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Luminescence characteristics of strontium borate phosphate phosphors

Chung-Hsin Lu*, S.V. Godbole[1], V. Natarajan

Electronic and Electro-optical Ceramics Lab, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, ROC

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Abstract

New green emitting phosphors based on $SrBPO_5$ with high brightness are prepared via solid-state reactions at high temperatures in reducing atmosphere. $SrBPO_5$ doped with trivalent terbium ions emit weakly in blue and orange light region and strongly in green light region on excitation at 220 nm. The blue and green-orange emissions are ascribed to $^5D_3 \rightarrow {}^7F_J$ and $^5D_4 \rightarrow {}^7F_J$ (where $J = 3$–6) transitions of Tb^{3+} ions, respectively. The co-doping of Ce^{3+} and Tb^{3+} in $SrBPO_5$ phosphors results in strong emission from Tb^{3+} ions on excitation in the UV region corresponding to excitation bands of Ce^{3+} ions. The enhanced luminescence observed in $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$ and $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ phosphors is understood as due to a reduction in the non-radiative energy transfer. $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ synthesized in reducing atmosphere show nearly two-order enhancement in emission intensity of 542 nm peak on excitation at 254 nm as compared with the intensity of 542 nm emission in $Sr_{0.99}Tb_{0.01}BPO_5$. These results suggest the possibility of the potential of $SrBPO_5$-related phosphors in tri-color lamps.

Keywords: $SrBPO_5$; Luminescence; Energy transfer; Co-doping

1. Introduction

Since the introduction of tricolor fluorescent lamps based on rare earth ions, the research in the field of luminescence applications has been focused on developing new phosphors using rare earth ions. The newly developed devices, such as plasma display panels and field emission displays, also demand phosphors with improved properties. These displays require phosphors having good luminescence yield, small particles, and uniform spherical morphology [1]. Trivalent terbium ions based phosphors play an important role in the field of illumination and displays in view of its sharp green emission at around 545 nm. $LaPO_4$, Y_2SiO_5, $CeMgAl_{11}O_{19}$, and $GdMgB_5O_{10}$ are certain well-established phosphors based on energy transfer from Ce^{3+} to Tb^{3+} for green emission in lamps [2]. The phosphor materials such as $LaOBr:Tb^{3+}$, $Ln_2O_2S:Tb^{3+}$ (where Ln = Gd, La, and Y) and $Y_3Al_5O_{12}:Tb^{3+}$ are utilized in X-ray imaging and cathode ray tube [3,4]. Terbium doped matrices such as zirconium pyrophosphate, lanthanum borophosphate, gadolinium oxybromide, zinc silicate, calcium aluminate and vaterite, have lately been investigated for their spectroscopic properties [5–11].

Strontium borate phosphate ($SrBPO_5$) having a crystal structure corresponding to mineral stillwellite has been investigated in detail in recent years. The effects of doping Eu^{2+} and Ce^{3+} ions on the luminescent properties are reported in literature [12–14]. In the present work, luminescent properties of Tb^{3+}, Ce^{3+} and Na^+ doped $SrBPO_5$ are investigated. The photoluminescence investigations are performed to explore the luminescence and energy transfer characteristics of the doped ions in the host matrix. The observation of intense green luminescence from $SrBPO_5:Tb^{3+}$, Ce^{3+} and Na^+ on 254 nm excitation suggests a possibility of applying the newly developed phosphors to tri-color lamps.

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* Corresponding author. Tel.: +886 2 23651428; fax: +886 2 23623040.
E-mail address: chlu@ccms.ntu.edu.tw (C.-H. Lu).

[1] Permanent address: Radiochemistry Division, BARC, Mumbai 400085, India.

