THERMOLUMINESCENCE CHARACTERISTICS OF ZnS:Cu NANOPOSPHORS

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The thermoluminescence (TL) characteristics of copper doped zincsulphide nanoparticles under UV radiations have been studied. The average particle size of the nanoparticles was found to be 2 – 3 nm, which is confirmed by TEM micrograph. The TL glow curve shows a single peak at 540K. TL intensity was found optimum for 5 minutes UV exposure. Further increase in the dose results into a decrease of TL intensity. Variation in TL intensity as a function of cerium concentration is studied and 2milliMole is found to be the optimum concentration for TL. The trap parameters namely, activation energy (E), order of kinetics (b) and frequency factor (s) of ZnS:Cu (2mM) sample have been determined using Chen’s method. The order of Kinetics is found to be 1 indicating re-trapping of charge carriers in ZnS:Cu nanoparticles. The PL emission spectrum shows peaks at 369nm, 398 and 518nm when excited at 254nm.

(Received June 6, 2015; Accepted August 4, 2015)

*Keywords:*Thermoluminescence, ZnS:Cu, TEM, UV

1. Introduction

Thermoluminescence (TL) is the emission of light from a solid either inorganic, semiconductor or an insulator when it is heated after its exposure to some radiation [1]. TL is directly related to band structure of solids and particularly to just centers that may occur when ions of either signs move away from their original sites, thus leaving vacant sites that are able to interact with free charge carriers [2-5]. Materials having TL property emits light that can be best described by a glow curve, which may present several glow peaks during the heating process [6]. The most widespread applications of TL phenomenon is the radiation dosimetery in health physics, biological science and radiation protection. Besides this TL is an important and convenient methods of investigating nature of traps and trapping levels presents in solids [7,8].

Sodium Sulphide, a member of II-IV family has been long investigated for its dosimeteric properties[9,10] for various radiations such as UV,gamma rays and beta rays. ZnS crystals are knows as a material having high photoluminescence (PL) and TL properties and are widely used in opto-electronic devices for their photoluminescence properties [11].There is a scarcity of the works reported on TL from ZnSnanophases. Zaheedifar et al.[12] studied the thermoluminescence of ZnS:Mn^{2+} nanoparticles, with its intensity depending on concentration of the Mn dopant. Yazici et al.[13] studied the TL properties of copper (Cu) doped ZnS nanophosphors after beta irradiation at room temperature and found that TL intensity was increased with a decrease in the size of particles. In this paper we report the TL characteristics of ZnS:Cu nanophosphors exposed to UV radiation. The effect of different dopant concentrations on the glow curves has been studied. Chen's et al. [14], first order kinetic equation is applied to experimentally obtained glow curve and it describes quite satisfactorily the single glow curve.

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2. Experimental

2.1 Method of preparation

The nanoparticles for the study are prepared by wet chemical synthesis method [15]. Analytical reagent grade chemicals zinc acetate ($C_4H_6O_4Zn$), copper acetate ($C_4H_6O_4Cu$), sodium sulfide (Na_2S) and Sodium Hexa Meta Phosphate SHMP $(NaPO_3)_6$ were obtained commercially. Double distilled water was used for sample preparation and dilution. 5 gm of SHMP was dissolve in double distilled water and added in to a solution of 0.25M zinc acetate and 1mM coper acetate, drop wise with continuous stirring. White precipitate was formed which subsequently dissolved during the stirring process. The mixture was then heated till boiling. After cooling to room temperature, 0.25M sodium sulphide was added drop wise in above mixture in an ice bath with constant stirring. The white precipitate so formed was isolated by centrifugation, washed several times with distilled water and finally air dried at room temperature. Different samples were prepared by changing the concentration of copper.

2.2 Characterization

To measure the structure of the ZnS host and the size of the crystallites, X-ray powder diffraction (XRD) patterns were determined on a Bruker D8 Advance X-Ray Diffractometer using CuKα radiation (λ = 0.15428 nm). Transmission Electron Microscopy (TEM) micrograph has been obtained by TECHNAI G2 by FEI. For recording TL samples were exposed to UV radiations from UV lamp operating at 230V-50Hz (emitting 253nm). TL glow curves were recorded on a TLD reader TL 1009I Nucleonix, at a heating rate of 10°C/s in temperature range from 50 to 400°C.Every time 5mg of irradiated phosphor was taken for TL measurements. The excitation and emission spectra were measured by a spectrofluorophotometer (SHIMADZU, RF-5301 PC).

