Luminescence induced by elastic and plastic deformation of II – VI semiconductors at fixed strain rates

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The mechanoluminescence (ML) emission during the elastic deformation of ZnS:Mn crystals occurs due to the electrostatic interaction between dislocation segments and filled electron traps, and the ML emission during the plastic deformation of II-VI semiconductors takes place due to the mechanical interaction between the moving dislocations and filled electron traps. In the elastic region, the ML intensity increases linearly with the strain or deformation time, and in this case, the saturation region could not be observed because of the beginning of plastic deformation before the start of saturation in the ML intensity. In the plastic region, initially the ML intensity also increases linearly with the strain or deformation time, and later on it attains a saturation value for large deformation. When the deformation is stopped, then at low temperature the ML intensity decreases with time whereby the decay time of ML gives the relaxation time of dislocation segments or pinning time of the dislocations. For the deformation at fast strain rate, there are two components of ML decay, in which the fast decay gives the relaxation time of dislocation segments or pinning time of dislocations, and the slow decay gives the lifetime of electrons in the shallow traps The saturation value of the ML intensity increases linearly with the strain rate and also with the density of filled electron traps in the crystals. The saturation value of ML intensity decreases with increasing temperature of the crystals because of the decreases of the luminescence efficiency and radius of interaction of dislocations with filled electron traps with increasing temperature. From the ML measurements the relaxation time of dislocation segments, pinning time of dislocations, and the lifetime of electrons in shallow traps can be determined. Expressions derived for the ML induced by elastic and plastic deformation of II-VI semiconductors at fixed strain rate, indicate that the ML intensity depends on the strain, strain rate, stress, density of filled electron traps, size of crystals, temperature, luminescence efficiency, etc. A good agreement is found between the theoretical and experimental results.

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1. Introduction

Mechanoluminescence (ML) is the phenomenon of light emission from a solid as a response to the mechanical stimulus given to it. The light emission induced by elastic deformation, plastic deformation and fracture of solids is 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 investigated, 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 II – VI semiconductors have been the model materials for ML studies as ZnS: Mn exhibits ML during its elastic and plastic deformation as well as during its fracture, and all other II – VI semiconductors show ML during their plastic deformation and fracture. In the past,

the ML of II-IV semiconductors has attracted the attention of a large number of workers. Although, it has come into knowledge long back that the rubbing of the surface of sphalerite minerals (ZnS) shows the visible trails of light, the light produced from natural and synthetic zinc sulphide was studied in detail only in the last century. Levision [9] was the first to measure the ML spectra of sphelarite (largely ZnS:Mn) and observed by naked eyes that the ML spectrum was extended from 550nm to 650 nm. Subsequently, Karl [10, 11] observed visually the relative ML intensity of the new materials obtained by fusing zinc sulphides with a verity of new compounds, e.g., oxides of manganese, tin or silicon. The ML spectra of different samples of ZnS:Mn was measured by Waggoner [12]. He observed that the ML spectra of different samples had their maximum intensity at a mean value of 557 ±5 nm, which compares well with the mean value of 557 ± 3 nm, at which maximum intensity was found to occur in the phosphorescence spectrum excited by X-rays Later on, (Nelson [13], Chaudacck [14], Obrikat et al. [15], Meyer and Obrikat [16], Thelssen [17], Meyer et al. [18] photographed the ML spectra of ZnS phosphor with different activators and co-activators and they observed

that the ML spectra were most closely to the electroluminescence (EL) spectra . Curie and Prost [12] also suggested that EL might be responsible for the ML of ZnS.

The correlation between ML and EL was also observed In addition to the spectroscopy method, with respect to others points. The ML intensity was shown to have the same functional dependence on force, as the EL intensity has on voltage. Also the temperature dependence and time decay characteristics in both ML and EL are found to be of similar nature [18]. Alzetta et al. [20] reported that when a top-hat compression pulse is applied to Mn doped ZnS powder suspended in oil in a pressure cell, then a burst of light was emitted at both the instances of rise and fall of the compression pulse. Meyer et al. [18] and Alzetta et al. [21] also found that the ML pulse due to the application of pressure pulse to the ML cell was most closely the same as the ML pulse created after applying the voltage pulse to the EL cell. This fact also showed a kind of similarity between the ML and EL phenomena, and therefore, it is concluded that the ML may be the deformation-induced electroluminescence.