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2. Experimental

$SrBPO_5$-based phosphors were prepared via the solid-state reactions at high temperatures. For synthesizing $Sr_{0.99}Tb_{0.01}BPO_5$, reagent-grade $SrCO_3$, Tb_4O_7, $(NH_4)_2HPO_4$, and H_3BO_3 were thoroughly mixed by grinding. To investigate the effects of energy transfer and co-doping on the luminescent properties, Na^+ and Ce^{3+} ions were also incorporated with Tb^{3+}ions in the host matrix. Na_2HPO_4 and CeO_2 were added along with other ingredients during grinding stage to obtain $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$, $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$, and $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$. During the synthesis of $Sr_{1-(x+y+z)}Tb_xCe_yNa_zBPO_5$ (where $x = 0.01$, $y = 0$ or 0.05 and $z = 0$ or 0.05), corresponding mixtures were initially heated at 400 °C for 2 h in air, followed by thoroughly regrinding for 30 min before heating at higher temperatures. The 400 °C-heated mixtures of $Sr_{0.99}Tb_{0.01}BPO_5$, $Sr_{0.95}Ce_{0.05}BPO_5$, and $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ were heated at 1000 °C for 4 h. For synthesizing $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$ and $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$, the 400 °C-heated mixtures were further heated at 900 °C for 4 h. As for the reducing treatment, the samples prepared in air were further heated at 900 °C for 4 h in mixed gas (N_2 (95 vol.%) and H_2 (5 vol.%)). The crystal structures of the prepared powders were examined using an X-ray diffractometer (MAC M03 XHF). Photoluminescence studies were conducted using a fluorescence spectrometer (Hitachi F-4500).

3. Results and discussion

3.1. Luminescent characteristics of Tb^{3+} ions in $SrBPO_5$

Fig. 1 illustrates the XRD patterns for 1000 °C-heated $Sr_{0.99}Tb_{0.01}BPO_5$ (curve a) and $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (curve b), and 900 °C-heated $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$ (curve c) and $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ (curve d). All of the above samples were heated in air. The above XRD patterns are similar to that reported for the compound strontium borate phosphate (ICDD file No.18-1270), indicating the formation of the stillwellite phase. They could be indexed to a hexagonal space group. In the case of $Sr_{0.99}Tb_{0.01}BPO_5$, the unit cell parameters obtained are $a = b = 0.68119$ nm and $c = 0.67696$ nm. Further heating these samples at 900 °C in the reducing atmosphere did not result in any change in the XRD patterns.

Fig. 2 illustrates the emission spectra ($\lambda_{excitation.} = 220$ nm) for 900 °C-heated $Sr_{0.94}Tb_{0.01}Na_{.05}BPO_5$ (curve a) and 1000 °C-heated $Sr_{0.99}Tb_{0.01}BPO_5$ (curve b) prepared in air. The emission spectra show weak blue emission in the region of 380–450 nm and strong green emission in 475–630 nm. The emission peaks at 385, 417 and 438 nm are due to transitions from excited level $^5D_3$ to $^7F_6$, $^7F_5$, and $^7F_4$ levels of Tb^{3+} ions, respectively. The emission peaks due to $^5D_4 \rightarrow {}^7F_6$, $^7F_5$, $^7F_4$, and $^7F_3$ transitions are observed at 492, 542, 582 and 618 nm, respectively [16]. Owing to the crystal field splitting of the levels into several sublevels, the observed spectra are complicated in appearance. The emission intensity of 542 nm peak corresponding to $^5D_4 \rightarrow {}^7F_5$ transition shows a two-fold increase in $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$ in comparison with that of $Sr_{0.99}Tb_{0.01}BPO_5$.

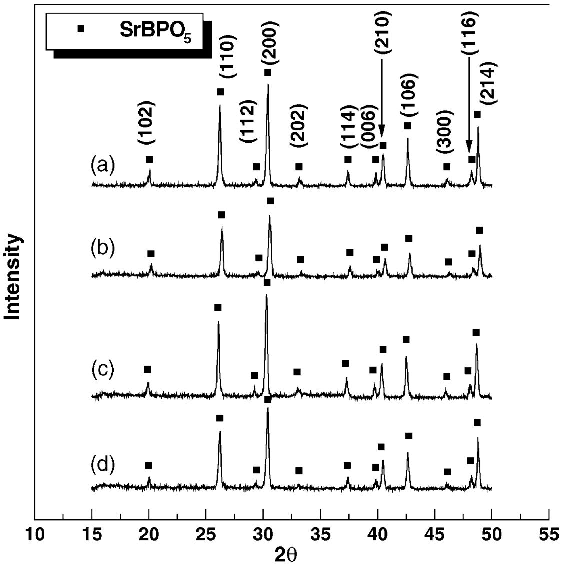

Fig. 1. XRD patterns of (a) 1000 °C-heated $Sr_{0.99}Tb_{0.01}BPO_5$ (air), (b) 1000 °C-heated $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (air), (c) 900 °C-heated $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$ (air), and (d) 900 °C-heated $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ (air).

