Nanoparticles of $BaSO_4$:Eu as detectors for high doses of different ionizing radiations

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ABSTRACT

Nanoparticles of $BaSO_4$:Eu phosphor with a particle size of around 40 nm have been irradiated by 48 MeV $^7Li^{3+}$, 75 MeV C^{6+} and 90 MeV O^{7+} ion beams at the fluence range 1×10^9-1×10^{13} ions/cm^2. Thermoluminescence (TL) glow curves of the irradiated samples were recorded and studied. The microcrystalline form of this sample is included in the study with the aim of reporting a comparative measurement. TL results of this material in its nano and microforms exposed to gamma rays of ^{60}Co are also included and investigated in more details. The TL analysis shows that the glow curves of the nanomaterial exposed to these ions are similar to that exposed to gamma rays with a dosimetric peak at 462 K beside a smaller one at 503 K, while those of the microcrystalline sample exposed to both ion beams and gamma rays have their prominent peak at 503 K beside a smaller one at 462 K. The observed TL sensitivity of the prepared nanocrystalline material is less than that of the microcrystalline sample at low fluences/doses, while it is more at higher fluences/doses. This nanophosphor exhibits a linear/sublinear TL response to energetic ions and gamma radiation over a very wide range of exposures, which is much wider comparing to that of the microcrystalline counterpart. This response over a large span of exposures makes the nanostructure form of $BaSO_4$:Eu useful for its application to estimate the high doses of different ionizing radiations that are in use for radiotherapy or food/seed irradiation.

1. INTRODUCTION

Thermoluminescence (TL) is a powerful technique used for estimations of doses of high-energy ionizing radiations as the energy absorbed during irradiation and the TL intensity on stimulation (heating) is proportional to the radiation flux (doses). There are a number of commercially available thermoluminesent dosimeters (TLD) for this purpose [Fox, 1988; Noh, 2001]. However, efforts are still being made to improve the TL characteristics of these materials by preparing them using different techniques.

Recently, heavy ion beams have been used for diagnostic and therapeutic purposes [Barth, 2003; Strehl, 1999]. The treatment with highly energetic ion beams has several advantages in comparison with the conventional irradiation with photons. The physical advantage is significantly more favorable dose deposition profile. Whereas with conventional irradiation the dose deposition decreases in proportion to the penetration depth, with ion beams it gradually increases, and then declines rapidly beyond a sharply defined maximum known as the Bragg Peak near the end of range of ion beam. However, the fluences of energetic ions need to be measured with great precision and accuracy while dealing with human beings. Moreover, cosmic rays span a very wide range of energies (keV to GeV) and include light charged particles such as electrons and protons as well as heavy charged particles (HCP). They constitute a serious dosimetric problem, particularly high-energy particle radiation, near the low earth orbit, where the components used in various subsystems of the spacecraft get exposed to such radiation. These have triggered detailed investigations of suitable thermoluminescent dosimeters (TLD) for dose verification in heavy ion irradiation.

Currently, nanotechnology and nanomaterials have attracted several researchers from different fields [Nalwa, 2000], especially from the field of luminescence. It has been found that the physical properties of individual nanoparticles can be very different from those of their bulk counterparts. Recent studies on different luminescent nanomaterials have showed that they have a potential application in dosimetry of ionizing radiations for the measurements of high doses using TL technique, where the conventional microcrystalline phosphors saturate [Salah, 2006a; 2006b; Sahare, 2007; Lochab, 2007a; 2007b]. This saturation occurs due to the ionised zones overlapping each other in the micromaterial at higher doses. However, with the use of very tiny particles such as nanoscale TLD materials, this problem is overcome to a major extent [Salah, 2006a; 2006b; Sahare, 2007; Lochab, 2007a; 2007b]. The TL results of the reported nanomaterials have revealed very imperative characteristics such as high sensitivity and saturation at very high doses. This has encouraged us to study further the TL response of nanocrystalline $BaSO_4$:Eu to different ionizing radiations such as heavy charged particles (HCP) as its microcrystalline form has showed excellent TL performance for measuring the gamma-rays exposures [Madhusoodanan, 1999].

