Materials Physics and Mechanics 19 (2014) 25-38 Received: March 19, 2014

EXACT MODEL FOR THE ELASTICO MECHANOLUMINESCENCE OF II-VI PHOSPHORS

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Abstract. The mechanoluminescence (ML) emission during the elastic deformation of II-VI crystals occurs either due to the electrostatic interaction between dislocation segments and filled electron traps or due to the piezoelectrically-induced electron detrapping. According to electrostatic interaction model, bending of dislocation segments causes electron from the electron traps tunnel to the conduction band. The recombination of electron-hole emit energy which is absorbed by the Mn^{2+} centers and the subsequent de-excitation gives rise to the light emission and according to piezoelectrically-induced electron detrapping the local piezoelectric field near the detect centers reduces the trap-depth, and therefore, the detrapping of filled electron traps takes place, and subsequently the energy released non-radiatively during the electron-hole recombination excites the Mn^{2+} centers and de-excitation gives rise to the ML. The present paper reports that piezoelectrically-induced electron detrapping model is more suitable to explain the elastico ML of II-VI phosphors.

1. Introduction

Mechanoluminescence (ML) is a phenomenon, in which light emission from a solid take place as a response to the mechanical stimulus given to it. The light emissions induced by elastic deformation, plastic deformation and fracture of solids are known as elastico ML, plastico ML and fracto ML, respectively. The ML induced by rubbing of solids or separation of two solids in contact is known as tribo ML or triboluminescence [1]. In the recent past, several materials have been reported, which emit intense ML during their elastic deformation, plastic deformation, and fracture. These materials have been reported to be useful in stress sensor [2, 3], fracture sensor [4, 5], damage sensor [6], and in the fuse-system for army warhead [7]. The ML has also been reported to be useful in the online monitoring of grinding in milling machines [8], and in radiation dosimetry [1]. The ML has also been useful the design of safety management monitoring system.

Recently, we found that several materials show strong ML in the elastic region. The examples of elastico mechanoluminescent materials are colored alkali halide crystals, ZnS:Mn, $SrAl_2O_4$:Eu, $SrAl_2O_4$:Eu,Dy, $ZnGa_2O_4$:Mn, $MgGa_2O_4$:Mn, $BaAl_2Si_2O_8$: rare earth element, $Ca_2Al_2SiO_4$: rare earth element, $Ca_2Al_2SiO_7$:Ce (Gehlenite, one of the brightest elastico mechanoluminescent materials), ZnMnTe, and ZrO_2:Ti. The dopant shown as rare earth element can be Eu. A few polymers have also been reported to be elastico mechanoluminescent. The II – VI semiconductors have been the model materials for ML studies as ZnS: Mn exhibits ML duringits elastic and plastic deformation as well as during its fracture, and all other II – VI semiconductors show ML during their plastic deformation and

fracture.

The II – VI semiconductors are piezoelectric as well as they possess charge dislocation. As the matter of the fact the elastico ML of ZnS:Mn can be excited either by piezoelectrically or by charge dislocation or by both the processes. This fact has not been clarified till now. In the present paper such studies are made and it is found that piezoelectricity is responsible for elastico ML of ZnS:Mn crystals.

2. Mechanism of the EML of ZnS:Mn crystals

2.1. Dislocation electrostatic interaction model of the EML of ZnS:Mn crystals. Figure 1 shows the schematic diagram for the mechanism of the dislocation electrostatic interaction model of the EML of ZnS:Mn crystals.

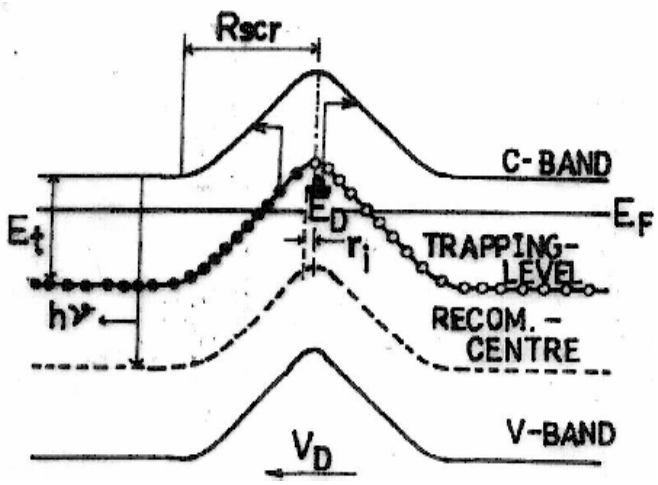

Fig. 1. Schematic diagram for the mechanism of the dislocation electrostatic interaction model of the EML of ZnS:Mn crystals.

The mechanism of the dislocation electrostatic interaction model of the Elasico ML of ZnS:Mn crystals during elastic deformation occur in the following steps [1]:

(i) The elastic deformation causes bending of the dislocation segments.

(ii) The electric field of the charged dislocation segments causes bending of the valance band and conduction band as well as dislocation bands.