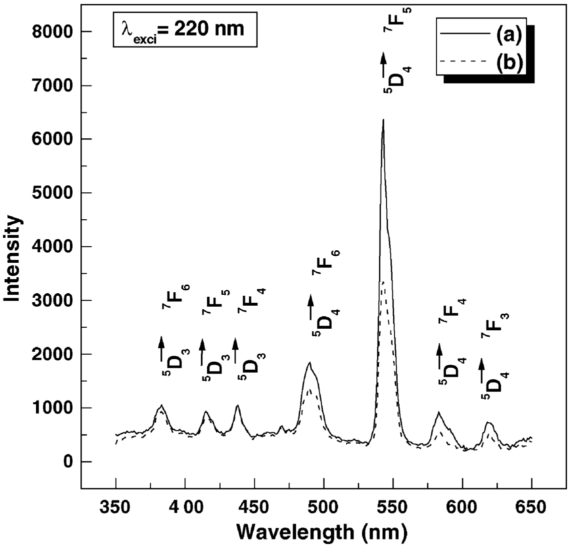

Fig. 2. Emission spectra ($\lambda_{excitation} = 220$ nm) of (a) $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$ heated at 900 °C in air and (b) $Sr_{0.99}Tb_{0.01}BPO_5$ heated at1000 °C in air.

Fig. 3 illustrates the excitation spectra ($\lambda_{emission} = 542$ nm) for 900 °C-heated $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$ (curve a) and 1000 °C-heated $Sr_{0.99}Tb_{0.01}BPO_5$ (curve b) prepared in air. The inset in the figure reveals weak excitation peaks observed for these phosphors in the wavelength range of 250–400 nm. A strong excitation peak at 220 nm along with a number

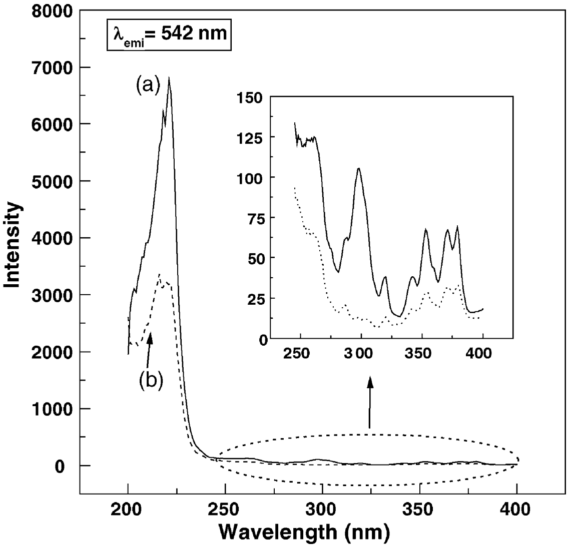

Fig. 3. Excitation spectra ($\lambda_{emission}$ = 542 nm) of (a) $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$ heated at 900 °C in air and (b) $Sr_{0.99}Tb_{0.01}BPO_5$ heated at 1000 °C in air. The inset: enlarged excitation spectra at 250–400 nm.

of comparatively weak excitation peaks in the wavelength range of 280–380 nm are observed. The relatively strong excitation band at 220 nm can be attributed to $4f^8 \rightarrow 4f^7 5d^1$ transition [15]. The weak excitations shown in the inset are due to various excited states of Tb^{3+} ions belonging to $4f^8$ electronic configuration, including the $^5D_3$ excited state at 380 nm. The excitation spectra also reveal a similar degree of enhancement in the intensity, as a result of co-doping Na^+ and Tb^{3+} ions in $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$. Introduction of Ce^{3+} or Tb^{3+} ions without the coexistence of charge compensating ions requires the formation of cation vacancies. Moreover, heating in air produces oxygen vacancies as well. It is probable that the starting material with the composition of $Sr_{0.94}Tb_{0.01}Na_{0.05}BPO_5$ can lead to $Sr_{0.98}Tb_{0.01}Na_{0.02}BPO_5$ formation with excess Na, B and P either volatilized or present as a minor phase that undetected by XRD. In that case, the observed enhancement in the Tb^{3+} emission can be attributed to the charge compensation by Na^+ ions that alleviates the need for formation of defects. These defects, such as cation vacancies and oxygen vacancies, are expected in the case of $Sr_{0.99}Tb_{0.01}BPO_5$ samples which usually lead to non-radiative energy losses.

