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# Theoretical Approach to the Fracto-Stimulated Luminescence in Coloured Alkali Halide Crystals

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**Abstract**

The first peak in the ML intensity versus time curve occurs in the deformation region of the crystals which is primarily due to the recombination of dislocation electrons with the $V_2$-centres. The occurrence of second peak in the post deformation region of the crystals may be understood as follows. In alkali halide crystals there are deep surface states. The absorbed ions, for instance can play the role of such traps. Calculations performed within the model of point ions show that the electron traps on potassium ions absorbed into the KCl (100) perfect surface and near a step are located at 4.27 and 4.01 eV, respectively, from the bottom of the conduction band. Since the dislocation accepter band in the KCl is situated at approximately 2eV below the conduction band bottom, the recombination between deep traps and the electrons carried by dislocation the KCl surface can cause the Auger ionization of other dislocation electrons to the conduction bottom. Thus, if the shallow traps near the conduction band of the crystal may be populated during the process of Auger ionization of the electrons, then the subsequent thermal stimulation may transfer electrons from the shallow traps to the conduction band. Later on the recombination of electrons with $V_2$-centres in the crystal may give rise to the delayed luminescence where the delay time will depend on the life time of the electrons in the shallow traps.

An expression is derived for the time dependence of the ML intensity in coloured alkali halide crystals, which suggest that there should be two peaks in the ML intensity versus time curves of the crystals, where one peak should be in the deformation region and the other should be in post deformation region in the crystals. The expression derived for $t_{m_1}, I_{m_1}, t_{m_2}, I_{m_2}$ and $I_T$ are as follows

$$t_{m_1} = \frac{1}{\alpha_1} \ln\left(\frac{\alpha_1}{\alpha}\right)$$

$$I_{m_1} = \frac{\eta_1 \alpha_1^{'}}{\alpha_1} A \lambda_d P_F n_F r_F M_o v_o \exp(-v_d / v_o)$$

$$t_{m_2} = \frac{1}{\alpha} \ln \frac{\eta_2 \alpha_1^{''} \alpha_2^2}{\eta_1 \alpha_1^1 \alpha^2}$$

$$I_{m_2} = \frac{\eta_2 \alpha_1^{''} \alpha_2}{\alpha_1 \beta_o} \lambda_d P_F n_F r_F M_o V \exp(-v_c + v_d) / v_d)$$

and

$$I_T = \frac{\left(\eta_1 \alpha_1^{'} + \eta_2 \alpha_1^{''}\right) V \lambda_d P_F n_F r_F M_o}{\beta_o} \exp\left[-\left(\frac{v_c + v_d}{v_o}\right)\right]$$

## Introduction

Cold emission of light is known as luminescence. Luminescence is the non equilibrium phenomenon of excess emission over and above the thermal emission of a body, in which emission has a duration considerably exceeding the period of light oscillations. Luminescence induced during mechanical deformation of solids is known as mechanoluminescence (ML). It can be excited by rubbing, grinding, cutting, cleaving, shaking, scratching, compressing or crushing of solids. ML can also be excited by thermal shocks caused by drastic cooling or heating of material or by the shock waves produced during exposure of samples to powerful laser pulse. ML also appears during the deformation caused by the phase transition or growth of certain crystals as well as during separation of two dissimilar materials in contact. The phenomenon of ML has also been called by many other names such as trennugslicht, tribo, piezo, deformation and stress activated luminescence. The ML likes mechanical, spectroscopic, electrical, structural and other properties of solids. A large number of organic, inorganic crystals and amorphous solids exhibit the phenomena of ML [1-4]. It is known that coloured alkali halide crystals exhibit intense ML during their plastic deformation [5]. The present paper reports that the fracto-stimulated luminescence in coloured alkali halide crystals which is able to explain the dependence of ML intensity on strain-rate, stress, temperature, dopant concentration, annealing temperature, storage time, irradiation doses etc. The theory is also able to explain the efficiency, spectroscopy and the kinetics of ML.

