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MECHANOLUMINESCENCE GLOW CURVE OF ZnS:Mn

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The curve between mechanoluminescence (ML) intensity and deformation and post-deformation time of a solid is known as ML glow curve. When a ZnS:Mn crystal is elastically deformed by applying a load at a fixed rate, then initially the ML intensity increases with time, attains a peak value I_m at a particular time t_m, and later on it decreases with time. After t_m, initially the EML intensity decreases exponentially at a fast rate and then it decreases exponentially at a slow rate, in which the decay time of fast decrease in EML intensity is equal to half of the decay time of piezoelectric charges. For a given strain rate, whereas the peak intensity I_m increases linearly with the magnitude of applied pressure, the total EML intensity I_T increases quadratically with the magnitude of the applied pressure. The ML spectra of ZnS:Mn crystals are similar to their photoluminescence and electroluminescence spectra. The elastico ML in ZnS:Mn crystals can be understood on the basis of the piezoelectrically-stimulated electron detrapping model ,in which the local piezoelectric field near the Mn^{2+} centres 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+} centres and de-excitation gives rise to the ML. On the basis of the piezoelectrically-stimulated electron detrapping model, expressions are derived for different characteristics of the EML of ZnS:Mn crystals and a good agreement is found between the theoretical and experimental results. The expressions explored for the dependence of EML intensity on several parameters may be useful in tailoring the suitable materials capable of exhibiting ML during their elastic deformation. The values of the decay time of piezoelectric charges, time-constant for the rise of pressure, pressing rate, strain rate and the threshold pressure for EML emission can be determined from the measurement of the ML glow curve.

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1. Introduction

The luminescence induced by any mechanical action on solids is known as mechanoluminescence (ML). The light emissions produced during the elastic deformation ,plastic deformation, and fracture of solids are called elastico ML, plastico ML and fracto ML, respectively, and the light induced by rubbing of solids or separation of two solids in contact is known as tribo ML or triboluminescence. Whereas nearly 50% of all inorganic salts and organic molecular solids show ML during their fracture, only a few solids exhibit ML during their elastic and plastic deformations. The examples of elastico mechanoluminescent materials are coloured

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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. In addition to all the elastico mechanoluminescent materials mentioned above, alkaline-earth oxides, certain varieties of rubber, and certain metals also exhibit plastico ML. To date, most studies on ML have been made on coloured and non-coloured alkali halide crystals, II-VI semiconductors, sugar crystals and divalent rare earth doped $SrAl_2O_4$ phosphors [1-8]. For better understanding of the mechanoluminescent materials significant theoretical studies have also been made on the EML, PML and FML [8-14]. In the recent past the intense elastico and fracto mechanoluminescent materials have been found to have the potential for the stress sensor, fracture sensor, damage sensor, and for the visualizations of stress field near the crack-tip, stress distribution in the solids, and quasidynamic crack-propagation in solids [12,15-19].
When a load is applied on to a solid, initially the ML intensity increases with time, attains a peak value and then it decreases with time. Such a curve between the ML intensity and deformation and post-deformation time of a solid is known as the ML glow curve.The present paper reports the ML glow curve of ZnS:Mn crystals where the ML is induced by elastic deformation. Moreover, a comparison is made between the theoretical and experimental results, and the importance of ML glow curve is explored.

2. Mechanism of the EML of ZnS:Mn crystals

ZnS crystals are non-centrocemetric [20], hence, the piezoelectrifiction caused by elastic deformation may give rise to the light emission [1-15].The other possibility for the occurrence of ML in ZnS:Mn crystals may be the electrostatic interaction between charged dislocations and filled electrons traps [1,21]. The dislocation model has been found to be suitable for the plastico ML of II-VI semiconductor [1].

The following experimental facts support the suitability of piezoelectrically-stimulated electron detrapping model for the elastico ML in ZnS:Mn crystals.

(i) In dislocation electrostatic interaction model of elastico 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 [9]. In piezoelectrically-stimulated 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 crystals depends quadratically on the applied stress,[5], hence, this results supports the piezoelectric origin of the elastico ML of ZnS:Mn crystals.

