Study of Thermoluminescence Dosimetric Properties of Submicron $BaSO_4$ Phosphor

M. S. Nikam[1,a], Y.K. More[2], S. P. Wankhede[3], Sharmila Bhonsule[4], S. B. Kondawar[1] Milind Jog[5] and S. V. Moharil[1]

[1]*Department of Physics, R. T. M. Nagpur University, Nagpur, 440033, India.*
[2] *Department of Physics, Bhiwapur Mahavidyalaya, Bhiwapur 441201, India.*
[3] *Department of Physics, K.D.K. College of Engineering, Nagpur, 440009, India.*
[4] *Department of Physics, Priyadarshani College of Engineering, Nagpur, 440019, India.*
[5] *Department of Physics, Kirti M. Doongursee College, Dadar (West), Mumbai 400028, India.*

[a] minakshinikam58@gmail.com

Abstract: Dosimetric properties of submicron $BaSO_4$:Eu phosphor have been studied. Top down approach (ball billing) has been adopted to reduce the grain size of the material to submicron level. Phosphor showed good thermoluminescence (TL) properties. The TL properties of the phosphor were altered due to the particle size reduction on ball milling. Ball milling affected the kinetics of TL Processes. TL dose response of the phosphor has been linearly increased upto 4 kGy on ball milling which makes it useful in high dose dosimetric applications.

INTRODUCTION

Rare earth doped $BaSO_4$ was firstly reported by Dixon et al in 1974 [1]. Out of several doped samples, intense thermoluminescence (TL) was observed in Tb and Eu doped samples. Yamashita et al. [2] and other researchers [3,4] also studied thermoluminescence and photoluminescence (PL) of Eu doped $BaSO_4$. They confirmed that Eu enters $BaSO_4$ lattice in Eu^{2+} state. TL emission spectra in these samples are similar to PL spectra of Eu^{2+} which indicates that Eu^{2+} acts as a center for emission in TL process**.** Atone et al. [5] made $BaSO_4$:Eu by co-precipitation method and annealed the precipitate at 973 K in air. The TL peak was observed at 450 K but its sensitivity to gamma rays was found to be 3.5 times less than that of $CaSO_4$:Dy. Shinde et al. synthesized and characterized $BaSO_4$:Eu,P phosphor as highly sensitive TL dosimeter [6]. $BaSO_4$: Eu phosphor was also developed by Madhusoodanan et al. [7, 8] using co-precipitation technique and solid state reaction with TL sensitivity higher than that of $CaSO_4$: Dy. However the sample exhibited fading due to presence of lower temperature peak. Recently Bhatt and et al. [9] reported the thermoluminescence and optically stimulated luminescence (OSL) of $BaSO_4$:Eu. P.R. González et al. [10] reported the thermoluminescence properties of Eu doped $BaSO_4$ at different concentrations. They have also investigated the kinetic parameters such as activation energy, the frequency factor, the pre-exponential factor and the kinetic order by initial-rise and deconvolution methods. Kinetic parameters of the TL curve of $BaSO_4$ doped with Eu and Dy were also investigated by Y. Rangeela Devi and Dorendrajit Singh using computerized glow curve deconvolution (CGCD) method [11].

Nanoparticles of $BaSO_4$:Eu with grain size in the range of 30–50 nm were prepared by Numan Salah et al [12] by the chemical co-precipitation method. Thermoluminescence glow curve of these $BaSO_4$:Eu nanoparticles was studied and found to exhibit a linear/sublinear TL response to gamma radiation over a very wide range of exposures.

In this work efforts were made to increase the dose linearity of the phosphor to the wide dose range of gamma exposure. For this a top down approach (ball milling) was employed to reduce the size of the material to submicron level. The TL results on submicron Eu doped $BaSO_4$ phosphor are reported. We investigated that the linearity of dose

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response for submicron Eu doped $BaSO_4$ phosphor has been increased, hence this phosphor can be prove promising candidate for high dose dosimetry.

