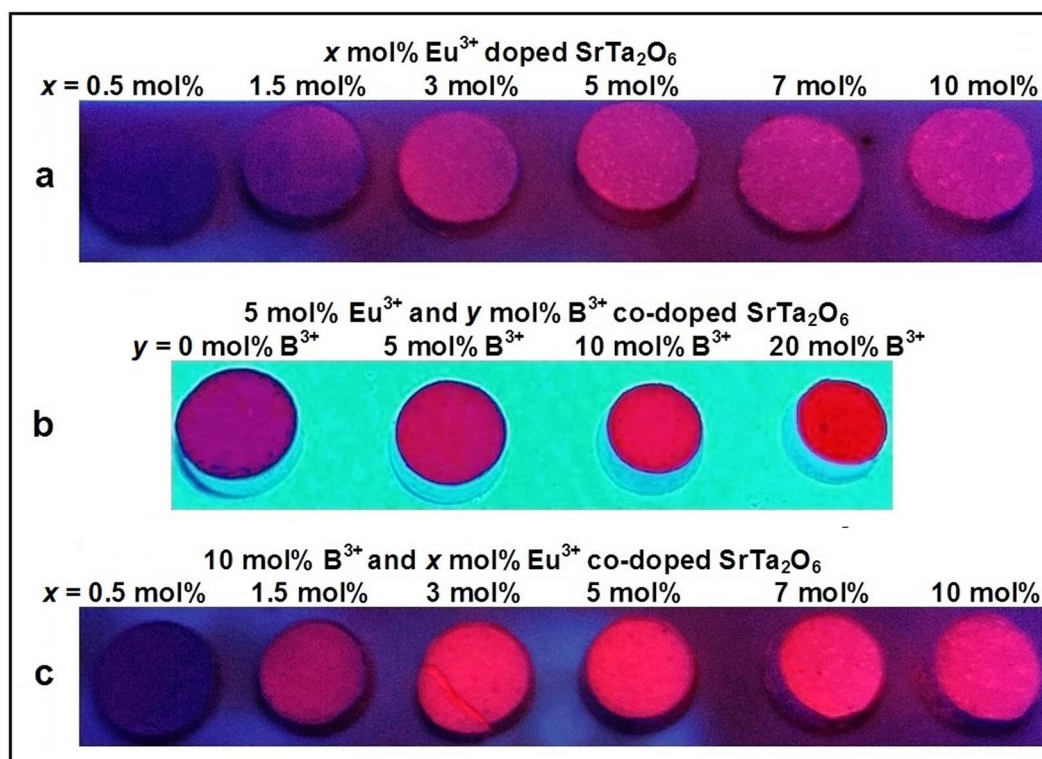


Fig. 8 UV lamp photos of (a)  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$ , (b)  $\text{SrTa}_2\text{O}_6:0.05\text{Eu}^{3+}, \text{yB}^{3+}$  (c)  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+}$  phosphors at 365 nm.

**Table 1** Judd–Ofelt intensity parameters ( $\Omega_2, \Omega_4$ ) for  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$  ( $x = 0.5, 1.5, 3, 5, 7, 10$  mol%) and  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, \text{yB}^{3+}$  ( $x = 0.5, 1.5, 3, 5, 7, 10$  mol%,  $y = 10$  mol%) phosphors

$\text{Eu}^{3+}$ conc. ( $x$ mol%)	$\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$		$\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+}$	
	$\Omega_2 (\times 10^{-20} \text{ cm}^2)$	$\Omega_4 (\times 10^{-20} \text{ cm}^2)$	$\Omega_2 (\times 10^{-20} \text{ cm}^2)$	$\Omega_4 (\times 10^{-20} \text{ cm}^2)$
0.5	2.963	1.670	3.586	2.800
1.5	3.315	1.764	3.692	3.101
3	3.343	1.943	3.806	3.130
5	3.201	1.906	4.070	2.887
7	3.292	2.018	4.162	3.055
10	3.367	2.196	4.183	2.913

