Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2012, Article ID 239182, 8 pages
doi:10.1155/2012/239182

Research Article

Particle Size Effect on TL Emission of ZnS Nanoparticles and Determination of Its Kinetic Parameters

L. Robindro Singh[1,2] and S. Dorendrajit Singh[3]

[1] *Department of Physics, Mizoram University, P U College, Aizawl 796 001, India*
[2] *Department of Nanotechnology, North-Eastern Hill University, Shillong 793 002, India*
[3] *Department of Physics, Manipur University, Manipur 795 003, Canchipur, India*

Correspondence should be addressed to L. Robindro Singh, robindro001@yahoo.co.in

Received 17 March 2012; Accepted 3 May 2012

Academic Editor: Leonard Deepak Francis

Nanoparticles have large surface area, and most of the ions are lying on its surface. Could these surface ions be contributed in thermoluminescence emission or enhanced nonradiative transition? In view of this, we have prepared small sizes of ZnS nanoparticles at low temperature and made two samples, one as-prepared (size ~3 nm) and the other heat-treated at 1073 K (size ~32 nm). Characterization of the samples shows that the prepared phosphors are pure. Thermoluminescence (TL) glow curves could not be recorded in both samples without irradiation. Even for higher dose of γ-radiation the as-prepared samples could not show TL signal, but 1073 K heat-treated sample shows the TL signal. This may be due to the fact that smaller particles have large surface area compared to bigger particles, the surface ions may produce the nonradiative transitions. The kinetic parameters of the TL glow curves are evaluated by the conventional methods and compared with curve fitting computerised glow curve deconvolution (CGCD) technique. The variations in both techniques are found only ±0.02. The shape factor of all the glow curves ~0.48, and these TL glow curves could be fitted with order of kinetics 1.5.

1. Introduction

The semiconductor nanoparticles in the groups II–VI have been studied extensively due to their intriguing physical properties compared to their bulk counterparts [1–10]. Optical properties of such materials can be tuned due to quantum size effects which effectively lead to a size-dependent variation of band gap. Among the most studied II–VI semiconductors are ZnO, CdS, ZnS, and so forth [11–15] for their wide range of luminescence emissions from ultraviolet to infrared regions. ZnS is a blue emitting direct band gap semiconductor of energy gap 3.6 eV with low phonon energy suitable in display devices and lighting applications. Extensive studies on the luminescence emissions of ZnS nanoparticles doped with transition metals or lanthanide ions at different sizes, pH, cappants, and so forth have been carried out since the past decades [16–22]. There are few reports on the study of thermoluminescence characteristics of these materials in nanosize; in view of this, the present paper is prepared to study their luminescence characteristics at different particle sizes.

Thermoluminescence (TL) continues to be an active area of research because of its immense contribution in the fields of personnel and environmental dosimetry, dating of archeological artifacts, sediments and study of defects in solids. Irradiation on many insulating and semiconducting materials creates sufficient defects to act as trap centers for electron and holes. Upon heating the materials containing large number of electrons and holes trapped in their respective trap centers, these electrons and holes are released and recombine with opposite charges resulting luminescence called TL (thermoluminescence). In the case of nanomaterials, the surface-to-volume ratio is large resulting in larger concentrations of surface states. The surface states are responsible for the production of TL glow curves, that is why Chen et al. [23] record TL glow curves in ZnS nanoparticle prior to irradiation. They also observed that the TL intensity increases with the decrease of particle sizes and concluded that the surface

ions on the nanoparticles were responsible for the production of TL glow curves. Crystalline sizes of the particles take important role in producting luminescence emission of the phosphors, many researchers are working in this regard on different phosphors [24–29]. Studying the luminescence characteristics of phosphors on particle sizes will be beneficial in lighting applications.

The present work studies the photoluminescence and thermoluminescence (TL) of as-prepared and 1073 K heat-treated undoped (pure) ZnS nanoparticles. Kinetic parameters such as the activation energy (E), order of kinetics (b), and frequency factor (s) of the glow peaks are determined by initial rise [30], curve fitting [31] and compared with computerised glow curve deconvolution method [32].

