

## Fracto-ml induced by slow deformation of n- acetyanthranilic acid and hexaphenylcarbodiphosphorane crystals

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**Abstract :** The present paper gives study of Fracto-mechanoluminescence induced by slow deformation of fluorescent and phosphorescent crystals. In slow deformation of a crystal, the number of ML pulses emitted indicates the number of cracks moved in the crystal. Thus, there is one-to-one correspondence between the number of cracks formed and the number of ML pulses emitted during the deformation of crystal. The study of fracto-ML gives important information that the number of cracks increases linearly with the deformation of crystals and the area of newly created surfaces at slow strain increases linearly with the strain of crystals.

### I. INTRODUCTION

As ML is produced during deformation of solids, a systematic correlation between the ML intensity and the material deformation is expected. The emission of photons due to deformation is an interesting example of energy transfer between system and potentially useful probe of deformation process specially in understanding the basic mechanisms of crack-growth. Different techniques have been used nowadays for deforming the materials.

Because archaeological dating techniques usually involve grinding the sample, they may inadvertently change the thermoluminescence and thus the age. Mechanoluminescence and thermoluminescence studies may be needed to improve the accuracy. Models of deformation and fracture to explain mechanoluminescence may help to explain and predict earthquakes. Laboratory studies on minerals and theories that focus on piezoelectric voltage, dislocation motion, electric field oscillations, coronal discharge or dielectric breakdown (Cress et al. 1987, Brady and Rowell 1986), have already improved our understanding.

The new surfaces of crystals that follow the tip of the crack are totally unlike the bulk. When the mechanical energy of the fracture is still primarily in a layer, a few atoms thick from a new surface and has yet to be transferred to the entire chunk of material, the new surface is disrupted far more than the surfaces of the plastically deformed material. Depending on the

material the new surface is pock marked with patches of charge, broken bonds and huge crystal defects, and it is criss-crossed by dislocations. High levels of surface roughness are observed even after annealing (Watanabe et al. 1994). Dislocations popping out of this new surface concentrate energy and electrons that probably could cause chemical reactions, e.g., expulsion of sodium from glass (Langford et al 1991), carbon dioxide from calcite (Dickinson et al. 1991b) and carbon monoxide from polycarbonate (Dickinson et al. 1993b). Electrons are expelled from this surface with high energies and accelerated back to positive sites on the surface (Mathison et al. 1989). The energy of this bombardment is sufficient to heat the surface (Dickinson and Jensen 1985), eject more electrons (Dickinson 1990) and/or excite the photoluminescence of material on or near the surface (defects, dopants or host). Some of the electrons may strike the molecules of the surrounding gas as they are accelerated towards the surface, exciting its luminescence in a coronal discharge. When the fracture is done in high vacuum, the discharge is through a gas consisting of molecular fragments expelled by the energetic surface (Dickinson et al. 1982b, Dickinson et al. 1986a, Li and Haneman 1999, Klyuev et al. 1979, Larson et al. 1979). In addition, electrons can recombine with positive sites by tunneling either along the surface (Batylin et al. 1992, Molotskii 1987) or between two surfaces less than 1nm apart (Dickinson et al. 1997) exciting luminescence in some cases.

Chandra and Zink (1980a,b) were the first to report the ML emission induced by the fracture of fluorescent and phosphorescent crystals during their deformation at fixed rate. They found that the ML pulses appear concurrently with the steps occurring in the stress-strain curve of the crystals. As the steps in the stress-strain curve of the crystals occurs due to the movement of cracks moved in the crystals, it was shown that the cracks are responsible for fracto-ML of crystals. In this study, the crystals were compressed slowly at a fixed strain rate using a table model Instron testing machine, in which stress was measured by a load cell, strain was measured by a LVDT transducer, and the ML intensity was measured by a photomultiplier tube.

In the past attempts have been made to understand the systematic correlation between number of cracks and deformation and area of newly-created surfaces and deformation, but such correlations have not been established to date. The present chapter reports the fracto-ML produced during the slow deformation of crystals and explores the correlation between the number of cracks formed and the number of ML pulses emitted and also establishes the correlation between the number of cracks and deformation and the area of newly created surfaces and deformation of crystals. Furthermore, a comparison is made between the theoretical and experimental results.

