CHAPTER II

THEORETICAL APPROACH TO THE FRACTOMECHANOLUMINESCENCE PRODUCED DURING CLEAVAGE OF PIEZOELECTRIC CRYSTALS
2.1 INTRODUCTION

The mechanoluminescence of piezoelectric crystals has been widely studied. Tschugaeff (1901) found that high proportion of crystalline mechanoluminescent materials lack a centre of symmetry in their structure. Vernadsky (1910) proposed that the piezoelectrification may be one of the reasons for the ML excitation. Later on, Langevin (1921) explored the piezoelectric model of ML.

Longchambon in 1925 also found that most of the crystals which exhibit the phenomenon of ML were non-centrosymmetric and, therefore, supported the piezoelectric origin of ML. Longchambon further showed that the single crystals of sugar and tartaric acid did not exhibit ML, when cleaved parallel to their pyroelectric axis, though they show intense mechanoluminescence when cleaved in all other directions. Hoof and Boord (1950) found that cis-4-octene shows ML while trans 4-octene does not show ML, when subjected to rapid cooling by immersing a test tube containing these compounds in liquid air. The emission of flashes from cis 4-octene was interpreted as an electrical discharge generated by crystal fracture resulting from uneven cooling. The characteristic ML flashes was of red-orange colour when the crystallization took place under an atmosphere of neon. Because ‘cis’ and ‘trans’ isomers may have different crystal structures, it is very likely that the ML is piezoelectrically induced and that ‘cis’ and ‘trans’ forms have different crystal structures.

Hardy et al (1976, 1981) examined structurally the two polymorphic systems, namely hexaphenyldicarbodiphosphorence and anthranilic acid containing both ML-active and ML-inactive to determine what physical characteristics are related to the presence or absence of ML. A general observation of the differences between the polymorphs which appears to be relevant to ML is that crystals which have polar space groups demonstrate ML, while those with non-polar space group are not ML active. Such correlation between the crystal structure and ML is also found to be valid for other molecular crystals. This observation suggests that piezoelectricity could play
role in the production of ML. Chandra and his co-workers have made a detailed investigation on the ML and they have determined the spectroscopy, intensity and crystal structure, ML correlation for 162 inorganic crystals and 234 organic crystals (Chandra and Elyas 1979, Chandra and Shrivastava 1979, Chandra et al 1980, 1987, Chandra and Verma 1980, Chandra 1981, 1985, Chandra and Tutakne 1981). They have found that generally all the piezoelectric crystals show ML and the crystals which do not show ML are non-piezoelectric. Nowack et al (1983) have suggested that the ML in polar molecular crystals is related rather to the pyroelectricity than to piezoelectricity. Kitamura et al (1986) have investigated the ML in N-alkyl and N-alkyl 3-substitued carbazole crystals. They have found that the ML active carbazole crystals belong to polar space groups, while the non-ML active crystals belong to non-polar ones. This fact led them to conclude that the ML activity in carbazole derivatives is closely related to structure, in particular to the space group polarity and thus, to the generation of piezo or pyroelectric charges. Hocking et al (1989) have investigated the ML in crystals of 1,2,5- triphenyl-phosphole and looking to their non-centrosymetric nature, they have also suggested the piezoelectric origin of ML. Sweeting et al (1992) have also reported the piezoelectric origin of ML in organic crystals.

For the piezoelectric crystals, the deformation characteristics, stress dependence, strain-rate dependence, temperature dependence and crystals-size dependence of ML etc have been studied experimentally and considerable results related to these facts are available (Longchambon 1925, Meyer et al 1970, Chandra 1981, 1985, 1998). However, least theoretical studies have been made on the ML of piezoelectric crystals to date.

The present chapter explores the theory of fracto-ML produced during cleavage of piezoelectric crystals and makes a comparison between the theoretical and experimental results.
2.2 MECHANISM OF THE ML PRODUCED DURING THE CLEAVAGE OF PIEZOELECTRIC CRYSTALS

Following are the important facts which indicate the piezoelectric origin of ML in non-centrosymmetric crystals.

(i) Generally the crystals exhibiting ML, belong to twenty non-centrosymmetric (piezoelectric) point groups and the crystals belonging to centrosymmetric (non-piezoelectric) point group do not exhibit ML. In inorganic crystals the newly created surfaces may get charged by the piezoelectrification as well as by other mechanisms, hence, the correlation between the ML and piezoelectric behaviour does not hold as satisfactory as in the case of organic crystals. There are some exceptions, that is, certain non-piezoelectric crystals, such as chemically impure saccharin, salicylamide, phthalic acid etc. exhibit ML, but these crystals do not show ML after their purification. The ML of such impure crystals may be due to the presence of a piezoelectric phase near the defects.