There are several studies on microcrystalline $BaSO_4$:Eu for its TL [Madhusoodanan, 1999; Dixon, 1974; Gupta, 1974; Gundu Rao, 1995; Bhatt, 1997]. However, the TL response of $BaSO_4$:Eu nanoparticles to HCP has not been reported. In this work, the nanostructure form of $BaSO_4$:Eu was prepared by the chemical co-precipitation method and irradiated by 48 MeV $^7Li^{3+}$, 75 MeV C^{6+} and 90 MeV O^{7+} ion beams at the fluence range 1×10^9-1×10^{13} ions/cm^2. The microcrystalline form of this sample is also included in the study with the aim of reporting a comparative measurement. Thermoluminescence (TL) glow curves of the irradiated samples were recorded and studied. The TL results of

this sample in its nano and microforms exposed to ^{60}Co gamma rays are also included here and investigated in more details.

2. EXPERIMENTAL

The nanocrystalline form of $BaSO_4$:Eu was prepared by the chemical co-precipitation method. In this method analytical reagent (AR) grade Barium chloride ($BaCl_2$) was dissolved in triply distilled water. Europium chloride ($EuCl_3$) of AR grade (0.2 mol %) was then added to the solution. The solution was then mixed with ammonium sulfate ($(NH_4)_2SO_4$) solution stoichiometrically in the presence of ethanol. Ammonium sulfate was added drop wise to the solution until the precipitation was complete. The precipitate was filtered out and washed several times with distilled water. The nanophosphor was finally obtained by drying the precipitate at 363 K for 2 h. The nanocrystalline powder thus obtained was further annealed in a quartz crucible at 1123 K for 1 hour in Argon atmosphere. Microcystalline powder of $BaSO_4$:Eu sample was prepared by the same method adopted by Madhusoodanan *et al* (1999).

The shape and size of the prepared nanocrystalline powder materials were determined by the scanning electron microscope (SEM). SEM images were obtained, on JEOL, JSM-6360LV scanning electron microscope. To confirm the formation of the compound, XRD was studied at room temperature for the nanocrystalline samples by using Cu-target (Cu-Kα1 line, λ = 1.5045 Å) on Philips-X'Pert Model-98 XRD machine and matched with the standard data available (JCPDS card No. 24-1035).

Pellets form of $BaSO_4$:Eu nanoparticles of approximately 0.6 mm thickness and 1 cm diameter were prepared by taking ~ 50 mg of the nanocrystalline sample, putting in a die and applying ~ 0.1 ton/cm^2 pressures each time by a hydraulic press. These pellets were exposed to 48 MeV $^7Li^{3+}$, 75 MeV C^{6+} and 90 MeV O^{7+} ion beams at the fluence range 1×10^9-1×10^{13} ions/cm^2 using a 16 MV Tandem Van de Graaff type Electrostatic Accelerator (15 UD Pelletron) at the Inter-University Accelerator Center (IUAC), New Delhi, India. The full details of this set up are given by Kanjilal *et al* (1993). The dose rate for 48 MeV ^{7}Li ions was 18.75×10^9 particle/sec. The detailed procedure for sample irradiation is similar to that given by Salah *et al* (2007). For taking TL the irradiated surface of the pellet was kept facing upwards towards the detector (PMT) of the TLD reader. TL glow curves were recorded using a Harshow TLD reader (Model 3500). The heating rate was 5 Ks^{-1}. The obtained nanoparticles were also irradiated with different doses of ^{60}Co gamma-rays, ranging from 0.1 Gy to 14.5 kGy at room temperature.

3. RESULTS

3.1 Particle size

The shape and size of the prepared $BaSO_4$:Eu nanocrystalline powder were determined by the scanning electron microscope (SEM). SEM image given in the inset of figure 1 shows particles of semispherical shape with grain size in the range 30-50 nm (The average is 40 nm). Formation of $BaSO_4$:Eu compound was confirmed by studying the X-ray diffraction (XRD) pattern (inset of figure 1). These diffracted peaks are in agreement with the JCPDS card for $BaSO_4$ (JCPDS card No. 24-1035).

The XRD pattern is fitted well with the orthorhombic structure of $BaSO_4$. Moreover, there are a considerable broadenings in the X-ray diffraction lines, which are due to the reduction in the grains sizes.