Sodomka and his co-workers have studied the ML of II-VI semiconductors [22-29]. They came to a conclusion that the instantaneous ML intensity of the phosphors depends on the instantaneous change of pressure with time and the ML does not occur until a minimum pressure I_m is attained Sodomka [23] recorded both the pressure and ML brightness during impact of a load on the ZnS:Mn and ZnS:Cu powders placed in a solid binder. It was suggested that the ML in these materials was caused by elastic and plastic deformation and fracture. Myazdrikov et al. [30] have reported that the ML intensity of ZnS:Mn,Cu electroluminescent panel is proportional to the impact energy of the ball dropped on the sample. Chudacek [25], Alzetta et al. [20], and Meyer et al. [18] have reported the following relation for the pressure dependence of the ML of semiconductors.

$$\begin{split} I_{ML} &\sim \ \underline{P} \ d\underline{P}/dt \\ I_{ML} &\sim \ exp \ (\alpha_0 \underline{P}^2) \end{split}$$

and,

$$\mathbf{I}_{\mathrm{ML}} \sim \exp\left(-\gamma_0 \,/\, \underline{\mathbf{P}}^{1/2}\,\right)$$

where and α_0 and γ_0 are the quantitics not explicitly dependent on the pressure.

Warschaner and Reynolds [31] have reported that when UV-irradiated CdS crystals cooled at liquid nitrogen temperature is gently tapped, then a green flash of light is emitted from the body of the crystals. It was shown that impulses involving energies of 750 cgs or smaller is sufficient to excite the effect. The ML flashes were found to appear by dropping spheres of known weight from a calibrated height to the surface of the crystal. It was found that the impact was most effective when applied parallel to the c-axis of the crystals. Repeated tapping produces a flash for each tap. Of the order of one thousands flashes may be obtained from a well-stimulated crystal by tapping more or less uniformly over the whole surface. After the stimulation has exhausted, the crystals can be re-activated by a brief illumination, and the process of obtaining multiple flashes by tapping can be repeated. Kulp and Gale [32] have reported that when the uniaxial pressure is applied on to the CdS crystals of low resistivity, then the ML emission takes place. In this case, the ML consisted of the characteristics green edge emission and a red luminescence centring at about 660nm.

Although Sodomka [23] Chaudacck [29] and Meyer et al. [18] reported the occurrence of ML in ZnS:Mn during its elastic deformation, the systematic demonstration of the ML emission from ZnS:Mn was given by Alzetta et al. [33] by deforming the ZnS:Mn crystal at a fixed strain rate and measuring the ML-strain and stress-strain curves of the crystals. Results of Zns:Mn indicated that 5% of the emitted light was observed in the elastic region, 80% observed during plastic region, and the rest 15% at fracture. The emission of ML pulses is found to occur concurrently with the steps occurring in the stress-strain curve of the crystals. As the step in the stress-strain curve occurs due to the unpinning or gliding of the dislocations, it was inferred that the Mn²⁺ centres are excited during the unpinning of dislocations. Scarmozzino [34] also supported the dislocation origin of ML in ZnS:Mn Bredikhin and Shmurak [35] reported that ZnS:Cu crystals do not show ML during their elastic deformation and it starts to appear only during the plastic deformation. They suggested that the electrostatic interaction between the dislocations and filled electron traps is responsible for the ML. The electrostatic interacting mechanism of the ML in II-VIsemiconductor was also supported by many workers [36-42].

In, ZnS crystal with a sufficiently high resistivity, pulsed ML occurs during their deformation[43-46]. The charged dislocations of opposite sings move in opposite directions and bring out charges to the crystal surface. The potential difference across the crystals increases as deformation proceeds until it reaches a breakdown value at which the pulse of surface EL is emitted and this process is repeated continuously with increasing deformation of the crystal. The pulsed ML is suppressed by immersing the crystals in the conducting liquid or by using a crystal of insufficient high resistivity or by short-circuiting the lateral surfaces of the crystals, and then in these cases continuous ML is observed.

Diorvdivic [47] has studied the ML induced by the impulsive deformation of ZnF₂:Mn, ZnS:Ag, ZnS:Mn CaP₂O₇:Dy and (ZnCd)S phosphors. The overall purpose of his work was to apply the ML concept to a wireless fuse system for army warhead [2,48,49].