(iii) Subsequently, the electrons from the electron traps tunnel to the conduction band.

(iv) The recombination of electrons with the holes gives rise to the light emission characteristic of the activator centers. In the case of Mn doped II – VI semiconductors, the impact of accelerated electrons in presence of electric field of dislocations, with the Mn^{2+} centers causes the excitation of Mn^{2+} centers and the subsequent de-excitation gives rise to the light emission characteristic of Mn^{2+} ions.

2.2. Piezoelectrically- stimulated electron detrapping model of the EML of ZnS:Mn crystals. Figure 2 shows the schematic diagram for the mechanism of the piezoelectrically- stimulated electron detrapping model of the EML of ZnS:Mn crystals

The mechanism of the piezoelectrically- stimulated electron detrapping model of the elastico ZnS:Mn crystals may be understood in the following way:

(i). The deformation of ZnS:Mn nanocrystals produces piezoelectric field because crystal – structure of ZnS is non-centrosymmetric [9].

(ii). Because of the decrease in the trap-depth due to the piezoelectric field, the detrapping of electrons from filled-electron traps takes place, and therefore, electrons reach the conduction band.

(iii). The electrons reaching the conduction band may recombine with the holes trapped in the

defect centres or they may jump to the valence band and subsequently energy may be released non-radiatively.

(iv). The energy released non-radiatively during electron hole recombination may be transferred to the Mn^{2+} ions, whereby Mn^{2+} ions may get excited [10, 11].

(v). The de-excitation of excited. Mn^{2+} ions gives rise to the light emission characteristic of the Mn^{2+} ions.

(vi). As the piezoelectric field is also produced during the release of pressure, the ML may also be produced when the pressure is released from ZnS:Mn thin film. Therefore, the mechanism of the occurrence of ML during the release of pressure should be similar to that for the application of pressure.

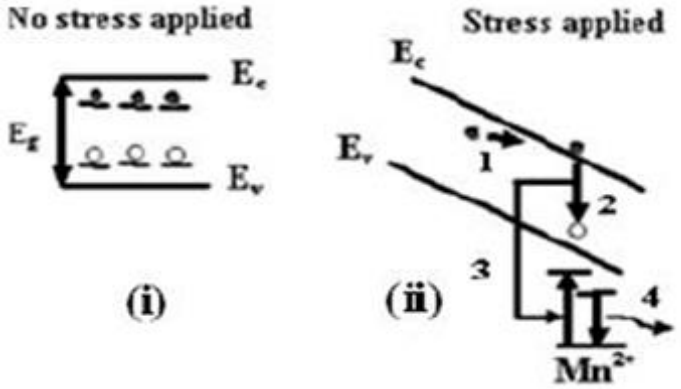

Fig. 2. Schematic diagram for the EML emission in ZnS:Mn Crystals (1-detrapping of electron and its movement in conduction band, 2-electron-hole recombination, 3- transfer of energy to Mn^{2+}, ion and excitation of Mn^{2+} ion, and 4- emission of light).

3. Theory

3.1. Electrostatically induced detrapping of charge carriers. When a crystal is deformed in the elastic region, then bending of the dislocation segments between the pinning points takes place. If g_s is the rate of generation of bending dislocation segments and τ_s is the relaxation time of the bending dislocations segments, then we may write the following rate equation

$$\left(\frac{dN_s}{dt}\right) = g_s - \frac{N_s}{\tau_s} = g_s - \varphi N_s, \tag{1}$$

where $\phi = 1/\tau_s$, and N_s is the number of bending dislocation segments at any time t.
Integrating Eq. (1) and taking $N_s = 0$, at t = 0, we get

$$N_s = \frac{g_s}{\phi}\left[1 - \exp(-\phi t)\right]. \tag{2}$$

If v_s is the average velocity of the bending segments of dislocations, then the rate of the sweeping of the surface area by the dislocation segments can be expressed as

$$\left(\frac{dS}{dt}\right) = \frac{g_s v_s}{\varphi}\left[1 - \exp(-\varphi t)\right], \tag{3}$$

where S is the surface area swept out by the dislocation segments at any time t.

As $\frac{g_s}{\varphi} = g_s \tau_s$ is the number of bending dislocation segments in equilibrium, $\frac{g_s v_s}{\varphi}$ will

be the rate of sweeping out the area by dislocation segments in equilibrium. Considering that the area swept out by the dislocation segments should be proportional to the strain ε, we can write S = B ε = B $\dot{\varepsilon}$ t, where B is the proportionality constant. Thus $\left(\frac{dS}{dt}\right)$ can be expressed as

$$\left(\frac{dS}{dt}\right)_{equilibrium} = B\,\dot{\varepsilon}. \tag{4}$$

It is to be noted that in the plastic region, the rate of sweeping of the surface area is proportional to the strain rate; hence, the validity of Eq. (4) seems to be justified.