2. Experimental Section

2.1. Preparation. Quantum sizes of undoped (pure) ZnS nanoparticles were prepared by coprecipitation reaction at low temperature. In order to get small sizes of the particles, slow release of the reactants at controlled manner would be needed [33, 34]. Ethylene glycol acts as the reaction medium as well as the capping ligand. The precursors used for the production of Zn^{2+} was $Zn(CH_3COO)_2 \cdot 2H_2O$ (99.05%, E-Merck), and thiourea (AR) for the production of S^{2-}. 1 gm of $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 25 mL ethylene glycol; warming the solution, a clear solution could be observed. This solution contained Zn^{2+} ions. In this solution, 2.0 g of thiourea (AR) was simply added and warmed the mixture at 353 K, the solution again became transparent. The reaction medium was kept in nitrogen atmosphere, in order to avoid oxidation during reaction. The whole mixture was heated linearly up to 403 K. After half an hour, light yellowish-white colloidal precipitate could be observed, the reaction temperature maintained at this temperature and continues another two hours. The precipitates so obtained are extracted by centrifugation and washed several times in excess methanol (AR). Special care has been taken to avoid oxidation, the powder samples so obtained were dried at room temperature.

2.2. Characterization. X-ray diffraction studies were carried out using a Philips powder X-ray diffractometer (model PW 1071) with Ni-filtered Cu-k_α radiation. The lattice parameters were calculated from the least square fitting of the diffraction peaks. The average crystallite sizes were calculated from the diffraction line-width based on Scherrer relation: $d = 0.9\lambda/\beta \cos\theta$, where λ is the wavelength of X-rays, and β is the half maximum line width. To record UV-visible spectra, EDX and AFM, the powder samples were dispersed in dimethyl formide (DMF), then multiple dipping were carried out on ultrasonically cleaned glass slides.

Photoluminescence measurements were carried out at room temperature with a resolution of 3 nm, using a Hitachi Instrument (F-4500) having a 150 W Xe lamp as the excitation source. Powder samples (5 mg) were mixed with methanol, spread over a quartz plate, dried at 373 K, and mounted inside the sample chamber for photoluminescence measurements. Thermoluminescence glow curves of the powder samples were recorded using TLD-1404 recorder.

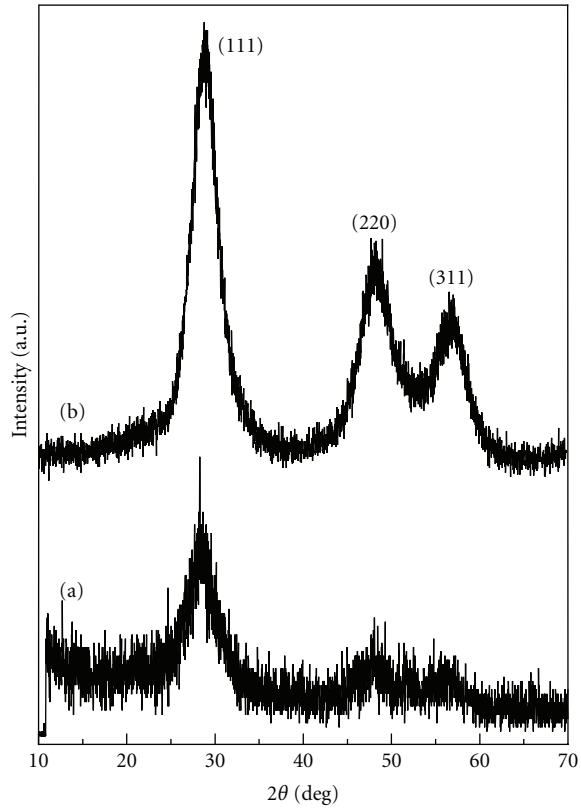

Figure 1: XRD pattern of (a) as-prepared and (b) 1073 K heat-treated ZnS nanoparticles.

