Effect of Silver Concentration on Thermoluminescence Studies of (Cd$_{0.95}$Zn$_{0.05}$)S Phosphors with Trap Depth Parameters Synthesized by Solid State Reaction Method

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Received 12 July 2014; Published online 6 September 2014

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Abstract

The present paper reports the synthesis and characterization of Ag$^+$ doped (Cd$_{0.95}$Zn$_{0.05}$)S phosphors. The effect of variable concentration of silver on thermoluminescence (TL) studies was investigated. The samples were prepared by solid state synthesis technique which is suitable for large scale production for phosphors. The starting materials used for sample preparation were CdS, ZnS, (Ag(NO$_3$)$_3$) and sodium chloride was used as a flux during synthesis. The prepared sample was characterized by X-ray diffraction technique (XRD). Sample shows hexagonal structure and the particle size calculated by Scherer's formula. The prepared phosphors were also examined by thermoluminescence technique. For recording TL glow curve every time 2mg phosphor was irradiated by 254nm UV source and fixed the heating rate at 8°C s$^{-1}$. Sample shows well-resolved peak at 102°C for different concentration of Ag$^+$. In addition, the effect of Ag$^+$ concentration at fixed UV exposure time was studied. The effect of UV exposure time and dose versus intensity plot was studied. Sample shows linear response with dose and broaden peak with lower temperature shows the less stability and more fading in TL glow curve. Trapping parameters were calculated for every recorded glow curve. The heating rate effect on TL glow curve was also studied. The sample shows the shifting of TL glow curve towards to lower temperature side with increasing of heating rate. The kinetic parameters like trap depth, frequency factor were calculated by using the Peak shape method, which are discussed in details. The TL Glow curves were fitted in CGCD (computerized glow curve convolution deconvolution) technique & trapping parameters calculated.

Keywords: (Cd$_{0.95}$Zn$_{0.05}$)S phosphors; XRD; TEM; TL; Deconvolution

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1. Introduction

In recent years, micro and nano materials in various fields of pure and applied sciences have attracted a great interest amongst the researchers. Research in the field of II–VI semiconductors material doped with transition metals have steadily increased (Bisen et al, 2009; Kumar et al, 2009; Tamrakar et al, 2012). Micro and nano range these material having great interests of research. Because of their fascinating and tremendous properties with great potential in many applications such as solid state lasers, lamp industry, colour displays, etc (Senthil et al, 2001; Tamrakar et al, 2013“a”; Tamrakar et al, 2013“b”; Tamrakar et al, 2014“a”; Tamrakar et al, 2014“b”).

Measurement of incident radiation dose is of truly important, where ionizing radiation is used. Much research has been carried out to find a better dosimetric material for such application (Zahedifar et al, 2012). Transition ion doped (Cd, Zn)S phosphors may play an important role as radiation detectors in many fields of fundamental and applied research (Tamrakar et al, 2013“b”; Tamrakar et al, 2014“b”; Tiwari et al, 2014 “a”; Tiwari et al, 2014 “b”). Thermoluminescence (TL) is a radiation dosimetric method that is widely used to personal, environmental and clinical dosimetry places. The peak area and the peak intensity of a TL dosimeter are proportional to the received dose from the radiation field (Zahedifar et al, 2012; Tamrakar et al, 2013“a”).

The TL phenomenon is the result of releasing electrons trapped by some defects within the material lattice when exposed to any type of ionizing radiation. The stimulation energy to release these electrons trapped is usually thermal and those defects are in the form of electrons or holes traps. If these traps are energetically deep enough, charge carriers may remain trapped for an extended period until they acquire enough thermal-energy to increase the probability to escape, producing electromagnetic radiation after a radiative recombination process takes place (Rosa et al, 2007; Raunak et al, 2014; Kulkarni et al, 2001; Chen et al, 1981).

