

# EXACT MODEL FOR THE ELASTICO MECHANOLUMINESCENCE OF II-VI PHOSPHORS

Ratnesh Tiwari<sup>1</sup>, Vikas Dubey<sup>1</sup>, B.P. Chandra<sup>2\*</sup>

<sup>1</sup>Department of Physics, Bhilai Institute of Technology, Kendri, Raipur (C.G.) 493661, India

<sup>2</sup>Department of Postgraduate Studies and Research in Physics, Rani Durgawati University,  
Jabalpur (M.P.) 482001, India

\*e-mail: bpchandra@yahoo.co.in

**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 defect 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<sub>2</sub>O<sub>4</sub>:Eu, SrAl<sub>2</sub>O<sub>4</sub>:Eu,Dy, ZnGa<sub>2</sub>O<sub>4</sub>:Mn, MgGa<sub>2</sub>O<sub>4</sub>:Mn, BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>: rare earth element, Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>4</sub>: rare earth element, Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>:Ce (Gehlenite, one of the brightest elastico mechanoluminescent materials), ZnMnTe, and ZrO<sub>2</sub>: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 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

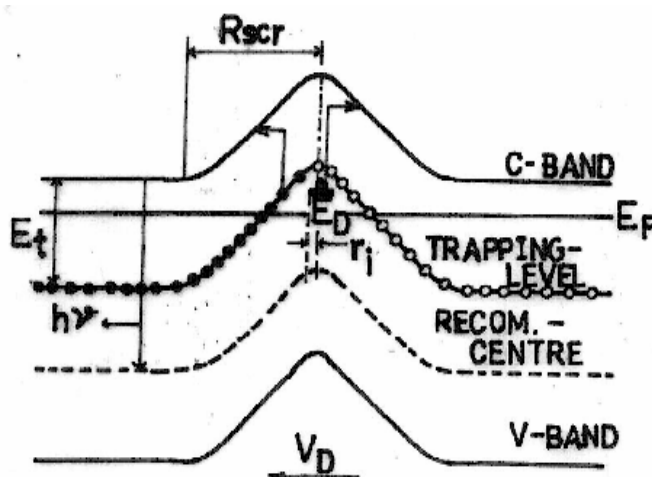
fracture.

The II – VI semiconductors are piezoelectric as well as they possess charge dislocation. As the matter of the fact the elástico 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 elástico 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 Elástico 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 elástico 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



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  $\varepsilon$ , we can write  $S = B \varepsilon = B \dot{\varepsilon} t$ , where  $B$  is the proportionality constant. Thus  $\left(\frac{dS}{dt}\right)$  can be expressed as

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

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

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

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

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

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  $\alpha_1$  is the rate constant for the transfer of electrons from the interacting filled electron traps to the dislocation band, and  $\alpha_2$  is the rate constant for the transfer of interacting filled electron traps to other traps, then we can write

$$\begin{aligned} \frac{dn_i}{dt} &= g_i - \alpha_1 n_i - \alpha_2 n_i, \\ \frac{dn_i}{dt} &= 2 B \dot{\varepsilon} r_t n_t [1 - \exp(-\phi t)] - \alpha n_i, \end{aligned} \quad (7)$$

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  $\alpha \gg \phi$ , we get

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

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

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

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:



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 rise to the light emission. If  $t_c$  is the time at which the velocity of dislocation become negligible and  $\tau_{ph}$  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. Piezoelectrically induced detrapping of charge carriers.** The crystals of ZnS:Mn exhibit elástico ML only in the presence of Mn. As the elástico ML has electrical origin, it seems that there is the presence of local non-centrosymmetric 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  $\Omega$  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  $\dot{\epsilon}$ , then  $Q$  can be written as

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

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

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

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  $\Omega N_l$ .