3. Results and Discussion

3.1. X-Ray Diffraction (XRD) Study. Figure 1 shows the X-ray diffraction patterns of (a) as-prepared and (b) 1073 K heat-treated ZnS nanoparticles and corresponds to cubic phase (JCPDS-77-2100) of space group F43m. No extra peaks of impurity could be detected even for higher heat-treated sample within the resolution of limit diffractometer. The lattice parameter of the as-prepared ZnS nanoparticle is $a = 5.359(1)$ Å with unit cell volume 153.948(1) Å^3 and that of 1073 K heat-treated ZnS nanoparticle is $a = 5.369(1)$ Å with unit cell volume $V = 154.825(1)$ Å^3. The unit cell volume of heat-treated ZnS gives higher value compared to as-prepared ZnS nanoparticle. The increase of the unit cell volume with the increase of heat-treatment temperature may be due to the decrease in ionicity. The particle sizes calculated from Scherrer relation are found to be 3 and 32 nm, respectively for as-prepared and 1073 K heat-treatment samples, respectively. The intensity of the diffraction peaks increases with the increase of the heat-treatment temperature showing an increase in the crystallinity of the samples with heat-treatment.

3.2. EDX (Energy Dispersive X-ray) and AFM (Atomic Force Microscopy) Study. Figure 2 shows the EDX of as-prepared

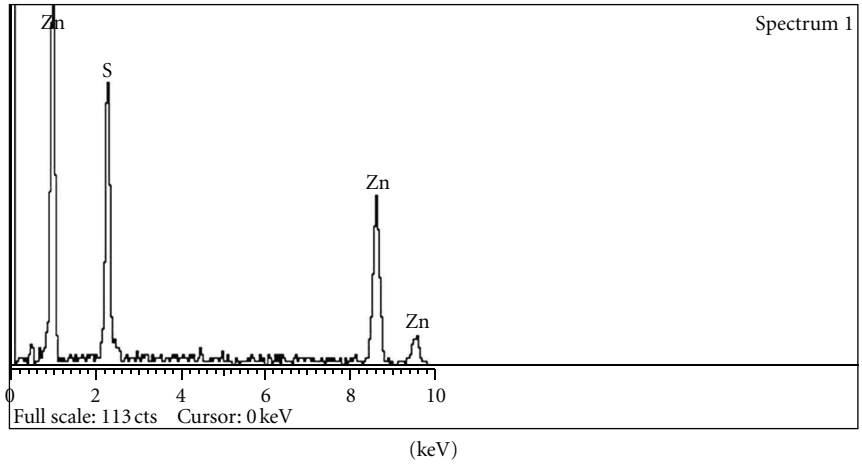

Figure 2: EDX spectra of as-prepared ZnS nanoparticles.

ZnS nanoparticles. As-prepared sample gives the atomic %Zn = 54 and S = 46, while the heat-treated sample gives atomic %Zn = 51 and S = 49. Figure 3 shows the 2-dimensional AFM picture of (a) as-prepared and (b) 1073 K heat-treated ZnS nanoparticles. The particles sizes determined by AFM are 12 and 87 nm, respectively for the as-prepared and heat-treated ZnS nanocrystals. The particles in as-prepared samples are spherical in shape and agglomerated. Figure 3(c) is the log-normal distribution of as-prepared sample showing the particle size of this sample is 13 nm. In the 1073 K heat-treated samples, the particles are spherical in shape and homogenous. It is obvious that the ethylene glycol can significantly resist agglomeration of nanoparticles.

4. Luminescence Study

4.1. TL Theory. Thermoluminescence is the thermally stimulated emission of light from insulators or semiconductors following previous absorption of energy from radiation. The electrons in the valance band gain energy due to exposure in radiation may come either to the conduction band or trapped in a metastable state as trapped electrons causing defect states in the material. On heating the phosphor, the trapped electrons in the metastable gain in energy then are released from the trapped level, if these electrons return to ground state with radiative recombination with the holes near the ground state, there is observation of thermoluminescence. When the recombination probability dominates the retrapping probability or retrapping probability is zero, Randall and Wilkins [35] had reported an expression for TL intensity of the first-order kinetics ($b = 1$) at a temperature T as

$$I(T) = n_0 s \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{s}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) dT'\right], \quad (1)$$

where n_0 is the initial concentration of trap electrons, s the frequency factor, E the activation energy, k the Boltzmann constant, and β the linear heating rate.

When the retrapping probability is the same as recombination probability then the expression for TL intensity of the second-order kinetics is given by [30]:

$$I(T) = \frac{n_0^2 s' \exp(-E/kT)}{\left[1 + (n_0 s'/\beta)\int_{T_0}^{T} \exp(-E/kT')\, dT'\right]^2}, \quad (2)$$

where $s = n_0 s'$.