(ii) When the plastico ML including elastico ML of ZnS:Mn crystals is induced by the application of hydrostatic pressure, then intense ML emission is observed [22]. As the dislocations cannot move under hydrostatic pressure [23], the part of plastico ML induced by moving dislocations is suppressed, and the observed ML emission may be attributed to the piezoelectrically –induced plastico ML and elastico ML.

The mechanism of the elastico ML in ZnS:Mn crystals may be understood in the following way :

(i) The deformation of ZnS:Mn crystals produces piezoelectric field because crystal – structure of ZnS is non-centrosymmetric [20].

(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 fall to the valence band and subsequently energy may be released non-radiatively.

(iv) The energy released non-radiatively during electron-hole recombination and falling of electrons from the conduction band to the valence band may be transferred to the Mn^{2+} ions, whereby Mn^{2+} ions may get excited [24-27].

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

3. Theory

3.1 Rise of ML intensity

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 ion have lower value of the piezoelectric constant, there should exist a gradient of electric field. Thus, filled electrons traps near Mn^{2+} ions may be detrapped for 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 a 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 ,$Q = d_0P$. If the crystal is compressed at a fixed pressing rate $\dot{P}$ or strain rate ἐ, then Q can be written as

$$Q = d_0 P = d_0 \dot{P} t = d_0 Y \dot{\varepsilon}\, t \tag{1}$$

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

$$-\frac{dn_t}{dF} = \frac{n_t}{F_c} = Zn_t \tag{2}$$

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

$$n_t = n_{t0} \exp[-Z(F - F_{th})] \tag{3}$$

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

Using Eq. (3), the total number of detrapped electrons can be expressed as

$$n_d = (n_{t0} - n_t) = n_{t0}[1 - \exp\{-Z(F - F_{th})\}] \tag{4}$$

In the elastic region, $Z(F\text{-}F_{th})$ is low, hence, Eq. (4) can be written as

$$n_d = n_{t0}[1 - 1 + Z(F - F_{th})] = n_{t0} Z(F - F_{th}) \tag{5}$$

Now, differentiating Eq. (5), we get

$$\frac{dn_d}{dt} = n_{t0} Z \frac{dF}{dt} \tag{6}$$

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

$$g = n_{t0} Z \frac{dF}{dt} \tag{7}$$

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

$$\Delta n = g\tau = n_{t0} Z \frac{dF}{dt} \tau \tag{8}$$

Using Eq. (8), the discharge current j flowing in the crystal can be written as

$$j = \Delta n \, q v_d \tag{9}$$

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. (9) can be expressed as

$$j = \Delta n \, q \, \mu \, \mathrm{F} \tag{10}$$

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

$$r = \frac{j}{q} = \Delta n v_d = \Delta n \, \mu F \tag{11}$$

From Eqs. (8) and (11), we get

$$r = \Delta n v_d = n_{t0} Z \tau \, \mu F \frac{dF}{dt} \tag{12}$$

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

$$R = \sigma \, n_h \Delta n v_d = \sigma \, n_h n_{t0} Z \tau \, \mu F \frac{dF}{dt} \tag{13}$$

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

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

or,

$$I = \eta \, \sigma \, \Omega \, \mathrm{N_l N_t} \, n_h Z \tau \, \mu (F - F_{th}) \frac{dF}{dt} \tag{14}$$

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. (14) can be written as

$$I = \eta\,\sigma\,\Omega\,N_1 N_t\,n_h Z\tau\,\mu B^2 (Q - Q_{th})\frac{dQ}{dt} \tag{15}$$

where $F_{th} = B\,Q_{th}$

From Eqs. (1) and (15), we get

$$I = \eta\,\sigma\,\Omega\,N_1 N_t\,n_h Z\tau\,\mu B^2 d_0^2 (P - P_{th})\frac{dP}{dt} \tag{16}$$

In terms of strain rate, Eq. (16) can be expressed as

$$I = \eta\,\sigma\,\Omega\,N_1 N_t\,n_h Z\tau\,\mu B^2 d_0^2 Y(P - P_{th})\dot{\varepsilon} \tag{17}$$

Equation (17) 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.