Thus taking $g_s v_s/\phi = B\,\dot{\varepsilon}$, Eq. (3) can be written as

$$\left(\frac{dS}{dt}\right) = B\,\dot{\varepsilon}\,\left[1 - \exp(-\varphi t)\right]. \tag{5}$$

If r_t is the radius of interaction of bending dislocation segments with filled electron traps and n_t is density of electrons in the traps in the crystal, then the rate of generation g_i of interacting filled electron traps can be expressed as

$$g_i = \left(\frac{dS}{dt}\right) r_t\, n_t = 2B\dot{\varepsilon}\, r_t\, n_t\, \left[1 - \exp(-\varphi t)\right]. \tag{6}$$

In Eq. (6) coefficient 2 has been taken because in II – VI semiconductors, the filled electron traps lying along both the sides of the dislocations may tunnel to the conduction band.

If α_1 is the rate constant for the transfer of electrons from the interacting filled electron traps to the dislocation band, and α_2 is the rate constant for the transfer of interacting filled electron traps to other traps, then we can write

$$\frac{dn_i}{dt} = g_i - \alpha_1 n_i - \alpha_2 n_i,$$

$$\frac{dn_i}{dt} = 2B\dot{\varepsilon}\, r_t\, n_t\, \left[1 - \exp(-\varphi t)\right] - \alpha n_i, \tag{7}$$

where $\alpha = (\alpha_1 + \alpha_2)$ and $\frac{1}{\alpha} = \tau_i$ is the lifetime of electrons in the interacting filled electron traps.

Integrating Eq. (7), and taking $n_i = 0$ at t = 0, for $\alpha >> \phi$, we get

$$n_i = \frac{2B\dot{\varepsilon}\, r_t\, n_t}{\alpha}\left[1 - \exp(-\phi t)\right]. \tag{8}$$

Thus, the rate of generation of electrons in the conduction band can be written as

$$g_c = \alpha_1 n_i = 2B\dot{\varepsilon}\, p_t\, r_t\, n_t\, \left[1 - \exp(-\phi t)\right], \tag{9}$$

where $p_t = \frac{\alpha_1}{\alpha}$ is the probability of the transfer of electrons from the interacting filled electron traps to the dislocation band. Now we can write the following rate equation:

$$\frac{dn_c}{dt} = g_c - \frac{n_d}{\tau_d}, \text{ or}$$

$$\frac{dn_c}{dt} = 2B\dot{\varepsilon} p_t r_t n_t \left[1 - \exp(-\phi t)\right] - \beta n_d, \tag{10}$$

where $\beta = \frac{1}{\tau}$, and n_d is the number of electrons in the conduction band at any time t.

Integrating Eq. (10) and taking $n_c = 0$, at t=0 for $\beta >> \phi$, we get

$$n_c = \frac{2B\dot{\varepsilon} P_t r_t n_t}{\beta}\left[1 - \exp(-\phi t)\right], \tag{11}$$

If η is the luminescence efficiency, then the ML intensity can be expressed as

$$I = \eta\beta n_c = 2\eta B\dot{\varepsilon} p_t r_t n_t \left[1 - \exp(-\phi t)\right]. \tag{12}$$

(i) Rise of ML intensity

For $\phi t >> 1$, Eq. (12) can be written as

$$I_r = 2\eta B\dot{\varepsilon} p_t r_t n_t \phi t = 2\eta B P_t r_t n_t \phi\varepsilon. \tag{13}$$

Equation (13) indicates that initially the ML should increase linearly with the deformation time or strain of the crystals.

(ii) Saturation value of the ML intensity

For $\phi t >> 1$, from Eq. (12) the saturation value of the ML intensity can be expressed as

$$I_s = 2\eta B\dot{\varepsilon} p_t r_t n_t. \tag{14}$$

(iii) Dependence of the ML intensity on the strain rate

Equation (13) indicates that for a given deformation time, the ML intensity should increase linearly with the strain rate. Equation (14) shows that the saturation value of the ML intensity should increase linearly with the strain rate of the crystals.

(iv) Dependence of the ML intensity on the density of filled electron traps

Equation (13) shows that for a given strain the ML intensity should increase linearly with the density of filled electron traps in the crystals. Eq. (14) shows that the saturation value of the ML intensity should increase linearly with the density of filled electron traps in the crystals.

(v) Decay of ML intensity

When the crosshead of the machine deforming the crystal is stopped at $t = t_c$, then $g_s = 0$, at $t = t_c$, and from Eq. (1), we get

$$\frac{dN_s}{dt} = -\phi N_s. \tag{15}$$

Integrating Eq. (15) and taking $N_s = N_o$, at $t = t_c$, we get

$$N_s = N_0 \exp[-\phi(t - t_c)]. \tag{16}$$

Following the procedure used previously, fast decay of the ML intensity can be expressed by

the following expression:

$$I_{df} = I_o \exp[-\phi(t - t_c)]. \quad (17)$$

During the deformation of the crystal, some of the detrapped electrons reaching the conduction band may get trapped in the shallow traps. Subsequently, the thermal vibration of the lattice may cause the detrapping and the electron-hole radiative recombination may give rese to the light emission. If t_c is the time at which the velocity of dislocation become negligible and τ_{ph} is the lifetime of electrons in the shallow traps, then the slow decay of the ML intensity can be expressed as

$$I_{ds} = I_0^{'} \exp[-\chi(t - t_c^{'})], \quad (18)$$

where $\chi = \frac{1}{\tau_{ph}}$, and $I_0^{'}$ is the ML intensity at $t = t_c^{'}$.

