Structural and thermoluminescence property of Y$_6$Ba$_4$(SiO$_4$)$_6$F$_2$:Ce,Tb

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Abstract. Present paper reports the synthesis, structural, morphological and thermoluminescence behavior of Y$_6$Ba$_4$(SiO$_4$)$_6$F$_2$:Ce,Tb apatite phosphors prepared by solid state reaction method. X-ray diffraction pattern confirms the formation of Y$_6$Ba$_4$(SiO$_4$)$_6$:Ce,Tb into apatite structure. Morphological study was done by scanning electron microscope (SEM) and it reveals that the prepared phosphors have rod-like structure with different orientation. Energy dispersive spectrooscope (EDX) confirms the presence of initial reactant. Thermoluminescence glow curve of the prepared phosphors were studied and its frequency factors, activation energy, order of kinetics etc are calculated and reported in the present paper.

1. Introduction

Inorganic compounds doped with rare earth ions have wide range of applications in the domain of luminescence like Photoluminescence, Electroluminescence, Cathodoluminescence, thermoluminescence etc. Thermoluminescence (TL) is observed from a material called phosphors [1]. Thermoluminescence arises from a phosphor when it is thermally stimulated subjected to prior irradiation of the phosphor by any form of light energy. Emission of light from the phosphor is due to the trapped charges and energy transfer mechanism. A TL glow curve contains the information regarding the mechanism involved. By analysis of TL glow curve various kinetic parameters are evaluated like order of kinetics (I order, II order or general order), Trap depth, frequency factor etc [2]. For the generation of TL from a phosphor three conditions must be satisfied-(i) Phosphor must be a semiconductor or insulator; metal do not exhibit TL. (ii) Phosphor must have exposed to some form of light energy, which results in the absorbance of this energy. (iii)Finally the TL is observed by heating the phosphors [3,4].

Apatite group of compound have general structural formula A(I)$_{10}$-xA(II)$_{x}$(ZO$_4$)$_6$Q$_2$ with space group P6$_3$/m. There are two distinct crystallographic sites namely 4f and 6h for A(I) and A(II) which are occupied by rare earth, alkali or alkaline. Phosphorous, vanadium, silicon, boron or germanium resides in Z site and Q denotes the anion site. Apatite compound has showed good results for the generation of cathodoluminescence and white LED’s [5–7].

In the past few decades, many researchers have worked on the thermoluminescence phosphors and have reported several phosphors such as potassium fluoride, CaF$_2$,K$_2$YF$_5$, CaSrAl$_2$SiO$_7$, NaBaBO$_3$, K$_2$Ca$_2$(SiO$_4$)$_3$ etc which are used in radiation dosimetry [8–12]. As per our literature survey TL properties of apatite compounds have not been widely explored. This motivated us for the experimental study of the thermoluminescence behaviour of Y$_6$Ba$_4$(SiO$_4$)$_6$F$_2$. 

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2. Experimental

Y$_2$Ba$_6$(SiO$_4$)$_6$F$_2$:0.6Ce,xTb phosphors were synthesized by keeping the ratio of cerium fixed at 0.6mol% whereas doping of terbium ion was taken as 0.2mol%, 0.4mol%, 0.6mol%, 0.8mol% and 1mol% by solid state reaction method. Initial reactant used for synthesis are Y$_2$O$_3$, BaCO$_3$, SiO$_2$, NH$_4$F, CeO$_2$ and Tb$_2$O$_3$. Stoichiometric amount of initial reactant were taken and weighed accordingly with excess amount of NH$_4$F by 50mol% apart from the stoichiometric ratio to compensate the loss of fluorine ion during the synthesis process. By using acetone as a mixing agent all the initial reactant were thoroughly mixed in an agate mortar and pestle for about 30 minutes. After that the mixture were transferred in alumina crucible and kept in a muffle furnace at 1250°C for 4 hours with a heating rate of 5°c/s. The mixture were air cooled and was ground for 35 minutes by using agate mortar and pestle and again kept in a muffle furnace at 1500°C for 5 hours with a heating rate of 5°c/s and cooled naturally to room temperature. The obtained product was ground to make the final product in powder form.