3.2 TL glow curves

Figure 1 shows typical TL glow curves of $BaSO_4$:Eu nanocrystalline powder exposed to 1×10^{10} ions/cm^2 of 48 MeV $^7Li^{3+}$, 75 MeV C^{6+} and 90 MeV O^{7+} ion beams (curves a, b and c, respectively). Glow curve of the nanomaterial exposed to 10 Gy of ^{60}Co gamma rays is also shown in this figure (curve d). Moreover, TL glow curves of the microcrystalline form of this sample irradiated by10 Gy of ^{60}Co gamma rays and1×10^{10} ions/cm^2 of 90 MeV O^{7+} ion beam are also given for comparison (curves e and f, respectively). As can be seen in this figure that the glow curves of the nanomaterial exposed to these ions are similar to that exposed to gamma rays with a dosimetric peak at 462 K beside a smaller one at 503 K, while those of the microcrystalline sample exposed to both ion beams and gamma rays (curves e and f, respectively) have their prominent peak at 503 K along with a smaller one at 462 K. The TL intensity of the ion beams irradiated nanomaterials is found to decrease, while going from low to high atomic number (Z) ions (i.e., $Li^{3+}\rightarrow O^{7+}$). The observed TL sensitivity of the prepared nanocrystalline powder is less than that of the microcrystalline sample at low fluences/doses, while it is more at higher fluences/doses.

3.3 TL response

The TL response curves of the $BaSO_4$:Eu nano and microcrystalline samples exposed to different fluences of 48 MeV $^7Li^{3+}$, 75 MeV C^{6+} and 90 MeV O^{7+} ion beams are given in figure 2 (curves a, b, c and d). The same for the samples exposed to different doses of ^{60}Co gamma rays are also shown in the inset. The peak heights were used for measuring the TL intensities. On exposing the nanophosphor to a wide range of gamma ray doses it is found that it exhibits a linear/sublinear response over a very wide range 0.1 Gy–7 KGy, whereas its corresponding microphosphor has a linear range only from 0.1 to 10 Gy. Beyond 7 KGy the nanophosphor shows saturation of TL. Similarly the TL response curves of the ion beams irradiated nanophosphor samples show linear behaviours in a wider range (curve a, b and c) than the corresponding microcrystalline sample (curve d). The response curves of the nanomaterials are linear in the fluence range1×10^9 -1×10^{12} ions/cm^2, then they show saturation, while that of the microphosphor is linear only in the range 1×10^9-1×10^{10} ions/cm^2, then it becomes sublinear in the range1×10^{10} -1×10^{12} ions/cm^2 and finally the TL intensity goes down at higher fluences. These are remarkable results for the nanomaterial to be used as a dosimeter for measuring the high doses/fluences of different ionizing radiations such as gamma rays and energetic ion beams.

