

# Photoluminescence properties of $X_5SiO_4Cl_6:Tb^{3+}$ ( $X = Sr, Ba$ ) green phosphor prepared via modified solid state method

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**Abstract.** Luminescence property of a new halo silicate phosphor,  $X_5SiO_4Cl_6:Tb^{3+}$  ( $X = Sr, Ba$ ) prepared by modified solid state method is reported here. It is characterized by powder X-ray diffraction and studied by photoluminescence excitation and emission spectra. In the emission spectra of  $X_5SiO_4Cl_6:Tb^{3+}$  ( $X = Sr, Ba$ ) phosphor, characteristic blue and green emission peaks are present corresponding to  $Tb^{3+}$  intra  $4f$  transition. Emission spectrum shows a dominant peak at 544 nm due to the  $^5D_4 \rightarrow ^7F_5$  transition of  $Tb^{3+}$ .

**Keywords.** Luminescence; X-ray diffraction; solid state method; phosphor; solid state lighting.

## 1. Introduction

Rare-earth-activated phosphors have attracted much attention for their well-defined transitions within the  $4f$  shell (Blasse 1979). Rare earth (RE) elements have been considered as the most important and promising activators for phosphors due to their emission characteristics in ultraviolet and visible region.  $Tb^{3+}$ -doped materials have been widely used as the green-emitting phosphors due to their intense  $^5D_4 \rightarrow ^7F_5$  emission in the green spectral region.  $Tb^{3+}$  has been widely used as green-emitting activator for luminescent materials and one of its characters is the cross-relaxation represented by the quenching of transitions from  $^5D_3$  to  $^7F_J$  and predominating those from  $^5D_4$  with increase in concentration of  $Tb^{3+}$  (Berdowski *et al* 1985; Van Uitert and Johnson 1966; Zhou *et al* 2008). Recently, halo silicate phosphors have attracted more attention due to their potential applications as highly stable, efficient phosphors with high luminescence efficiency and lower synthesis temperature. Introduction of RE ions as luminescent centres into host matrix has been an improvement in the field of luminescent materials. However, there are only few studies on halosilicate-based material such as  $Ca_3Al_2Si_2O_8Cl_4:Eu^{2+}, Mn^{2+}$  (Xia *et al* 2010),  $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$  (Guo *et al* 2011),  $Ca_3SiO_4Cl_2:Eu^{2+}$  (Zhuang *et al* 2011),  $Ca_2SiO_3C_{12}:Eu^{2+}:Mn^{2+}$  (Ning *et al* 2011),  $Ca_3SiO_4Cl_2:Eu^{2+}$  (Liu *et al* 2005). There are no studies related to  $Tb$ -doped halo silicate material.  $Tb^{3+}$  ion is known to emit visible emission in green region and advantage of using  $Tb^{3+}$  ions is that they exhibit high luminous efficiency under UV excitation in several hosts. The relevant green emission is a key component of the tricolour luminescence. However, to the best of our knowledge,

studies on luminescence properties of  $X_5SiO_4Cl_6:Tb^{3+}$  ( $X = Sr, Ba$ ) phosphors have not been reported. Therefore, special attention has been focused on  $Tb^{3+}$ -doped phosphors. We have synthesized  $X_5SiO_4Cl_6:Tb^{3+}$  ( $X = Sr, Ba$ ) green phosphor by modified solid state method and investigated its photoluminescent characteristics.