3.2 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 τq is the decay time of the piezoelectric charges, then the rate of relaxation of surface charges can be expressed as

$$-\frac{dQ}{dt} = Q \Big/ \tau_q = \gamma\,Q \tag{18}$$

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

Integrating Eq. (18) and taking $Q = Q_m$ at $t = t_m$, we get

$$Q = Q_m[-\gamma(t - t_m)] \tag{19}$$

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

Using Eqs. (16) and (19), the decay of ML intensity can be expressed as

$$I_d = I_m \exp[-2\gamma(t - t_m)] \tag{20}$$

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

3.3 Estimation of I_m and I_T

If the crystals is compressed at a fixed strain rate for a time t_m , where the pressure is P_m, then from Eqs. (16) and (17), the maximum intensity I_m of the ML is given by

$$I_m = \eta\,\sigma\,\Omega\,N_1 N_t\,n_h Z\tau\,\mu B^2 d_0^2 (t_m - t_{th})\eta\,\sigma\,\Omega\,N_1 N_t\,n_h Z\tau\,\mu B^2 d_0^2 Y(t_m - t_{th})\dot{\varepsilon} \tag{21}$$

It is evident from Eq. (21) 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. (16) gives that the total ML intensity I_{TD} during the deformation of the sample can be expressed as

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

or,

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

or,

$$I_{TD} \simeq \eta \sigma \Omega \, \mathrm{N_l N_t} n_h Z \tau \, \mu B^2 d_0^2 \frac{P_m^2}{2} \tag{22}$$

Equation (22) indicates that the total ML intensity in the deformation region should increase quardratically with the applied pressure.

Using Eq. (20), the value of total ML intensity from t_m to ∞ is given by

$$I_{TPD} = \int_{t_m}^{\infty} I_m \exp[-2\gamma(t - t_m)] dt = \frac{I_m}{2\gamma} \tag{23}$$

From Eqs. (22) and (23), the total ML intensity is given by

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

or,

$$I_T = \frac{\eta \sigma \Omega \, \mathrm{N_l N_t} \, n_h Z \tau \, \mu B^2 d_0^2 (P_m - P_{th})}{2} \left(1 + \frac{\tau_q}{t_m} \right) \tag{24}$$

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

4. Experimental support of the proposed theory

Xu et al. [15] 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 1050^0C for 3h 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 160^0C. 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.

Fig. 1 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 [15]. 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. 1. The threshold pressure for the appearance of EML in ZnS:Mn nanoparticles is nearly equal to 1 MPa.

Fig. 2 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. 2. 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. 2 using Eq. (20), 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.

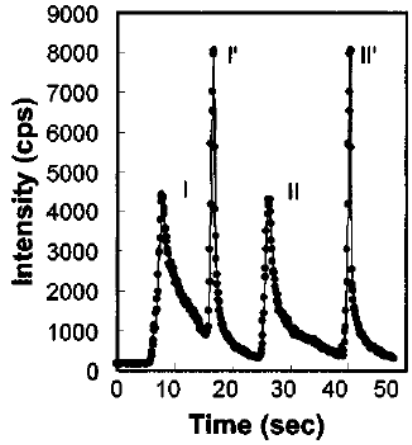

Fig. 1 ML response of ZnS:Mn nanoparticles coated on a quartz plate for the compression stress of 500 N, which was applied by a material test machine with a cross-head speed of 0.10 mm/min. (after Xu. et al. ref.[15].