Chandra [50] has studied the ML induced by impulsive deformation of the phosphors of II-VI semiconductors and he has found that the ML intensity is directly related to the rate of creation of new surfaces and the total ML intensity is directly related to the total surface area created during the fracture of samples. Bergeon et al. [51, 52] have studied the ML of ZnS:Mn phosphors induced by an impact of a projective at a hypervelocity. Reddy and Reddy [53] have reported laser-like ML in the Zn Mn Te and Rao et al.[54] have studied the ML of $(ZnS)_{1-x}$ (MnTe)_x Tiwari et al. [55] have studied the effect of temperature on the ML of gold-doped(ZnCd)S phosphors and Choudhary et al. [56] have reported the ML produced during the cleavage of II-VI semiconductor. Xu at el. [57-60] and Agyeman et al. [61] have studied the ML induced by elastic deformation of ZnS:Mn thin film and shown that the ML can be used are stress indicator or stress sensor. Chandra et al. [62] have studied the ML induced by elastic deformation of ZnS:Mn nanocrystals, in which the ML excitation is caused not by the charged dislocations but occurs due to by the piezoelectrification of nanocrystals.

In recent years, it has been found that II-VI semiconductors and SrAl₂O₄:Eu can be used as smart materials for designing mechano-optical sensors such as stress sensor, fracture sensor, damage sensor, etc. In this regard, a satisfactory understanding of the ML in II-VI semiconductors is required. The present paper reports the theoretical approach made on the ML of II-VI semiconductors induced by their elastic and plastic deformation at fixed strain rates and makes a comparison between the theoretical and experimental results. It is shown that many parameters of the ML of II-VI semiconductors can be determined from the measurements of their ML at fixed strain rates.

2. Mechanism of ML

Fig. 1 shows the schematic diagram for the mechanism of the ML in II-IV semiconductors.



Fig. 1. Schematic diagram for the mecahnism of ML in II-VI semiconductors.

Elastico ML

The Elasico ML of II - VI semiconductors 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 moving in the conduction band with the holes gives rise to the light emission characteristic of the activator centres. In the case of ZnS:Mn, the impact of accelerated electrons excites the Mn^{2+} centres and the subsequent de-excitation give rise to the light emission, characteristic of Mn^{2+} ions.

Plastico ML

The ML of II - VI semiconductors during plastic deformation occurs in the following steps [1]:

(i) The plastic deformation causes movement of dislocations.

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

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

(iv) The recombination of electrons with the holes gives rise to the light emission characteristic of the activator centres. 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+} centres causes the excitation of Mn^{2+} centres and the subsequent de-excitation gives rise to the light emission characteristic of Mn^{2+} ions.

3. Theory

3.1 Elastico ML of II - VI semiconductors

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

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

where $\phi=1/\tau_r$, 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

$$N_{s} = \frac{g_{s}}{\phi} \left[1 - \exp(-\phi t) \right]$$
 (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

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

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

or,

As
$$\frac{g_s}{\phi} = g_s \tau_s$$
, is the number of bending

dislocation segments in equilibrium, $\frac{g_s v_s}{\phi}$, 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 $S = B \varepsilon = B \dot{\varepsilon} t$, where B is the proportionality constant. Thus $\left(\frac{d\dot{S}}{dt}\right)$ can be expressed

as

$$\left(\frac{\mathrm{dS}}{\mathrm{dt}}\right)_{\mathrm{equilibriu m}} = \mathbf{B} \overset{\bullet}{\varepsilon} \tag{4}$$

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 $g_r v_r / \phi = B \xi$, Eq. (3) can be written as

$$\left(\frac{\mathrm{dS}}{\mathrm{dt}}\right) = \mathrm{B} \stackrel{\bullet}{\epsilon} \left[1 - \exp\left(-\phi t\right)\right] \tag{5}$$

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

$$\mathbf{g}_{i} = \left(\frac{\mathrm{dS}}{\mathrm{dt}}\right) \mathbf{r}_{t} \mathbf{n}_{t} = 2 \operatorname{B} \overset{\bullet}{\boldsymbol{\varepsilon}} \mathbf{r}_{t} \mathbf{n}_{t} \left[\mathbf{l} - \exp\left(-\phi t\right)\right] \quad (6)$$