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

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



$$I = \eta \sigma \Omega N_1 N_t n_h Z \tau \mu (F - F_{th}) \frac{dF}{dt}, \quad (32)$$

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

$$I = \eta \sigma \Omega N_1 N_t n_h Z \tau \mu B^2 (Q - Q_{th}) \frac{dQ}{dt}, \quad (33)$$

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

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

$$I = \eta \sigma \Omega N_1 N_t n_h Z \tau \mu B^2 d_0^2 (P - P_{th}) \frac{dP}{dt}. \quad (34)$$

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

$$I = \eta \sigma \Omega N_1 N_t n_h Z \tau \mu B^2 d_0^2 Y (P - P_{th}) \dot{\epsilon}. \quad (35)$$

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  $\tau_q$  is the decay time of the piezoelectric charges, then the rate of relaxation of surface charges can be expressed as

$$-\frac{dQ}{dt} = \frac{Q}{\tau_q} = \gamma Q, \quad (36)$$

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

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

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

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

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

$$I_m = \eta \sigma \Omega N_1 N_t n_h Z \tau \mu B^2 d_0^2 (P_m - P_{th}) \dot{P} = \eta \sigma \Omega N_1 N_t n_h Z \tau \mu B^2 d_0^2 Y (P_m - P_{th}) \dot{\epsilon}. \quad (39)$$

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.

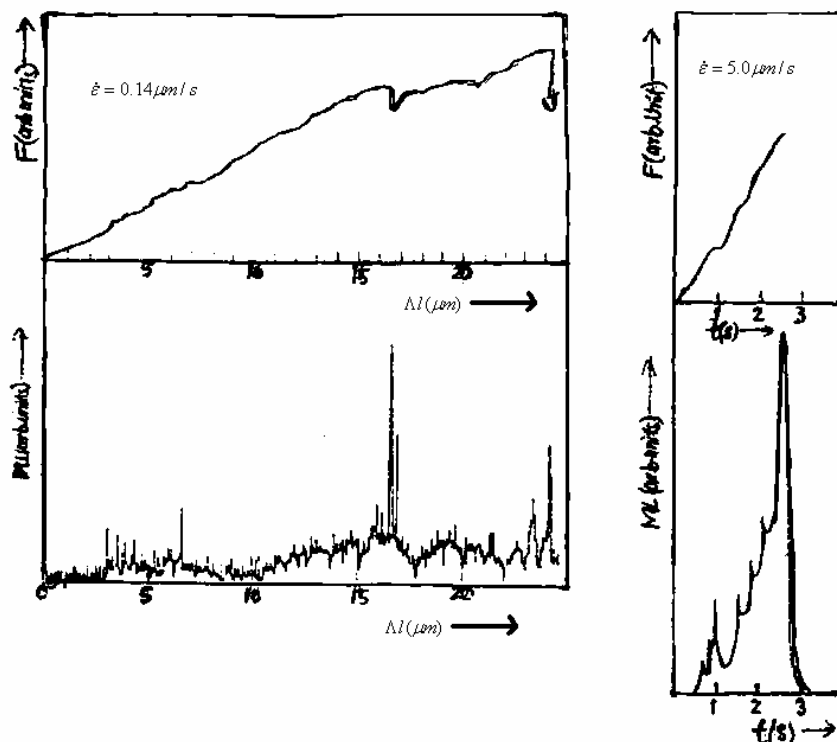
Integration of Eq. (34) gives that the total ML intensity  $I_{TD}$  during the deformation of the sample can be expressed as

$$I_{TD} = \int_0^{t_m} I dt = \int_0^{P_m} \eta \sigma \Omega N_1 N_t n_h Z \tau \mu B^2 d_0^2 (P - P_{th}) dP \quad \text{or,}$$