EXPERIMENTAL

The $BaSO_4$:Eu phosphor was synthesized using recrystallization method. In this case GR grade $BaCl_2$ dissolved in double distilled water was taken in a beaker. Stoichiometric amount of Eu_2O_3 was dissolved in nitric acid and added to $BaCl_2$ solution. The entire solution was then transferred to the flask containing excess amount of distilled H_2SO_4. The solution was then allowed to evaporate slowly in acid distillation plant. The powder thus obtained was washed thoroughly with double distilled water and dried under lamp. The dried powder was then annealed at 850 ^{0}C in air and quenched to room temperature. This sample was referred as bulk sample. The Eu concentration was optimized to 0.5 mol%. Eu incorporated in the lattice in Eu^{2+} form which was confirmed from the PL study of the phosphor. The top down approach was employed for particle size reduction to the submicron level using high energy planetary ball mill (RETSCH GmbH Germany make). The bulk material thus obtained was dry ball milled with 10 mm zirconium balls for 8 hours. The mass of balls was taken in the ratio of 25:1 g of the phosphor. Particle size analysis was carried out on Master sizer 2000 E particle size analyzer with water as a dispersant.

The thermoluminescence study of the phosphor was carried out on PC controlled TL reader system [Polltech TL Reader (Model PSI-TLD1)]. It is equipped with PM tube EMI6255S with S11 response. HA3 (Chance Pilkington) infra-red filter was used in this setup in order to reduce the thermal noise to a considerable extent.

The OSL measurements were carried out on PC Controlled TL/OSL Reader (TL/OSL 1008) manufactured by Nucleonix systems fitted with Blue LEDs cluster, each of 3 watt output placed 180 degrees opposite which gives stimulation output with peak wavelength emission of 465 nm, having Luminous flux radiometric power of 30 mW & emission wave length band ranging from 460 to 470 nm. ^{60}Co source was used for irradiating the samples.

RESULTS AND DISCUSSION

After 8 hours of dry ball milling, the particle size of the phosphor was found to be reduced to 3-10 μm with an average grain size of 5 μm which was confirmed by particle size analysis (Figure 1). Figure 1a shows the SEM images of the sample ball milled for 8 hrs. From figure it can be seen that the particle size was uniformly reduced to submicron range. This fact was well supported by the particle size distribution of the phosphor (figure 1 b).

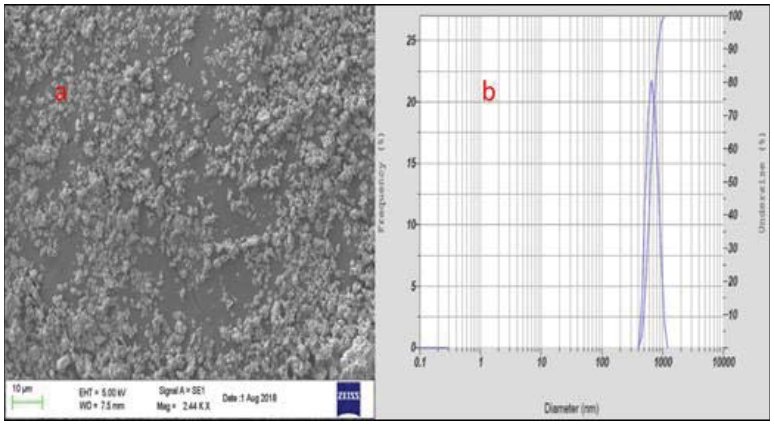

FIGURE 1. a) SEM image and b) Particle size distribution of the ball milled $BaSO_4$:Eu phosphor

The phase purity of the $BaSO_4$ samples was confirmed from the XRD patterns obtained using Cu Kα x-rays with wavelength 1.5046 Å. The XRD patterns of the bulk and ball milled samples were compared with the ICDD data 83-2053. From the results it is clear that ball milling does not modify the host lattice structure or even the phase of the material. From XRD data it was observed that both the samples belongs to orthorhombic system with a=8.884, b= 5.455 and c= 7.156.

The thermoluminescence glow curves of the bulk and submicron phosphors were recorded at the heating rate of 5º C/s for the gamma dose of 25 Gy. The TL intensities were normalized for 1 mg of the phosphor. Figure 2 shows

the comparative TL spectra of the bulk and submicron samples. For bulk sample broad TL glow curve was obtained. The glow peak for bulk sample was observed at 200 ºC with a prominent shoulder at 225 ºC and a sub-shoulder at 295 ºC. On ball milling, glow peak structure for the phosphor was found to be altered. A sharp glow peak was observed at 170 ºC. The TL intensity in the phosphor was drastically reduced in ball milled sample. The TL intensity in ball milled sample was only 1.5 % of the bulk sample. This may be due to the surface accommodation of the charge carriers. The particle size reduction causes the energy level modification by converting deep traps into shallow traps which led to the change in glow peak structure and shifting glow peak temperature from 200 ºC to 170 ºC.

