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CGCD technique to find the kinetic parameters of TL glow curves

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ABSTRACT

The behavior of ZnS:Mn,Cu,Cl phosphor by the effect of pressure was studied on the thermoluminescence (TL). Two prominent peaks were visible, increasing pressure the prominent peaks were also shifting to the higher temperature. Kinetic parameters of the glow curves were determined by computerized glow curve deconvolution (CGCD) technique. The order of kinetics (b) was found to be independent of pressure. All the peaks can be fitted with b=1.5. Computerised glow curve deconvolution (CGCG) method was used to determine the activation energy (E) order of kinetics (b) and frequency factor (s) of the different peaks present in the phosphor.

Key words: Computerized glow curve deconvolution; glow curve; kinetics; thermoluminescnece.

INTRODUCTION

Thermoluminescence (TL) appears as a very complex phenomenon. It is an indispensible tool for the exhaustive study of the nature, thermal stability and concentration of electron and hole trapping centres in luminescent materials. Extensive studies on the photoluminescence (PL) and TL properties of ZnS have been carried out since the past decades for both bulk as well as nanocrystalline form. ZnS is a direct band gap II-VI compound semiconductor having a band gap of 3.6 eV at room temperature with low phonon energy which is suitable for applications in display devices. Chen *et al*.[1] could successfully prepare ZnS nanoparticles and probed the surface ions present on the surface of the particles. They reported that the surface ions are responsible for the production of TL glow curves. Thus, without irradiation, TL glow curves of ZnS nanoparticles could be recorded. They also reported that TL intensity increases as the particle size is decreased and the glow curve with peak temperature at 357K can be fitted with activation energy of 0.83 eV[2].[2] Singh *et al*.[3] studied TL glow curve of bulk ZnS powder irradiated with gamma rays. It shows a broad peak with a peak temperature at 374 K and 390 K. The shape factor is 0.53 and 0.47. The glow curve could be fitted with two TL peaks at 376 and 406_K with activation energies 0.7 and 1.0 eV, respectively. Both the peaks obeyed the non-first order kinetics (order of kinetics b=1.5). The comput-

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erized glow curve deconvolution (CGCD) technique for the analysis of a composite TL glow curve into its individual glow peaks has been applied.[4] Many functions describing a single glow peak have been proposed, which are summarized extensively.[5-9]

Lang *et al*.[10] recorded high pressure and low temperature TL glow curve of ZnS:Mn,Cu,Cl phosphor with a linear heating rate of (b) = 0.74°Cs^{-1}. They reported the presence of two-peak system. As pressure increases new shallower traps are appeared. The pressure dependence of four traps are established. By comparison with pressure measurements on ZnS doped Mn^{+2} and only with defects Cu^{+} and Cl^{-}, they established that the deepest trap is associated with defects introduced by Mn^{+2}, while the two traps next lower in energy are associated with defects introduced by Cl^{-}. The shallowest trap could not be assigned to a specific defect.

A number of methods are developed to determine the kinetic parameters such as activation energy, frequency factor and order of kinetics. The value of activation energy of a TL peak indicates the stability of the electrons trapped in a defect centre. This concept has implications about the applicability of the material for dating and dosimetry purposes. In this paper, we used the CGCD to decode the different trap levels of the ZnS:Mn,Cu,Cl phosphor. The glow curves were subjected to CGCD in the kinetics formalism.

THEORY

The equation of motion governing trafficking of charge carriers can be written as[11]

$$I(t) = -\frac{dm}{dt} = A_m m n_c \tag{1}$$

$$\frac{dn}{dt} = -sne^{-\frac{E}{kT}} + (N-n)n_c A_n \tag{2}$$

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn}{dt} \tag{3}$$

where m, n_c and n represent the concentration of holes trapped in recombination centres, electrons in the conduction band and electron traps of density N. E and s denote the activation energy and frequency factor. A_m and A_n are respectively recombination and retrapping probabilities respectively. The TL intensity I (t) is directly proportional to the rate of decreasing the number of holes in the recombination centres. As one uses linear heating profile ($T=T_0+\beta t$) in recording TL glow curves, it is convenient to express the rate equation in terms of temperature in absolute scale involving heating rate β.

When the recombination probability dominates the retrapping probability the expression for TL intensity follow the first order kinetics (b=1) and rate equations (1-3) gives the expression for TL intensity as[12]

$$I(T) = n_0 s \exp(-E/kT)\exp\left[-\frac{s}{\beta}\int_{T_0}^{T}\exp(-E/kT')dT'\right] \tag{4}$$

where n_0 is the initial concentration of trap electrons, T_0 the initial temperature before heating the sample, 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 following the second order kinetics becomes[13]

$$I(T) = n_0^2 s' \exp(-E/kT)/[1+(n_0 s'/\beta)\int_{T_0}^{T}\exp(-E/kT')dT']^2 \tag{5}$$

where s=Ns' and N is the number of electron traps.

For the non-first order kinetics (b≠1). Gartia *et al*.[13] and Rasheedy[14] reported an expression for TL intensity as

$$I(T) = Nf^b s \exp(-E/kT)[1+(b-1)f^{b-1}\frac{s}{\beta}\int_{T_0}^{T}\exp(-E/kT')dT']^{-b/(b-1)} \tag{6}$$

where filling factor $f=n_0/N$.

