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Original Research

Sci Vis Vol 13 Issue No 3
July-September 2013
ISSN (print) 0975-6175
ISSN (online) 2229-6026

Thermoluminescence (TL) characteristics of $Ba_{1-x}Ca_xSO_4$:Eu nanophosphor

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Received 22 April 2013 | Revised 17 July 2013 | Accepted 22 July 2013

Abstract

TL phosphor based on $Ba_{1-x}Ca_xSO_4$:Eu (1 at %) ($0 < x < 1$) was prepared using the chemical co-precipitation technique. XRD shows orthorhombic structure. It was found that the TL sensitivity of the material changes on varying the concentration of Ca and maximum sensitivity is found for $Ba_{0.98}Ca_{0.01}SO_4$:$Eu_{.01}$. Moreover, the phosphor had constant glow curve shape over a dose range of 100-1000Gy. The dose response is linear/sub-linear over the dose range 100-500 Gy, above which TL sensitivity saturates.

Key words: Thermoluminescence; dose response; sensitivity; TL; XRD.

Introduction

Sulphate based phosphors, because of its high sensitivity, ease of preparation and stability of response in adverse climates, have already been very popular for use in radiation dosimetry, personnel dosimetry and environmental monitoring.[1-4] $CaSO_4$ is the first one used to measure ionizing radiation in 1895[5]. Studies on thermoluminescence (TL), ESR, photoluminescence (PL) and various display applications of $CaSO_4$:RE (RE = rare earth) under different conditions continue to be an active area of interest.[6-10] $CaSO_4$:Eu is useful in photo gated optical hole-burning studies.[11] It is also highly sensitive to UV-rays. It has been proposed for use in radio-photoluminescence dosimetry.[12] $BaSO_4$ phosphor is another material that is getting more and more attention as useful luminescent host and are suited for many applications. The TL sensitivity of $BaSO_4$:Eu is higher than that of $CaSO_4$:Dy.[13] Okamoto *et al.*[14] developed a very sensitive $BaSO_4$:Eu TL phosphor–based screens for the study of hadronic and electromagnetic cascade showers in ultra-high interactions. Azorin *et al.*[15] suggest that $BaSO_4$:Eu^+ PTFE (polytetrafluoro-ethylene) discs can be used to measure absorbed doses in cases in which lack of quantum equivalence of detector material is without importance.

Numan *et al.*[16] studied the TL properties of

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$BaSO_4$:Eu irradiated with 48MeV Li^{3+} and 150MeV Ag^{12+} ions and found $BaSO_4$:Eu phosphor, a good candidate to be used as a dosimeter for cosmic rays and medical applications. Xiong *et al.*[17] studied the effect of γ-irradiation on structures and luminescent properties of nanocrystalline $MSO_4:Eu_x^{+3}$ (M = Ca, Ba, Sr, x = 0.001-0.005). Lochab *et al.*[18] studied the dosimetric characteristics and determined the kinetic parameters of microcrystalline $BaCaSO_4$:Eu. In our earlier studies, it was reported that when $BaSO_4$ is doped with different concentrations of Eu, $Ba_{0.99}SO_4$: $Eu_{0.01}$ phosphor has the highest TL intensity.[19] The aim of this paper is to report on a new preparation of $Ba_{1-x}Ca_xSO_4:Eu_{.01}$ ($0.01 \leq x \leq 0.07$) phosphor and study their TL characteristics. The TL sensitivity response at different gamma ray dose is also recorded.

Methodology

The $Ba_{1-x}Ca_xSO_4$:Eu thermoluminescence phosphors have been prepared by using the conventional chemical route technique. In this technique, analytical reagent (AR) grade barium chloride ($BaCl_2.2H_2O$), europium chloride, $EuCl_2.2H_2O$ (1 at %) and calcium chloride ($CaCl_2.2H_2O$), mixed in stoichiometric ratio are dissolved in de-ionised water. Ammonium sulphate $(NH_4)_2SO_4$ is added to the solution in the presence of ethanol. The precipitate settled at the bottom of the beaker is collected and washed repeatedly with deionised water. The samples thus obtained are dried at 100°C for 1 hour to remove ethanol and water molecules present in the sample. The samples are further annealed at 600°C for 1hr in a quartz boat.

The formation of all the samples of $Ba_{1-x}Ca_xSO_4:Eu_{.01}$ are confirmed by XRD taken at room temperature using PANalytical X-ray diffractometer with Cu target (Cu-Kα_1 line, λ = 1.5406 Å) having Ni filter. All patterns have been recorded over the angular range $20° \leq 2\theta \leq 80°$ with a step size $\Delta 2\theta = 0.02°$.