3. Result and discussion

3.1 X-Ray diffraction pattern

"3 kW PANalytical Xpert powder diffractometer” with generator voltage 40kV and tube current 30mA was used to determine the crystal structure and phase purity of the prepared phosphors parameter for XRD graph in 2θ angle range from 20° to 70° with scan step size of 0.1 were taken. La$_6$Ba$_4$(SiO$_4$)$_6$F$_2$ with ICDD card number 98-017-0852 was taken as a reference pattern for matching the obtained XRD pattern [13]. The XRD pattern for undoped Y$_6$Ba$_4$(SiO$_4$)$_6$F$_2$ is shown in figure 1.

![XRD graph](image)

Figure 1. XRD graph.

The lattice parameter and unit cell volume was calculated for Y$_6$Ba$_4$(SiO$_4$)$_6$F$_2$ and Y$_6$Ba$_4$(SiO$_4$)$_6$F$_2$:0.6Ce,0.4Tb from the obtained graph. The lattice parameter for Y$_6$Ba$_4$(SiO$_4$)$_6$F$_2$ and Y$_6$Ba$_4$(SiO$_4$)$_6$F$_2$:0.6Ce,0.4Tb phosphors are a = 3.43Å & c = 5.445Å and a = 4.3Å & c = 6.8Å. Axial ratio for undoped and doped samples are 1.587Å and 1.581Å respectively. There is no significant change in the axial ratio of the prepared phosphors and the Change in the lattice parameter is due to the presence of doping ions. The unit cell volume for undoped and doped phosphors are 55.477Å$^3$ and 108.887Å$^3$ respectively, which shows an increase in the volume of the unit cell due to the presence of cerium and terbium ions. The average crystalline size of the prepared phosphors was calculated from X-ray diffraction pattern by using debye scherrer formula [14] and was found to be 7.9nm for undoped and 11.08nm for Y$_6$Ba$_4$(SiO$_4$)$_6$F$_2$:0.6Ce,0.4Tb. Figure 2 shows the unit cell of Y$_6$Ba$_4$(SiO$_4$)$_6$F$_2$[13,15,16].
3.2 Scanning electron microscopy (SEM)
Zeiss-Oxford SEM analyzer was used to obtain SEM image of the prepared phosphors. The SEM image of the prepared phosphors shows elongated rod-like structure randomly oriented in different direction as shown in figure 3 and the average particle size for \( \text{Y}_6\text{Ba}_4(\text{SiO}_4)_6\text{F}_2:0.6\text{Ce},0.4\text{Tb} \) was calculated and is found to be 34μm.

3.3 Energy Dispersive X-ray spectroscopy (EDX)
EDX spectrums of the prepared phosphors were obtained and the results confirms the present of all initial reactants. Figure 4 shows the EDX spectrum for \( \text{Y}_6\text{Ba}_4(\text{SiO}_4)_6\text{F}_2:0.6\text{Ce},0.4\text{Tb} \).

![Figure 2. Unit cell of \( \text{Y}_6\text{Ba}_4(\text{SiO}_4)_6\text{F}_2 \)](image)

![Figure 3. SEM image of \( \text{Y}_6\text{Ba}_4(\text{SiO}_4)_6\text{F}_2:0.6\text{Ce},0.4\text{Tb} \)](image)

![Figure 4. EDX spectrum.](image)
3.4 Thermoluminescence (TL) study

TL study of the prepared phosphors YBSF:0.6Ce,xTb(x = 0.2,0.4,0.6,0.8 & 1mol%) was carried out by using Thermoluminescence Reader TL 1008 manufactured by Nucleonix system private limited. Samples were exposed to UV light of wavelength 254nm in UV chamber with exposure time of 2 min. Constant heating rate(β) of 3°C/s was kept and samples were heated from room temperature to 450°C with a holding time of 10 second at 450°C. Parameters like activation energy E(eV), order of kinetics(b) etc was calculated by using methods proposed by Chen (Equation 1). Figure 5 represents a TL glow curve and definition of symbol used during the analysis of TL glow curve.

Figure 5. Schematic view of TL glow curve.