(ii) The ML has been measured in many polymorphic crystals, e.g. anthranilic acid, hexacarbodiphosphorane, acetamide, glycine, p-mannitol, p-anisidine etc. (Hardy et al 1981, Chandra 1981) and it has been found that only the piezoelectric forms exhibit ML and the other forms do not.

(iii) Certain crystals, e.g. sucrose, tartaric acid, ethylene diamine tartrates etc. do not show ML when they are cleaved in a plane parallel to their pyroelectric axis, although ML is produced from all other cleavage planes.

(iv) Near the curie temperature of ferroelectric crystals, where the crystal structure transforms from one phase to another, a drastic change in the ML intensity takes place.

The ML excitation in piezoelectric crystals can be understood on the basis of the piezoelectricfication of newly created surfaces of crystals. Fig 2.1
Fig 2.1 : Creation of charged surfaces during propagation of a crack in piezoelectric crystals.
shows the Langevin's model of the creation of charged surfaces during movement of a crack in a piezoelectric crystal (Langevin 1921). When a stress is applied to a piezoelectric crystal, its one surface gets positively charged and the opposite surface gets negatively charged. Due to the movement of a crack in the crystal, new surfaces are created. The newly created surface nearer to the positively charged surface of the crystal, gets negatively charged and the newly created surface nearer to the negatively charged surface of the crystals gets positively charged. Thus, an electric field may be produced between the newly created oppositely charged surfaces of the crystal.

For simplification of the estimation of electric field, let us make the following assumptions; (i) that the piezoelectric constants remain unchanged upto the fracture stress of the crystal, (ii) that the stress near tip of the mobile crack acts along a polar direction of the crystals, and (iii) that the stress near tip of the mobile crack is not relaxed before the luminescence excitation. The electric field produced may be estimated from the equation $e = p/e_0$, where $e_0$ is the permittivity of space ($8.85 \times 10^{-12}$ coulomb N$^{-1}$m$^{-2}$) and $p$ is the charge density of the newly created surface. The charge density $\rho$ will be $d \cdot \sigma_f$, where $d$ is the piezoelectric constant and $\sigma_f$ is fracture stress which is determined from $1/30^\text{th}$ of the Young's modulus (Cottrell 1964). It is known that the piezoelectric constants and the stress needed to separate the surfaces of the crystals are generally of the order of $10^{-11}$ coulomb m$^{-1}$ and $10^{-8}$ Nm$^{-2}$, respectively (Meson 1950, Cottrell 1964). Thus, the surface charge density is of the order of $10^3$ coulomb m$^{-2}$ and thereby an intense electric field of the order $10^8$ Vm$^{-1}$ may be produced between the newly created oppositely charged surfaces. This field may cause the dielectric breakdown of the intervening gases as well as the crystals. The surface charge can be neutralized by the carriers and ions produced due to the dielectric breakdown of the intervening gases and the crystal. Thus, depending on the prevailing condition, the light emission
resembling either gas discharge or luminescence of solids or that having these two characters may be obtained.

2.3 THEORY OF THE FRACTO-ML PRODUCED DURING CLEAVAGE OF PIEZOELECTRIC CRYSTALS

Consider a crystal having length L, breadth W and thickness H. If the crystal is cleaved along the plane parallel to its breadth side, then the rate of the creation of new surfaces is given by $2Wv$, where $v$ is the average velocity of separation of cleavage plane or, in other words, the velocity of crack propagation. If $\rho$ is the charge density of the newly created surface of the crystal, then the rate of generation of surface charges is given by

$$g_s = 2\rho Wv \quad \text{---(2.1)}$$

The charged surface may be created due to the piezoelectrification, movement of charged dislocations, baro-diffusion of charged defects etc. (Walton 1977, Chandra 1998, Molteski 1989). When the charged surfaces are created, the surface charge density may get relaxed, firstly, by the charge carriers produced due to the breakdown of the crystal, and secondly, by the electrons and ions produced due to the breakdown of intervening gases. If $\alpha_1$ and $\alpha_2$ are the rate constants for the relaxation of charges on the newly created surfaces by the crystal and gaseous breakdown processes, respectively, then we may write the following rate equation

$$\frac{dQ}{dt} = g_s - \alpha_1 Q - \alpha_2 Q$$

or,

$$\frac{dQ}{dt} = g_s - \alpha Q \quad \text{---(2.2)}$$

where $\alpha = (\alpha_1 + \alpha_2)$ and $Q$ is the surface charge at any time $t$.