3. Result and Discussion

The X-ray diffraction pattern (XRD) of Cu- doped ZnS sample is shown in fig.1. It is clear from this figure that there are three major peaks, which are consistent with cubic (sphalerite) ZnS phase with lattice constant a = 5.33Å and they are polycrystalline with preferential orientation along (111) (JCPDS no.05-05660 [16].The three major diffraction peaks corresponds to the (111), (220) and (311) lattice planes. The average crystallite size of the nanoparticles is calculated from FWHM of the most intense XRD peak using Debye Scherrer formula[17].

$$D= 0.89\, \lambda / \beta \cos\theta$$

Where D is the average gain size of the crystallite, λ is the wavelength of CuKα (0.154nm) radiation, β is the diffracted full-width at half- maximum (in radian) caused by the crystallite and θ is the Bragg's angle. The average size was found to be approximately 2.33nm.

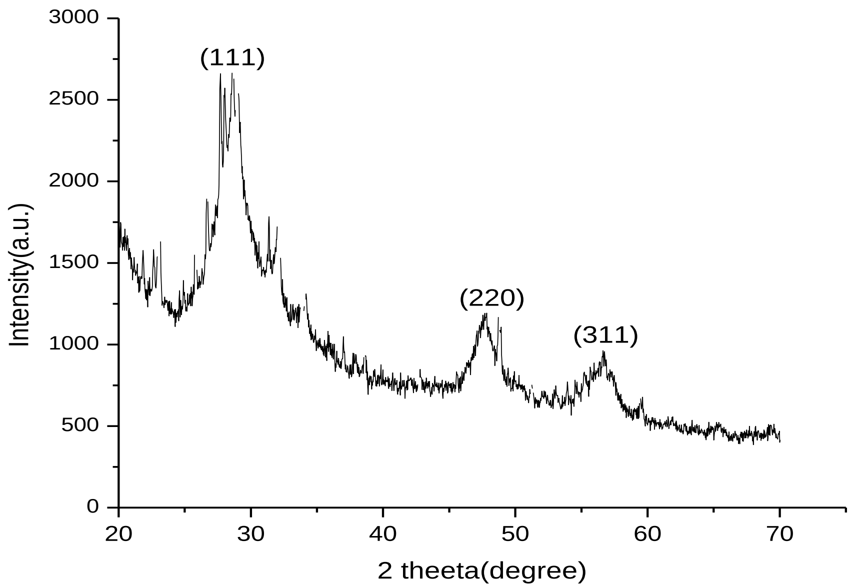

Fig.1 XRD pattern of ZnS:Cu

The particle shape and size of the prepared nanocrystalline powdered materials was determined by TEM. The TEM micrographs are shown in fig. 2 which indicates an average size of the nanoparticles which are aggregated and an irregular shape. TEM micrograph confirms the XRD result.

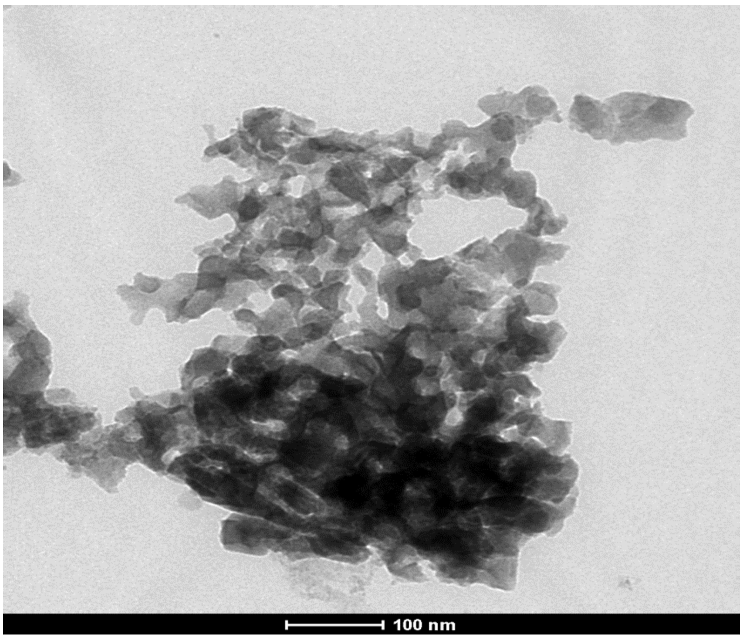

Fig. 2 TEM image from ZnS:Cu

Fig. 3 shows the TL glow curves for different concentrations of copper in millimole for a UV exposure of 5 minutes. Luminescence of a phosphor is affected largely bythe impurity concentration in it. If the concentration of impurities increases from a particular amount, they may act as self quenchers by non- radiative transitions resulting in fall in the intensity of the luminescence. In the present case the TL intensity increases with copper concentration up to 2mM and afterwards it decreases. The fall in the TL intensity may be attributed to the well known concentration quenching effect of dopant. Hence the optimum impurity concentration of Cu in ZnS for 5 minutes UV exposure is 2mM since at higher concentrations the TL intensity falls.