In Eq. (6), 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 another traps, then we can write

$$\frac{\mathrm{dn}_{i}}{\mathrm{dt}} = g_{i} - \alpha_{1} n_{i} - \alpha_{2} n_{i}$$

$$\frac{\mathrm{dn}_{i}}{\mathrm{dt}} = 2 \operatorname{B} \overset{\bullet}{\epsilon} r_{t} n_{t} \left[1 - \exp(-\phi t) \right] - \alpha n_{i} \quad (7)$$

where $\alpha = (\alpha_1 + \alpha_2)$ and $\frac{1}{\alpha_1} = \tau_i$, 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

$$n_{i} = \frac{2 \operatorname{Be} r_{i} n_{t}}{\alpha} \left[1 - \exp(-\phi t) \right]$$
(8)

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

$$g_{c} = \alpha_{1} \mathbf{n}_{i} = 2 \mathbf{B} \overset{\bullet}{\varepsilon} \mathbf{p}_{t} \mathbf{r}_{t} \mathbf{n}_{t} \left[1 - \exp(-\phi t) \right] (9)$$

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

$$\frac{\mathrm{dn}_{\mathrm{c}}}{\mathrm{dt}} = \mathrm{g}_{\mathrm{c}} - \frac{\mathrm{n}_{\mathrm{d}}}{\tau_{\mathrm{d}}}$$

$$\frac{\mathrm{dn}_{\mathrm{c}}}{\mathrm{dt}} = 2 \operatorname{B} \overset{\bullet}{\varepsilon} \operatorname{p}_{\mathrm{t}} \operatorname{r}_{\mathrm{t}} \operatorname{n}_{\mathrm{t}} \left[1 - \exp\left(-\phi \, \mathrm{t} \right) \right] - \beta \operatorname{n}_{\mathrm{d}} \quad (10)$$

where $\beta = \frac{1}{\tau_c}$, and n_c 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

$$n_{c} = \frac{2 \operatorname{B} \varepsilon \operatorname{P}_{t} \operatorname{r}_{t} \operatorname{n}_{t}}{\beta} \left[1 - \exp\left(-\phi t\right)\right]$$
(11)

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

$$I = \eta \beta n_{d} = 2\eta B \varepsilon p_{t} r_{t} n_{t} [1 - \exp(-\phi t)]$$
(12)

(i) Rise of ML intensity

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

$$I_{r} = 2\eta B \varepsilon p_{t} r_{t} n_{t} \phi t = 2\eta B P_{t} r_{t} n_{t} \phi \varepsilon$$
(13)

Eq. (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

$$I_s = 2\eta B \varepsilon p_t r_t n_t$$
(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

$$\frac{d N_s}{dt} = -\phi N_s$$
(15)

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

$$N_s = N_0 \exp[-\phi(t - t_c)]$$
(16)

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

$$I_{df} = I_o \exp\left[-\phi \left(t - t_c\right)\right]$$
(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

$$I_{ds} = I'_{0} \exp \left[-\chi \left(t - t'_{c} \right) \right]$$
 (18)

where $\chi = \frac{1}{\tau_{ph}}$, and I_0 is the ML intensity at $t = t_c$.

(vi) Temperature dependence of the ML intensity

As η and r_t decrease with increasing temperature of the crystals, Eqs. (13) and (14) indicate that the ML intensity should decrease with increasing temperature of II-IV semiconductors.

3.2 Plastico ML of II - VI semiconductors

If G_d is rate of generation of moving dislocations caused by the deformation of a crystals at a fixed strain rate, and if $\tau_p = \frac{1}{\phi^t}$ is the pinning of dislocations, then we

can write the following equation

$$\frac{\mathrm{dN}_{\mathrm{m}}}{\mathrm{dt}} = \mathrm{G}_{\mathrm{d}} - \frac{\mathrm{N}_{\mathrm{m}}}{\tau_{\mathrm{p}}} = \mathrm{G}_{\mathrm{d}} - \phi' \mathrm{N}_{\mathrm{m}} \qquad (19)$$