## II. MECHANISM OF FRACTO-MECHANOLUMINESCENCE OF CRYSTALS

### Mechanoluminescence Excitation in Piezoelectric Crystals

The ML excitation in piezoelectric crystals can be understood on the basis of piezoelectrification of newly created surfaces. The Langevin (1921) model of the creation of charged surfaces during movement of a crack in a piezoelectric crystals. When a stress is applied onto a piezoelectric crystal, its one surface is positively charged and the opposite surface is negatively charged. Due to the movement of a crack in the crystal, new surfaces are created. The newly created surfaces nearer to the positively charged surface of the crystal are negatively charged and the newly created surface nearer to the negatively charged surface of the crystal is positively charged. Thus, an intense electric field may be produced between the newly created surfaces of the crystal. For the simplification of the estimation of the electric field, let us make certain assumptions: (i) that the piezoelectric constants remain unchanged upto the fracture stress of the crystal, (ii) that the stress near the tip of the mobile crack acts along a polar direction of the crystal, and (iii) that the stress near the tip of the crack is not relaxed before the ML excitation. It is known that the piezoelectric constants and the stress needed to separate the surface of the crystal are generally of the order of  $10^{-12}$  coulomb  $N^{-1}$  and  $10^{-8}$   $Nm^{-2}$ , respectively (Mason 1950, Cottrel 1964). Thus, the surface charge density  $\rho$  is of the order of  $10^{-4}$  Coulomb  $m^{-2}$  and

thereby an intense electric field  $\frac{\rho}{\epsilon_0}$  of the order of  $10^7$   $Vm^{-1}$  is created between the newly created oppositely charged surfaces, where  $\epsilon_0$  is the permittivity of the space ( $\epsilon_0 = 0.85 \times 10^{-12} C^2 N^{-1} m^{-2}$ ).

This field may cause the dielectric breakdown of the intervening gasses and, in turn, may give rise to gas discharge ML. The field may also cause the dielectric breakdown of the crystals and the recombination of free carriers may give rise to the recombination

luminescence (Thomson and Thomson 1933). The impact of accelerated electrons on the positively charged surfaces may also give rise to the cathodoluminescence.

## III. THEORY

In fact, fracture denotes the separation of a solid into two or more parts by the application of stress. Fractures are termed ductile or brittle, depending on whether or not plastic deformation occurs before fractures. The classification depends not only on the material but also on size, shape, mode of loading and scale of observation. The transition from ductile to brittle fracture takes place at large size of crystals, at low temperature and at higher strain rates.

In the experiment of fracto-mechanoluminescence induced by slow deformation, a crosshead presses the sample very slowly and the ML is produced during fracture of the sample.

If  $\epsilon$  is the strain rate of the crystal, then the increase of strain  $\epsilon$  with time is given by

$$\epsilon = \epsilon \cdot t \quad \dots(1)$$

Experimentally, it has been found from the stress versus strain curve of the materials that, beyond the fracture stress or strain, the stress increases with strain. For a small value of strain, as the fracture occurs the stress decreases slightly and then the force increases again with increasing strain, and fracture of the sample takes place again, and subsequently the stress decreases with strain of the sample. Overall beyond the fracture strain, the stress increases with strain  $\epsilon$ . When the sample is compressed beyond the fracture strain, then more and more cracks are produced in the sample. For large strain, the crack starts at the cleavage planes having more and more fracture strength for the movement of cracks. Thus, after the fracture stress  $\Omega_f$  the dependence of stress  $\Omega$  on the strain  $\epsilon$  of the crystal can be expressed as

$$\Omega = \Omega_f + [P(\epsilon - \epsilon_f)]^n \quad \dots(2)$$

where  $\epsilon_f$  is the fracture strain of the crystal, P is a constant and n is an exponent.

From the stress-strain curve of the crystals beyond  $\Omega_f$ , at slow strain rate, n has been found to equal to 1. Thus, Eq. (2) can be written as

$$\Omega = \Omega_f + P(\epsilon - \epsilon_f) \quad \dots(3)$$

Differentiating Eq. (3), we get

$$\frac{d\Omega}{dt} = P \frac{d\epsilon}{dt} \quad \dots(4)$$

If there is uniform distribution of the cleavage planes in the sample where the stress amplification and fracture are possible by increasing the stress with increasing the

strain, then for a constant strain rate, the stress will increase to a given value in a given time interval and also the number of cleavages will also increase with increasing volume  $V$  of the sample. Thus, the rate of increase of the number of cracks with time can be expressed as