increase of grain size in SEM micrographs is associated with the vitrification effect that accelerates agglomeration in boron grains. By evaluating the SEM micrographs and the decay components, it is seen that there is a correlation between grain growth and the increase in the short components. Similar behavior has been observed in  $\text{Sm}^{3+}$  doped  $\text{BaTa}_2\text{O}_6$  phosphor, where grain growth with increasing sintering temperature leads to an increase in short components.<sup>5</sup> Although this requires further observation, it shows that grain growth may be related to the increase of  $\text{Eu}^{3+}$  luminescence centers on grain surfaces and a decrease in crystal field symmetry. The quantum efficiency ( $\eta_{\text{QE}}$ ) of  $^5\text{D}_0$  level can be found from the ratio of the average (observed) lifetime ( $\tau$ ) to the radiative lifetime ( $\tau_r$ ) by eqn (8):

$$\eta_{\text{QE}} = \frac{1}{\frac{A_r + A_{\text{nr}}}{A_r}} = \frac{\tau}{\tau_r} \quad (8)$$

where the radiative and nonradiative transitions of  $^5\text{D}_0$  are  $A_r$  and  $A_{\text{nr}}$ , respectively. The radiative lifetimes ( $\tau_r$ ) and quantum efficiencies ( $\eta_{\text{QE}}$ ) are tabulated in Table 2. The values of the  $\eta_{\text{QE}}$  for  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$  and  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+}$  phosphors varied between 36.03–30.30% and 42.72–36.08%, respectively. The  $\eta_{\text{QE}}$  for  $\text{Eu}^{3+}$  and  $\text{B}^{3+}$  co-doped phosphors corresponds to an approximate increase of 15–21%. The quantum efficiency of the highest luminescent (or  $0.05\text{Eu}^{3+}, 0.1\text{B}^{3+}$  co-doped) phosphor increased by about 21%. As mentioned in the previous sections, the low symmetry of the  $\text{Eu}^{3+}$  sites and some



