

Tunneling Mechanoluminescence Produced During Deformation of II-VI Semiconductor Nanoparticles

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Abstract

The present paper reports the tunneling mechanoluminescence (ML) produced during deformation of II-VI semiconductor nanoparticles. The ionization of trapped electrons may occur by the tunneling of electron from the trapping level to the conduction band under the operation of strong electric field close to the charged dislocations. The electrons released from the filled traps may move in this conduction band and they may recombine with the luminescence center, giving rise to the luminescence characteristics of activator centers. Based on this fact, equations are derived for rise and decay of ML intensity and also for the saturation value of the ML intensity. It is found that the ML intensity should depend on the number of filled trap N_c , radius of interaction r_i , strain rate $\dot{\epsilon}$ and volume of crystal V . It is found that there is a good agreement between theoretical and experimental results.

Keywords: Luminescence, Tunneling Mechanoluminescence, Mechanical deformation

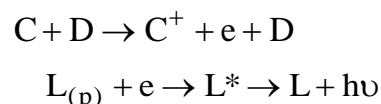
INTRODUCTION

Luminescence induced during mechanical deformation of solids is known as fracto-mechanoluminescence (ML) or tribo-luminescence. The ML links mechanical spectroscopic, electrical structural and other properties of solid. A large number of organic and inorganic crystals and amorphous solids exhibits the phenomenon of ML[1-4]. It is known that II-VI compounds exhibit instance ML during their plastic deformation and fracture [5-7]. The present paper reports that the ML in II-VI semiconductor nanoparticles are due to the tunneling of trapped electrons into the conduction band, arising as a result of the instance electric field in the vicinity of charged dislocations.

THEORY OF TUNNELING MECHANOLUMINESCENCE

An analysis of the possible ML mechanisms has shown that the interacting between charged dislocations and activator centers leads to ionization of traps. Ionization may occur by tunneling of electrons from the trapping levels to the conduction band under the operation of strong electric field close to a charged dislocation. The electric field at a distance r from the core of a charged dislocation is given by $E = 2q / \epsilon_0 r$, where ϵ_0 is the dielectric permittivity and r is the distance between the charged dislocation and trapping

center. At $q = 0.35 e/\text{units}$ [8], where e is the electron charge, the electric field voltage at a distance $r=10^{-7}$ to 10^{-8} from the dislocation core is $E = 3.4 \times 10^6$ volt/cm¹ and then they may recombine with the luminescence centers, gives rise light emission characteristic of the activator centers. This process can be represented as follows :



where C is a trap filled electrons, C^+ is empty trap and $L_{(p)}$ is the activator containing hole.

If N_c is the number of filled traps per unit volume, then the rate of generation of electrons is given by

$$g = \frac{2N_c r_i \dot{\epsilon}}{b} \quad (1)$$

where N_c is the number of ionization centers (filled traps) per unit volume. The rate equation for the change in number of electrons in the conduction band may be given by

$$\frac{dn}{dt} = g - N_a \sigma_a v n \quad (2)$$

where σ_a is the capture cross-section of the activator containing hole.

The ML intensity for a crystal of volume V may be expressed as

$$I = I_s [1 - \exp(-t / \tau)] \quad (3)$$

where, $\tau = \frac{1}{N_a \sigma_a v}$ (4)

and $I_s = \frac{2\eta N_c r_i \dot{\epsilon} v}{b}$ (5)

Equation (5) shows that the saturation value of ML intensity is directly proportional to the strain rate $\dot{\epsilon}$.

When the cross-head of the deforming machine is stopped at a time $t = t_c$, at which the ML intensity had attained a saturation value I_s , the deformation rate will decrease exponentially with time and from equation (2), we get

$$\frac{dn}{dt} = 2N_d N_c r_i v_{do} \exp[-\alpha(t - t_c)] - N_a \sigma_a v n \quad (6)$$

As $N_a \sigma_a v n \gg \frac{dn}{dt}$, the solution of above equation gives

$$n = \frac{2N_d N_c r_i v_{do}}{(N_a \sigma_a v - \alpha)} \left\{ \exp[-\alpha(t - t_c)] - \exp(-N_a \sigma_a v)(t - t_c) \right\}$$

As $N_a \sigma_a v \gg \alpha$, n may be written as

$$n = \frac{2N_d N_c r_i v_{do}}{N_a \sigma_a v} \exp[-\alpha(t - t_c)] \quad (7)$$

$$I = \frac{2\eta N_d N_c r_i v_{do}}{N_a \sigma_a v} \exp[-\alpha(t - t_c)] \quad (8)$$

The above equation shows that the ML intensity should decrease exponentially with a decay time controlled by the stress relaxation process.