$$\frac{dN}{dt} = ZV^m \frac{d\Omega}{dt} = ZPV^m \frac{d\varepsilon}{dt} \quad \dots(5)$$

where  $Z$  is the proportionality constant, and  $m$  is an exponent

Now, the integration of Eq. (2.5) gives

$$N = ZPV^m \varepsilon + C \quad \dots(6)$$

where  $C$  is the constant of integration

As  $N = 0$ , for  $\varepsilon = \varepsilon_f$ , we get,  $C = -ZK\varepsilon_f$ , and therefore, Eq. (6), can be written as

$$N = ZPV^m (\varepsilon - \varepsilon_f) \quad \dots(7)$$

Equation (7) indicates that beyond the fracture strain  $\varepsilon_f$ , the number of cracks should increase linearly with the strain.

As movement of each crack produces one ML pulse, the number  $N_p$  of ML pulses will be equal to the number  $N$  of the cracks. Thus,  $N_p$  is given by

$$N_p = N = ZPV^m (\varepsilon - \varepsilon_f) \quad \dots(8)$$

From Eq. (8), the rate of emission of ML pulses per unit time is given by

$$\frac{dN_p}{dt} = ZPV^m \dot{\varepsilon} \quad \dots(9)$$

It is evident from Eq. (9) that the number of ML pulses emitted per unit time is proportional to the strain rate of the sample, and also it increases with the volume of sample. If  $s$  is the average surface area produced by the movement of a single crack, then the total surface area produced during the movement of cracks will be  $S = Ns$ . Thus, using Eq. (7) the total surface area produced can be expressed as

$$S = sN = ZPsV^m (\varepsilon - \varepsilon_f) \quad \dots(10)$$

As the ML intensity is directly proportional to the area of newly created surfaces, (Chandra 1998, 2011), the total ML intensity  $I_T$  can be expressed as

$$I_T = \eta ZPsV^m (\varepsilon - \varepsilon_f) \quad \dots(11)$$

where  $\eta$  is the ML efficiency, that is, the number of photons produced during the creation of unit surface area.

The value of  $s$  increases with the product  $WH$ , where  $W$  is the width of crystal and  $H$  is the height of crystal, that is,  $s = bV^{m'}$ , where  $b$  is a constant and  $m'$  is an exponent. Thus Eq. (11) can be expressed as

$$I_T = \eta ZPbV^{(m+m')} (\varepsilon - \varepsilon_f) \quad \dots(12)$$

As  $I_T$  is proportional to  $V$ , we can take  $m' = 1$  and Eq. (2.12) can be written as

$$I_T = \eta ZPbV (\varepsilon - \varepsilon_f) \quad \dots(13)$$

Generally, the number of cleavage planes increases with increasing perimeter of the crystals, and therefore,  $m = 1/3$ , as the perimeter is proportional to. However, the area of newly created surface for the first crack increases linearly with the product of width  $W$  and height  $H$  of the crystal, and therefore,  $m'$  is equal to  $2/3$ , as  $WH$  is proportional to.

#### IV. EXPERIMENTAL SUPPORT TO THE PROPOSED THEORY

Fig. 1 and Fig. 2 show the ML versus strain curve and stress versus stress curve of a fluorescent N-acetylanthranilic acid and hexaphenylcarbodiphosphorane crystals, respectively. It is seen that the ML appears concurrently with the steps occurring in the stress-strain curve of the crystals. As the steps in the stress-strain curve correspond to the movement of a crack in the crystal, it seems that the creation of new surfaces is responsible for the ML emission.

The ML-strain and stress-strain curves of the sample were determined by Chandra and Zink (1980a,b) by slowly compressing the crystals at a fixed strain rate using a table model Instron testing machine, where the stress was measured by a load cell, the strain was measured using a different linear variable transducer (LVDT) and the ML intensity was measured using a photomultiplier tube.

Fig. 3 and fig. 4 show that both for fluorescent and phosphorescent crystals  $N_p$  increases linearly with  $(\varepsilon - \varepsilon_f)$ . This is in accordance with Eq. (8). Fig. 5 and Fig 6 show the plot of  $I_T (= \sum I)$  versus strain of the crystals. It is seen that the  $I_T$  increases linearly with increasing strain of the fluorescent and phosphorescent crystals. This result follows Eq. (13). Fig. 7 shows that the ML spectra of N-acetylanthranilic acid crystals are similar to their photoluminescent spectra (Duignan et al. 2002). Fig. 8 shows that the ML spectra of hexaphenylcarbodiphosphorane crystals are also similar to their photoluminescent spectra (Chandra 1991).