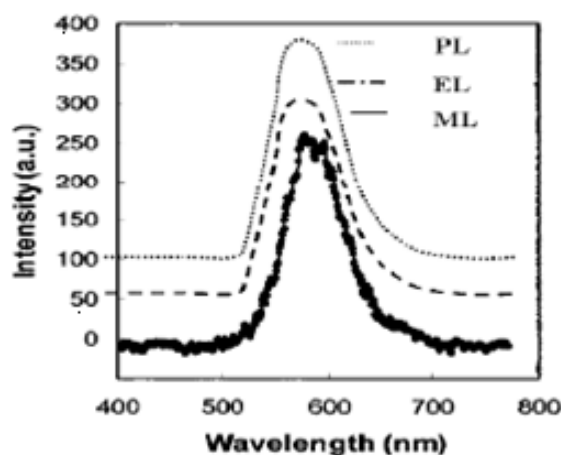


concentration of the crystals. Initially the ML intensity increases with increasing concentration of  $Mn^{2+}$  as the number of luminescence centres increases, however, for higher concentration of  $Mn^{2+}$  the ML intensity decreases because of the concentration quenching. Thus the intensity is optimum 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]).

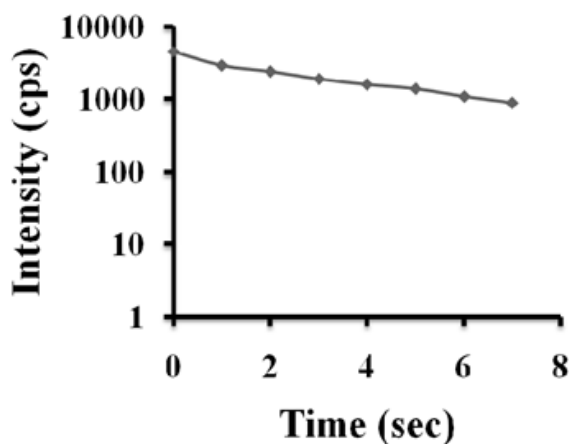
Figure 5 shows the ML spectra of II – VI semiconductors. It is evident that the ML spectra are similar to the PL and EL spectra. This fact shows that although the excitation mechanism is different in ML, and PL, and EL, the emission of photons occurs from the similar transitions.



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

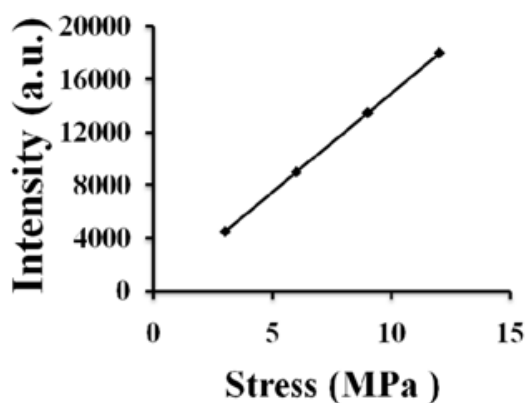


is determined from a slope of the Fig. 7 using Eq. (38), and it is found to be  $0.11 \text{ sec}^{-1}$  and this gives that the decay time of EML intensity should be equal to 9.1 sec.



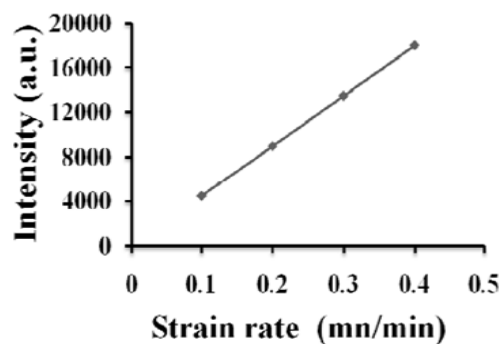
**Fig. 7.** Plot of  $\log I$  versus  $(t-t_m)$ .

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  $\text{Mn}^{2+}$  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 phosphors

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 piezoelectrically induced detrapping model is responsible for elastico ML of ZnS:Mn crystals.

## 6. Conclusions

As ZnS crystals is non-centrosymmetric [9], the piezoelectrification 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.