The literature revels many authors have already studied various properties of (Cd, Zn)S. We have already reported the mechanoluminescence properties of (Cd$_{0.95}$Zn$_{0.05}$)S mixed nanoparticles doped with silver in our previous studies (Tiwari et al, 2014 “b”). Recently, many researchers have been devoted to the TL properties of different micro sized materials that show some outstanding characteristics for instance high sensitivity and saturation at very high dose levels (Tamrakar et al, 2014“a”; Tamrakar et al, 2014“b”; Tamrakar et al, 2014“c”; Tamrakar et al, 2014“d”). The Sao et al (2013) have synthesized the Ag$^+$ doped (Cd$_{0.95}$Zn$_{0.05}$)S phosphors in air atmosphere with KCl as a flux, and studies the ML and TL properties with a fix amount of silver (Sao, 2014). Tiwari et al (2014“a”) studies the TL properties of the Ag$^+$ doped (Cd$_{0.95}$Zn$_{0.05}$)S phosphors for fixed concentration of Ag$^+$ ion with higher temperature synthesis at 1300˚C (Tiwari et al, 2014“a”). The effect of silver ion on thermoluminescence properties of (Cd$_{0.95}$Zn$_{0.05}$)S phosphors was not studied in detail.

In this paper, we studies the TL response for different Concentration of Ag$^+$ ions on (Cd$_{0.95}$Zn$_{0.05}$)S. The (Cd, Zn)S host matrix shows more thermal and electrical stability and good luminescence material as compared to pure ZnS and CdS with composition of Cd (95%) and Zn (5%) (Kaur et al 2011). Effect of heating rate for on TL phonon on Ag$^+$ ions doped (Cd$_{0.95}$Zn$_{0.05}$)S phosphors. The kinetic parameters like trap depth, frequency factor etc. by using the Glow Curve of present phosphor were calculated. Peak shape method is found to be suitable amongst all reported
methods. This method provides the nearest possible values of all studied kinetic parameters that are discussed in details. The variable concentration of Ag⁺ ion on TL glow curve have been fitted by applying computerized glow curve convolution deconvolution (CGCD) and kinetic parameters were calculated (Tamrakar et al, 2014“b”).

2. Experimental details

Solid state reaction method was used to prepare the pure and silver-doped (Cd₀.₉₅Zn₀.₅₅)S phosphor. The AR grade CdS, ZnS and Silver nitrate (Ag(NO₃)₃) were used. Sodium chloride (NaCl) was used as a flux. The contents of CdS and ZnS were fixed at 0.95, 0.05 percent, and different Ag⁺ ion concentration (1-5 mols %) were added to it for the preparation of phosphors. The mixture was placed in an alumina crucible. The heating was done in a silica tubular furnace maintained at 900°C in the inert atmosphere of flowing nitrogen gas. After completion of heating, the mixture was cooled up to room temperature in the same furnace followed by immediate crushing to convert in the fine powder form to have uniform particle size. (Scheme 1) (Sao et al, 2014; Tiwari et al, 2014“b”).

![Scheme 1. Mechanism of solid state synthesis method of (Cd₀.₉₅Zn₀.₅₅)S: Ag⁺(1-5%)](image)

To determine the average particle size and the phase of the samples, Powder X-ray diffraction (PXRD) pattern was measured by using a D-8 Advance X-ray generator with Cu Kα radiation. The X-rays were produced using a sealed tube and the wave length of X-ray was 0.154 nm. The X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker Lynx Eye detector). The Thermoluminescence (TL) glow curve was recorded with the help of TLD reader (Model 1009I) made by Nucleonix fitted with 931B photomultiplier tube (PMT) by taking 1 mg of sample each time. For recording TL, samples were exposed to UV radiation from UVGL-58 handled UV lamp operating at 230V-50 Hz (emitting 254nm) for 5 to 25 minutes.

3. Results and discussion

3.1 X-ray diffraction technique

Figure 1 shows the XRD pattern of solid-state synthesized Ag⁺ doped (Cd₀.₉₅Zn₀.₅₅)S phosphor for 5mol% of silver. The characteristic XRD pattern of the (Cd₀.₉₅Zn₀.₅₅)S:Ag(5%) phosphor exhibit many prominent peaks, they are about 24.15, 25.89, 27.98, 49.01, 53.35 and 60.02. These diffraction patterns are in good agreement with JCPDS card number 49-1302 confirmed hexagonal
structure. The average particle size (D) of the as-formed \((Cd_{0.95}Zn_{0.05})S:Ag(5\%)\) phosphor was estimated from the full width at half maximum (FWHM) of the diffraction peak of the powder, using Scherrer's formula (Klug et al, 1954).