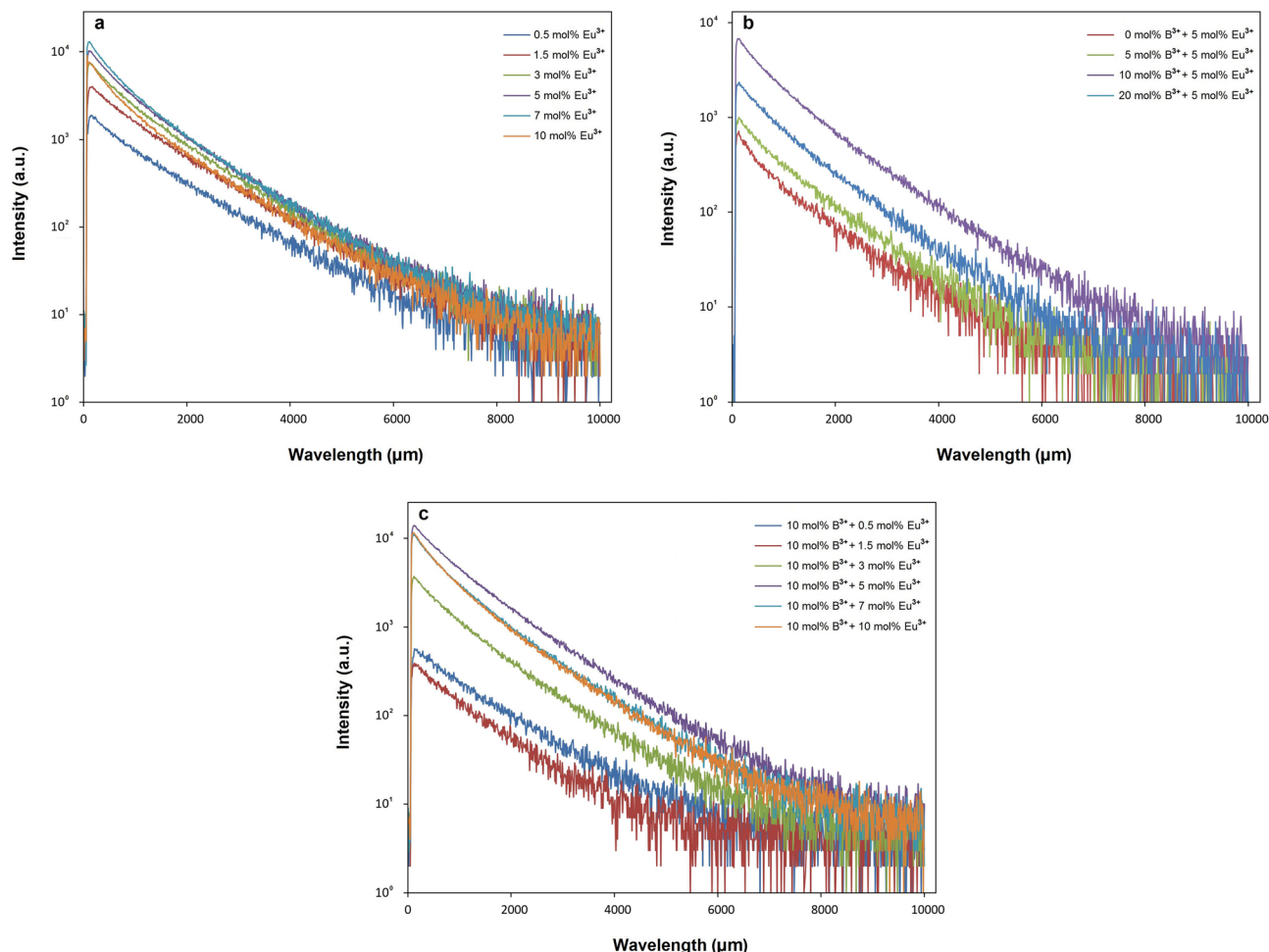


Fig. 9 Decay curves of (a)  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$ , (b)  $\text{SrTa}_2\text{O}_6:0.05\text{Eu}^{3+}, \text{yB}^{3+}$  (c)  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+}$  phosphors with emission of 618 nm and excitation of 465 nm.

Table 2 Long ( $\tau_1$ ) and short ( $\tau_2$ ) lifetimes, average (observed) lifetimes ( $\tau$ ), radiative lifetimes ( $\tau_r$ ), quantum efficiencies ( $\eta_{\text{QE}}$ ) and chi-square ( $\chi^2$ ) values for  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$  ( $x = 0.5, 1.5, 3, 5, 7, 10$  mol%) and  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, \text{yB}^{3+}$  ( $x = 0.5, 1.5, 3, 5, 7, 10$  mol%,  $y = 10$  mol%) phosphors

$\text{Eu}^{3+}$ conc. ( $x$ mol%)	$\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$						$\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, 0.1\text{B}^{3+}$					
	$\tau_1$ (ms)	$\tau_2$ (ms)	$\tau$ (ms)	$\tau_r$ (ms)	$\eta_{\text{QE}}$ (%)	$\chi^2$	$\tau_1$ (ms)	$\tau_2$ (ms)	$\tau$ (ms)	$\tau_r$ (ms)	$\eta_{\text{QE}}$ (%)	$\chi^2$
0.5	1.293	0.504	1.178	3.283	35.88	1.190	1.259	0.429	1.162	2.720	42.72	1.106
1.5	1.274	0.319	1.101	3.056	36.03	1.151	1.205	0.521	1.086	2.619	41.47	1.196
3	1.198	0.421	1.012	3.025	33.45	1.179	1.183	0.452	1.003	2.570	39.03	1.108
5	1.147	0.462	0.978	3.110	31.45	1.156	1.135	0.425	0.959	2.516	38.12	1.225
7	1.112	0.387	0.919	3.033	30.30	1.142	1.104	0.437	0.902	2.456	36.73	1.208
10	1.148	0.395	0.904	2.952	30.62	1.360	1.113	0.423	0.892	2.472	36.08	1.194
Avg	1.195	0.415	1.015	3.077	32.96	—	1.167	0.448	1.001	2.559	39.03	—

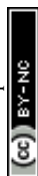
Table 3 Long ( $\tau_1$ ) and short ( $\tau_2$ ) lifetimes, average (observed) lifetimes ( $\tau$ ) and chi-square ( $\chi^2$ ) values for  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}, \text{yB}^{3+}$  ( $x = 5$  mol%,  $y = 0, 5, 10, 20$  mol%) phosphors