3.2. Piezoelectically induced detrapping of charge carriers. The crystals of ZnS:Mn exhibit elastico ML only in the presence of Mn. As the elastico ML has electrical origin, it seems that there is the presence of local non-centrosymetric structure near Mn ions, whereby the piezoelectric constant is high. As the space near Mn^{2+} ions has higher piezoelectric constant and normal regions away from Mn^{2+} ion have lower value of the piezoelectric constant, there should be the existence of a gradient of electric field. Thus, filled electrons traps near Mn^{2+} ions may be detrapped by low value of stress and the detrapping of electron traps lying at larger distance from Mn^{2+} ions needs higher value of the stress. The detrapping may take place either due to tunneling process or due to the thermal ionization of traps owing to the reduction in trap-depth caused by the piezoelectric field.

If Ω is the activation volume near an Mn^{2+} ion, where the local structure has high value of the piezoelectric constant and N_l and N_t are the concentrations of Mn^{2+} ions and filled electron traps, respectively, then the total number of detrapable traps is, $n_{t0} = \Omega N_l N_t$. If d_0 is the piezoelectric constant near Mn^{2+} ions, then for the applied pressure P, the piezoelectric charge Q near Mn^{2+} ions is given by, $Q = d_0 P$. If the crystal is compressed at a fixed pressing rate $\dot{P}$ or strain rate ε̇, then Q can be written as

$$Q = d_0 P = d_0 \dot{P} t = d_0 Y \dot{\varepsilon} t, \quad (19)$$

where Y is the Young's modulus of the elasticity of the crystal.

If F_c is the characteristic piezoelectric field, that is, the field needed for reducing n_{t0} to n_{t0}/e caused by the detrapping of the filled electrons traps in ZnS:Mn crystals, then we can write the following equation

$$-\frac{dn_t}{dF} = \frac{n_t}{F_c} = Zn_t, \quad (20)$$

where F is the piezoelectric field near Mn^{2+} ions, n_t is the number of filled electron traps at any time t and $Z = 1/F_c$.

Integrating Eq. (20) and taking $n_t = n_{t0}$, for the threshold field $F = F_{th}$, we get

$$n_t = n_{t0} \exp[-Z(F - F_{th})], \quad (21)$$

where n_{t0} is the total number of the filled electron traps in the activation volume ΩN_l.

Using Eq. (21), the total number of detrapped electrons can be expressed as

$$n_d = (n_{t0} - n_t) = n_{t0}[1 - \exp\{-Z(F - F_{th})\}]. \quad (22)$$

In the elastic region, Z(F-F_{th}) is low, that is Z(F-F_{th}) <<1, hence, Eq. (22) can be written as

$$n_d = n_{t0}[1-1+Z(F-F_{th})] = n_{t0}Z(F-F_{th}). \quad (23)$$

Now, differentiating Eq. (23), we get

$$\frac{dn_d}{dt} = n_{t0}Z\frac{dF}{dt}. \quad (24)$$

As the rate of generation g of electrons in the conduction band will be equal to the rate of detrapping of electrons, we can write

$$g = n_{t0}Z\frac{dF}{dt}. \quad (25)$$

If τ is the lifetime of electrons in the conduction band, then the change in the number of electrons in the conduction band can be expressed as

$$\Delta n = g\tau = n_{t0}Z\frac{dF}{dt}\tau. \quad (26)$$

Using Eq. (26), the current j flowing in the crystal can be written as

$$j = \Delta n\, qv_d, \quad (27)$$

where q is the electronic charge and v_d is the drift velocity.

If μ is the mobility of electrons in the crystals, then Eq. (27) can be expressed as

$$j = \Delta n\, q\, \mu \mathrm{F}. \quad (28)$$

Thus, the rate of flow of electrons in the conduction band of the crystal is given by

$$r = \frac{j}{q} = \Delta n v_d = \Delta n\, \mu F. \quad (29)$$

From Eqs. (26) and (29), we get

$$r = \Delta n v_d = n_{t0}Z\tau\, \mu F\frac{dF}{dt}. \quad (30)$$

If σ and n_h are the capture-cross section and the concentration of the hole centres, respectively, then the rate of electron- hole recombination can be expressed as

$$R = \sigma n_h \Delta n v_d = \sigma n_h n_{t0}Z\tau\, \mu F\frac{dF}{dt}. \quad (31)$$

(i) Rise of ML intensity

If η is the efficiency of the Mn^{2+} ions, to emit light during the absorption of non-radiative energy produced during electron-hole recombination, then the EML intensity can be expressed as

$$I = \eta\sigma n_h n_{t0}Z\tau\, \mu(F-F_{th})\frac{dF}{dt} \text{ or,}$$

$$I = \eta\ \sigma\ \Omega\ \mathrm{N_l N_t}\ n_h Z\tau\ \mu(F - F_{th})\frac{dF}{dt}, \tag{32}$$

where F_{th} is the threshold piezoelectric field for the ML emission.