The thermoluminescence glow curves of the samples irradiated with γ-rays by using Co^{60}-gamma irradiator have been recorded on the TL recording system (model TL 1404, supplied by Indotherm Instruments Pvt. Ltd., Bombay, India) with linear heating rate of 2.2 K/sec. Samples in powder form are kept directly on the Kanthal heater which facilitates rapid heating and cooling of the system due to its low thermal inertia. The photocathode of the photomultiplier tube (RCA 931A PMT) has an S4 response, which extends from 300-700 nm. A filter holder drawn is located between the heater strip and a PMT, basically to cut- off infrared using quartz filter. The duration between irradiation and TL reading is same for all the samples. The irradiated samples are read out in air at room temperature.

Results and Discussion

XRD results

Fig. 1 shows the X-ray diffraction pattern of the $Ba_{1-x}Ca_xSO_4:Eu_{.01}$ ($0.01 \leq x \leq 0.07$) samples with (hkl) values. All the XRD peaks of the compounds are fitted well with orthorhombic structure of $BaSO_4$ (JCPDS no. 832053). But it is seen in Fig. 1 (b), (c) and (d), there is a peak having (1 2 2) observed at 2θ = 44.82° corresponding to monoclinic structure of $CaSO_4$. The

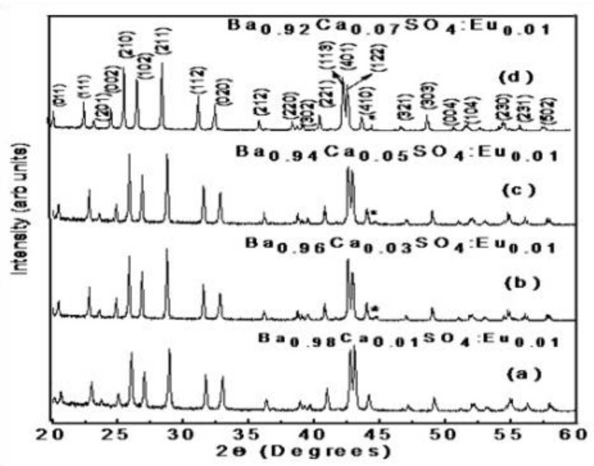

Figure 1. XRD patterns of $Ba_{0.99-x}Ca_xSO_4:Eu_{.01}$ annealed at 600°C with x = 0.01 (a), 0.03 (b), 0.05 (c), 0.07 (d). *Peaks corresponding to $CaSO_4$.

Table1. Crystallite sizes calculated from different XRD peaks of $Ba_{1-x}Ca_xSO_4:Eu_{.01}$ ($0.01 \le x \le 0.07$) phosphors annealed at 600°C for 1 hr.

Sample	D_1 (nm)	D_2 (nm)	D_3 (nm)	D_4 (nm)	D_5 (nm)	D_6 (nm)	D_7 (nm)	D_8 (nm)	D_{avg} (nm)
$Ba_{0.98}Ca_{0.01}SO_4:Eu_{.01}$	73	79	75	71	74	70	69	73	73
$Ba_{0.96}Ca_{0.03}SO_4:Eu_{.01}$	63	66	61	62	68	62	67	66	64
$Ba_{0.94}Ca_{0.05}SO_4:Eu_{.01}$	73	78	66	72	74	75	69	66	72
$Ba_{0.92}Ca_{0.07}SO_4:Eu_{.01}$	89	79	75	89	72	75	74	71	78

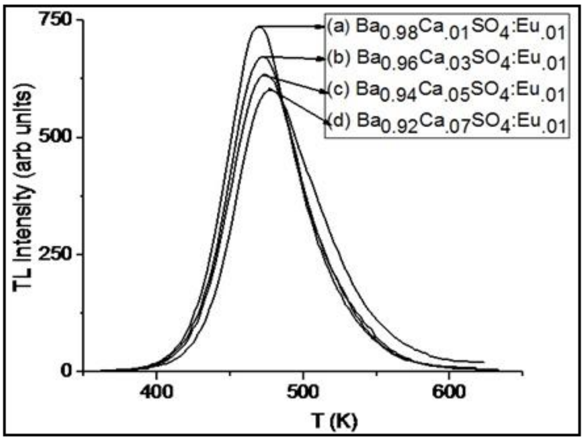

Figure 2. TL glow curves of $Ba_{0.99-x}Ca_xSO_4:Eu_{.01}$ annealed at 600°C and irradiated with 150 Gy.