For the non-first-order kinetics ($b \neq 1$), Gartia et al. [36] and Rasheedy [37] reported an expression for TL intensity as

$$I(T) = N f^b s \exp\left(-\frac{E}{kT}\right) \times \left[1 + (b-1) f^{b-1} \frac{s}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) dT'\right]^{-b/(b-1)}, \quad (3)$$

where N is the electron traps and filling factor $f = n_0/N$.

The condition for maximum intensity for the glow curve obeying (3) is given by

$$1 + (b-1) f^{b-1}\left(\frac{s}{\beta}\right)\int_{T_0}^{T_m} \exp\left(-\frac{E}{kT'}\right) dT' = \frac{bsk\, T_m^2}{\beta E} f^{b-1} \exp\left(-\frac{E}{kT_m}\right). \quad (4)$$

The shape factor μ_g, of the glow curve can also be determined from the relation [32]:

$$\mu_g = \frac{\delta}{\omega} = \frac{(T_2 - T_m)}{(T_2 - T_1)}, \quad (5)$$

where T_m is the peak temperature of the glow curve, and T_1, and T_2 are the temperatures at half of the maximum intensity on the rising and falling sides of the glow curves.

4.2. Photoluminescence and Thermoluminescence Study. Figure 4 shows the photoluminescence emissions of as-prepared and 1073 K heat-treated ZnS nanoparticles excited at