3.2. Luminescent characteristics of Ce^{3+} ions in $SrBPO_5$

The luminescent characteristics of Ce^{3+} ions are known to depend upon whether the charge compensatory vacancy is associated with Ce^{3+} ions in the cases of similar aliovalent substitution [17,18]. Our earlier investigations on $Sr_{0.95}Ce_{0.05}BPO_5$ have revealed that Ce^{3+} ions situated at Sr^{2+} sites with no associated vacancy show a broad emission peak at 317 nm with a shoulder around 330 nm upon 275 nm excitation [19]. On the other hand, Ce^{3+} ions substituting at Sr^{2+} sites with associated vacancy show red shifted emission with peaks at 330 and 350 nm upon excitation at 295 nm.

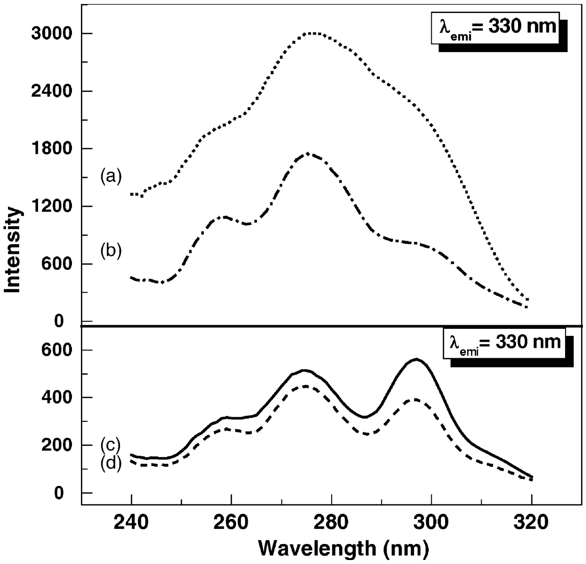

Fig. 4. Excitation spectra ($\lambda_{emission}$ = 330 nm) of (a) 900 °C-heated $Sr_{.89}Tb_{.01}Ce_{.05}Na_{0.05}BPO_5$ (reducing atmosphere), (b) 900 °C-heated $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (reducing atmosphere), (c) 900 °C-heated $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ (air), and (d) 1000 °C-heated $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (air).

3.3. Energy transfer from Ce^{3+} ions to Tb^{3+} ions in $SrBPO_5$

Fig. 4 illustrates the excitation spectra for Ce^{3+} ions for $\lambda_{emission}$ = 330 nm in 900 °C-heated $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ and 1000 °C-heated $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ samples prepared in the reducing atmosphere (curves a and b) and in air (curves c and d). For the samples prepared in air, the excitation peaks are observed at 295, 275 and 260 nm with the former two peaks comparable in intensity; while, the excitation peak at 260 nm is relatively weak. The excitation spectra for the samples prepared in the reducing atmosphere (curve a and b) show strong intensities. The positions of the excitation peaks of these samples are nearly the same. Among three excitation peaks illustrated in curves a and b, the one at 275 nm is the most intense, while those at 260 and 295 nm appear as shoulders to the peak at 275 nm. The emission intensities of Ce^{3+} ions in the samples heated in the reducing atmosphere are noted to increase, suggesting nearly complete reduction of Ce^{4+} ions to Ce^{3+} ions.