## 2. Experimental

Powder samples of  $X_5SiO_4Cl_6:Tb^{3+}$  ( $X = Sr, Ba$ ) with  $Tb$ -doping concentration of 1 mol% were synthesized by the modified solid state method. Starting raw materials used were  $SiO_2$ ,  $BaCO_3$ ,  $SrCO_3$ ,  $BaCl_2$  and  $Tb_4O_7$  (purity,  $\geq 99.99\%$ ). Stoichiometric amounts of corresponding raw materials were thoroughly mixed and ground in an agate mortar. The mixture was preheated at 400 °C for 1 h using porcelain crucibles in air atmosphere. After 1 h of preheating the samples, they were again crushed in an agate mortar. Then these samples were calcined at 800 °C for 18 h in preheated furnace followed by subsequent air-cooling to room temperature. Finally, efficient phosphor was obtained. The prepared host lattice was characterized for phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer ( $CuK\alpha$  radiation) at a scanning step of 0.010, continue time 20 s, in the  $2\theta$  range from 10° to 80°; the average crystallite size was calculated from the broadening of the X-ray line (311) using Scherrer's equation. Photoluminescence measurement of excitation and emission was recorded on Shimadzu RFPC5301 spectrofluorophotometer. The same amount of sample (2 g) was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. All the luminescence properties of the phosphors were studied at room temperature.

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### 3. Results and discussion

#### 3.1 XRD phase analysis

XRD patterns of  $\text{Ba}_5\text{SiO}_4\text{Cl}_6$  are shown in figure 1. XRD peaks of the present host closely matched with the standard JCPDS file no. 00-034-1410. It is found that the main phase does not agree with any available JCPDS file. XRD patterns of  $\text{Sr}_5\text{SiO}_4\text{Cl}_6$  closely matched with the standard JCPDS file no. 00-045-0704, recently we have reported the same method (Yerpude and Dhoble 2012).

#### 3.2 Luminescence of $X_5\text{SiO}_4\text{Cl}_6:\text{Tb}^{3+}$ ( $X = \text{Sr}, \text{Ba}$ )

Excitation spectrum of  $\text{Tb}^{3+}$  singly doped sample,  $\text{Ba}_5\text{SiO}_4\text{Cl}_6$ , is shown in figure 2 and the excitation spectrum of  $\text{Sr}_5\text{SiO}_4\text{Cl}_6:\text{Tb}^{3+}$  is shown in figure 3, by monitoring the emission at 544 nm. Figures 4 and 5 present the emission

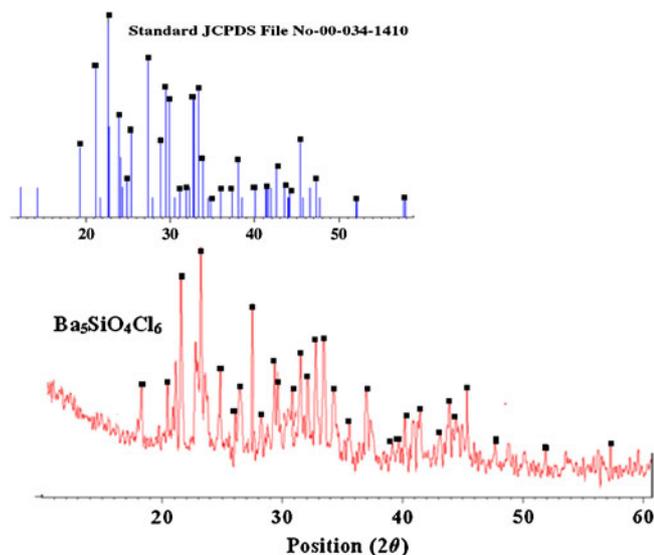


Figure 1. XRD of  $\text{Ba}_5\text{SiO}_4\text{Cl}_6$  host.

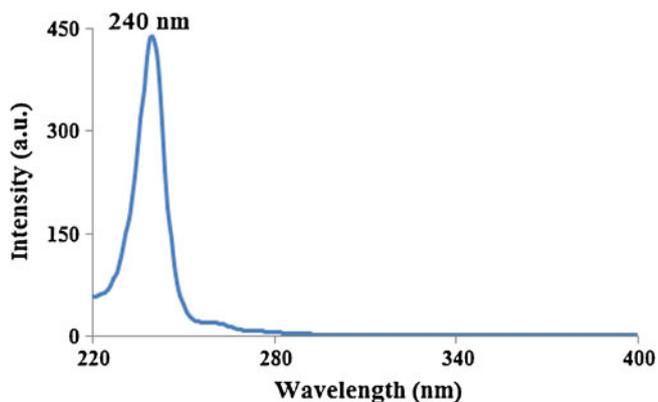


Figure 2. Excitation spectra of  $\text{Ba}_5\text{SiO}_4\text{Cl}_6:\text{Tb}^{3+}$  phosphor.