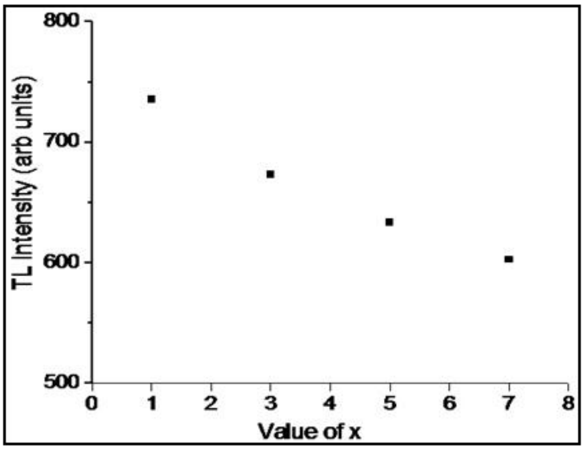

Figure 3. A plot of TL peak intensities with different values of x of $Ba_{0.99-x}Ca_xSO_4:Eu_{.01}$.

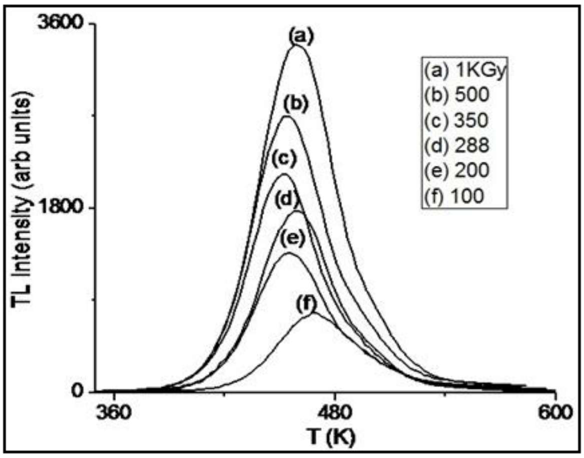

Figure 4. TL glow curves of $Ba_{0.98}Ca_{0.01}SO_4:Eu_{0.01}$ irradiated with different doses of γ –rays.

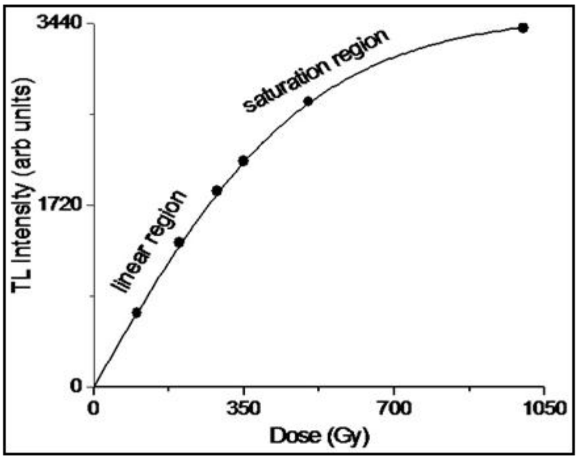

Figure 5. TL response of $Ba_{0.98}Ca_{0.01}SO_4:Eu_{.01}$.

crystallite sizes, calculated using the Scherrer relation for the crystalline samples are in the range 64 to 78 nm. Sample sizes of the phosphors calculated from different XRD peaks are shown in Table 1.

Thermoluminescence study

***Characteristics of thermoluminescence (TL) glow curves of** $Ba_{1-x}Ca_xSO_4$:$Eu_{.01}$* : Fig. 2 shows the TL glow curves of $BaCaSO_4$:Eu with Eu = 1 at % and different concentrations of Ba and Ca, annealed at 600 °C for 1 hr and irradiated with 150 Gy of γ-rays. The glow curves have similar shape but with different peak intensities and peak temperature. The most intense TL glow curve with peak temperature 470 K corresponds to the TL phosphor with x = 0.01. With increasing the concentration of Ca the TL sensitivity is found decreasing. There is a systematic shifting of peak temperature towards higher temperature with the increase of Ca concentration. The peak temperatures of the phosphor with Ca concentrations 3, 5 and 7 at % are 472, 474 and 477 K respectively. The phosphor $Ba_{0.96}SO_4$:$Eu_{0.02}$,$Dy_{0.02}$ having the highest TL intensity is selected for further investigation.

TL glow curves of $Ba_{0.98}Ca_{0.01}SO_4$:$Eu_{0.01}$ phosphor annealed at 600°C and exposed to different doses of γ-rays ranging from 100-1000 Gy are shown in Fig. 4. As expected, there is increase in thermoluminescence intensity with the increase of gamma doses.

It is observed that over this range, the TL glow curves have the same structure but the peak temperatures are slightly different. The TL response as a function of the absorbed dose was obtained using a Co^{60} source and the result is shown in Fig. 5.

Conclusion

It can be concluded that the prepared $Ba_{0.99-x}Ca_xSO_4$:$Eu_{.01}$ ($0.01 \leq x \leq 0.07$) samples have orthorhombic structure of $BaSO_4$ with monoclinic structure of $CaSO_4$ for the samples with x = 0.03, 0.05, 0.07. The crystallite size of the samples ranges from 64 to 78 nm. For x = 0.01 the phosphor shows the maximum TL sensitivity. It has a linear/sublinear response only up to 350 Gy. So, this phosphor is suitable for TL dosimetry of low doses.