**Theory**

From the comparison of the ML spectra with the spectra of other types of luminescence in X or $\gamma$ -irradiated pure alkali halide crystals and it has been proved that the ML arises due to the recombination of electrons from F-centres with the holes in $V_2$ centres . This is confirmed by the fact that pure additively coloured alkali halide crystals do not show ML during their plastic deformation due to the absence of holes schematically, the ML process can be described by the following equations:

$$F + D \rightarrow e_d + [-]$$

$$V_2\left(= X^- + X^- + X^\circ\right) + e_d \rightarrow 3X^- + h\upsilon + D$$

where F and D represent F-centres and dislocation respectively, $e_d$ is the dislocation electron i.e. the electron captured by dislocation [-] is the negative ion vacancy, X is halogen ion, $X^\circ$ is the self-trapped hole.

In X- or $\gamma$ -irradiated impurity doped alkali halide crystals, some of the holes may be in impurities and their recombination with the dislocation electrons may induce the impurity emissions .

Consider a crystal having $N_d$ dislocations of unit length per unit volume. If $V_d$ is the average velocity of the dislocation, then in time dt each dislocation will move a distance $g_i = N_d V_d r_F n_F = \frac{\dot{\varepsilon}}{b} r_F n_F$. If $r_F$ is the radius of interaction of a dislocation with F-centres, then the volume of interaction per unit time will be $N_d V_d r_F$. If $n_F$ is the density of F-centres, then the rate of interaction of dislocations with F-centres may be given by

$$g_i = N_d V_d r_F n_F = \frac{\dot{\varepsilon}}{b} r_F n_F \qquad \text{-------(1)}$$

where $\dot{\varepsilon} = N_d V_d b$, and b is the Burgers vector.The rate equation for the change in number of electron in dislocation band is

$$\frac{dN_d}{dt} = \frac{M_o v_o}{H} \exp\left(\frac{-v_d}{v_o}\right) \exp(-\alpha t) \qquad \text{----(2)}$$

If $\lambda_d$ is the mean free path of dislocations, then the number of F-centres excited by a dislocation is $\lambda_d P_F n_F r_F$. Therefore, the rate of generation of electrons in the dislocation band may be expressed as

$$g = \lambda_d P_F n_F \frac{dN_d}{dt}$$

Substituting the value of $\frac{dN_d}{dt}$ from equation (2), we get

$$g = \lambda_d P_F n_F \frac{M_o v_o}{H} \exp\left(\frac{-v_d}{v_o}\right) \exp(-\alpha t)$$

$$\text{or } g = g_o \exp(-\alpha t) \qquad \text{-----(3)}$$

where $g_o = \frac{1}{H}\lambda_d P_F n_F M_o v_o \exp\left(\frac{-v_d}{v_o}\right)$ -----(4)

If $\alpha_1$ is the rate of transfer of electrons from dislocation band to other centers, then we have

$$d\Delta n_1 = g_o \exp(-\alpha t)dt - \alpha_1 \Delta n_1 dt \quad \text{-----(5)}$$

where $\Delta n_1$ is the concentration of electrons in the dislocation band at any time t,

Integrating equation (5) and taking $\Delta n_1 = 0$ , at t = 0, we get

$$\Delta n_1 = \frac{g_o}{(\alpha_1 - \alpha)}[\exp(-\alpha t) - \exp(-\alpha_1 t)]$$

$$\text{or } \Delta n_1 = \frac{g_o}{(\alpha - \alpha_1)}[\exp(-\alpha_1 t) - \exp(-\alpha t)] \quad \text{-----(6)}$$

Similarly the number of electron in shallow traps at any time t

$$\Delta n_2 = g_o \alpha_1'' \left[ \frac{\exp(-\alpha t)}{(\alpha - \alpha_1)(\alpha - \alpha_2)} - \frac{\exp(-\alpha_1 t)}{(\alpha - \alpha_1)(\alpha - \alpha_2)} + \frac{\exp(-\alpha_2 t)}{(\alpha - \alpha_2)(\alpha_1 - \alpha_2)} \right] \quad \text{-----(7)}$$

Luminescence is produced during the recombination of dislocation electrons with the centres containing holes and also during the release of electrons the shallow traps and their subsequent recombination with hole containing centre. Thus, the luminescence intensity I may be written as

$$I = I_1 + I_2$$

$$\text{or } I = \left[\alpha_1' \Delta n_1 \eta_1 + \alpha_2 \Delta n_2 \eta_2\right] \quad \text{-----(8)}$$

where $\eta_1$ and $\eta_2$ are the probability of radiative electron-hole recombination.