## References

- [1] B.P. Chandra, In: *Luminescence of Solids*, ed. by D.R. Vij (Plenum Press, New York, 1998), p. 361.
- [2] C.N. Xu, T. Watanabe, M. Akiyama, X.G. Zheng // *Applied Physics Letters* **74** (1996) 1236.
- [3] C. Li, C. N. Xu, H. Yamada, Y. Imai, H. Zheng, I. Zhang // *Key Engineering Materials*

- 368, 1401 (2008).
- [4] B.P. Chandra, J.I. Zink // *Physical Review B* **21** (1980) 816.
- [5] J.S. Kim, Y.M. Kwon, N. Shin, K.S. Sohn // *Applied Physics Letters* **90** (2007) 241916.
- [6] I. Sage, L. Humberstone, N. Geddes, M. Kemp, S. Bishop, G. Bourhill // *Smart Materials and Structures* **10** (2001) 3312.
- [7] J.G. Dante, In: *Reports by the Secretary of Army* (USA, 1983).
- [8] S. Aman, J. Tomas // *Journal of Materials Science* **39** (2007) 5247.
- [9] H.-Y. Lu, S.-Y. Chu // *Journal of Crystal Growth* **265** (2004) 476.
- [10] L. Grmela, R. Macku, P. Tomanek // *Journal of Microscopy* **229** (2008) 275.
- [11] J.F. Suyver, S.F. Wuister, J.J. Kelly, A. Meijerink // *Nano Letters* **1** (2001) 429.
- [12] G. Alzelta, I. Chudacek, R. Scarmozzino // *Physica Status Solidi (a)* **1** (1970) 775.
- [13] C.N. Xu, T. Watanabe, M. Akiyama, X.G. Zheng // *Applied Physics Letters* **74** (1999) 1236.
- [14] I. Chudáček // *Czechoslovak Journal of Physics B* **16(6)** (1966) 520.
- [15] K. Meyer, D. Obrikat, D. Rossberg // *Physica Status Solidi B* **35(1)** (1969) K13.
- [16] M.I. Molotskii, *Electronic Excitation during Plastic Deformation and Fracture of Crystals: Chemistry Reviews; Soviet Scientific Reviews, Section B, Chemistry Reviews* V. 13 Part 3 (Taylor & Francis, 1989).
- [17] Yu.A. Osip'yan, V.F. Petrenko, A.V. Zaretskii, R.W. Whitworth // *Advances in Physics* **35** (1986) 115.
- [18] B.P. Chandra // *Radiation Effects and Defects in Solids* **138** (1996) 883.
- [19] R.L. Penn, J.F. Banfield // *Science* **281** (1998) 969.
- [20] J.F. Banfield, H. Zhang, In: *Nanoparticles and the Environment Reviews in Mineralogy and Geochemistry*, ed. by J.F. Banfield, A. Navrotsky (Mineralogical Society of America, 2001), Vol. 44, p. 1.
- [21] B. Gilbert, F. Huang, H. Zhang, G.A. Waychunas, J.F. Banfield // *Science* **305** (2004) 651.
- [22] H. Zhang, B. Gilbert, F. Huang, J.F. Banfield // *Nature* **424** (2003) 1025.
- [23] B.P. Chandra, C.N. Xu, H. Yamada, X.G. Zheng // *Journal of Luminescence* **130** (2010) 442.
- [24] C.-N. Xu, M. Akiyama, K. Nonaka, T. Watanabe // *IEEE Transactions on Ultrasonics, Ferroelectrics and Frequency Control* **45(4)** (1998) 1065.
- [25] B.P. Chandra // *Journal of Luminescence* **128** (2008) 1217.
- [26] G. Alzetta, N. Minnaja, S. Santucci // *Nuovo Cimento* **33** (1962) 911.
- [27] R. Scarmozzino // *Solid State Communications* **9** (1971) 1759.