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

where \(\lambda\) is the wavelength of X-ray used, \(\theta\) the Bragg angle and \(\beta\) is the Full width at half maxima (FWHM) of corresponding peaks. The crystallite size was found in the range of 1.5\(\mu\)m. As compared to high temperature at 1300\(^\circ\)C synthesize by Tiwari et al (2014\"b\"), we found that the particle size was reduced.

![XRD patterns of \((Cd_{0.95}Zn_{0.05})S:Ag(5\%)\)](image)

**Fig. 1.** XRD patterns of \((Cd_{0.95}Zn_{0.05})S:Ag(5\%)\)

### 3.2 Transmission Electron Microscope

The morphology of silver-doped \((Cd_{0.95}Zn_{0.05})S\) phosphor was determined by Transmission electron microscopy (Figure 2). TEM analysis shows the crystalline behavior of the prepared phosphor with particle size in the range of few microns, which is identical with XRD result.
3.3 Energy Dispersive X-ray Spectrometer

In the EDX spectra, it should be clear that Ag\(^+\) Doped \((\text{Cd}_{0.95}\text{Zn}_{0.05})\)S phosphor is prepared. There is no other impurity present here to incorporate in our results.
3.4 Thermoluminescence(TL) Glow curve studies of Ag⁺ Doped (Cd₀.₉₅Zn₀.₀₅)S Phosphor

Thermoluminescence (TL) glow curves recorded by TLD reader 1009I (Nucleonix). TL readers work by heating the TL materials and measuring the light output from the photon emissions via de-excitation of electrons trapped in the forbidden band of the crystals. The TL material is placed on a planchet that is heated via a thermocouple. The light emission is focused through a filter or wave shifter which serves to convert the emitted photon wave frequency to a visible spectrum photon which can then be collected in a photomultiplier tube (PMT).

3.4.1 TL glow Curve response for UV Ray Ag⁺ doped (Cd₀.₉₅Zn₀.₀₅)S phosphor

TL glow curve for different UV exposure time recorded for (Cd₀.₉₅Zn₀.₀₅)S:Ag phosphor at fixed concentration (1mol%) of Ag shows well-resolved peak 102°C (figure 3(a)). It shows linear response with UV dose (figure 3(b)). For UV radiation the formation of shallow, trap in the sample. The impurity doped in the material could help in generating more number of traps (electron traps and hole traps/luminescent centers) responsible for TL (Chen et al 1981). These created defects are responsible for thermoluminescence glow curve (Tamrakar et al, 20144’a”; Tamrakar et al, 20144”d”).

![Thermoluminescence Glow curve of (Cd₀.₉₅Zn₀.₀₅)S:Ag(1%) phosphor](image)

Fig. 3(a). Thermoluminescence Glow curve of (Cd₀.₉₅Zn₀.₀₅)S:Ag(1%) phosphor
Fig. 3(b). Dose $V_s$ Intensity plot of $(\text{Cd}_{0.95}\text{Zn}_{0.05})\text{S}:\text{Ag}(1\%)$ phosphor

3.4.2 TL glow Curve response for different $\text{Ag}^+$ concentration Doped $(\text{Cd}_{0.95}\text{Zn}_{0.05})\text{S}$ phosphor for fixed 25 min UV Ray

Fig. 4(a). The Glow curves for the $(\text{Cd}_{0.95}\text{Zn}_{0.05})\text{S}$ samples with different concentrations of impurity $\text{Ag}^+$
Curves 1-6 for Ag concentrations 1.0-6.0 mol\% (figure 4(a)) Peak 1 for each curve is almost overlapping on the glow curve (green in color) while peak 2 (high temperature peak of low intensities) could be seen distinctly. The upward arrow shows increase in intensity with concentration up to 5.0 mol\% (curve 1-5) while intensity decreases for increasing the concentration further (Tamrakar et al, 2014"a"; Tamrakar et al, 2014"d"). TL glow curve for Ag concentration 6.0 mol\% (curve 6) found to consist of a single peak (i.e., it does not consist of Peak 2). The curves in symbols are the theoretically fitted curves and a very good fit could be seen between the experimental and theoretical curves. The TL parameters such as activation energy for deconvoluted peak were found in the range of 0.64eV to 1.97 eV. The frequency factor is of the order of between $1.08 \times 10^8$ to $1.3 \times 10^{24}$ s$^{-1}$ (Chen et al, 1997; Chen et al, 2011).