Integrating Eq. (19) and taking $N_m = 0$, at t = 0, we get

$$N_{m} = \frac{G_{d}}{\phi'} \left[1 - \exp(-\phi' t) \right]$$
(20)

If v_d is the velocity of dislocations, then the rate of sweeping out the area by the dislocation can be expressed as

$$\frac{\mathrm{dS}}{\mathrm{dt}} = \frac{G_d v_d}{\phi'} \left[1 - \exp(-\phi' t) \right]$$
(21)

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

As
$$\frac{G_d v_d}{\phi} = G_d v_d \tau_p$$
, and $G_d \tau_p$ is the number N_d

of dislocations moving in equilibrium, $G_d v_d \tau_p$ will be

equal to $N_d v_d$. From the relation $\mathcal{E} = N_d v_d b$, we

get $n_d v_d = \frac{\varepsilon}{b}$ (where b is the Burgers vector). Thus Eq. (26) can be written as

(26) can be written as

$$\frac{\mathrm{dS}}{\mathrm{dt}} = \frac{\varepsilon}{\mathrm{b}} \left[1 - \exp(-\phi' t) \right] \tag{22}$$

Following the procedure, the ML intensity in the present case, can be given by

$$I = \frac{2\eta \varepsilon}{b} p_t r_t n_t [1 - \exp(-\phi' t)]$$
(23)

Equation (22) indicates that initially the ML intensity should increase linearly with time and for ϕ 't>>1, it should attain a saturation. Thus I_r and I_s are given by the following equations

$$I_{r} = \frac{2\eta \varepsilon}{b} p_{t} r_{t} n_{t} \phi' t = \frac{2\eta}{b} P_{t} r_{t} n_{t} \phi' \varepsilon \quad (24)$$

and,

$$I_{s} = \frac{2\eta \varepsilon}{b} p_{t} r_{t} n_{t}$$
(25)

(26)

(27)

Equation (25) indicates that the saturation value of the ML intensity should increase linearly with the strain rate and also with the density of Mn^{2+} centres in the crystals. It is to be noted that for higher values of Mn²⁺ concentration quchching takes place and thus the ML intensity should be optimum for the particular concentration of the Mn^{2+} centres in the crystals

Similar to the case of electro ML the fast and slow decay of the ML intensity in this case, can be given by the following equations, respectively

 $I_{df} = I_0 \exp[-\phi'(t - t_c)]$

and

$$I_{ds} = I_{0}^{'} \exp[-\chi(t - t_{c}^{'})]$$
(27)

It is to be noted that the slow component of ML decay will be observed only when
$$\phi' >> \chi$$
, that is only for very high strain rate of the crystals.

4. Experimental support to the proposed theory

Fig. 2 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 Fig. 2(c) that the ML pulses appear concurrently with the steps occurring in the stress-strain curve of the crystal. As the step in the stress strain curve is related with the movement of dislocations, 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. 2. (a) stress-strain and, (b) ML -strain curves of ZnS:Mn crystal when deformed by bending at a fixed strain rate.(c) is the magnified portion of two curves shown in (a) and (b) (after Alzelta et al., ref.[33]).

Fig. 3 shows the dependence of the ML intensity on the deformation or deformation time for ZnS: Cu, Cl crystals deformed at a fixed strain rate. It is seen that initially the ML intensity increases linearly with time, and then it attains a saturation value. These results are in accordance with Eqs. (24) and (25).



Fig. 3. ML intensity versus deformation time and stress versus deformation time curves of ZnS:Cu, Al crystals deformed at a strain rate of 10 µm/min (after Bredikhin and Shmuralk, ref. [35]).

Fig. 4 shows the plot of log I versus (t - t_c). It is seen that the plot is a straight line with negative slope. This result follows Eq. (26). From the inverse of the slope of this plot the value of the pinning time of dislocations is determined and it is found to be 90.91 sec: As the pinning time of dislocations is less, the fast decay of the ML intensity could not be observed.



Fig. 4. In I versus (t-t_c) plot for the decaying portion of the ML intensity of ZnS:Cu,Al crystal for $\varepsilon = 10 \mu m/min$.

Fig. 5 shows that the ML intensity of ZnS:Mn crystals increases with the strain rate. This result is in accordance with Eq. (25). 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 as the number of luminescence centres increases, however, for higher concentration of Mn the ML intensity decreases decreases because of the concentration quenching. Thus the intensity is optimum for a particular concentration of Mn in ZnS.