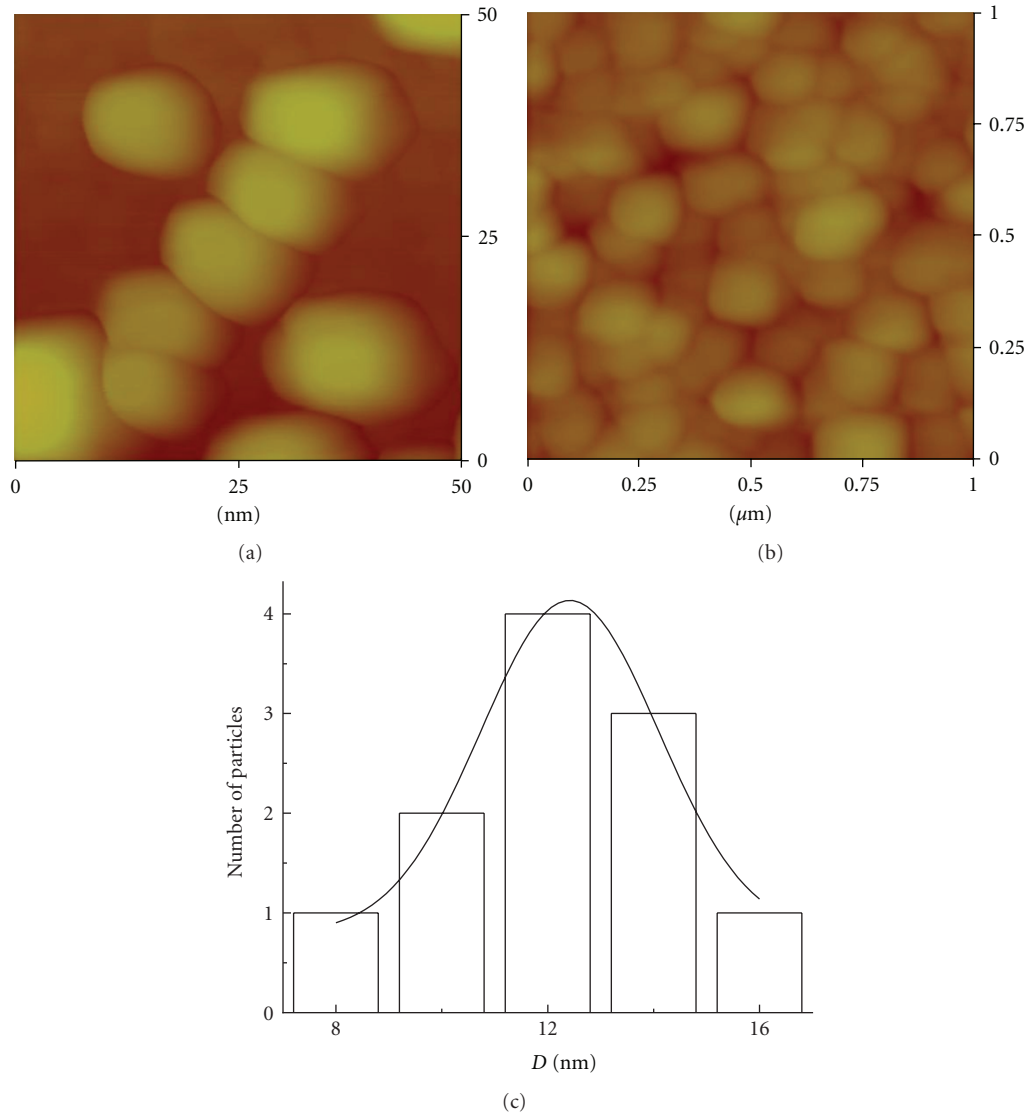

Figure 3: AFM picture of (a) as-prepared, (b) 1073 K heat-treated ZnS nanoparticles, and (c) log-normal distribution of the as-prepared nanoparticles showing that most of the particles are 13 nm in size.

290 nm. Strong blue emissions are observed, these emissions are the due to native intrinsic defects such as vacancies and interstitial form energy levels in ZnS, such as donor levels of V_S and Z_{ni} and acceptor level of V_{zn}. The emission intensity increases with the increase of heat-treatment temperature, this observation may be due to increase in crystallinity of the particles which in turn reduces the iconicity and the surface effects of the nanoparticles.

Thermoluminescence (TL) glow curves were recorded for both as-prepared and heat-treated ZnS nanoparticles without irradiation, but no TL signal could be recorded. Both the as-prepared and heat-treated samples were irradiated with different doses of γ radiation, but as-prepared sample does not show TL signals even for higher dose of γ radiation. The 1073 K heat-treated ZnS nanoparticles were irradiated with 126 and 252 Gy of γ-rays, and TL glow curves could be recorded. Chen et al. [23] could get TL glow curves of ZnS nanoparticles without irradiation. They observed that the TL intensity increases with the reduction of particle sizes. Their observations had open vehement argument for further understandings on the luminescence characteristics of small particles. They suggested that the surface ions on the nanoparticles took a vital role in the production of TL signals. But our observations are contrary to their findings. It is expected that that the surface ions on the surface of nanoparticles enhance the nonradiative transition that is why TL signal cannot be detected for as-prepared samples. It is well accepted that small particles have large surface area, and most of the ions lie on its surface. To confirm these observations, the as-prepared nanoparticles are heat-treated at 1073 K for one hour to get bigger particle sizes. Bigger nanoparticles have less number of surface ions and the non-radiative transition due to phonon-phonon interactions could be reduced extensively. Even this sample

Table 1: Peak parameters of the TL glow curves irradiated with 126 and 252 Gy of γ-rays.

Dose	T_m (K)	I_m	τ	$\delta = T_2 - T_m$	$\omega = T_2 - T_1$	$\mu_g = \delta/\omega$
126	374.0	66.3	43.5	50.5	101.0	0.50
252	390.0	112.9	43.5	39.5	83.0	0.48

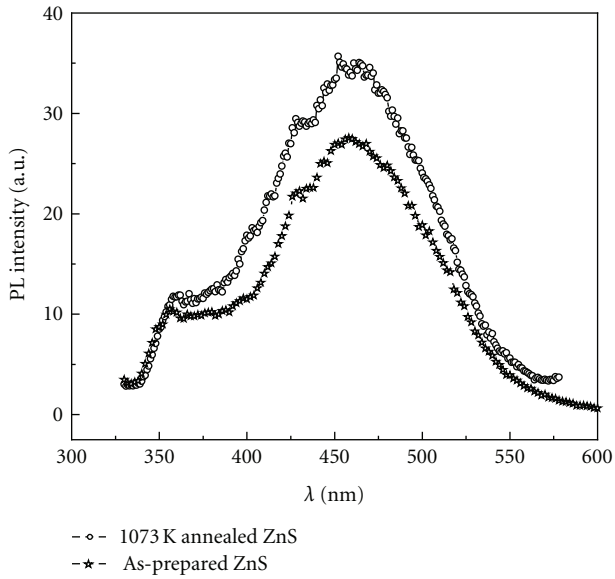

Figure 4: Photoluminescence emission spectra of as-prepared and 1073 K heat-treatment ZnS nanoparticles showing the native blue emission.