**Table 1** Trapping parameters of a typical glow curve. There are no any appreciable changes in the peak temperatures of the deconvoluted peaks and the trapping parameters with the impurity concentration.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>$T_1$ (K)</th>
<th>$T_m$ (K)</th>
<th>$T_2$ (K)</th>
<th>$\mu_g$</th>
<th>$\beta$</th>
<th>E (eV)</th>
<th>S (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>346</td>
<td>375</td>
<td>405</td>
<td>0.51</td>
<td>2.0</td>
<td>0.64</td>
<td>$1.0 \times 10^8$</td>
</tr>
<tr>
<td>Peak 2</td>
<td>399</td>
<td>409</td>
<td>416</td>
<td>0.41</td>
<td>1.0</td>
<td>1.97</td>
<td>$1.3 \times 10^{24}$</td>
</tr>
</tbody>
</table>
3.4.3 Effect of Heating rate for fixed Ag$^{+}$ concentration Doped (Cd$_{0.95}$Zn$_{0.05}$)S phosphor for fixed 25 min UV Ray

The heating rate effect of UV irradiated phosphors shows the linear response with increase in heating rate the peak shift towards to lower temperature side. The heating rate effect of TL glow curve for fixed concentration of Ag$^{2+}$ (5mol%) and fixed UV exposure time shows the linear response with heating rate (Figure 5(a) & 5(b)). In this behavior shows the peak temperature shifted...
towards the lower temperature side on increase of heating rate. The heating rate effect of TL studies for 5 mol% of Ag and fixed UV exposure time shows the decrease the peak temperature when increase of heating rate this is the novel behavior proposed by so many authors and also Mckeever in his book thermoluminescence of solids (McKeever et al, 1985; Furetta et al, 2006; Tamrakar et al, 2014”).

4. Conclusion

It is concluded that the prepared phosphor shows hexagonal structure when sample was prepared by solid state reaction method. The structural analysis and particle size was determined by XRD techniques the particle size of prepared phosphor found ~1.5µm. The exact particle size was calculated by TEM study that shows the ranging of particle size distribution along few microns range. The TEM study shows the formation of micro phosphors with the good surface morphology some defects found because the sample prepared by high temperature synthesis method. The thermoluminescence behavior for the variable concentration of Ag+ as well as the variable UV exposure time shows well resolved peak at 102°C. The peak is lower temperature peak shows the formation of shallower trap described by the trap model. According to the given models, irradiation of sample by electron beam creates two types of traps (one type are of shallower traps and other of deeper traps) in the forbidden band gap of material. When sample is irradiated by UV rays it forms shallower traps which confirmed by lower temperature peak at TL glow curve. (Furetta et al, 1985) In addition, the effect of heating rate on optimized sample with fixed UV exposure time shows the shifting of TL glow peak in lower temperature side. This phenomenon indicates that the prepared phosphor shows high fading and less stability. Peaks if fitted by CGCD technique the curves in symbols are the theoretically fitted curves and a very good fit could be seen between the experimental and theoretical curves for 1-6 mol% of silver in (Cd0.95Zn.05)S phosphor. The impurity doped in the material could help in generating more number of traps (electron traps and hole traps/luminescent centers) responsible for TL. The TL parameters such as activation energy for deconvoluted peak was found in the range of 0.64eV to 1.97 eV. The frequency factor is of the order of between 1.08 ×10^8 to 1.3 ×10^24 s^-1.

Acknowledgement

We are very grateful to IUC Indore for XRD characterization and also thankful to Dr. Mukul Gupta for his cooperation. I am very thankful to SAIF IIT, Bombay for other characterization such as TEM and EDX.

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