The condition for maximum intensity for the glow curve obeying equation (6) is given by

$$1+(b-1)f^{b-1}(\frac{s}{\beta})\int_{T_0}^{T_m}\exp(-E/kT')dT' = \frac{bskT_m^2}{\beta E}f^{b-1}\exp(-E/kT_m) \quad (7)$$

The shape factor μ_g, of the glow curve can also be determined from the relation[8]

$$\mu g=\delta/\omega = (T2 - Tm)/ (T2 - T1) \quad (8)$$

where T_m is the peak temperature of the glow curve and T_1, T_2 are the temperatures at half of the maximum intensity on the raising and falling sides of the glow curves. Equation (4-6) are conveniently used in fitting TL glow peaks. Nonlinear least square fitting is generally used in curve fitting . Chi squared test or figure of merit[7] was used for the criteria of best fitting.

RESULTS AND DISCUSSION

Figure 1 shows typical set of TL glow curves of ZnS:Mn,Cu,Cl recorded with a linear heating rate β=0.74 K/sec[10]. As reported,

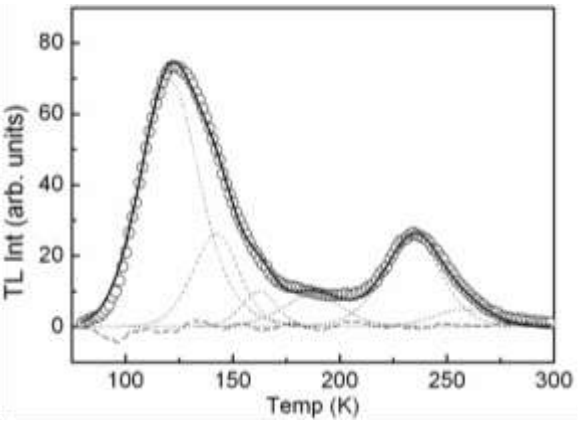

Figure 1. Deconvolution TL glow curves of ZnS:Mn,Cu,Cl phosphor of pressure =0 kbar. The symbols ooo indicates the experimental curves, ….. the deconvoluted curves and ___ Sum of the deconvoluted curves.

there is an intense TL peak at 133 K and a less intense peak at 236 K at ambient pressure. These peaks shift to higher temperature with increasing pressure. At 10 kbar pressure a new peak appears at low temperature. At 25 kbar another peak appears between 133 and 236 K. Lang *et al.*[10] evaluated the activation energy of TL peaks using various heating rate method. The values of activation energies are 0.15, 0.3 and 0.5 eV. For the same peak the activation energies are reported to increase with increase of pressure.

Table 1. Trapping parameters of the glow curves of ZnS:Mn,Cu,Cl phosphor for 0 kbar & 10 = kbar pressure.

Tm (K)	Energy (eV)	b (order)	S (sec^{-1})	FOM
120.56	0.1	1.5	$8.2x10^2$	
142.4	0.19	1.5	$4.0x10^5$	
162.68	0.34	1.5	$3.6x10^9$	0.000946
187.64	0.26	1.5	$5.7x10^5$	
234.44	0.42	1.5	$6.7x10^7$	
257.84	0.52	1.5	$9.4x10^8$	
117.2	0.1	1.5	$1.1x10^3$	
154.5	0.18	1.5	$4.5x10^4$	
179.2	0.28	1.5	$5.3x10^6$	
204	0.42	1.5	$1.9x10^6$	0.046417
225.7	0.53	1.5	$5.9x10^{10}$	
247.4	0.72	1.5	$4.3x10^{13}$	
273.2	0.72	1.5	$1.7x10^{12}$	

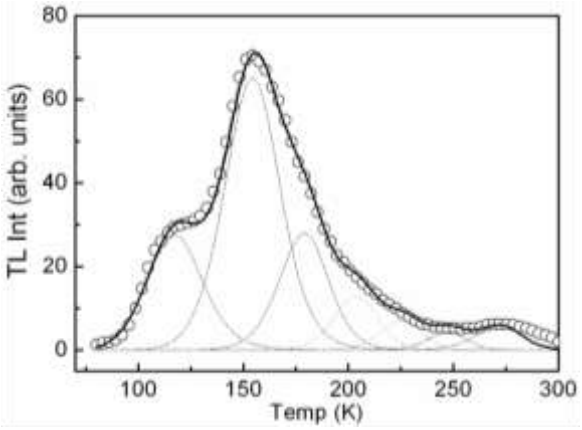

Figure 2. Deconvolution of glow curves of ZnS:Mn,Cu,Cl phosphor at pressure 10 kbar.