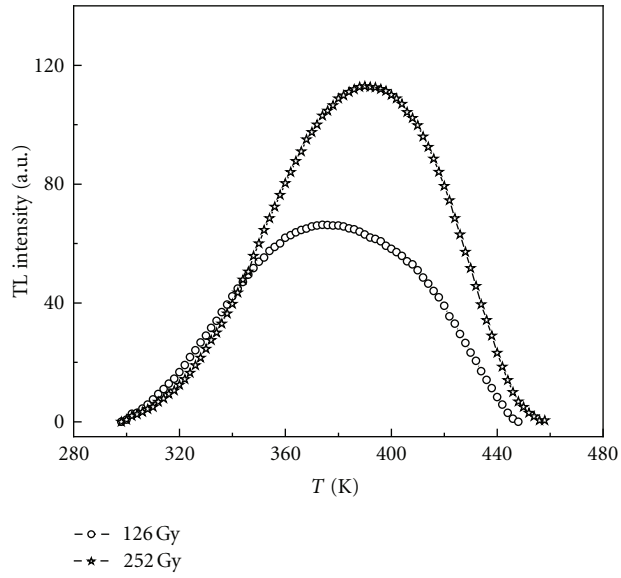

Figure 5: TL glow curves of nanoparticle ZnS irradiated with (a) 126 Gy and (b) 252 Gy of γ-rays with a linear heating rate $\beta = 1.73^{\circ}$C/s.

the TL signal could not be recorded prior to irradiation. Then the samples are again irradiated with γ radiations, and TL signal could be recorded for different doses of radiations. With irradiation different trap centers could be developed, even though there are surface ions on the nanoparticles. The radiative transitions due to trap levels dominates over the non-radiative transitions due to surface ions. That is why, TL signals could be recorded in heat-treated and irradiated samples. The above observations revealed that the surface ions on the surface of the nanoparticles could not contribute to the luminescence emissions, but only the trap centers could give luminescence emissions. Figure 5 shows the TL glow curves of 1073 K heat-treated ZnS nanoparticle irradiated with 126 and 252 Gy of γ-rays with a linear heating rate of 1.73 K/s, and the peak temperatures of the glow curves are around 374 and 390 K, respectively. The TL intensity of the glow curves varies with the different doses of γ-rays. The sample irradiated with higher dose of γ-ray has more intense in TL signal than the sample irradiated with lower γ dose. The full widths (ω) of the glow curves are found to be 83 K and 101 K, which are exceptionally large. In general, such a broad peak must contain at least two or more TL peaks. The shape factor μ_g is found to be 0.48, which are the characteristics of the non-first-order kinetics model [30, 31]. Table 1 indicates the characteristic peak parameters of the recorded glow curves of Figure 7.

Figure 6 shows the TL glow curves of 1073 K heat-treated ZnS nanoparticles irradiated with 126 Gy and 252 Gy of γ-rays after thermal cleaning up to 393 K. The peak temperatures of the glow curves (126 Gy and 252 Gy) are observed around 419 K, and the full widths at half maximum (ω) of the glow curves become 41 and 47 K, respectively. The shape factors of the glow curves are still at 0.48. The 252 Gy irradiated sample has been thermally cleaned to different temperatures 373, 393, 413, and 443 K, and then the glow curves are recorded. The peak temperatures of the recorded glow curves are 409.15, 415.82, 423.38, and 434.2 K, respectively as shown in Figure 7. The full width (ω) becomes narrower as compared to the glow curves before thermal cleaning. The value of the shape factor of the glow curves is at ~0.48, which is the characteristic of the non-first-order kinetics. Physically, it signifies that during heating parts of the electrons released from the traps are recombining with the holes in the hole centers resulting TL, and the remaining part of electrons are retrapped back to the electron traps. If significant numbers of electrons are retrapped back to the earlier electron trap centres such that retrapping probability is equal to recombination probability, the shape factor should be nearly 0.52. Table 2 describes the peak parameters of the glow curves, which are thermally cleaned at temperatures 373, 393, 413, and 443 K. It is clearly observed that all the peaks are non-first-order kinetics.