Equation (2.2) may be written as

$$dQ + \alpha Q dt = g_s dt$$

Multiplying both side by $e^{\alpha t}$ and integrating it, then we get

$$\int e^{\alpha t} dQ + \int e^{\alpha t} \alpha Q dt = \int g_s e^{\alpha t} dt$$

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or, \[ Qe^{at} = \frac{g_s e^{at}}{\alpha} + C \] ---(2.3)

As \( Q = 0 \) at \( t = 0 \), we get

\[ C = -\frac{g_s}{\alpha} \]

Thus, eq. (2.3) becomes,

\[ Qe^{at} = \frac{g_s e^{at}}{\alpha} - \frac{g_s}{\alpha} \]

or,

\[ Qe^{at} = \frac{g_s}{\alpha} \left[ e^{at} - 1 \right] \]

or, \( Q = \frac{g_s}{\alpha} [1 - \exp(-\alpha t)] \) ---(2.4)

The ML intensity \( I \) will be directly proportional to the rate of discharge \((-dQ/dt)\). If \( \eta_1 \) is the luminescence efficiency related to the movement of carriers produced due to the dielectric breakdown of crystals and \( \eta_2 \) is the luminescence efficiency related to the movement of electrons and ions produced due to the dielectric breakdown of intervening gases, then the ML intensity may be expressed as

\[ I = \eta_1 \alpha_1 Q + \eta_2 \alpha_2 Q \] ---(2.5)

From eqs. (2.4) and (2.5), we get

\[ I = \frac{\left( \eta_1 \alpha_1 + \eta_2 \alpha_2 \right) g_s}{\alpha} [1 - \exp(-\alpha t)] \] ---(2.6)

Now, on the basis of eq. (2.6), we shall discuss certain characteristics of the cleavage ML in piezoelectric crystals.

2.3.1 KINETICS OF ML

For \( \alpha t < 1 \), eq. (2.6) may be written as

\[ I = \frac{\left( \eta_1 \alpha_1 + \eta_2 \alpha_2 \right) g_s}{\alpha} t \]

or, \[ I = 2(\eta_1 \alpha_1 + \eta_2 \alpha_2) R W v t \] ---(2.7)
The above equation shows that when a crystal will be cleaved, initially the ML intensity should rise linearly with time \( t \).

After the completion of cleavage of the crystal at \( t = t_m \), \( v \) becomes zero and hence \( g_s = 0 \), at \( t = t_m \). Thus, from eq. (2.2) we get

\[
\frac{dQ}{dt} = -\alpha Q \tag{2.8}
\]

or,

\[
\frac{dQ}{Q} = -\alpha dt \tag{2.8'}
\]

or,

\[
\log Q = -\alpha t + C \tag{2.9}
\]

For \( Q = Q_0 \), at \( t = t_m \), eq. (2.9) gives

\[
\log Q_0 = -\alpha t_m + C \tag{2.10}
\]

or,

\[
C = \log Q_0 + \alpha t_m \tag{2.10'}
\]

From eqs. (2.9) and (2.10), we get

\[
\log Q = -\alpha t + \log Q_0 + \alpha t_m \tag{2.11}
\]

As \( t_m \) is very short, negligible discharge occurs within the time duration, from zero to \( t_m \) and, therefore, we may take, \( Q_0 = 2WHp \), i.e. the total charge of newly created surfaces. Thus, from eqs. (2.5) and (2.11), we get

\[
I = (\eta_1 \alpha_1 + \eta_2 \alpha_2)Q_0 \exp[-\alpha(t - t_m)] \tag{2.12}
\]

Equation (2.12) shows the exponential decay of the ML intensity after cleavage of crystals, where the decay rate will be controlled by \( \alpha = (\alpha_1 + \alpha_2) \).

### 2.3.2 ESTIMATION OF \( t_m \)

For the thickness \( H \) of the crystal, the time \( t_m \) taken for cleaving of crystal is given by

\[
t_m = \frac{H}{v} \tag{2.13}
\]

The above equation shows that the velocity of crack propagation may be given by
Thus, the ML may provide a new tool for determining the velocity of crack propagation in crystals.