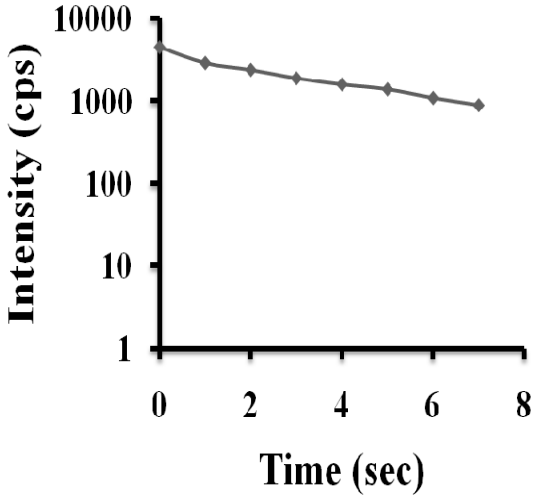

Fig. 2. Plot of log I versus ($t-t_m$).

It is seen from Fig. 3 that for a given strain rate the EML intensity increases linearly with the the applied stress. This is in accord with Eq. (21) . Fig. 4 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.

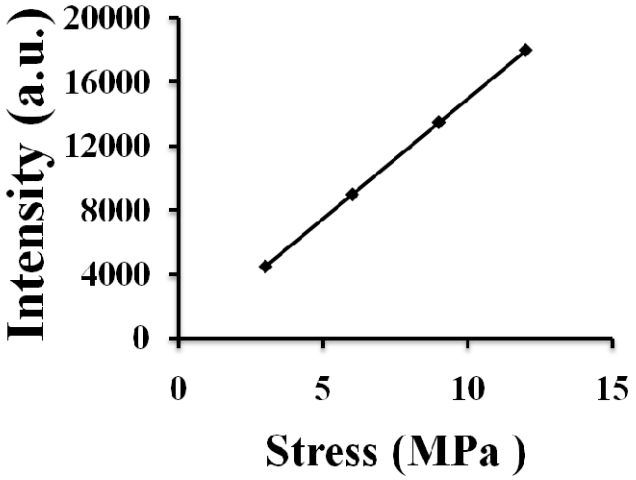

Fig. 3 Stress dependence of the EML intensity (Theoretical).

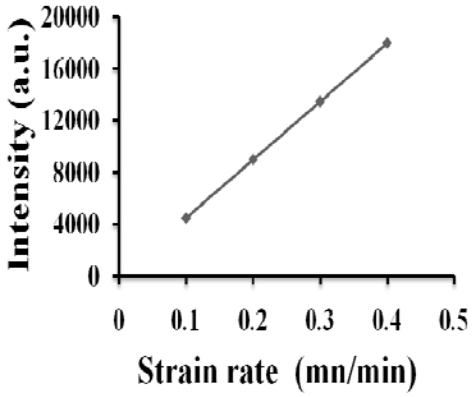

Fig. 4 Strain rate dependence of the EML intensity (Theoretical).

5. Conclusions

When a ZnS:Mn crystal is elastically deformed by applying a load at a fixed rate, then initially the ML intensity increases with time, attains a peak value I_m at a particular time $t_{m,}$, and later on it decreases with time. After $t_{m,}$ initially the EML intensity decreases exponentially at a fast rate and then it decreases exponentially at a slow rate, in which the decay time of fast decrease in EML intensity is equal to half of the decay time of piezoelectric charges. For a given strain rate, whereas the peak intensity I_m increases linearly with the magnitude of applied pressure, the total EML intensity I_T increases quadratically with the magnitude of the applied pressure. The ML spectra of ZnS:Mn crystals are similar to their photoluminescence and electroluminescence spectra.

The elastico ML in ZnS:Mn crystals can be understood on the basis of the piezoelectrically-stimulated electron detrapping model ,in which the local piezoelectric field near the Mn^{2+} centres 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+} centres and de-excitation gives rise to the ML. On the basis of the piezoelectrically-stimulated electron detrapping model, expressions are derived for different characteristics of the EML of ZnS:Mn crystals and a good agreement is found between the theoretical and experimental results. The expressions explored for the dependence of EML

intensity on several parameters may be useful in tailoring the suitable materials capable of exhibiting ML during their elastic deformation.

The values of the decay time of piezoelectric charges, time-constant for the rise of pressure, pressing rate, strain rate and the threshold pressure for EML emission can be determined from the measurement of the ML glow curve.

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