If B is the correlating factor between the piezoelectric field F and the piezoelectric charge Q, then, F = BQ, and Eq. (32) can be written as

$$I = \eta\ \sigma\ \Omega\ \mathrm{N_l N_t}\ n_h Z\tau\ \mu B^2(Q - Q_{th})\frac{dQ}{dt}, \tag{33}$$

where F_{th}= B Q_{th}.

From Eqs. (19) and (33) we get

$$I = \eta\ \sigma\ \Omega\ \mathrm{N_l N_t}\ n_h Z\tau\ \mu B^2 d_0^2(P - P_{th})\frac{dp}{dt}. \tag{34}$$

In terms of strain rate, Eq. (34) can be expressed as

$$I = \eta\ \sigma\ \Omega\ \mathrm{N_l N_t}\ n_h Z\tau\ \mu B^2 d_0^2 Y(P - P_{th})\dot{\varepsilon}. \tag{35}$$

Equation (35) indicates that for a given strain rate the ML intensity should increase linearly with the pressure, and for a given pressure, the ML intensity should increase linearly with the strain rate.

(ii) Decay of ML intensity

If the deformation of the crystals is stopped at $t = t_m$, then the generation of charges is stopped and relaxation of piezoelectric charges takes place. If τ_q is the decay time of the piezoelectric charges, then the rate of relaxation of surface charges can be expressed as

$$-\frac{dQ}{dt} = Q \Big/ \tau_q = \gamma\ Q, \tag{36}$$

where $\gamma = 1/\tau_q$, is the rate constant for the relaxation of piezoelectric charges.

Integrating Eq. (36) and taking $Q = Q_m$ at $t = t_m$, we get

$$Q = Q_m \exp[-\gamma(t - t_m)], \tag{37}$$

where Q_m is the piezoelectric charges at $t = t_m$.

Using Eqs. (34) and (37), the decay of ML intensity can be expressed as

$$I_d = I_m \exp[-2\gamma(t - t_m)], \tag{38}$$

where I_m is the ML intensity at $t = t_m$.

(iii) Estimation of I_m and I_T

If the crystal is compressed at a fixed strain rate for a time t_m, where the pressure is P_m, then from Eqs. (34) and (35), the maximum intensity I_m of the ML is given by

$$I_m = \eta\sigma\Omega\ \mathrm{N_l N_t}\ n_h Z\tau\ \mu B^2 d_0^2(P_m - P_{th})\dot{P} = \eta\sigma\Omega\ \mathrm{N_l N_t}\ n_h Z\tau\ \mu B^2 d_0^2 Y(P_m - P_{th})\dot{\varepsilon}. \tag{39}$$

It is evident from Eq. (39) that the ML intensity will be maximum for the pressure P_m corresponding to time t_m at which the cross-head of the machine is stopped.

Integration of Eq. (34) gives that the total ML intensity I_{TD} during the deformation of the sample can be expressed as

$$I_{TD} = \int_0^{t_m} I dt = \int_0^{P_m} \eta\ \sigma\ \Omega\ \mathrm{N_l N_t}\ n_h Z\tau\ \mu B^2 d_0^2(P - P_{th})dP \quad \text{or,}$$

$$I_{TD} = \eta\,\sigma\,\Omega\,\mathrm{N_l N_t}\,n_h Z\tau\,\mu B^2 d_0^2\,\frac{(P_m^2 - 2P_m P_{th})}{2} \qquad \text{or,}$$

$$I_{TD} \simeq \eta\,\sigma\,\Omega\,\mathrm{N_l N_t} n_h Z\tau\,\mu B^2 d_0^2\,\frac{P_m^2}{2}. \tag{40}$$

Equation (40) indicates that the total ML intensity in the deformation region should increase quardratically with the applied pressure.

Using Eq. (38), the value of total ML intensity from t_m to ∞ is given by

$$I_{TPD} = \int_{t_m}^{\infty} I_m \exp[-2\gamma(t - t_m)]dt = \frac{I_m}{2\gamma}. \tag{41}$$

From Eqs. (40) and (41), the total ML intensity is given by

$$I_T = I_{DT} + I_{TPD} = \left(\frac{I_m P_m}{2} + \frac{I_m}{2\gamma}\right) \qquad \text{or,}$$

$$I_T = \frac{\eta\,\sigma\,\Omega\,\mathrm{N_l N_t}\,n_h Z\tau\,\mu B^2 d_0^2 P_m^{\,2}}{2}\left(1 + \frac{\tau_q}{t_m}\right), \tag{42}$$

where $P_m = Y\dot{\varepsilon}\,t_m$.