2.3.3 ESTIMATION OF $I_m$

From eqs. (2.7) and (2.13), the value of the peak of ML intensity at time $t_m$ given by

$$I_m = 2(\eta_1 \alpha_1 + \eta_2 \alpha_2) \rho W H$$

As $2WH$ is the area $A$ of the newly created surfaces, we have

$$I_m = (\eta_1 \alpha_1 + \eta_2 \alpha_2) \rho A$$

The above equation shows that $I_m$ should increase linearly with the area of newly created surfaces $A$, and it should also increase linearly with the surface charge density $\rho$.

2.3.4 ESTIMATION OF THE TOTAL ML INTENSITY $I_T$

The total ML intensity $I_T$, i.e. the integrated area below the ML intensity versus time curve may be given by

$$I_T = \int_0^t dt = \int_0^{t_m} dt + \int_{t_m}^\infty dt$$

From eqs. (2.7), (2.12) and (2.17), we may express the total ML intensity as

$$I_T = \int_0^{t_m} dt + \int_{t_m}^\infty \left[ (\eta_1 \alpha_1 + \eta_2 \alpha_2) \rho W H \right] dt$$

or,

$$I_T = (\eta_1 \alpha_1 + \eta_2 \alpha_2) \rho A \left[ \frac{1}{\alpha} + \frac{H}{2\alpha v} \right]$$

As $1/\alpha >> H/2v$, equation (2.19) may be expressed as

$$I_T = \frac{(\eta_1 \alpha_1 + \eta_2 \alpha_2) \rho A}{\alpha}$$
The above equation shows that the total ML intensity should be directly proportional to the area of newly created surfaces $A$. It is also evident that $I_T$ should be higher for the crystals having higher values of the surface charge density $\rho$.

2.3.5 TEMPERATURE DEPENDENCE OF ML

Equations (2.16) and (2.20) show that the temperature dependence of both $I_m$ and $I_T$ should be primarily due to the effect of temperature on $\eta_1, \eta_2$ and $\rho$. Since $\eta_1, \eta_2$ and $\rho$ decrease with increasing temperature of the crystals, $I_m$ and $I_T$ should decrease with increasing temperature of the crystals. Beyond a particular temperature, $\rho$ may decrease to such a value where the breakdown of gases and solids may not be possible and thereby the ML may not appear.

2.3.6 SPECTROSCOPY OF ML

For $\alpha_2 = 0$, there will be no gaseous discharge ML and the ML emission will primarily be due to the solid state ML. In this case, $\alpha = \alpha_1$ and eqs. (2.16) and (2.20) may written as

$$I_m = \eta_1 \alpha_1 \rho A \quad \text{----(2.21)}$$

and,

$$I_T = \eta_1 \rho A \quad \text{----(2.22)}$$

For $\alpha_1 = 0$, there will be no solid state ML and the ML emission will primarily be due to the gaseous discharge ML. In this case, $\alpha = \alpha_2$ and eqs. (2.16) and (2.20) may be written as

$$I_m = \eta_2 \alpha_2 \rho A$$

and,

$$I_T = \eta_2 \rho A$$

For the crystals, where $\alpha_1$ is comparable with $\alpha_2$, the ML emission should consist of both the solid state ML and gaseous discharge ML and in this case eqs (2.16) and (2.20) should be obeyed.
2.3.7 KINETICS OF ML IN PHOSPHORESCENT CRYSTALS

In phosphorescent crystals, some of the charge produced during fracture may get transferred to the shallow traps and this may rise to second peak in the ML versus time curve of the crystals.

2.4 EXPERIMENTAL SUPPORT TO THE PROPOSED THEORY

Fig 2.2(a,b,c) show the ML spectra of sucrose, triphenylamine and urnylnitrate hexahydrate crystals. It is seen that the ML spectra of sucrose resemble the gas discharge spectra. The ML spectra of triphenylamine are almost similar to the corresponding photoluminescence spectra. However, the ML spectra of urnylnitrate hexahydrate crystal consist of the photoluminescence spectra and gas discharge spectra. It is to be noted that sucrose, urnylnitrate hexahydrate and triphenylamine crystals belong to non-centrosymmetric space group, namely P2 space group, and Aa space group. (Chandra 1991, 1980). Thus, all these crystals are piezoelectric.