By substituting the value of $\Delta n_1$ and $\Delta n_2$ from equation (6) and (7) in equation (8) we get

$$I = \frac{\eta_1 g_o \alpha_1'}{(\alpha - \alpha_1)}[\exp(-\alpha_1 t) - \exp(-\alpha t)] +$$

$$\eta_2 g_o \alpha_1'' \alpha_2 \left[ \frac{\exp(-\alpha t)}{(\alpha - \alpha_1)(\alpha - \alpha_2)} - \frac{\exp(-\alpha_1 t)}{(\alpha - \alpha_1)(\alpha_1 - \alpha_2)} + \frac{\exp(-\alpha_2 t)}{(\alpha - \alpha_2)(\alpha_1 - \alpha_2)} \right]$$

$$\text{or } I = g_o [A \exp(-\alpha t) - B \exp(\alpha_1 t) + C \exp(-\alpha_2 t)] \quad \text{---(9)}$$

$$\text{where } A = \left[ \frac{\eta_2 \alpha_1'' \alpha_2}{(\alpha - \alpha_1)(\alpha - \alpha_2)} - \frac{\eta_1 \alpha_1'}{(\alpha - \alpha_1)} \right]$$

$$B = \left[ \frac{\eta_2 \alpha_1'' \alpha_2}{(\alpha - \alpha_1)(\alpha_1 - \alpha_2)} - \frac{\eta_1 \alpha_1'}{(\alpha - \alpha_1)} \right]$$

$$C = \left[ \frac{\eta_2 \alpha_1'' \alpha_2}{(\alpha - \alpha_2)(\alpha_1 - \alpha_2)} \right]$$

In the case of coloured alkali halide crystals, we assume $\alpha$ to be greater then $\alpha_2$ but less than $\alpha_1$. Thus we assume $\alpha_1 > \alpha > \alpha_2$ and then the value of A, B and C may be expressed as.

$$A = \frac{\eta_1 \alpha_1' \alpha - \eta_2 \alpha_1'' \alpha_2}{\alpha_1 \alpha} \quad \text{-----(10)}$$

$$B = \frac{\eta_1 \alpha_1' \alpha_1 - \eta_2 \alpha_1'' \alpha_2}{\alpha_1^2} \quad \text{-----(11)}$$

$$C = \frac{\eta_2 \alpha_1'' \alpha_2}{\alpha_1 \alpha} \quad \text{-----(12)}$$

**Estimation of $t_{m_1}, I_{m_1}, t_{m_2}, I_{m_2}$ and $I_T$**

During the deformation of crystals at high strain-rate, dislocations move with high velocity and it has been found that $\beta$ lies in between 1.2 and 1.5 for KCl crystal. In the experimental investigation being made in laboratory, for the highest value of $v_o = 280\,\text{cm sec}^{-1}$, and for the thickness for the crystal H = 0.1 c.m., the highest value of $\alpha = \frac{(\beta v_o)}{H}$, comes out to be $3 \times 10^3 \sec^{-1}$. $\alpha_1$ is the rate constant for the recombination and it is given by

$$\alpha_1 = \sigma_1 N_1 v_d$$

where $\sigma_1$ and $N_1$ are the capture cross-section and density of the recombination centre (holes), respectively and $v_d$ is the velocity of the dislocation electrons which is equal to the velocity of dislocation. For $N_1 = 10^{17}\,\text{cm}^{-3}$, $\sigma_1 = 10^{-15}\,\text{cm}^2$ and $v_d \approx 10^4 - 10^5\,\text{cm s}^{-1}$, in the case of impulsive deformation $\alpha_1$ comes out to be nearly equal to $10^6 - 10^7 \sec^{-1}$.