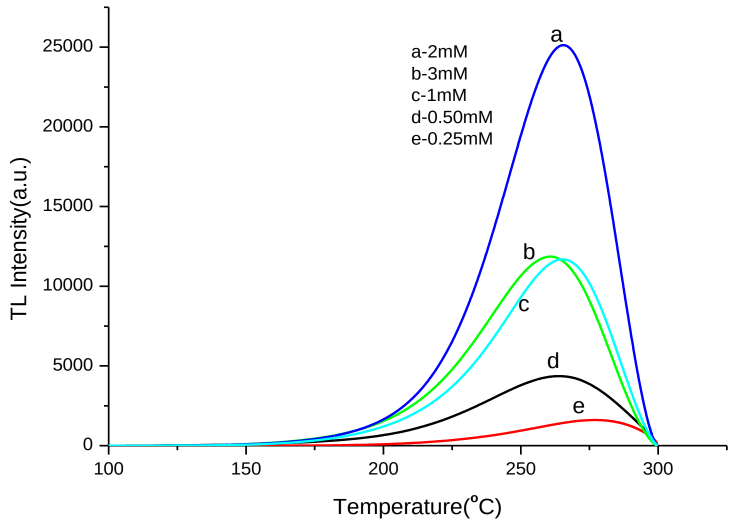

Fig.3 TL glow curves for ZnS:Cu with different concentrations of Cu

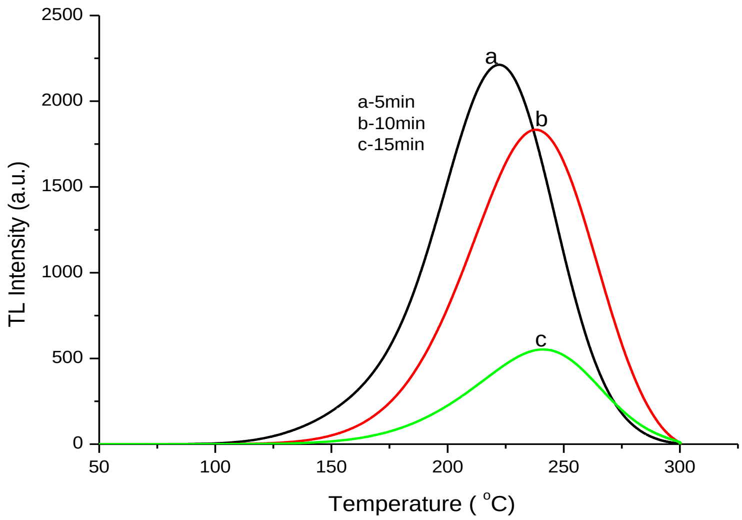

Fig. 4 Variation in the TL intensity for ZnS :Cu (2mM) as function of UV exposure time

The variation in the TL intensity for ZnS: Cu (2mM) as a function of UV exposure time is shown in fig. 4. The TL intensity increases maximum up to 5minutes UV exposure and afterwards it decrease. In case of UV irradiated phosphor response mainly generates from the surface traps, since these radiations cannot penetrate deeper and hence will not induce lattice defects. The density of surface defects increases with increase in the UV exposure leading to increase in peak intensity. The fall in the TL intensity at higher doses has been reported earlier by several authors [18,19].

The TL glow curve of ZnS:Cu from fig.4 it is seen that initially TL intensity increases with UV irradiation time. TL intensity are maximum for 5min UV exposure time, after that they start to decrease, it is predicted that with increasing UV radiation time greater number of charge carriers are released which increase the trap density result in increase of TL intensity (density of charge carriers may have been increasing),but after a specific exposure (5minutes) trap starts to destroy results in decrease in TL intensity. The decrease in charge carrier density may be a reason for the low TL intensity at higher irradiation time(10 minutes, 15 minutes)[20].