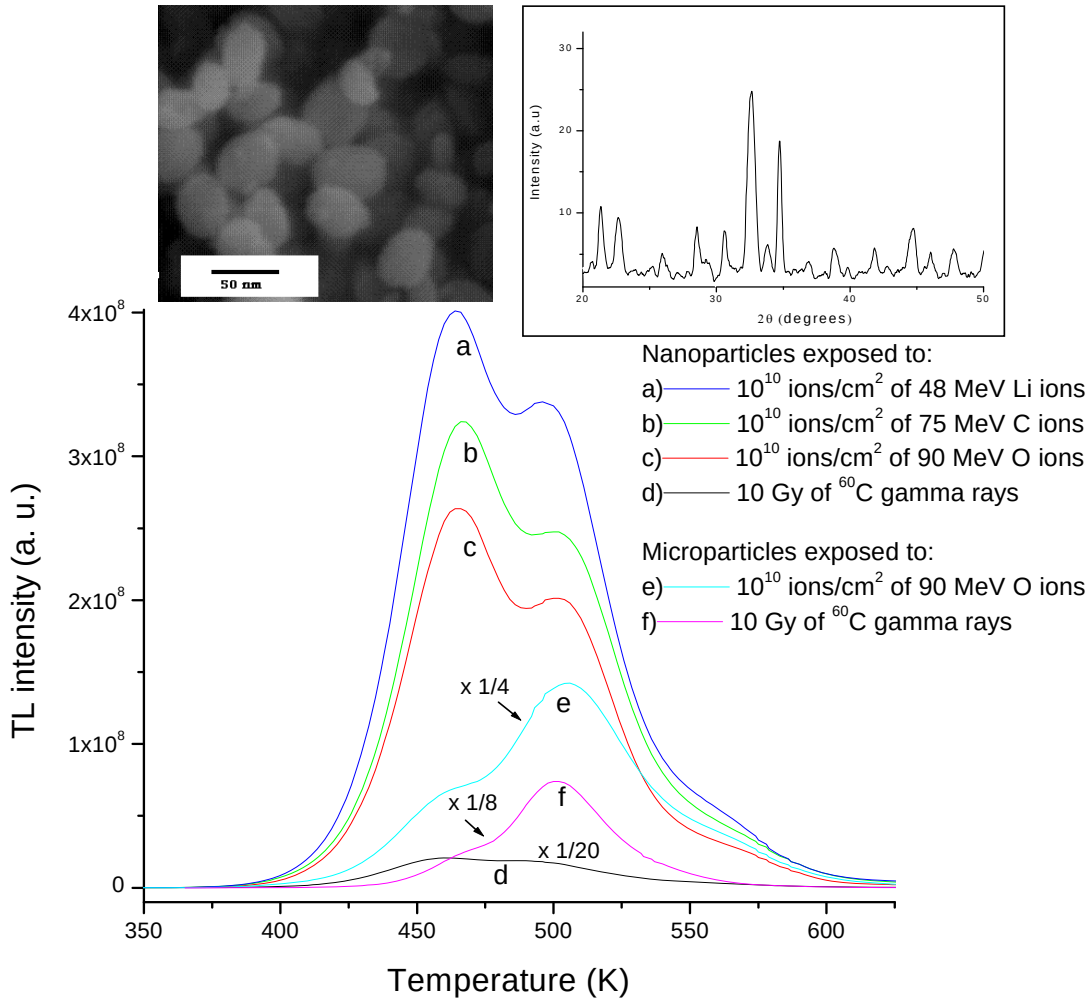

Figure 1: TL glow curves of $BaSO_4$:Eu nano and microcrystalline samples exposed to different ion beams and ^{60}Co gamma rays. The ordinate is to be multiplied by the numbers at the curves to get the relative intensities. X-Ray diffraction pattern of $BaSO_4$:Eu nanocrystalline powder and SEM image are also shown in the insets.