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

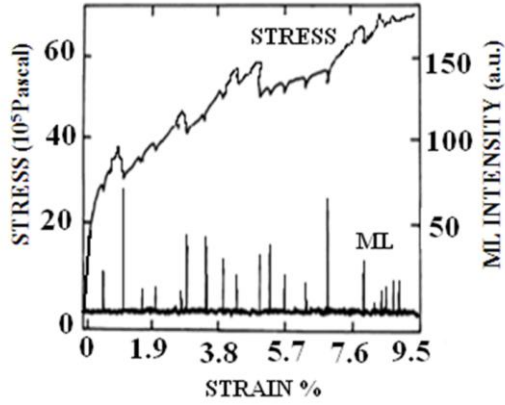


Figure 1: Stress-strain curve and ML-strain curve of N-acetylanthranilic acid fluorescent crystals (Optoelectronics lab. RDVV, Jabalpur).

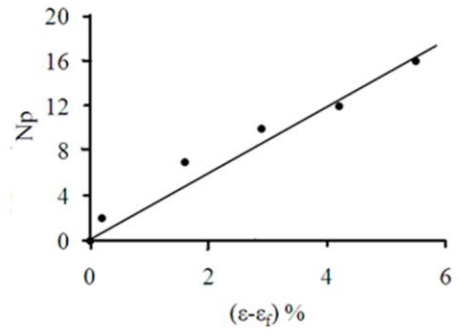


Figure 4: Dependence of number of ML pulses  $N_p$  on the strain  $\epsilon-\epsilon_f$  for hexaphenylcarbodiphosphorane phosphorescent crystals (Optoelectronics lab. RDVV, Jabalpur).

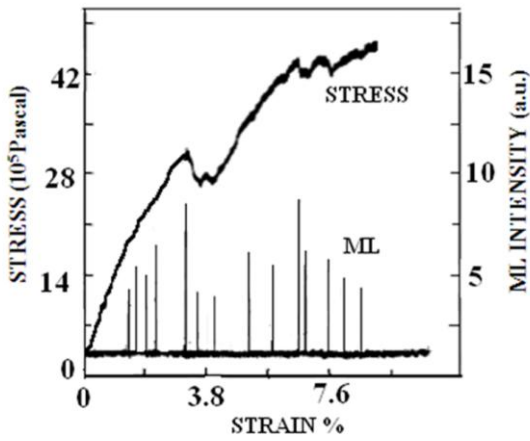


Figure 2: Stress-strain curve and ML-strain curve of hexaphenylcarbodiphosphorane phosphorescent crystals (Optoelectronics lab. RDVV, Jabalpur).

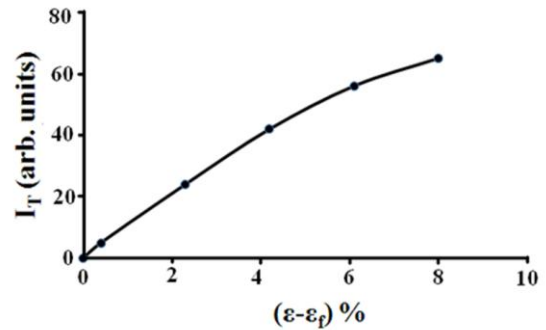


Figure 5: Dependence of total number of ML intensity  $I_T$  on the strain  $\epsilon[-\epsilon]_f$  for N-acetylanthranilic acid fluorescent crystals (Optoelectronics lab. RDVV, Jabalpur).

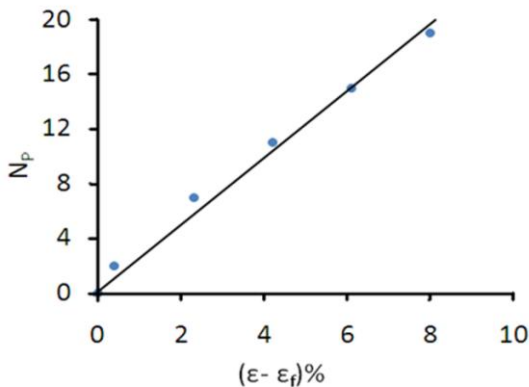


Figure 3: Dependence of number of ML pulses  $N_p$  on the strain  $\epsilon-\epsilon_f$  for N-acetylanthranilic acid fluorescent crystals (Optoelectronics lab. RDVV, Jabalpur).