Table 2: Peak parameters of γ-irradiated TL glow curves of 1073 K heat-treatment ZnS nanoparticles recorded with different thermal cleaning (Tc).

Tc (K)	T_m (K)	I_m	τ	$\delta = T_2 - T_m$	$\omega = T_2 - T_1$	$\mu_g = \delta/\omega$
373	409.15	99.2	38.4	30.0	64.8	0.47
393	415.82	89.6	36.1	29.1	60.8	0.48
413	423.38	63	31.4	24.6	51.4	0.48
443	434.20	16.6	16.1	22.35	44.7	0.50

Table 3: Comparison of activation energies calculated from CGCD and peak shape method of the γ-irradiated ZnS nanoparticles.

Dose (Gy)	T_m (K)	Ec (eV)	E_δ	b	s ($\sec^{-1}$)	FOM
	396.92	0.67	0.634	1.5	5.9×10^7	
126	427.16	0.95	0.891	1.5	2.3×10^{10}	0.0869
	391.25	0.70	0.732	1.5	1.5×10^7	
252	421.5	1.00	0.992	1.5	2.0×10^{10}	

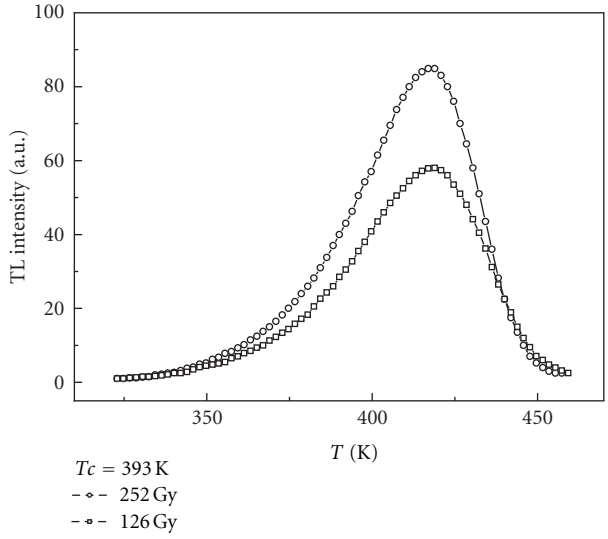

Figure 6: TL glow curves of nanoparticle ZnS irradiated with (a) 126 Gy and (b) 252 Gy of γ-rays recorded after thermal cleaning up to 393 K ($\beta = 1.73^\circ$C/s).

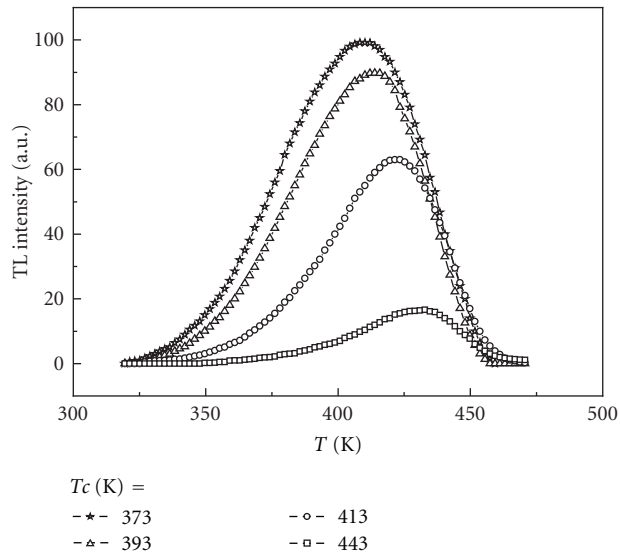

Figure 7: TL glow curves of ZnS irradiated with 252 Gy of γ-ray recorded after thermal cleaning at (a) 373 K, (b) 393 K, (c) 413 K, and (d) 443 K with linear heating rate 1.73°C/s.