Fig. 5 shows the excitation spectra of Tb^{3+} ions at 542 nm emission in different phosphors. The excitation peaks in the 240–380 nm region are relatively weak for 1000 °C-heated $Sr_{0.99}Tb_{0.01}BPO_5$ prepared in air (curve e). For the other samples co-doped with Ce^{3+} ions, additional strong excitation peaks occur in the region of 240–320 nm. Additional excitation peaks at 275 and 295 nm are observed for 900 °C-heated $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ (curve c) and 1000 °C-heated

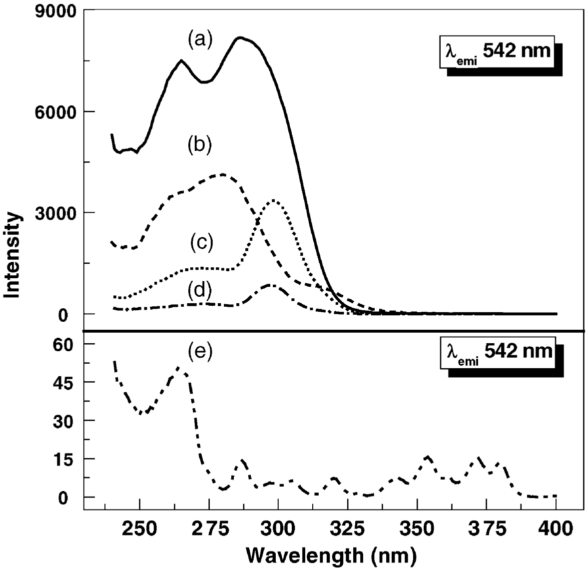

Fig. 5. Excitation spectra ($\lambda_{\text{emission}} = 542$ nm) of (a) 900 °C-heated $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ (reducing atmosphere), (b) 900 °C-heated $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (reducing atmosphere), (c) 900 °C-heated $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ (air), (d) 1000 °C-heated $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (air), and (e) 1000 °C-heated $Sr_{0.99}Tb_{0.01}BPO_5$ (air).

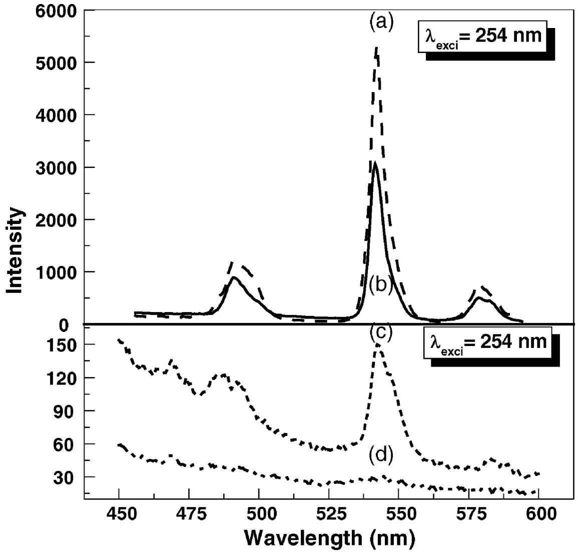

Fig. 6. Emission Spectra ($\lambda_{\text{excitation}} = 254$ nm) of (a) 900 °C-heated $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ (reducing atmosphere), (b) 900 °C-heated $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (reducing atmosphere), (c) 1000 °C-heated $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (air), and (d) 1000 °C-heated $Sr_{0.99}Tb_{0.01}BPO_5$ (air).

$Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (curve d) prepared in air as a result of co-doping with cerium ions. These peaks, observed for Tb^{3+} emission, correspond to the excitation bands of Ce^{3+} ions [19]. This observation clearly indicates the energy transfer amongst these ions.

For the samples prepared in the reducing atmosphere, shift in peak positions and changes and increase in relative excitation intensities are observed. Intense excitation peaks are found at 260 and 280 nm for $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (curve b) prepared in the reducing atmosphere. These correspond to the Ce^{3+} excitation peaks. However, for $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ (curve a) prepared in the reducing atmosphere, peaks due to Ce^{3+} absorption are observed at 285 and 265 nm. This shift can be explained by the changed crystal field environment of Ce^{3+} ions because of the co-doping of smaller Na^+ ions in $SrBPO_5$. The peak shifts and change in relative intensities of the excitation peaks in curves c and d are presumably due to the contribution from Ce^{3+} ions occupying sites with and without charge compensating cation/oxygen vacancies in varying proportion.