spectrum of  $\text{Tb}^{3+}$  singly doped phosphor  $\text{Ba}_5\text{SiO}_4\text{Cl}_6$ ,  $\text{Sr}_5\text{SiO}_4\text{Cl}_6$  excited with 240 nm. When the emission wavelength is monitored at 544 nm, the excitation spectrum consists of one band, due to the  $4f^8 \rightarrow 4f^7 5d$  transition ( $f-d$  transition) of  $\text{Tb}^{3+}$  in the shorter wavelength of 240 nm. Similar excitation peak was observed by Li *et al* (2006) at 238 nm due to the  $f-d$  transition of  $\text{Tb}^{3+}$ . This  $f-d$  transition type is allowed according to Laporte's rule (Vij 1998).  $\text{Tb}$ -activated phosphors always show strong  $4f-5d$  transition band absorption around 200–300 nm (Li 2006). Emission spectra consist of many specific relatively narrow

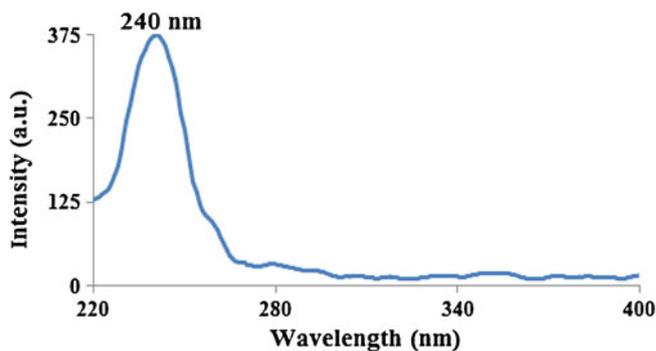


Figure 3. Excitation spectra of  $\text{Sr}_5\text{SiO}_4\text{Cl}_6:\text{Tb}^{3+}$  phosphor.

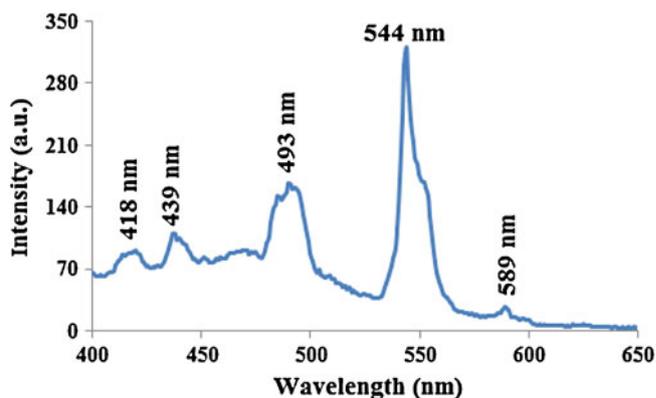


Figure 4. Emission spectra of  $\text{Ba}_5\text{SiO}_4\text{Cl}_6:\text{Tb}^{3+}$  phosphor.