As $\alpha_2$ is the rate constant for the detrapping of the shallow traps, its value will depend on the trap-depth and the temperature of crystals.

(i) Estimation of $\boxed{t_{m_1}}$

For $\alpha_1 > \alpha > \alpha_2$, $\alpha_1^{'} \approx \alpha_1$, $\alpha_1^{''} < \alpha_1^{'}$ and $\eta_1 \geq \eta_2$, and value of A and B are much greater than C. equations (10), (11) and (12). For low value of t, $\exp(-\alpha_2 t) \approx 1$, thus we can neglect the term, $C\exp(-\alpha_2 t)$ in equation (9) and I may therefore be expressed as

$$I = g_o\left[A\exp(-\alpha t) - B\exp(-\alpha_1 t)\right]$$

For maximum value of I, dI/dt is equal to zero, taking logarithm on both the sides and substituting $t = t_{m_1}$, we get

$$t_{m_1} \approx \frac{1}{\alpha_1}\text{In}\frac{B\alpha_1}{A\alpha} \qquad \text{-----(13)}$$

Substituting the values of A and B from equations (10) and (11) in the above equation, we get

$$t_{m_1} \approx \frac{1}{\alpha_1}\text{In}\left(\frac{\alpha_1}{\alpha}\right) \qquad \text{-----(14)}$$

$t_{m_1}$ should decreases slowly with increasing strain rate of the crystals.

(ii) **Estimation of** $I_{m_1}$

Substituting the value of $t_{m_1}$ from equation (14) in the following equation

$$I = g_o\left[A\exp(-\alpha t) - B\exp(-\alpha_1 t)\right]$$

and taking $I = I_{m_1}$, we get

$$I_{m_1} = g_o\left[A\exp\left(-\frac{\alpha}{\alpha_1}\text{In}\frac{\alpha_1}{\alpha}\right) - B\exp\left(-\text{In}\frac{\alpha_1}{\alpha}\right)\right]$$

The solution of above equation, gives

$$I_{m_1} \approx \frac{g_o\eta_1\alpha_1^{'}}{\alpha_1} \qquad \text{--------(15)}$$

The above equation indicates that $I_{m_1}$ should increase with increasing strain-rate or impact velocity of the piston used to deform the crystal, as $g_o$ increases with increasing value of $v_o$

(iii) Estimation of $v_o$

When t is large, $\exp(-\alpha_1 t) \approx o$,, since $\alpha_1$ is very high. Thus equation (9) for I becomes

$$I = g_o\left[A\exp(-\alpha t) + C\exp(-\alpha_2 t)\right]$$

For maximum value of I, $\frac{dI}{dt}$ is equal to zero, substituting the value of A and C from equation (10) and (12), and substituting $t = t_m$, we get

$$t_{m_2} = \frac{1}{\alpha} \text{In} \frac{\eta_2 \alpha_1'' \alpha_2^2}{\eta_1 \alpha_1^1 \alpha^2} \quad \text{----(16)}$$

Since the pre-exponential factor will be dominating, it is evident from equation (16) that $t_{m_2}$ should shift towards shorter time values with increasing strain-rate or impact velocity of the piston.

**(iv) Estimation of $t_{m_2}$**

Substituting the value of $t_{m_2}$ from equation (16) in the following equation and taking $I = I_{m_2}$, we get

$$I = g_o\left[A\exp(-\alpha t) + C\exp(-\alpha_2 t)\right]$$

The solution of the above equation gives

$$I_{m_2} \approx \frac{g_o \eta_2 \alpha_1'' \alpha_2}{\alpha_1 \alpha} \quad \text{-----(17)}$$

As $g_o$ depends on the strain-rate, the above equation indicates that $I_{m_2}$ should increase with the strain-rate or impact velocity. However, as $\alpha$ also depends on the strain-rate, the value of $I_{m_2}$ should increase slowly with the strain rate as compared to that of $I_{m_1}$.