$\text{B}^{3+}$ conc. ( $y$ mol%)	$\text{SrTa}_2\text{O}_6:0.1\text{Eu}^{3+}$			
	$\tau_1$ (ms)	$\tau_2$ (ms)	$\tau$ (ms)	$\chi^2$
0	1.131	0.306	0.979	1.057
5	1.111	0.346	0.991	1.003
10	1.147	0.436	0.950	1.178
20	1.110	0.440	0.958	1.107

enhancement in crystal structure properties are likely to increase the luminescence efficiency.

## 4. Conclusion

The effect of boron on the structural and spectral properties was studied by using  $\text{Eu}^{3+}$  doped orthorhombic  $\beta\text{-SrTa}_2\text{O}_6$  fabricated by solid-state method at 1400 °C for 20 h. The phase structure of



all the ceramics preserved up to 10 mol%, and the  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped samples have relatively slightly better crystallinity. SEM micrographs showed that the presence of boron promoted agglomeration and growth in grains. The increment in boron concentration led to an increase in PL up to 20 mol%, and the increase of PL may be related to the low symmetry of  $\text{Eu}^{3+}$  ions and the improvement of crystal properties. In  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped samples, the charge transfer band slightly shifted to the lower energy and asymmetry of phosphor increased. The trend of Judd–Ofelt ( $\Omega_2$ ,  $\Omega_4$ ) parameters was  $\text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$ ,  $0.1\text{B}^{3+} > \text{SrTa}_2\text{O}_6:\text{xEu}^{3+}$ . The high values of the  $\Omega_2$ , and  $\Omega_4$  for  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped phosphors related to a covalent Eu–O bond character with low symmetry of the  $\text{Eu}^{3+}$  ions and a reduced electron density in the ligands, respectively. While the increase of  $\text{Eu}^{3+}$  causes a slight decrease in the decay times, the decrease is slightly more in the  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped samples. The increase in  $\tau_2$  lifetimes may be associated with the activation of the  $\text{Eu}^{3+}$  luminescence centers at the grain surface and near the surface. The quantum efficiencies of the  $\text{Eu}^{3+}$ ,  $\text{B}^{3+}$  co-doped phosphors increased between 15–21%.

## Conflicts of interest

There are no conflicts to declare.