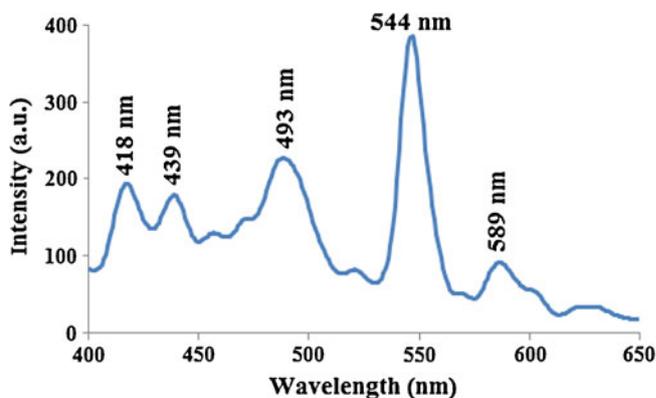
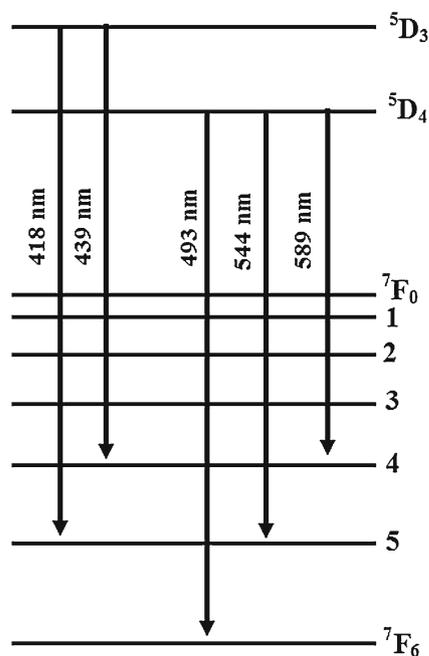


Figure 5. Emission spectra of  $\text{Sr}_5\text{SiO}_4\text{Cl}_6:\text{Tb}^{3+}$  phosphor.



**Figure 6.** Energy-level diagram of  $Tb^{3+}$  showing transitions that produce emission in visible region.

bands that are correlated with some  $4f \rightarrow 4f$  electronic transitions in the activating terbium ions. In the emission spectra of  $X_5SiO_4Cl_6:Tb^{3+}$  ( $X = Sr, Ba$ ) phosphor, characteristic blue and green emission peaks corresponding to  $Tb^{3+}$  intra  $4f$  transitions from the excited levels to lower levels,  $^5D_3 \rightarrow ^7F_J$  ( $J = 4, 5$ ) and  $^5D_4 \rightarrow ^7F_J$  ( $J = 4, 5, 6$ ) transitions, respectively are seen. Emission spectrum of  $Tb^{3+}$  is strongly dependent on  $Tb^{3+}$  concentration. Blue emissions at 419 and 439 nm, ascribed to the  $^5D_3 \rightarrow ^7F_J$  ( $J = 5, 4$ ) transitions occurring at wavelength below 485 nm, were observed at low  $Tb^{3+}$  concentrations. These blue emissions are attributed to the transition from  $^5D_3$  excited state to  $^7F_J$  ground states (Berdowski *et al* 1985). Blue emission was generally found to disappear when  $Tb^{3+}$  concentration is increased beyond the critical concentration for cross-relaxation to occur (Van Uitert and Johnson 1966). Green emission peaks are found at 493, 544 nm (the highest one) and 589 nm, corresponding to the  $^5D_4 \rightarrow ^7F_6$ ,  $^5D_4 \rightarrow ^7F_5$  and  $^5D_4 \rightarrow ^7F_4$  typical transitions of  $Tb^{3+}$  in the host lattice. The strongest  $^5D_4$  to  $^7F_5$  transition due to its largest probability for both electric-dipole and

magnetic-dipole induced transitions make the sample emit intense green light (Lei *et al* 2007). Photoluminescence (PL) results show that  $Sr_5SiO_4Cl_6:Tb^{3+}$  phosphors possess the highest emission intensity. The energy-level diagram of trivalent terbium, with labelled transitions that correspond to observed emission in both the phosphors is shown in figure 6. The main emission band, located at 544 nm, gives rise to the well known intense green luminescence of  $Tb^{3+}$ , which indicates that it could be a good green phosphor candidate for white lamp phosphor.

#### 4. Conclusions

$X_5SiO_4Cl_6:Tb^{3+}$  ( $X = Sr, Ba$ ) phosphors were synthesized by modified solid state method and their luminescent properties were investigated. Green emission from  $^5D_4 \rightarrow ^7F_5$  at 544 nm showed the highest intensity. PL results show that  $Sr_5SiO_4Cl_6:Tb^{3+}$  phosphors possess the highest emission intensity.  $Tb^{3+}$ -activated  $X_5SiO_4Cl_6$  ( $X = Sr, Ba$ ) phosphors having potential application in the field of lamp industry were prepared.

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