The order of kinetics(μ_g) and the activation energy(E) of glow curve (fig. 3) was found using Chen's empirical formulae[21].The form factor μ_g is found using formula

$$\mu_g = (T_2-T_m) / (T_2-T_1)$$

where T_m is the temperature corresponding to the maximum intensity, T_1 and T_2 are the temperature corresponding to the half of the intensities on the either side of the maximum. The value of form factor is 0.42 for first order kinetics and 0.52 for second order kinetics[22], ZnS :Cu shows the first order kinetics(μ_g = 0.35). The trap depth or the thermal energy needed to free the trapped electrons can be calculated using the Chen's formula in case of first- order kinetics

$$E = 1.52(kT_m^2) /\delta_1 - 1.58(2kT_m)$$

where $\delta_1 = T_m-T_1$and k is Boltzmann's constants. The frequency factor[23] was calculated from the equation

$$S = \beta E / k T_m^{2} * e^{(E/kTm)}$$

The calculated trap parameters have been summarized in table 1.

ZnS :Cu factor	T_m(K)	Order of Kinetics (μ_g)	Activation energyE(eV)	Frequency S(s^{-1})
(2mM) Heating rate 10°C/	540K	1(0.35)	0.74	7.89x10^{7}

The room temperature PL excitation and emission spectra of ZnS:Cu nanoparticles is shown in figure 5. PLE showed the peaks at 270 nm, 318 nm and 325nm. PL emission spectra were recorded at 254nm excitation. The excitation spectrum shows peaks around 369nm, 398nm and 518nm. PL spectra shows two emission peak at 369nm and 398nm, blue/purple emission peaks. A third peak was identified in the green region (~518nm). The 398nm peak in ZnS has been classically termed as self activated luminescence and known due to recombination of carriers between sulphur vacancy (Vs) related donor and valence band [24]. The 518nm peak in ZnS:Cu is thought to be due to recombination between Vs and Cu related acceptor center[25].

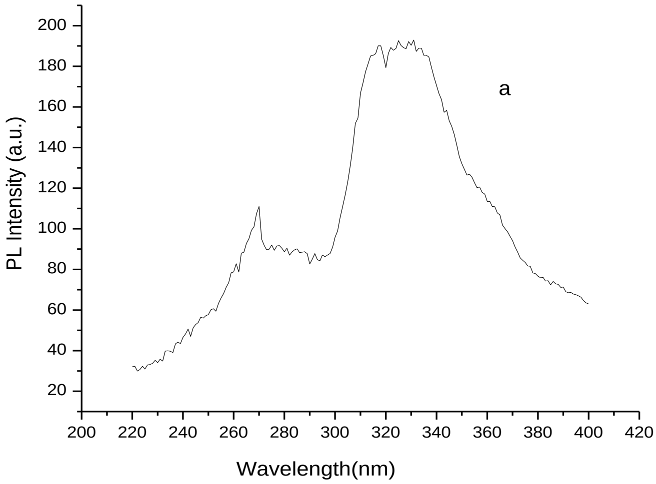

Fig. 5 (a) Excitation spectrum of ZnS:Cu

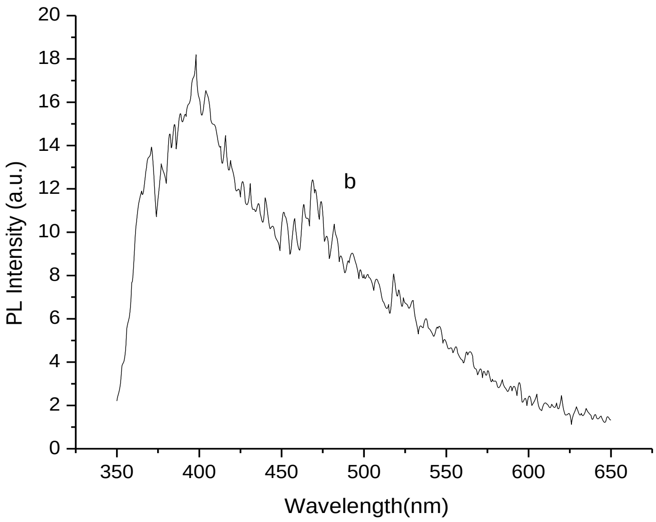

Fig. 5 (b) Emission Spectrum of ZnS:Cu

4. Conclusions

The TL properties of ZnS:Cu nanophospor has been investigated for UV irradiation. The optimum concentration of Cu is 2mMole. The trapping parameters were calculated. The phosphor ZnS:Cu is found to have first-order kinetics in TL emission suggesting re-trapping of charges. The TL intensity increases up to 5 minutes of UV exposure. Further increase in the dose results into decrease in TL intensity. PL emission spectrum shows peaks at around 369nm, 398nm and 518nm when excited at 254nm. The green emission (~518 nm) arises from the recombination between the shallow donor level (sulfur vacancy) and the t_2 levels of Cuions.

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