## References

- 1 K. Binnemans, *Coord. Chem. Rev.*, 2015, **295**, 1–45.
- 2 C. G. Walrand and K. Binnemans, *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, Belgium, 1998, pp. 101–264.
- 3 M. İlhan and İ. Ç. Keskin, *Physica B*, 2020, **85**, 412106.
- 4 M. İlhan, *Solid State Sci.*, 2014, **38**, 160–168.
- 5 M. İlhan and L. F. Güleriyüz, *Chem. Pap.*, 2022, **76**, 6963–6974.
- 6 M. İlhan, M. İ. Katı, İ. Ç. Keskin and L. F. Güleriyüz, *J. Alloys Compd.*, 2022, **901**, 163626.
- 7 M. İlhan, İ. Ç. Keskin, L. F. Güleriyüz and M. İ. Katı, *J. Mater. Sci.: Mater. Electron.*, 2022, **33**, 16606–16620.
- 8 E. Lee, C. H. Park, D. P. Shoemaker, M. Avdeev and Y. I. Kim, *J. Solid State Chem.*, 2012, **191**, 232–238.
- 9 J. Y. Kim and Y. I. Kim, *J. Ceram. Soc. Jpn.*, 2015, **123**, 419–422.
- 10 H. Kato and A. Kudo, *Chem. Lett.*, 1999, **28**, 1207–1208.
- 11 Y. Huang, Q. Feng, Y. Yang and H. J. Seo, *Phys. Lett. A*, 2005, **336**, 490–497.
- 12 D. Zhao, Y. Yu, C. Cao, J. Wang, E. Wang and Y. Cao, *Appl. Surf. Sci.*, 2015, **345**, 67–71.
- 13 N. Lu, H. Zhao, J. Li, X. Quan and S. Chen, *Sep. Purif. Technol.*, 2008, **62**, 668–673.
- 14 E. Finazzi, C. D. Valentin and G. Pacchioni, *J. Phys. Chem. C*, 2009, **133**, 220–228.
- 15 V. Vitola, I. Bite, D. Millers, A. Zolotarjovs, K. Laganovska, K. Smits and A. Spustaka, *Ceram. Int.*, 2020, **46**, 26377–26381.
- 16 A. S. Başak, M. K. Ekmekçi, M. Erdem, M. İlhan and A. Mergen, *J. Fluoresc.*, 2016, **26**, 719–724.
- 17 J. Kaduk and W. Wong-Ng, *International Center for Diffraction Data*, PDF code 00-051-1683.
- 18 W. E. Moddeman, A. R. Burke, W. C. Bowling and D. S. Foote, *Surf. Interface Anal.*, 1989, **14**, 224.
- 19 D. H. Quinones, A. Rey, P. M. Álvarez, F. J. Beltrán and G. L. Puma, *Appl. Catal., B*, 2015, **178**, 74–81.
- 20 W. Zhang, T. Hu, B. Yang, P. Sun and H. He, *J. Adv. Oxid. Technol.*, 2013, **16**, 261–267.
- 21 G. Blasse, *J. Solid State Chem.*, 1972, **4**, 52–54.
- 22 P. Dorenbos, *J. Lumin.*, 2005, **111**, 89–104.
- 23 D. E. Henrie, R. L. Fellows and G. R. Choppin, *Coord. Chem. Rev.*, 1976, **18**, 199–224.
- 24 Y. Hua, T. Wang, J. S. Yu, W. Ran and L. Li, *Inorg. Chem. Front.*, 2022, **9**, 6211–6224.
- 25 Q. Shao, H. Zhang, J. Dai, C. Yang, X. Chen, G. Feng and S. Zhou, *CrystEngComm*, 2020, **22**, 1359.
- 26 B. R. Judd, *Phys. Rev.*, 1962, **127**, 750.
- 27 G. S. Ofelt, *J. Chem. Phys.*, 1962, **37**, 511.
- 28 M. İlhan, M. K. Ekmekçi and İ. Ç. Keskin, *RSC Adv.*, 2021, **11**, 10451–10462.
- 29 M. İlhan and İ. Ç. Keskin, *Phys. Chem. Chem. Phys.*, 2020, **22**, 19769–19778.
- 30 R. Saraf, C. Shivakumara, S. Behera, H. Nagabhushana and N. Dhananjaya, *RSC Adv.*, 2015, **5**, 4109.
- 31 G. Blasse, *J. Phys. Chem. Solids*, 1989, **50**, 99.
- 32 J. W. Stouwdam and F. C. M. van Veggel, *Nano Lett.*, 2002, **2**, 733–737.
- 33 V. Sudarsan, F. C. J. M. van Veggel, R. A. Herring and M. Raudsepp, *J. Mater. Chem.*, 2005, **15**, 1332.
- 34 N. Yaiphaba, R. S. Ningthoujam, N. S. Singh, R. K. Vatsa, N. R. Singh, S. Dhara, N. L. Misra and R. Tewari, *J. Appl. Phys.*, 2010, **107**, 034301.
- 35 A. K. Parchur and R. S. Ningthoujam, *RSC Adv.*, 2012, **2**, 10859–10868.
- 36 B. Padlyak, M. Grinberg, B. Kukliński, Y. Oseledchik, O. Smyrnov, D. Kudryavtcev and A. Prosvirnin, *Opt. Appl.*, 2010, **2**, 413–426.
- 37 S. K. Gupta, B. Modak, M. Tyagi, N. S. Rawat, P. Modak and K. Sudarshan, *ACS Omega*, 2022, **7**, 5311–5323.
- 38 S. K. Gupta, C. Reghukumar and R. M. Kadam, *RSC Adv.*, 2016, **6**, 53614–53624.
- 39 M. İlhan, M. K. Ekmekçi, A. Mergen and C. Yaman, *J. Fluoresc.*, 2016, **26**, 1671–1678.