3.4. *Effects of co-doping of Na^+ ions on the luminescent properties*

The emission spectra for the prepared samples upon excitation at 254 nm were recorded for the interest in mercury-based fluorescent lamps and are shown in Fig. 6. Curves a and b illustrate the emission spectra obtained for $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ and $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ heated at 900 °C in the reducing atmosphere, respectively. The emission spectra for $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ and $Sr_{0.99}Tb_{0.01}BPO_5$ prepared in air are shown in curves c and d, respectively. Upon excitation at 254 nm, the green emission at 542 nm increases by nearly 100-fold in $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ (curve b) and 170 folds in $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ (curve a) in comparison with $Sr_{0.99}Tb_{0.01}BPO_5$ (curve d) prepared in air. The intensity of the emission peak of Tb^{3+} ions at 542 nm in $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ phosphor prepared in the reducing atmosphere was compared with that of the commercial green phosphor $LaPO_4$:Ce^{3+}, Tb^{3+} (Nichia, Japan), and the relative luminescence yield was found to be about 10%.

As illustrated in Figs. 2 and 6, the incorporation of sodium ions as co-dopants in the respective sample does not lead to changes in emission wavelengths; however, increased luminescence of Tb^{3+} and Ce^{3+} ions is observed. The enhancement in luminescence can arise due to several reasons such as energy transfer, decreased formation of charge compensating cation vacancies/oxygen vacancies due to Na^+ ion co-doping, and increased concentration of emitting ions. The monovalent sodium ions cannot involve directly in the energy transfer process, since their closed shell configuration cannot have matching energy levels with those of Tb^{3+} and Ce^{3+} ions. An increase in luminescence intensity of Ce^{3+} ions due to co-doping of monovalent lithium ions has been reported in lanthanum phosphate and is ascribed to the energy transfer from Ce^{4+} to Ce^{3+} ions facilitated by co-doping of Li^+ ions [20]. The preparation of the phosphors in the reducing atmosphere result in reduction of Ce^{4+} and Tb^{4+} ions to Ce^{3+} and Tb^{3+} ions, respectively. Since Ce^{4+} ions are expected to be absent in $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ and $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ prepared in the reducing atmosphere, the observed luminescence enhancement cannot be attributed to the energy transfer from Ce^{4+} ions. Furthermore, similar luminescence enhancement with co-doping of Na^+ ions has been reported in $CaSO_4$:Eu^{3+}, wherein this has been attributed to the decreased concentration of vacancies [21].

Hence the luminescence enhancement observed for the $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ samples prepared in the reducing atmosphere is understood as due to co-doping of Na^+ ions. Co-doping of Na^+ ions with Ce^{3+} and Tb^{3+} ions in the samples results in a significant reduction of charge compensating vacancies, which are expected to be formed in the host lattice. This is expected to cause a significant reduction in non-radiative transitions and lead to the enhanced luminescence intensity.

4. Conclusion

The trivalent terbium ions in the $SrBPO_5$ host show luminescence arising from various $^5D_3$ and $^5D_4 \rightarrow {}^7F_J$ transitions of Tb^{3+} ions upon excitation at 220 nm. The excitation band at 220 nm is ascribed to the lowest $4f^8 \rightarrow 4f^7 5d^1$ transition in the host. As a result of co-doping Ce^{3+} with Tb^{3+} ions in the host of $SrBPO_5$, the excitation spectra of Tb^{3+} ions show additional intense excitation occurring at 240–300 nm due to energy transfer from Ce^{3+} to Tb^{3+} ions. With excitation at 240–300 nm, increased luminescence is observed for $Sr_{0.94}Tb_{0.01}Ce_{0.05}BPO_5$ and $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ synthesized in the reducing atmosphere. The luminescence enhancement in these phosphors is attributed to the reduction of charge compensating cation vacancies/oxygen vacancies, resulting in higher concentration of Ce^{3+} ions and consequent energy transfer to Tb^{3+} ions. $Sr_{0.89}Tb_{0.01}Ce_{0.05}Na_{0.05}BPO_5$ prepared in the reducing atmosphere shows more than two-order magnitude increase in 254 nm excited green emission of Tb^{3+} ions in comparison with $Sr_{0.99}Tb_{0.01}BPO_5$ prepared in air. It is revealed that $SrBPO_5$-related phosphors exhibit enhanced luminescence and can be utilized as green phosphors in tricolor lamps.

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