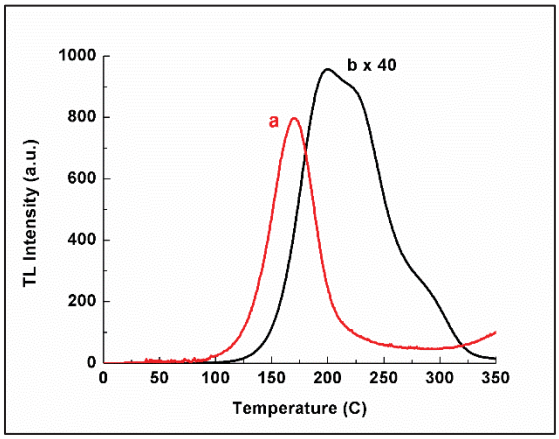

FIGURE 2. TL glow curves of (b) Bulk and (a) ball milled $BaSO_4$:Eu phosphor for a gamma dose of 25 Gy.

Ball milling also affected the kinetics of TL Process. Figure 3 shows the de-convoluted TL glow curves for the bulk and ball milled phosphors. The deconvolution was done by using glow-fit software [13]. From figure it is clear that ball milling affected the TL glow curve structure and modified the TL components originating from different trap levels. The glow curve (figure 3a) for Bulk sample was exactly fitted with three components at 194 ºC, 229 ºC and 264 ºC, however after ball milling the glow peak structure (figure 3b) was modified and exactly fitted with three components at 156 ºC, 170 ºC and 191ºC. Parameters for different components are listed in table 1.

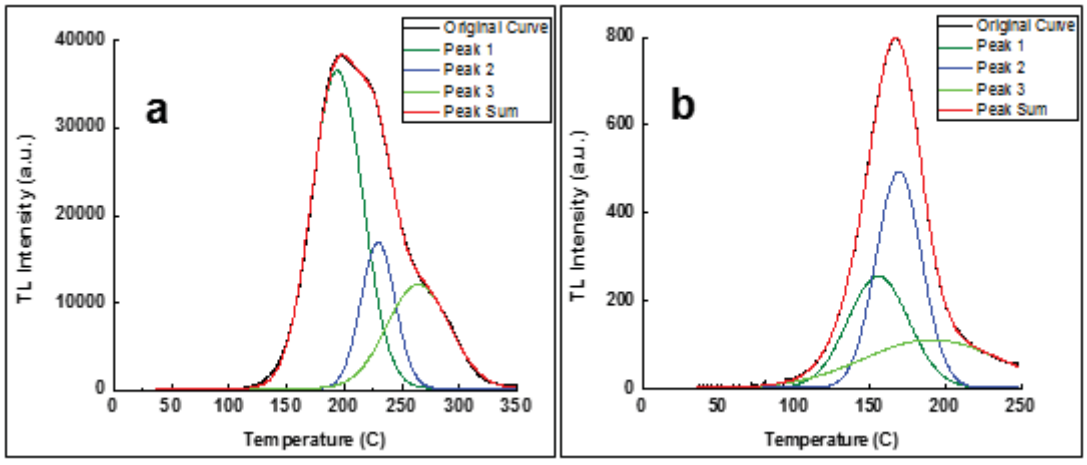

FIGURE 3. de-convoluted TL glow curves for the (a) bulk and (b) ball milled $BaSO_4$:Eu phosphors along with fitted components

From table 1, it is seen that the contribution of 194 ºC peak in bulk sample was about 57% of the total TL while the contributions of 229ºC and 264 ºC peaks were19% and 24% respectively. However in ball milled sample the contribution by almost all components is more or less equal. The contribution of 156 ºC peak was 29% while that

of 170 ºC and 191 ºC peaks was 43% and 28% respectively. This indicates that in both the samples TL was originated from different trap levels. However in bulk sample most of the TL was contributed by 229ºC component while in ball milled sample that was mostly contributed by 170 ºC peak confirming the transfer of charge carriers from deep to shallow traps on ball milling.