During the process of deformation some of the electrons reaching the conduction band may be transferred to the shallow traps which are not under the influence of the electric field of the moving charged dislocations. Later on, the thermo-stimulated luminescence may occur at room temperature and therefore, the delayed ML may appear in some crystals in their past deformation region and consequently two peaks may be observed in their ML kinetics.

DISCUSSION BETWEEN THEORETICAL AND EXPERIMENTAL RESULTS

The intensity of ML in the first process is given by equation (5) for $\eta = 0.1$, $N_a = 10^{19}$ atoms cm^{-3} , $r_i = 10^{-6}$ cm, $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$, $v = 1 \text{ cm}^3$, and $b = 3.83 \times 10^{-8}$ cm, comes out to be $10^{10} - 10^{11}$ photons $\text{s}^{-1} \text{ cm}^{-3}$, which is comparable with the experimental observations.

Fig. 1 shows that the ML spectra of impurity doped ZnS phosphors are similar to their PL spectra. Such results are expected from the theory of present investigation.

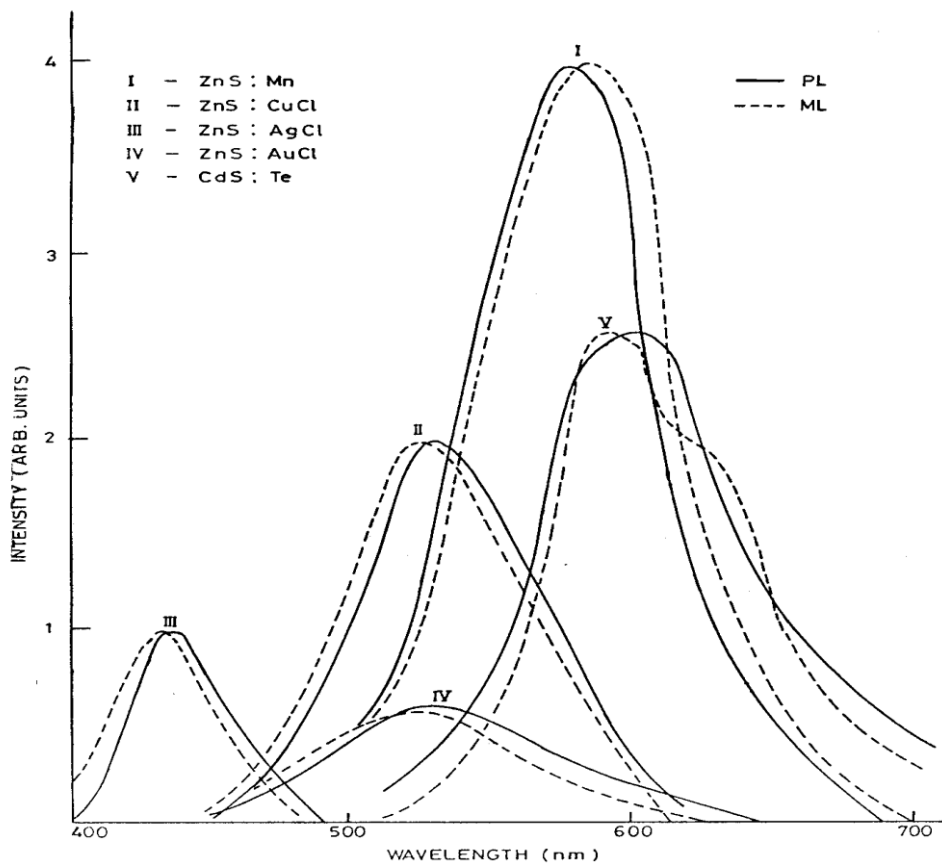


Fig.1.-ML and PL spectra of ZnS:Mn;ZnS:Cu, Cl; ZnS:Ag, Cl; ZnS:Au, Cl and CdS:Te phosphors.