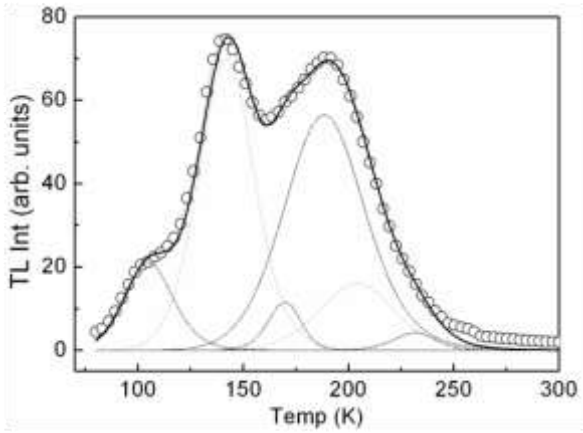

Figure 3. Deconvolution of glow curves of ZnS:Mn,Cu,Cl phosphor at pressure 25 kbar.

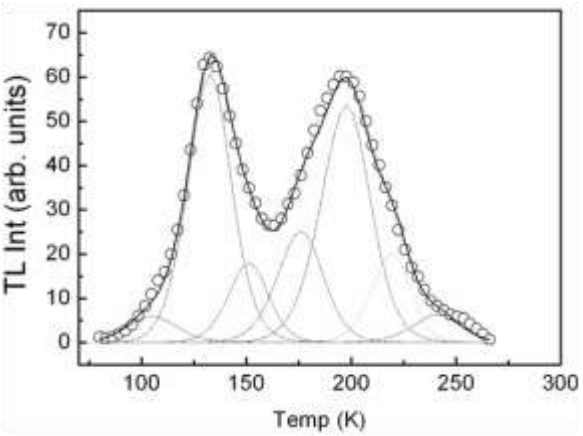

Figure 4. Deconvolution of glow curves of ZnS:Mn,Cu,Cl phosphor at pressure 58 kbar.

TL glow curve of ZnS:Mn,Cu,Cl phosphor without giving any pressure shows the presence of two prominent low temperature TL peaks at around 133 K and 234 K. The full width at half peak intensity points is considerably large. Large value of FWHM indicates that the glow curve is a composite one. The shape factor of the glow peak is also found to be above 0.48. This glow curve is deconvoluted with the *conventional glow curve deconvolution* technique to find out the trapping parameters of the glow curve. The composite curve appearing only two peaks can be deconvoluted into six TL peaks (Fig. 2). All the curves can be fitted with the same order of kinetics b=1.5. The kinetics parameters such as activation energy E, frequency factor s and order of kinetics are shown in Table 1. The figure of merit implies the validity of CGCD to extract kinetic parameters.

In order to study the effect of pressure on the characteristics of TL glow curves, a number of TL glow curves were recorded with different values of pressure. New TL peaks were observed after the application of pressure. Lang *et al*.[10] reported change in activation energy of TL peaks with the change of pressure. In this context, it is to be noted that the activation energy of a TL peak is an intrinsic parameter of the trap. This fact inspires us to investigate whether there is change in activation energy with increase of pressure. Accordingly CGCD technique is again applied to the TL peaks recorded with a pressure of 10 kbar. The glow curve clearly shows the presence of three TL peaks. The prominent peak is around 154 K shifting to the higher temperature followed by the shoulder peaks at 120 K and 272 K (Fig. 2). When CGCD is used it is evident that the glow curve can be deconvoluted to 7 peak systems. The trapping parameters of the seven peaks in Figure 2 along with the figure of merit are again given in Table 1.

Similarly TL glow curves of ZnS:Mn:Cu:Cl phosphor (Pressure = 25 kbar & 58 kbar) have been analysed by CGCD. It has been demonstrated that glow curves in

Table 1. Trapping parameters of the glow curves of ZnS:Mn,Cu,Cl phosphor for 25 & 58 kbar pressure.

Tm (K)	Energy(eV)	b (order)	S (sec-1)	FOM
120.56	0.1	1.5	8.2x102	
142.4	0.19	1.5	4.0x105	
162.68	0.34	1.5	3.6x109	0.000946
187.64	0.26	1.5	5.7x105	
234.44	0.42	1.5	6.7x107	
257.84	0.52	1.5	9.4x108	
117.2	0.1	1.5	1.1x103	
154.5	0.18	1.5	4.5x104	
179.2	0.28	1.5	5.3x106	
204	0.42	1.5	1.9x106	0.046417
225.7	0.53	1.5	5.9x1010	
247.4	0.72	1.5	4.3x1013	
273.2	0.72	1.5	1.7x1012	

reality are composite, consisting of a number of elementary peaks following general order (GO) of kinetics. The glow curve can be deconvoluted to 6 peak systems for pressure = 25 kbar (Fig. 4). The similar second curve for pressure 58 kbar is also shown (Fig. 5). It can be deconvoluted to 7 peak systems. The trapping parameters (E, s and b) and figure of merit (FOM) are quite acceptable and justifies the fitting (Table 2). In all cases it is observed that the order of kinetics remains constant. There is not much change in the values of activation energies with or without pressure.

CONCLUSION

The thermoluminescence (TL) glow curves of ZnS:Mn,Cu,Cl can be fitted to general order (GO) kinetics formalism. The order of kinetics of all the peaks was found to be 1.5 irrespective of pressure. The effect of pressure was manifested mainly in the location of the glow peak temperature. The activation energy was found to be independent of pressure.

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