TABLE 1. TL deconvolution parameters for different components

Sample	Peak	Total Integral area (a.u.)	Integral Area (a.u.)	Peak Temperature (C)	FWHM	Peak Height (a.u.)	COD (R^2)	FOM (%)
Bulk Sample	1	3512912	2017191	194	44.19	36417.19	0.99966	2.09
	2		621451	229	29.62	16741.71		
	3		812969	264	54.38	11928.56		
Ball milled Sample	1	43208	12761	156	40.28	252.76	0.99988	0.92
	2		18562	170	30.17	490.81		
	3		12240	191	89.70	108.87		

Figure of merit (FOM) for the deconvolution was calculated using formula

$$FOM(\%) = \frac{\sum_i \left| y_{peaksum} - y_{exp} \right|}{\sum_i y_{peaksum}} \times 100 \quad (1)$$

Where $y_{peak\ sum}$ = fitted TL intensity coordinates of peak sum and y_{exp}= experimental TL intensity coordinates. The FOMs for TL deconvolution of bulk and ball milled sample were found to be 2.09 % and 0.92 % respectively which ensures the quality of fitting.

TL dose response of the phosphor was studied for the high doses of ^{60}Co gamma radiation as shown in figure 5. The bulk sample show linear dose response up to 500 Gy however in ball milled sample the dose response was found to be linear up to 4 kGy.

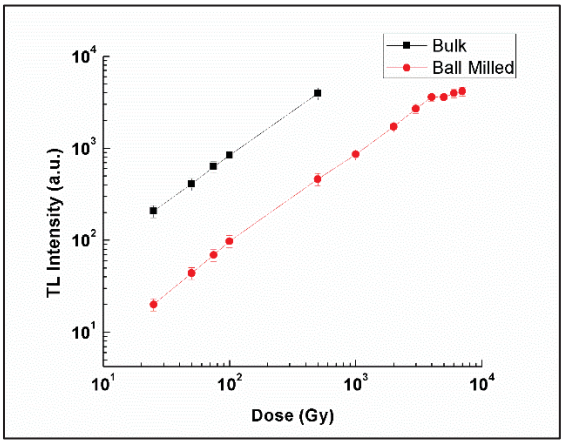

FIGURE 4. TL dose response plot of Bulk and Ball milled $BaSO_4$:Eu phosphor.

Minimum detectable dose in the ball milled samples was measured. For this background counts of the sample were recorded for six times. The mean deviation σ in the measurement was calculated. The phosphor was then exposed

to 25 Gy and the TL response of the sample was recorded. The minimum detectable dose for the phosphor was found to be 29 mGy. However for bulk sample, the minimum detectable dose was of the order of 10-100 μGy.

CONCLUSIONS

TL properties of the submicron $BaSO_4:Eu^{2+}$ phosphor were studied. The phosphor shows good TL response for gamma irradiation. TL properties of the phosphor were altered due to the particle size reduction on ball milling. The TL sensitivity of the phosphor was reduced drastically in ball milled sample. The TL intensities in ball milled sample were 1.5% of the TL intensities in bulk sample respectively. This may be due to the surface accommodation of the charge carriers.

Ball milling affected the kinetics of TL Processes. Ball milling also modified the TL components originating from different trap levels. In both bulk and ball milled samples, the TL glow curves were exactly fitted with three components. This indicates that in both the samples TL was originated from different trap levels. In bulk sample, most of the TL was contributed by 194°C peak (57 %) while the contribution of 229 °C and 264 °C peaks were19% and 24% respectively however in ball milled sample that was mostly contributed by 170 °C peak confirming the transfer of charge carriers from deep to shallow traps on ball milling. The TL dose response for gamma irradiation was studied in both the samples for the dose range from 25 Gy to 7 kGy. In bulk sample, TL dose response was observed to be linear up to 500 Gy which was increased up to 4 kGy after ball milling. Hence from the results so obtained, it is concluded that $BaSO_4$:Eu is the potential candidate which can be used as a dosimetric tool. On ball milling the dose response of the phosphor enhanced to higher doses in kGy range which makes it useful in high dose dosimetric applications.

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