Fig. 2 shows that the ML intensity of II-VI semiconductor nanoparticles decreases with temperature. This is in accord with the theory developed in the present investigation.

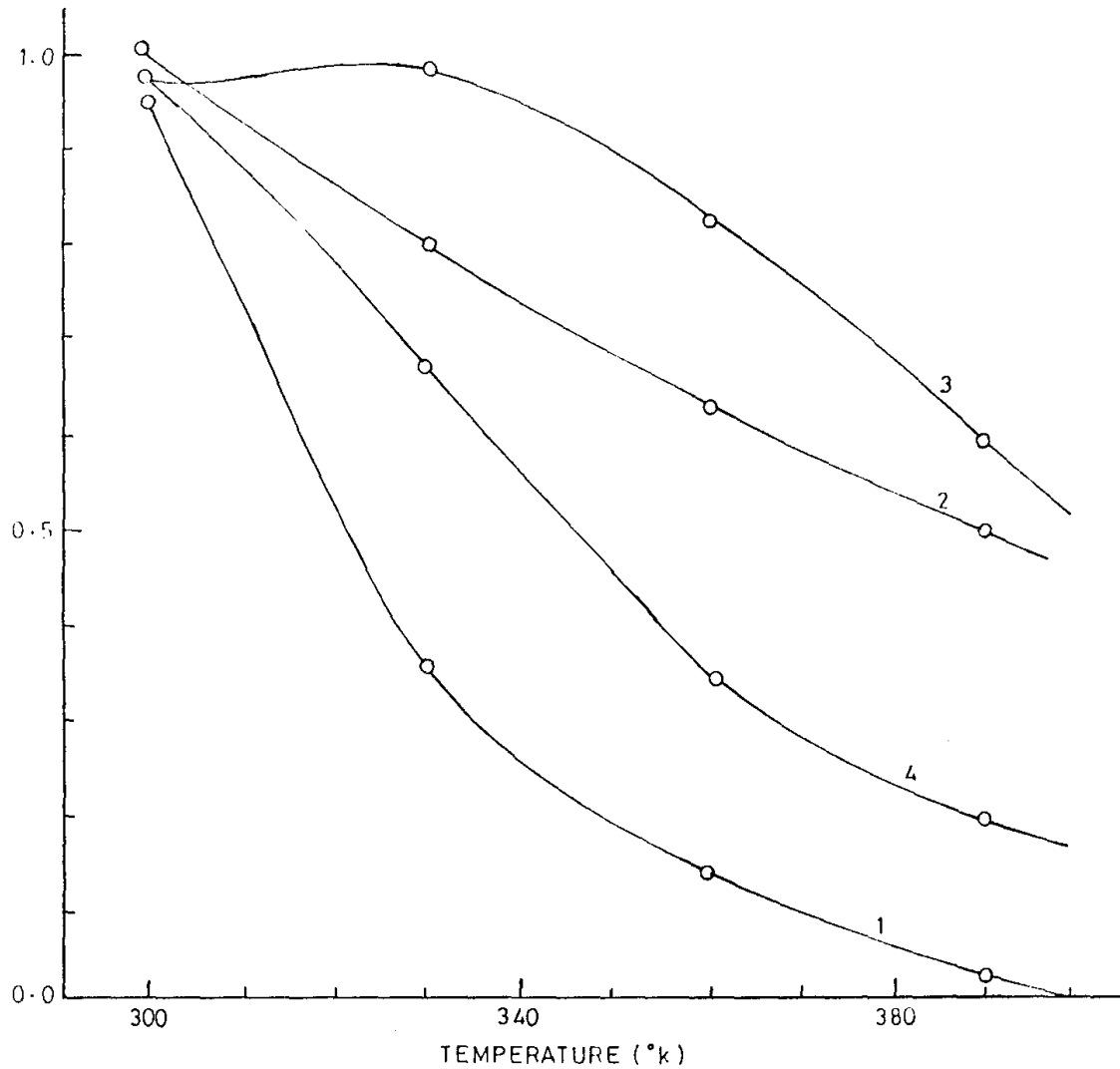


Fig2. Temperature dependence of the intensities of the deformation emission in ZnS:Cu, Al crystals

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