Chen’s formula

\[ E = C_\eta \frac{K T_m^2}{\eta} - b_\eta (2 K T_m) \]  
\( \eta = \delta, \tau \) and \( \omega \) (1)

Values of \( C_\delta \), \( C_\tau \), \( C_\omega \), \( b_\delta \), \( b_\tau \) and \( b_\omega \) are obtained by equation given below

\[ C_\delta = 1.51 + 3(\mu_g-0.42) \]  
(2)

\[ C_\tau = 0.976 + 7.3(\mu_g-0.42) \]  
(3)

\[ C_\omega = 2.52 + 10.2(\mu_g-0.42) \]  
(4)

\[ b_\delta = 1.58 + 4.2(\mu_g-0.42) \]  
(5)

\[ b_\tau = 0 \]  
(6)

\[ b_\omega = 1 \]  
(7)

Glow Curve Deconvolution (GCD) method [1,17,18] was used to determine the various parameters of the TL glow curve. YBSF:0.6Ce,0.4Tb and YBSF:0.6,1Tb showed better TL glow curve in comparison to YBSF:0.6Ce,xTb(x=0.2,0.6,0.8mol%). Figure 6 represents the deconvoluted glow curve of \( Y_6\text{Ba}_4(\text{SiO}_4)_6\text{F}_2:0.6\text{Ce},0.4\text{Tb} \) and Table 1 shows its various calculated parameter from chens formula. Figure 7 represents the deconvoluted glow curve of \( Y_6\text{Ba}_4(\text{SiO}_4)_6\text{F}_2:0.6\text{Ce},1\text{Tb} \) and Table 2 shows its various calculated parameter from chens formula. TL glow curve of \( Y_6\text{Ba}_4(\text{SiO}_4)_6\text{F}_2:0.6\text{Ce},0.4\text{Tb} \) and \( Y_6\text{Ba}_4(\text{SiO}_4)_6\text{F}_2:0.6\text{Ce},1\text{Tb} \) shows second order kinetics and the average activation energy calculated are 1.115ev and 0.99ev respectively.
Figure 6. Deconvulated TL glow curve of YBSF:0.6Ce,0.4Tb

Table 1. Parameters of TL glow curve for YBSF:0.6Ce,0.4Tb.

| Peak   | Tm(K)  | T1(K)  | T2(K)  | δ(K)  | ω(K)  | τ(K)  | μg  | γ   | Activation Energy(ev) |
|--------|--------|--------|--------|-------|-------|-------|-----|-----|-----------------------|
| Peak 1 | 365.82 | 340.8  | 394.23 | 28.41 | 53.43 | 25.02 | 0.53| 1.13| 0.71                  |
| Peak 2 | 423.41 | 391.165| 456.91 | 33.5  | 65.745| 32.245| 0.50| 1.03| 0.65                  |
| Peak 3 | 633.42 | 610.13 | 656.29 | 22.87 | 46.16 | 23.29 | 0.49| 0.98| 2.34                  |
| Peak 4 | 638.24 | 575.36 | 701.82 | 63.58 | 126.46| 62.88 | 0.50| 1.01| 0.76                  |

Figure 7. Deconvulated TL glow curve of YBSF:0.6Ce,1Tb.
Table 2. Parameters of TL glow curve for YBSF:0.6Ce,1Tb.

| Peak 1 | Tm(K) | T1(K) | T2(K) | δ(K) | ω(K) | τ(K) | μg | γ    | Activation Energy(ev) |
|--------|-------|-------|-------|------|------|------|-----|------|-----------------------|
|        | 369.462 | 339.13 | 401.23 | 31.77 | 62.1 | 30.33 | 0.51 | 1.04 | 0.565 |
| Peak 2 | 433.01 | 409.91 | 456.57 | 23.56 | 46.66 | 23.1 | 0.50 | 1.01 | 1.08 |
| Peak 3 | 630.79 | 540.47 | 721.11 | 90.32 | 180.64 | 90.32 | 0.5 | 1 | 0.45 |
| Peak 4 | 630.32 | 601.33 | 660.57 | 30.25 | 59.24 | 28.99 | 0.51 | 1.04 | 1.88 |

4. Conclusion

Y$_6$Ba$_2$(SiO$_4$)$_6$F$_2$:0.6Ce,xTb apatite structured phosphors were successfully synthesized by solid state reaction method. Prepared phosphors has rod like structure. TL glow curve of the synthesized sample shows second order kinetics with average activation energy of 1.115ev and 0.99. The prepared phosphors can be used in the field of radiation dosimetry.

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