Fig. 5. Stress-strain curve and ML- strain curve of ZnS:Mn for different strain rates (after Alzelta et al. ref. [33]).

Fig. 6 shows the effect of temperature on the ML intensity of ZnS:Cu, Cl crystals. It is seen that the decrease in the ML intensity with temperature is faster as compared to that of the photoluminescence (PL) intensity. As the ML intensity depends on η and charge density of the dislocations or the radius of the interaction, between charged dislocation and filled electron traps however, the PL intensity depends only on η , and both η and the charge density of the dislocations decrease with temperature, a faster decrease of ML intensity as compared to the PL intensity occurs with the increasing temperature of the crystals.



Fig. 6. Temperature dependence of the photoluminescence intensities of the blue (curve1), green (curve2), orange-red (curve3) photoluminescence bands, and the temperature dependence of the green band (curve4) of the ML in ZnS:Cu,Al crystals (after Brediktin and Shmurak, ref. [35]).

Fig. 7 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. 7. ML photoluminescence (PL) and electroluminescence spectra of ZnS:Mn film (afterXu et al., ref. [2]).

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

5. Conclusions

The important conclusions diagram from the present investigation are as given below:

(i) The ML emission from ZnS:Mn crystals takes place during its elastic and plastic deformation and the ML emission from other II-VI semiconductor takes place during their plastic deformations. The ML emission during the elastic deformation takes place due to the mechanical interaction between dislocations segments and F-centres, and the ML emission during the plastic deformation takes place due to the mechanical interaction between the moving dislocations and F-centres.

(ii) In the elastic region, the ML intensity increases linearly with the strain or deformation time and in this case, the saturation region could not be observed because of the beginning of the plastic deformation before the start of the saturation in the ML intensity.

(iii) In the ML in the plastic region, initially the ML intensity also increases linearly with the strain or deformation time, and later on it attain a saturation value for large deformation.

(iv) When the deformation is stopped, initially the ML intensity decreases at a fast rate and later on it decreases at a show rate. The decay time for the fast deceases in the ML intensity gives the relaxation time of bending dislocation segments or pinning time of dislocations, and the decay time of the slow decreases of the ML intensity gives the lifetime of electrons in the shallow traps in the crystals. The show component of the ML decay should appear only if the pinning time of dislocation will be less than the lifetime of electrons in the shallow traps in the crystals.

(v) The saturation value of the ML intensity increases linearly with the strain rate and also with the density of the filled electron traps in the crystals.

(vi) The ML intensity decreases with increasing temperature of the crystals because of the decreases in the luminescence efficiency and charge density of the dislocations.

(vii) From the ML measurements the relaxation time of dislocation segments, pinning time of dislocations and lifetime of the electrons in the shallow traps can be determined.

(viii) Expression are derived for the ML induced by elastic and plastic deformation of II-VI semiconductors at fixed strain rate. It is found that the ML intensity depends on the strain, strain rate, stress, density of filled electron traps, size of crystals, luminescence efficiency, and temperature. A good agreement is found between the theoretical and experimental results. The expressions derived are as given below:

Elastic region

$$I = \eta B \dot{\varepsilon} p_F r_F n_F \left[1 - \exp(-\phi t) \right]$$
$$I_r = \eta \dot{\varepsilon} p_F r_F n_F \phi t = \eta p_F r_F n_F \phi \varepsilon$$
$$I_s = \eta B \dot{\varepsilon} p_F r_F n_F$$

$$I_{df} = I_o \exp\left[-\phi(t-t_c)\right]$$

and,

$$I_{ds} = I'_o \exp\left[-\chi(t - t'_c)\right]$$

Plastic region

$$I = \frac{\eta \dot{\varepsilon}}{b} p_F r_F n_F \left[1 - \exp(-\phi' t) \right]$$
$$I_r = \frac{\eta \dot{\varepsilon}}{b} p_F r_F n_F \phi' t$$
$$I_s = \frac{\eta \varepsilon}{b} p_F r_F n_F$$
$$I_{df} = I_0 \exp[-\phi' (t - t_c)]$$

and

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 $I_{ds} = I'_{a} \exp\left[-y(t - t'_{c})\right]$

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