**(v) Estimation of total ML intensity $I_T$**

The expression for the total ML intensity $I_T$ can be written as

$$I_T = \int_0^\infty I dt$$

Substituting the value of I from equation (9) in the above equation, we get

$$I_T = g_o\left[\frac{A}{\alpha} - \frac{B}{\alpha_1} + \frac{C}{\alpha_2}\right]$$

Substituting, the value of A, B and C from equations (10), (11) and (12) above equation, we get

$$I_T = \frac{g_o}{\alpha_1 \alpha}\left[\eta_1 \alpha_1' + \eta_2 \alpha_1''\right]$$

As $\alpha_1 >> \alpha >> \alpha_2$, $I_T$ is given by

$$I_T \approx \frac{g_o}{\alpha}\left[\eta_1\alpha_1^{'} + \eta_2\alpha_1^{''}\right] \qquad \text{-----(18)}$$

It is evident from the above equation that should also increase with increasing strain-rate or impact velocity of the piston.

From equations (15), (17) and (18), the value of $I_{m_1}, I_{m_2}$ and $I_T$ for a crystal of volume V may be expressed by the following expression:

$$I_{m_1} = \frac{\eta_1\alpha_1^{'}}{\alpha_1} A\lambda_d P_F n_F r_F M_o v_o \exp(-v_d / v_o) \qquad \text{----(19)}$$

$$I_{m_2} = \frac{\eta_2\alpha_1^{''}\alpha_2}{\alpha_1\beta_o} \lambda_d P_F n_F r_F M_o V \exp(-v_c + v_d)/v_d) \qquad \text{-----(20)}$$

$$I_T = \frac{\left(\eta_1\alpha_1^{'} + \eta_2\alpha_1^{''}\right)V\lambda_d P_F n_F r_F M_o}{\beta_o} \exp\left[-\left(\frac{v_c + v_d}{v_o}\right)\right] \qquad \text{-----(21)}$$

**Comparison between the theoretical and experimental results**

Figure. 1 shows that both $I_{m_1}$ and $I_{m_2}$ increases non-linearly with increasing strain rate or impact velocity of the piston. $I_{m_1}$ does not saturate for higher values of the strain-rate or impact velocity ($v_o$), however, $I_{m_2}$ gets saturated for higher values of $v_o$. It is evident from Figure. 2 that $I_T$ initially increases and then tends to attain a saturation value for higher values of the impact velocity.

Figure. 3 shows that both $t_{m_1}$ and $t_{m_2}$ decreases with increasing impact velocity $v_o$ of the piston.

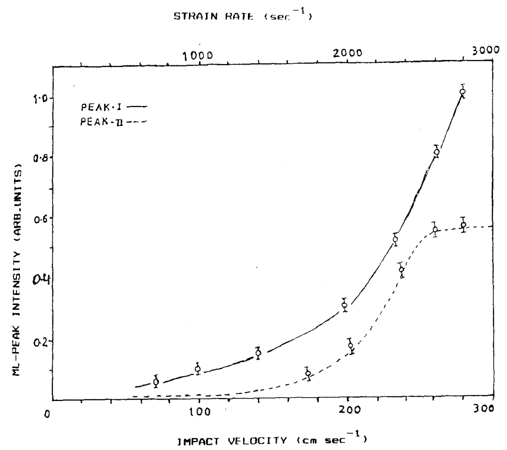


**Figure 1:** Dependence of ML intensities of peak 1 and peak II or $\gamma$-irradiated KCl crystals on different strain-rate or impact velocity impact velocity (crystal size $2\times2\times1\ mm^3$, $n_F \approx 10^{17}\ cm^{-3}$)