Fig. 2.3 shows that when the sucrose crystals are cleaved, initially the ML intensity increases linearly with time. This result is in accord with eq. (2.19). Fig 2.4 shows that the plot of lnI versus \((t - t_m)\) is a straight line with a negative slope. This result follows equation (2.22).

Fig. 2.5 shows that the time \(t_m\) determined from the peak of ML versus time curve is directly proportional to the thickness of the crystals. Such dependence of \(t_m\) on the thickness \(H\) is evident from eq. (2.13). Using eq. (2.14), the values of the average velocity of cracks, \(v\) is determined and is found to be \(4.3 \times 10^4\) cm/s for sucrose crystals.

Fig 2.6 shows that the ML peak intensity \(I_m\) and the total ML intensity \(I_T\) are directly related to the area of newly created surfaces of the crystals. These findings are in accord with eqs. (2.16) and (2.20), respectively.

Fig. 2.7 shows that the total ML intensity decreases and tends of disappear beyond a particular temperature of the crystals. Equation (2.24) indicates that the decrease in ML intensity with temperature may primarily be
Fig 2.2 (a) : Spectra of mechanoluminescence of sucrose crystals and gas discharge at atmospheric pressure ML, ......... discharge in air.
Fig 2.2 (b) : Mechanoluminescence and Photoluminescence spectra of triphenylamine crystals.
Fig. 2.2 (c): Mechanoluminescence and Photoluminescence spectra of uranyl nitrate hexahydrate crystals (*, o, ............. M; ----PL). Intensity * of position is increased by 100 times as compared to the intensity of o position of ML.
Fig 2.3

Fig 2.3: Time dependence of the ML during fracture of sucrose crystals.
Fig. 2.4

Fig 2.4 : Plot of lnI versus time (t-t_m).
Fig. 2.5

Fig. 2.5: Time $t_m$ versus thickness of the sucrose crystals.
Fig. 2.6

Fig. 2.6: ML peak intensity $I_m$ and total ML intensity versus surface of the crystals.
Fig. 2.7

Dependence of ML intensity on the temperature of phenanthrene, triphenylamine and resorcinol crystals.
Fig. 2.8: Time dependence of the mechanoluminescence intensity.
due to the decrease in $\eta_1, \eta_2$ and surface charge density $\rho$. Beyond a particular temperature of the crystals, the surface charge density may decrease below the threshold value, therefore, the ML may not appear beyond a critical temperature of the crystals.

Fig. 2.8 shows that when piezoelectric phosphorescent crystals like ditriphenylphosphine oxide manganese bromide are cleaved, then two peaks appear in the ML intensity versus time curve of the crystals, where the first peak lies in the deformation region and the second peak lies in the post deformation region. Thus is in accord with the theory discussed previously.

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

2.5 CONCLUSIONS

Following are the important conclusions drawn from the studies of the ML produced during the cleavage of piezoelectric crystals:

(i) When a piezoelectric crystal is cleaved, initially the ML intensity increases linearly with time, attains a peak value $I_m$ at a particular value of time $t_m$ and then decays exponentially with time.

(ii) Both, the peak ML intensity $I_m$ and total ML intensity $I_T$ of piezoelectric crystals increase linearly with the area of newly created surfaces as well as with the surface charge density $\rho$.

(iii) When piezoelectric phosphorescent crystals like ditriphenylphosphine oxide manganese bromide are cleaved, then two peaks appear in the ML intensity versus time curve of the crystals, where the first peak lies in the deformation region and the second peak lies in the post deformation region.

(iv) The ML intensity of piezoelectric crystals decreases with temperature primarily due to the decrease in $\eta_1, \eta_2$ and the surface charge density $\rho$. Beyond a particular temperature, the surface charge density may decrease to such a value where the breakdown of gases and solids may not be possible and thereby the ML may not appear.
(v) Depending on the prevailing conditions either the ML emission resembling gas discharge or other types of the luminescence of crystals, or that having these two characters may be obtained.

(vi) Fracto-ML provides a new tool to determine the velocity, \( v \) of cracks in crystals, and it may be given by \( v = H/t_m \), where \( H \) is the thickness of the crystal.

(vii) When a piezoelectric crystal is fractured, initially, the ML intensity increases with time. In fact, this is related to the increase in crack length with time. As a matter of fact, the ML intensity versus time plot autographs the increase in crack length with time. Thus, ML provides a new tool for studying the time-resolved fracture dynamics.