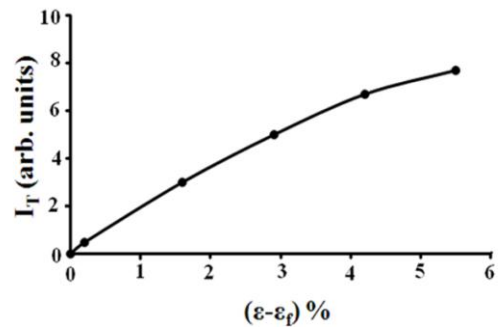


Figure 6: Dependence of number of ML intensity  $I_T$  on the strain  $\epsilon-\epsilon_f$  for hexaphenylcarbodiphosphorane phosphorescent crystals (Optoelectronics lab. RDVV, Jabalpur).

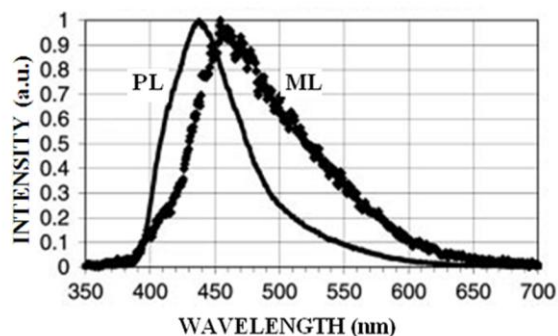


Figure 7: Mechanoluminescence and photoluminescence spectra of N-acetylanthranilic acid fluorescent crystals (Duignan et al. 2002).

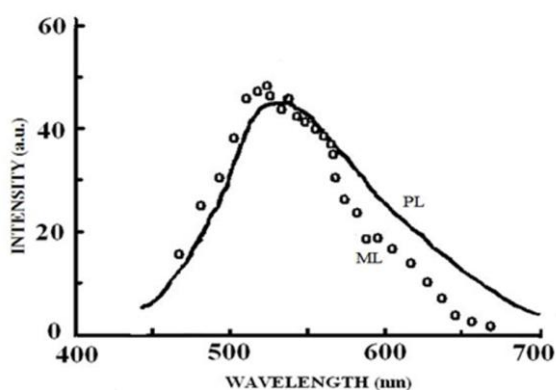


Figure 8: Mechanoluminescence and photoluminescence spectra of hexaphenylcarbodiphosphorane phosphorescent crystals (after Chandra, 1991, D.S.C. Thesis).

## V. CONCLUSIONS

The important conclusions drawn from the studies of the ML induced by slow deformation of fluorescent and phosphorescent are as given below:

- In slow deformation of a crystal, the number of ML pulses emitted indicates the number of cracks moved in the crystal. Thus, there is one-to-one correspondence between the number of cracks formed and the number of ML pulses emitted during the deformation of crystal.
- Initially, the total ML intensity related to the total area of the newly created surfaces created increases with the strain of a crystal. For larger strain, some nonlinearity is observed in the total ML intensity versus strain plot because the average surface area created by the movement of a single crack decreases with increasing strain of the crystals.
- As the decay time of ML is constant and it is of the order of microseconds, in the case of slow deformation, the peak of ML intensity induced by a single crack indicates the area of newly created surfaces.
- The study of fracto-ML gives important informations that the number of cracks increases linearly with the deformation of crystals and the area of newly

created surfaces at slow strain increases linearly with the strain of crystals.

- In slow deformation, although one-to-one correspondence occurs between the number of ML pulses and the number of cracks in the crystals, no difference can be noticed between the emission of ML pulses in fluorescent and phosphorescent crystals because of the short decay time of ML in phosphorescent crystals.

- Expressions are derived for the strain dependence of the number  $N_p$  of ML pulses, rate of appearance of ML pulses  $dN_p/dt$ , and the strain-dependence of the total ML intensity  $I_T$ , and they are as given below :

$$N_p = ZPV^m(\epsilon - \epsilon_f) = ZPV^{1/3}(\epsilon - \epsilon_f)$$

$$\frac{dN_p}{dt} = ZPV^m \dot{\epsilon} = ZPV^{1/3} \dot{\epsilon}$$

and,

$$I_T = \eta ZPbV(\epsilon - \epsilon_f)$$

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