To determine kinetic parameters such as activation energy (E), order of kinetics (b), and frequency factor (s) of the observed TL glow curves, we have used the conventional methods such as initial rise (IR) [30], peak shape method [31], and CGCD technique [32, 36, 38]. A series of initial rise (IR) thermoluminescence curves are recorded for the sample irradiated with 252 Gy of γ-ray by keeping the voltage across the photomultiplier tube to a high value such that TL intensity becomes large. The magnitude of the slope of In (I) versus $1/T$ gives E/k, and consequently E (activation energy) can be evaluated. The mean value of activation energy by using IR method is 0.78 eV. It is to be noted that the IR method to determine E is independent of the order of kinetics. Again the activation energy is evaluated using the peak shape formula of Gartia et al. [39]. The comparison between trapping parameters of ZnS nanoparticles evaluated by peak shape method and CGCD is shown in Table 3.

Figure 8 shows curve fitting of the glow curve of ZnS irradiated with 126 Gy of γ-rays after thermally cleaned up to 393 K. It can be fitted with two peaks with peak temperatures 396.92 and 427.16 K. The thermal activation energies of the deconvoluted curves are 0.7 and 1.0 eV, and frequency factors of the deconvoluted curves are 5.9×10^7 and 2.3×10^{10} s^{-1}. Both the deconvoluted peaks are non-first-order of kinetics $b = 1.5$. Similar pattern can be observed for higher Tc samples. Similar patterns are also observed for 252 Gy γ-ray irradiated sample. The deconvoluted glow curves have peak temperatures at 391.25 and 421.5 K, with order of kinetics $b = 1.5$. Table 3 indicates the activation energies calculated from CGCD and shape factor technique of ZnS nanoparticle irradiated with 126 and 252 Gy of γ-rays. The activation energy (Ec) determined from CGCD and shape factor (E_δ) is almost consistent, the difference is ± 0.02.

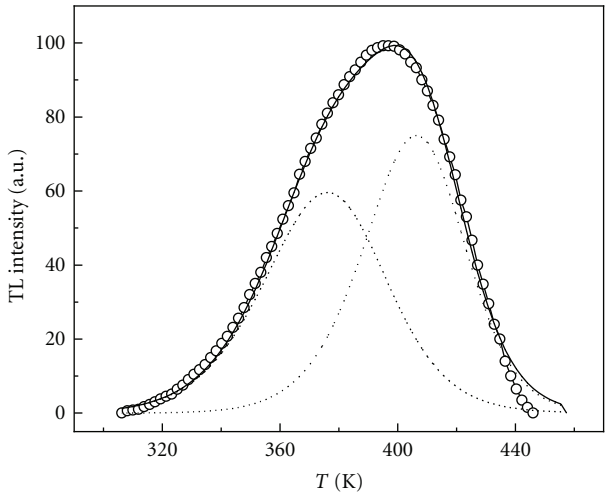

FIGURE 8: Computerised glow curve deconvolution of ZnS nanoparticles irradiated with 252 Gy of γ after thermal cleaning of 393 K with linear heating rate of 1.73°C/s, (ooo) Expt. Glow curve (—) sum of deconvoluted curves and (· · ·) deconvoluted curves.

5. Conclusion

Small sizes of ZnS nanoparticles could be prepared successfully at low temperature, it is evident that ethylene glycol can significantly resist agglomeration of the nanoparticles even heated at higher temperatures. As-prepared and 1073 K heat-treatment samples could not show TL signal without irradiation, reduction of surface ions on the nanoparticles might be responsible for the production of TL signals. The order of kinetics as evaluated by shape factor (non-first-order of kinetics) has the same pattern as evaluated by curve fitting technique. Peak shape method could be suitable to determine activation energy of the glow curves. Order of kinetics of the glow curves has the same value on order of kinetics $b = 1.5$ even for different doses of irradiation. The calculated value of activation energy using peak shape formula is in agreement with that of fitted value.

Acknowledgments

The authors owe R. S. Ningthoujam, scientific officer E. Chemistry Division, BARC, Mumbai for providing the facilities of characterizations and luminescence measurements. L. R. Singh thanks Dr. T. D. Singh, Swambung College, Imphal for his constant encouragement and suggestions while preparing this work. L. R. Singh thanks to DST-New Delhi for financial assistance under the scheme of DST Fast Tract Scheme for Young Scientist during execution of the present work.

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