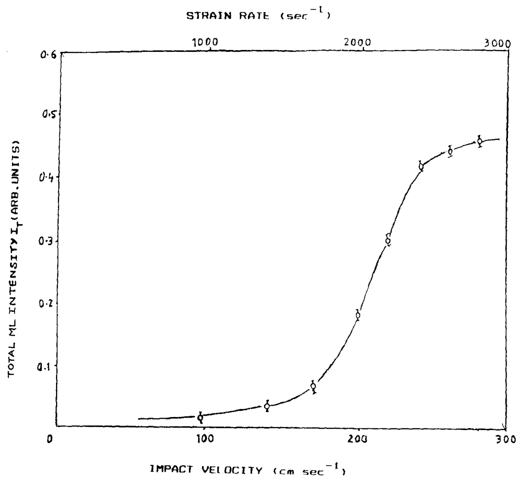


**Figure 2:** Strain-rate or impact velocity dependence of total ML intensities $I_T$ of $\gamma$ - irradiated KCl crystals (crystal size $2\times2\times1\ mm^3,\ n_F \approx 10^{17}\ cm^{-3}$ )

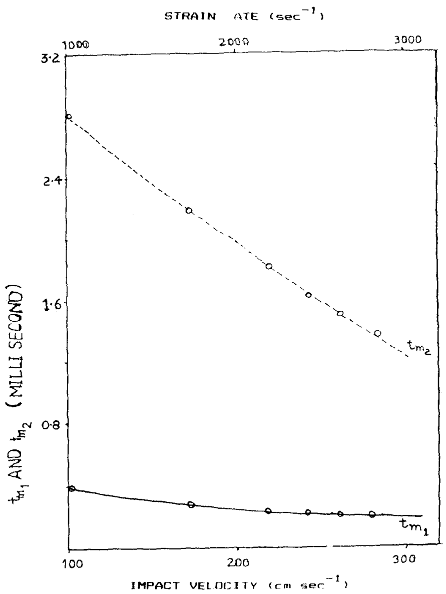


**Figure 3:** Dependence of $t_{m_1}$ and $t_{m_2}$ on strain-rate or impact velocity for KCl crystals (crystal size $2\times2\times1\ mm^3,\ n_F \approx 10^{17}\ cm^{-3}$ )

## Conclusions

(i) The fracto stimulated luminescence in coloured alkali crystals has dislocation origin, in which the dislocation moving during deformation of the crystal capture electrons from the F-centers and transport them to the hole containing defect centers, where by the radiative electron-hole recombination gives rise to luminescence.

(ii) The formula for the fracto ML intensity I derived

$$I = g_o\left[A\exp(-\alpha t) - B\exp(\alpha_1 t + C\exp(-\alpha_2 t)\right]$$

Where

$$A = \frac{\eta_1\alpha_1^{'}\alpha - \eta_2\alpha_1^{''}\alpha_2}{\alpha_1\alpha}$$

$$B = \frac{\eta_1\alpha_1^{'}\alpha_1 - \eta_2\alpha_1^{''}\alpha_2}{\alpha_1^{\ 2}}$$

$$C = \frac{\eta_2\alpha_1^{''}\alpha_2}{\alpha_1\alpha}$$

(iii) The time corresponding to first and second peak of fracto ML intensity are

$$t_{m_1} = \frac{1}{\alpha_1}\text{In}\left(\frac{\alpha_1}{\alpha}\right)$$

$$t_{m_2} = \frac{1}{\alpha}\text{In}\frac{\eta_2\alpha_1^{''}\alpha_2^2}{\eta_1\alpha_1^1}$$

(iv) Finally the ML intensity corresponding to the first peak lies in the deformation region the crystal and the second peak lies in the post-deformation region of crystal and total fracto ML intensities are derived

$$I_{m_1} = \frac{\eta_1\alpha_1^{'}}{\alpha_1}A\lambda_d P_F n_F r_F M_o v_o \exp(-v_d / v_o)$$

$$I_{m_2} = \frac{\eta_2\alpha_1^{''}\alpha_2}{\alpha_1\beta_o}\lambda_d P_F n_F r_F M_o v_o \exp(-v_c + v_d)/v_d)$$

$$I_T = \frac{\left(\eta_1\alpha_1^{'} + \eta_2\alpha_1^{''}\right)V\lambda_d P_F n_F r_F M_o}{\beta_o}\exp\left[-\left(\frac{v_c + v_d}{v_o}\right)\right]$$

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