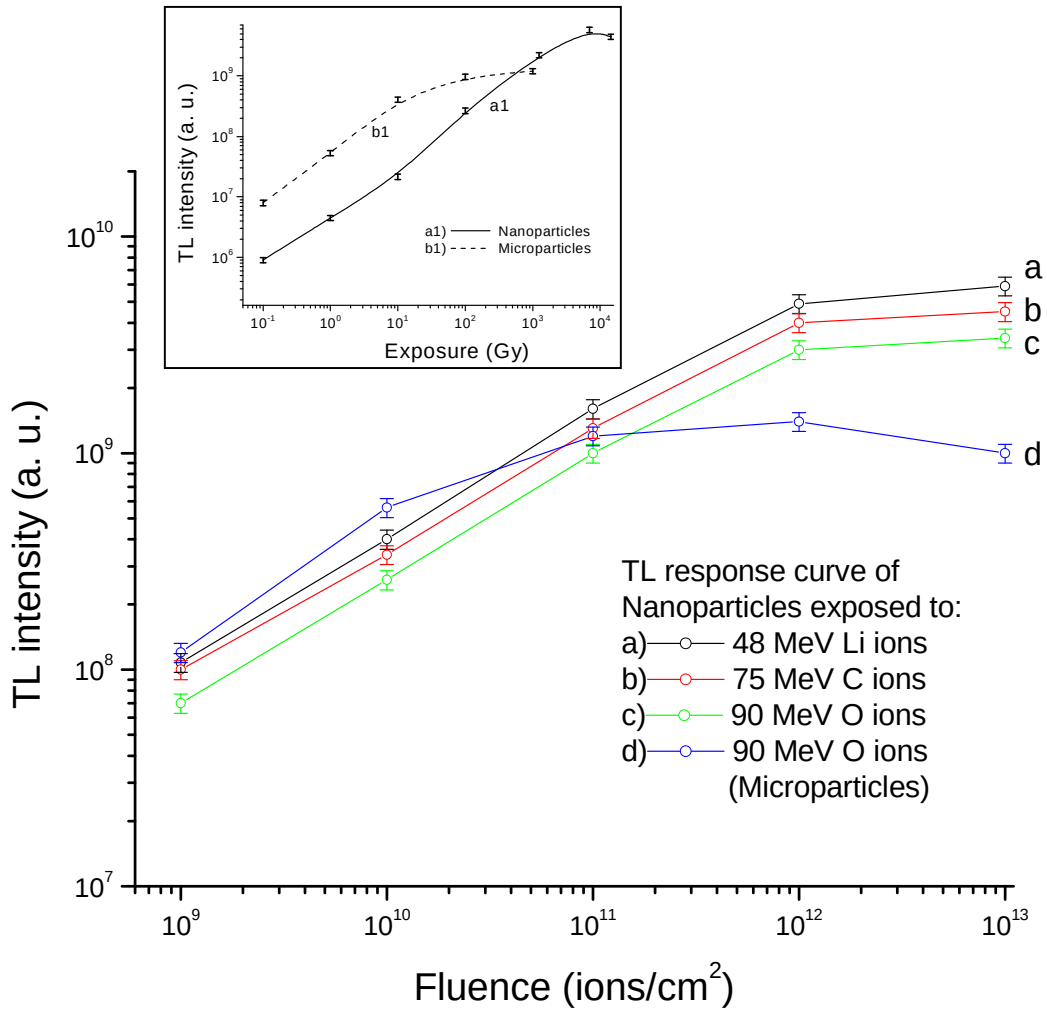

Figure 2: TL response curves of $BaSO_4$:Eu nano and microcrystalline samples exposed to different fluences of 48 MeV $^7Li^{3+}$, 75 MeV C^{6+} and 90 MeV O^{7+} ion beams. The response curves of these samples exposed to different doses of ^{60}Co gamma rays are also shown in the inst.

4. DISCUSSION

In this experiment we have exposed the nanocrystalline phosphor of $BaSO_4$:Eu to different fluences of 48 MeV $^7Li^{3+}$, 75 MeV C^{6+} and 90 MeV O^{7+} ion beams and various exposures of γ-rays from a ^{60}Co source . The TL consists of the most prominent peak at around 462 K beside other peak of lesser intensity at around 503 K. The peaks when compared with those of the microcrystalline powder, there is one-to-one correspondence i.e. the position of the peaks is almost the same in both cases. There is only a significant change in the relative intensity. This may be attributed to particle size effect. This effect seems to dominate in this material. It has been observed in many nanostructured materials that the energy level bands are altered or reorganized to the particle size effect due to the absence of crystal field effects [Gong, 2000; Moriarty, 2001]. It is known that on decreasing the particle size to nanoscale, the band gaps are widened [Moriarty, 2001]. Due to the widening of the band gap, the energy levels of the host of $BaSO_4$:Eu might also get reorganized. On irradiation to high-energy radiation the population of the trapping/luminescent centers (TC/LC) got changed, which could reflect on the occurrence of different intensity for the TL glow peaks (Fig. 1).

Linearity/sublinearity of the response curve of $BaSO_4$:Eu nanoparticles in a very wide range (Fig. 2) might be explained by the track interaction model (TIM) [Mahajna, 1997; Horowitz, 2001]. According to this model, the number of traps generated by the high-energy radiation in a track depends not only on the cross-section of the tracks but also on the length of the tracks inside the matrix. It is evident that in the case of a single crystal or a microcrystalline powder, high-energy radiation (such as γ-rays or ion beams having energy of the order of MeV) could generate a track of approximate length equal to dimensions of the crystal/crystallites while penetrating through it. This could be of the order of several mm. But in the case of nanocrystallites the length of such tracks will be only of the order of few tens of nanometres (dimensions of the nanoparticles). If we, therefore, compare the number of TC/LC generated in the nanocrystalline it would be much less than those in the case of a single crystal or microcrystalline powder sample for low doses/fluences. However, as the dose/fluence increases more overlapping tracks occur that may not give extra TL and saturation occurs in the case of a single crystal/microcrystalline powder material. While, in the case of nanoparticles, there are still exist some particles that would have been missed while being targeted by the high-energy radiation, due to the very tiny size of the particles. This will, however, slow down the process of generating the competing traps at different levels giving rise to a low sensitivity but a good linearity over a very wide range of the doses/fluences.

From the application point of few, the easy method of preparation, good sensitivity, simple glow curve structure, TL response over a wide range of exposure are some of the good characteristics of the presented $BaSO_4$:Eu nanophosphor. Therefore, it might be used as a dosimeter for high doses of ionizing radiations that has several applications such as radiotherapy, space dosimetry and irradiation of foods/seeds.

5. CONCLUSION

$BaSO_4$:Eu nanoparticles of average grain size around 40 nm have been exposed to 48 MeV $^7Li^{3+}$, 75 MeV C^{6+} and 90 MeV O^{7+} ion beams and various exposures of γ-rays from a ^{60}Co source . The nanophosphor exhibits a linear TL response to these ions and gamma radiation over a very wide range of exposures/fluences i. e.1×10^9 -1×10^{12} ions/cm^2 for these ions and 0.1 Gy–7 Kgy for gamma rays, whereas its corresponding microcrystalline powder has a linear range only from 1×10^9 to1×10^{10} ions/cm^2 for ion beams and from 0.1 to 10 Gy for gamma rays. This property makes the nanostructure form of $BaSO_4$:Eu useful for estimating the high doses of different ionising radiations that have applications in radiotherapy and food/seed irradiations.

6. ACKNOWLEDGMENTS

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