Research Article

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

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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 producing 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$_3$COO)$_2$·2H$_2$O (99.05%, E-Merck), and thiourea (AR) for the production of S$^{2-}$. 1 gm of Zn(CH$_3$COO)$_2$·2H$_2$O 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 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-$k_a$ 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 $\lambda$ is the wavelength of X-rays, and $\beta$ 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.

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 $a = 5.359(1) \, \text{Å}$ with unit cell volume 153.948(1) Å$^3$ and that of 1073 K heat-treated ZnS nanoparticle is $a = 5.369(1) \, \text{Å}$ with unit cell volume $V = 154.825(1) \, \text{Å}^3$. 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
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 retrapping probability is the same as recombination probability then the expression for TL intensity of the second-order kinetics is given by [30]:

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

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

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

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

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

The shape factor \(\mu_g\), of the glow curve can also be determined from the relation [32]:

\[
\mu_g = \frac{\delta}{\omega} = \frac{(T_2 - T_m)}{(T_2 - T_1)},
\]

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 due to native intrinsic defects such as vacancies and interstitial form energy levels in ZnS, such as donor levels of V$_S$ and Z$_m$ 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 $\gamma$ radiation, but as-prepared sample does not show TL signals even for higher dose of $\gamma$ radiation. The 1073 K heat-treated ZnS nanoparticles were irradiated with 126 and 252 Gy of $\gamma$-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 which 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.

<table>
<thead>
<tr>
<th>Dose</th>
<th>Tm (K)</th>
<th>Im</th>
<th>τ</th>
<th>δ = T2 - Tm</th>
<th>ω = T2 - T1</th>
<th>μg = δ/ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>126</td>
<td>374.0</td>
<td>66.3</td>
<td>43.5</td>
<td>50.5</td>
<td>101.0</td>
<td>0.50</td>
</tr>
<tr>
<td>252</td>
<td>390.0</td>
<td>112.9</td>
<td>43.5</td>
<td>39.5</td>
<td>83.0</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Figure 4: Photoluminescence emission spectra of as-prepared and 1073 K annealed 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 β = 1.73°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 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 up to 393 K. The peak temperatures of the glow curves after thermal cleaning up to 393 K 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).

<table>
<thead>
<tr>
<th>Tc (K)</th>
<th>Tm (K)</th>
<th>Im</th>
<th>τ</th>
<th>δ = T2 − Tm</th>
<th>ω = T2 − T1</th>
<th>μg = δ/ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>409.15</td>
<td>99.2</td>
<td>38.4</td>
<td>30.0</td>
<td>64.8</td>
<td>0.47</td>
</tr>
<tr>
<td>393</td>
<td>415.82</td>
<td>89.6</td>
<td>36.1</td>
<td>29.1</td>
<td>60.8</td>
<td>0.48</td>
</tr>
<tr>
<td>413</td>
<td>423.38</td>
<td>63</td>
<td>31.4</td>
<td>24.6</td>
<td>51.4</td>
<td>0.48</td>
</tr>
<tr>
<td>443</td>
<td>434.20</td>
<td>16.6</td>
<td>16.1</td>
<td>22.35</td>
<td>44.7</td>
<td>0.50</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>Tm (K)</th>
<th>Ec (eV)</th>
<th>Eδ b s (sec⁻¹)</th>
<th>FOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>126</td>
<td>396.92</td>
<td>0.67</td>
<td>0.634 1.5</td>
<td>5.9×10⁷</td>
</tr>
<tr>
<td>252</td>
<td>427.16</td>
<td>0.95</td>
<td>0.891 1.5</td>
<td>2.3×10¹⁰</td>
</tr>
</tbody>
</table>

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 (β = 1.73 °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.

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 5.9×10⁷ and 2.3×10¹⁰ 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 determined 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 (Eδ) is almost consistent, the difference is ±0.02.

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.
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. The 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.

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