4. Experimental support to the proposed theory

Figure 3 shows the ML –strain and stress-strain curves of ZnS:Mn crystals at a fixed strain rate. It is seen that the ML appears in the elastic region as well as in the plastic region. Initially the ML intensity increases with time and then it tends to attain a saturation value for larger value of the deformation. It is evident from it seems that the moving dislocations are responsible for the ML emission in ZnS:Mn crystals. It is to be noted that there is no time delay between the movement of dislocations and the appearance of ML pulses. This fact shows that the ML emission takes place as soon as the movement of dislocation starts.

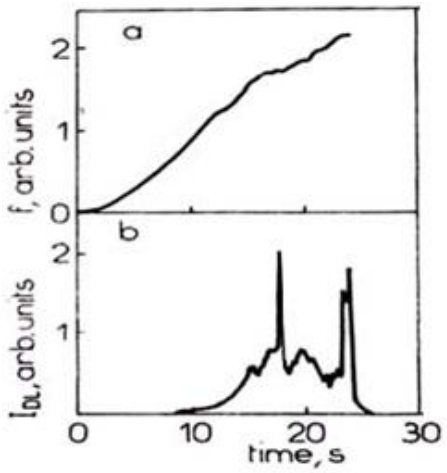

Fig. 3. (a) Stress-strain and, (b) ML -strain curves of ZnS:Mn crystal when deformed by bending at a fixed strain rate shown in (a) and (b) (after Alzelta et al., Ref. [12]).

Figure 4 shows that the ML intensity of ZnS:Mn crystals increases with the strain rate. It has been found that the ML intensity of ZnS:Mn crystals is optimum for a particular

concentration of the crystals. Initially the ML intensity increases with increasing concentration of Mn^{2+} as the number of luminescence centres increases, however, for higher concentration of Mn^{2+} the ML intensity decreases decreasesbecause of the concentration quenching. Thus the intensity is optimum for a particular concentration of Mn^{2+} centers in the phosphors.

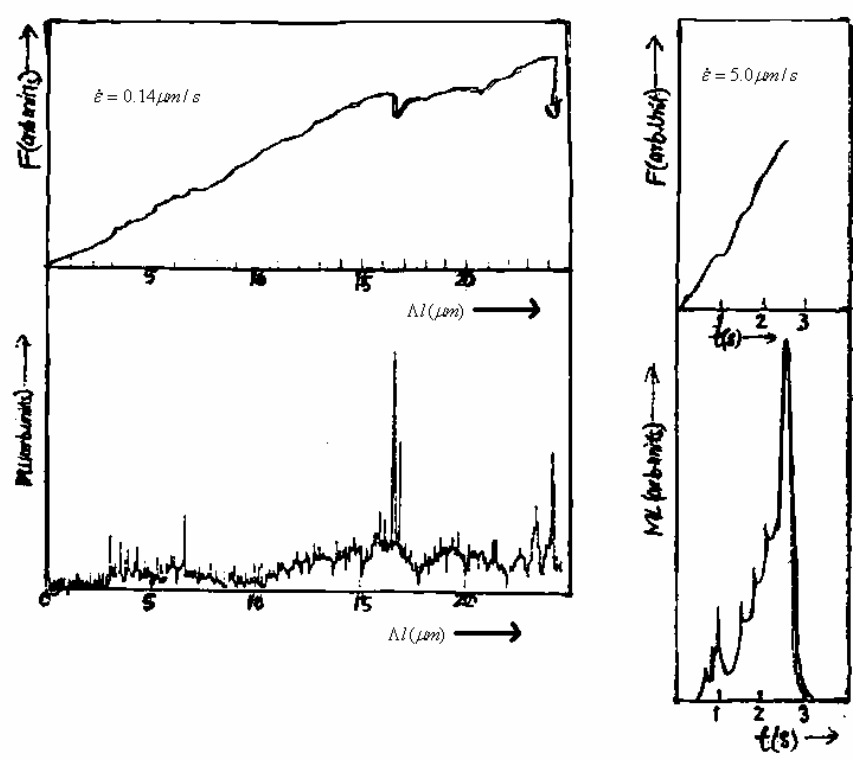

Fig. 4. Stress-strain curve and ML- strain curve of ZnS:Mn for different strain rates (after Alzelta et al. Ref. [12]).

Figure 5 shows the ML spectra of II – VI semiconductors. It is evident that the ML spectra are similar to the PL and EL spectra. This fact shows that although the excitation mechanism is different in ML, and PL, and EL, the emission of photons occurs from the similar transitions.