Acknowledgement

One of the authors, Y Rangeela Devi is thankful to Vice Chancellor, MZU and Principal, Pachhunga University College, Aizawl for giving one year study leave under FIP (No. 8-83/Estt.I/07/12744-47).

References

1. Lakshmanan AR (1999). Photoluminescence and thermoluminescence processes in rare earth doped $CaSO_4$ phosphors. *Prog Mater Sci*, **44**, 1-187.
2. Kim JL, Chang SY & Kim BH (1999). IAEA/RCA Personal dosemeter intercomparison results for the KAERI TLD system. *Radiat Prot Dosim,* **85**, 153-157.
3. Vohra KG, Bhatt RC, Bhuwan C, Pradhan AS, Lakshmanan AR & Shashtry SS (1980). A personnel dosimeter TLD badge based on CaSO4: Dy teflon TLD discs. *Health Phys,* **38**, 193-197.
4. Dixon RL & Ekstrand KE, 1974. Thermoluminescence of $SrSO_4$:Dy and $BaSO_4$:Dy. *Phys Med Biol*, **19,** 196-205.
5. Wiedemann E & Schmidt GC (1895). Thermoluminescence induced by electron beams in alkali halides. *Ann Phys Chem*, **54,** 604-625.
6. Danby RJ, Keith H, Manson NB (1988). Transient and photon-gated persistent spectral hole burning in $CaSO_4$:Sm. *J Lumin*, **42,** 83-88.
7. Bakshi AK, Patwe SJ, Bhide MK, Sanyal B, Natarajan V, Tyagi AK & Kher RK (2008). Thermoluminescence, ESR and x-ray diffraction studies of CaSO4 :Dy phosphor subjected to post preparation high temperature thermal treatment. *J Phys D: Appl Phy,* **41** (025402), 1-8.
8. Lakshmanan AR, Kim SB, Kum BG, Jang HM & Kang BK (2006). Rare earth doped CaSO4 luminescence phosphors for applications in novel displays – new recipes. *Phys Stat Sol (a),* **203**, 565-577.
9. Lakshmanan AR (2001). A new high sensitive $CaSO_4$:Dy thermostimulated luminescence phosphor. *Phys Stat Sol (a),* **186**, 153-166.
10. Nambi KSV, Bapat VN & Ganguly AK (1974). Thermoluminescence of $CaSO_4$, doped with rare earths. *J Phys C: Solid State Phys*, **7**, 4403-4415.
11. Lenth W & Moerner WE (1986). Gated spectral hole-

burning for frequency-domain optical-recording. *Opt Commun*, **58**, 249-254.

12. Danby RJ (1983). ESR of Eu^{2+} in X-irradiated $CaSO_4:Eu^{3+}$. *J Phys C,* **16**, 3573-3578.
13. Madhusoodanan U, Jose MT & Lakshmanan AR (1999). Development of $BaSO_4$:Eu thermoluminescence phosphors. *Radiat Meas*, **30,** 65-72.
14. Okamoto Y, Kawaguchi S, Kino S, Mino S, Kitijima T, Misaki A & Saito T (1986). Thermoluminescent sheets for the detection of high energy hadronic and electromagnetic showers. *Nucl Instrum Meth A,* **243**, 219-224.
15. Azorin J, Furetta C, Gutierrez A & Gonzales P (1991). *Appl Radiat Isot Int J Radiat Appl Instrum A,* **42(9),** 861-863.
16. Numan S, Lochab SP, Kanjilal D, Jyoti M, Sahare PD, Ranju R, Rupasov AA & Aleynikov VE (2008). Thermoluminescence of $BaSO_4$:Eu irradiated with 48 MeV Li^{+3} and 150 MeV Ag^{+12} ions. *J Phys D: Appl Phys,* **41** (085408) 1-6.
17. Xiong G, Pengfei W, Wai KC & Engju C (2000). Effect of γ-irradiation on structures and luminescent properties of nanocrystalline $MSO_4:Eu_x^{+3}$ (M = Ca, Ba, Sr, x = 0.001 -0.005). *J Phys Chem Solids*, **61**, 115-121.
18. Lochab S P, Sahare P D, Chauhan R S, Numan S & Pandey A (2006). Thermoluminescence and photoluminescence study of $Ba_{0.97}Ca_{0.03}SO_4$:Eu. *J Phys D: Appl Phys,* **39,** 1786-1792
19. Rangeela Y D & Doredrajit S S (2012). Synthesis and TL glow curve analysis of $BaSO_4$:Eu,Dy phosphor. *J Luminescence*, **132,** 1575-1580.