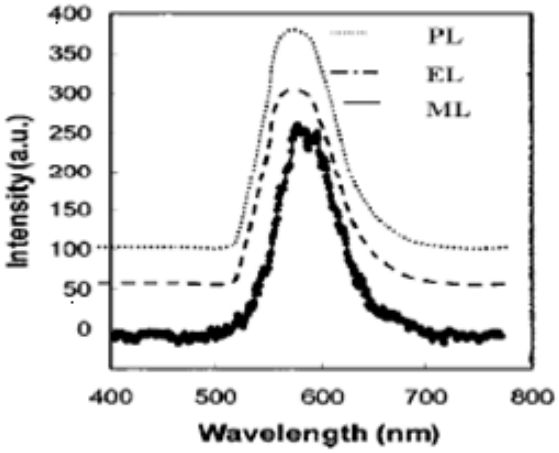

Fig. 5. ML photoluminescence (PL) and electroluminescence spectra of ZnS:Mn film (after Xu et al., Ref. [2]).

Thus, it seems that there is a good agreement between the theoretical and experimental results.

Xu et al. [13] fabricated the thin film of ZnS:Mn nanoparticles on various substrates by physical vapour deposition of ion plating or a sputtering method. The source material of ZnS:Mn was pretreated at 1050 ^{0}C for 3 h in a vacuum sealed quartz tube before deposition. A highly oriented film was achieved by selecting a deposition rate of 2nm/s and a substrate temperature of 160 ^{0}C. The chemical composition determined by X-ray diffraction pattern showed that the Mn amount in the film was the same as in the source material, i.e., 1.5 percent. Moreover, the X-ray diffraction pattern showed only one strong diffraction peak at 28.49 ^{0} in the 2θ range of 10 ^{0}-90 ^{0}, which was attributed to the (111) plane of ZnS, indicating that the film was highly oriented. The field emission scanning electron microscope (FE-SEM) and XRD techniques indicate that the ZnS:Mn film was composed of nano-sized crystallites with a mean size of 20 nm. The elastico ML was induced by compression stress of 500 N, which was applied by a material testing machine with a cross-head speed of 0.1 mm/minute. The EML intensity was measured by a photon counting system, and the EML spectra were recorded using a spectrometer attached to a photonic multichannel analyzer.

Figure 6 shows that when a load is applied on to the film of ZnS:Mn nanoparticles coated on a quartz substrate, then initially the EML intensity increases with time, attains a peak value and later on it decreases with time [13]. It is seen that when pressure is released, then the EML emission also takes place. It is evident from Fig. 1 that when the load is applied for the second time, then also the EML emission takes place during the application and release of the applied pressure. This fact shows the reproducibility of EML corresponding to the application and release of pressure, whereby two EML pulses I' and II', respectively are generated during one cycle of the applied pressure, and all of which were reproducible as shown in I' and II' in Fig. 6. The threshold pressure for the appearance of EML in ZnS:Mn nanoparticles is nearly equal to 1MPa.

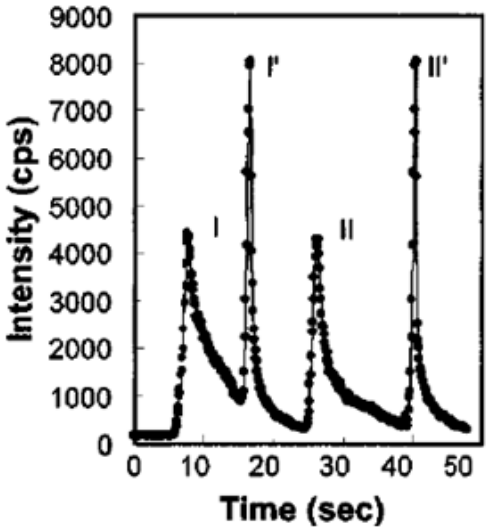

Fig. 6. ML response of ZnS:Mn nanoparticles coated on a quartz plate for the compression stress of 500 N, which was applied by a material test machine with a cross-head speed of 0.10 mm/min (after Xu. et al. Ref. [13].

Figure 7 shows the plot between the log of EML intensity I and $(t-t_m)$. The plot between log I and $(t-t_m)$ for the EML induced by release of pressure, is also similar to Fig. 7. In this case, the value of slope is higher because the rate of release pressure is high; however, the total EML intensity is equal to that obtained during the application of pressure. The value of γ

is determined from a slope of the Fig. 7 using Eq. (38), and it is found to be 0.11 sec^{-1} and this gives that the decay time of EML intensity should be equal to 9.1 sec.

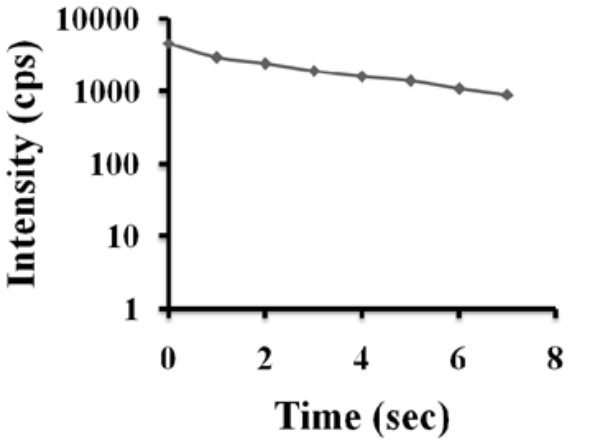

Fig. 7. Plot of log I versus $(t\text{-}t_m)$.

It is seen from Fig. 8 that for a given strain rate the EML intensity increases linearly with the applied stress. This is in accord with Eq. (39).

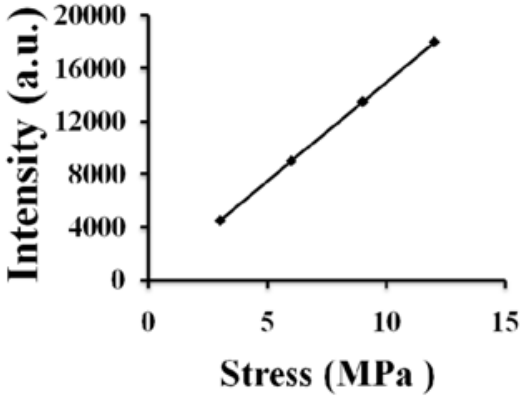

Fig. 8. Stress dependence of the EML intensity (theoretical).

Figure 9 shows that the EML intensity increases linearly with the strain rate. This finding follows Eq. (21) The EML spectra of ZnS:Mn phosphors are similar to their electroluminescence (EL)and photoluminescence (PL) spectra. The ML, EL and PL, emissions are related to $^4T_1$-$^6A_1$ transition of Mn^{2+} ions. Thus, there is a good agreement between the theoretical and experimental results.

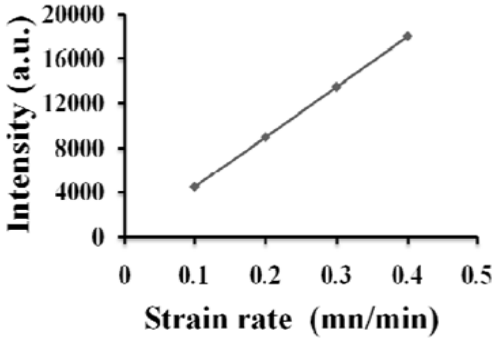

Fig. 9. Strain rate dependence of the EML intensity (theoretical).

5. Suitable model for the EML of Zns:Mn phoshphors

The II – VI semiconductors are piezoelectric as well as they possess charge dislocation. As the matter of the fact the elastico ML of ZnS:Mn phosphors can be excited either by piezoelectrically or by charge dislocation or by both the processes. This fact has not been clarified till today, yet an attempt has been made in this direction with the implementation of the above mentioned model, which opens new dimensions further. Such studies are made and it is found that piezoelectically induced detrapping model is responsible for elastico ML of ZnS:Mn crystals.

6. Conclusions

As ZnS crystals is non-centrosymmetric [9], the piezoelectrifiction caused by elastic deformation may give rise to the light emission [13, 14, 15]. The other possibility for the occurrence of ML in ZnS:Mn crystals may be the electrostatic interaction between charged dislocations and filled electrons traps [1,16,17,18]. The dislocation model has been found to be suitable for the plastico ML of II-VI semiconductors [1]. It is to be noted that thermodynamic analysis suggests that dislocations and stacking faults should be unstable in nanoparticles with respect to diffusion to the surface and annihilation. However, such defects may be retained by kinetic factors; for example, association with large scale shape features derived from the assembly of smaller nanoparticles precursors [19, 20], or be trapped at nanoparticles grain boundaries. The existence of dislocations in ZnS nanoparticles has also been reported [21, 22]. The following experimental facts support the suitability of piezoelectrically- induced electron detrapping model for the elastico ML in ZnS:Mn nanoparticles [23].

(i) ZnS crystal possesses non-centrosymmetric structure [9]; hence, piezoelectric origin of elastico ML may be possible.

(ii) The waveforms of ML induced by application of load, release of load, and impulsive deformation of ZnS:Mn crystals are similar to the waveforms of the piezoelectric charges produced during application of load, release of load, and impulsive deformation, respectively[13, 24].

(iii) In dislocation electrostatic interaction model of elastic ML, the bending of dislocation segments causes the ML excitation, in which the total ML emission increases linearly with the stress because the bending increases linearly with stress [25]. In piezoelectrically- induced electron detrapping model, electrical energy which depends on the mechanical energy is responsible for the ML excitation. As the mechanical energy, hence, the stress-induced electrical energy depends quadratically on the stress; the total ML emission depends quadratically on the applied stress. Practically, the total emission from elastico ML of ZnS:Mn nanocrystals depends quadratically on the applied stress, [13], hence, this results supports the piezoelectric origin of the elastico ML of ZnS:Mn nanocrystals.

(iv) When the plastico ML including elastico ML of ZnS:Mn crystals is induced by application of hydrostatic pressure, then intense ML emission is observed [26]. As the dislocations cannot move under hydrostatic pressure [27], the part of plastico ML and elastic ML induced by moving dislocations is suppressed, and the observed ML emission may be attributed to the piezoelectrically –induced plastico ML and elastico ML.

(v) In low temperature dislocation can not be moved but piezoelectric charge can be.

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