Mechanoluminescence studies by the impulsive deformation in crystals

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Abstract: Mechanoluminescence (ML) is the phenomenon of cold emission of light from a solid as a response to mechanical stimulus. When a crystal is deformed or fractured impulsively by the impact of a moving piston, then initially the ML increases with time, attains a peak value and later on it decreases with time. Considering that the gas discharge and solid state ML are excited due to the charging and subsequent production of electric field near the tip of moving cracks.It has been found that intensityI_m of the ML peak increases linearly with the increasing value of impact velocity and the total ML intensity I_T initially increases with increasing impact velocity and then it tends to attain a saturation value for higher values of the impact velocity of the piston. The total ML intensity I_T increases linearly with volume of mannitoland cinchonie sulphate crystal. The time t_m increases linearlywith the thickness of mannitol and cinchonine sulphate crystals.The importance of fracto ML induced by impulsive deformation of crystals is discussed.

Key Words: Mechanoluminescence, Impactvelocity, Crystals

I. INTRODUCTION:

Mechanoluminescence is a light emission phenomenon, which is induced by deformation or fracture of solids(1). ML can be excited by compressing, stretching, rubbing, grinding, cutting, cleaving shaking, scratching or crushing of solids. It can also be excited by thermal shocks caused by drastic cooling or heating or by the shocks waves produced during exposure of samples to powerful laser pulses. 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. It has been found that 50% of all inorganic salts and organic solids show ML(2),nearly one-half of all inorganic solid and from one-fourth to one-third of all organic solids exhibit ML both the crystalline and noncrystalline forms. ML has been observed in insulators, semiconductors as well as in certain conductors. Ditriphenylphosphine oxide-manganese bromide, europium tetrakis (dibenzoylmethide) triethyl ammonium, impure saccharin, Eu and Dy doped strontium aluminate, manganese doped zinc sulphide, acenaphthene, N-acetyl athranilic acid, coumarin, phenanthrene, cholesteryl, salicylate, urannylnitrate, hexahydrate, N-isopropyl carbazole, and sugar are examples of intense mechanoluminescent materials. The ML of first four materials are so intense that it can be seen in day light. The physical processes involved in including ML in solids, indicate that basically there should be two types of ML, firstly, the deformation ML and secondly, the tribo ML. Initially, fracture was used as a tool to induce ML, but now a days it is used to study the fracture of solids. The fracto ML provides a self-indicating method of monitoring the microscopic and macroscopic process occurring during fracture of solids and gives important information related to the initiation, propagation and interaction of cracks in solids. Rapid photographic methods and CCD cameras have been used effectively to photograph the active areas of the crystals by their own light arising due to ML. The ML technique makes possible the real time monitoring of crack-growth in solids (3,4,5) severity and location of damages (6,7,8,9) and the stress distribution near the tip of crack in solids (10). The fracto ML also provides the online monitoring of grinding in milling machine (11). Consequently, the ML technique is attracting the interest of many workers for fracture studies. Moreover, the emission of intense light during the earthquakes and mine-failure (12,13,14) has also created the curiosity for the studies of ML produced during fracture of solids.

II. EXPERIMENT:

Crystals are commercially purchases from sigma Aldrich**.** The sizes of the crystals used for the present investigation were 2x1.5x0.95 mm^3, 1.5x1.25x0.65 mm^3, 1.40x1.0x0.65 mm^3, 1x1x0.4 mm^3. Most observations were made for the crystals of size 1.5x1.25x0.65 mm^3. Since the ML is a volumetric phenomenon, care was taken to select the crystals of equal size.The experimental arrangement for the impulsive excitation of crystals is shown in Fig. 2.1. In this technique, a crystal was placed on the upper surface of a transparent lucite plate and then it was covered with a thin aluminum foil and fixed with an adhesive tape.

This arrangement prevents the scattering of crystalline fragments during the impact of the load or piston onto the crystal. By changing the distance between the piston to be dropped and the crystal placed on the lucite plate,

the impact velocity v_o of the load can be changed up to 300 cm/s. Lucite plate was kept inside the wooden box. Since there is a negligible friction between the pulley and guiding cylinder, the impact velocity v_o was taken as $\sqrt{2gh}$, where g is the acceleration due to gravity and h is the height through which the piston is dropped. The strain-rate έ was determined by using the relation

$$\acute{\varepsilon} = \frac{v_o}{H} = \frac{\sqrt{2gh}}{H} \qquad .....(2.1)$$

where H is the thickness of the crystal.

For making the ML measurements the mannitol or cinchonine sulphate crystal was placed on the transparent lucite plate inside the sample holder below the guiding cylinder and crushed impulsively by dropping a load onto it. The luminescence was recorded by an RCA-931A photomultiplier tube (PMT) placed just below the lucite plate. The output of the PMT was fed to a dual beam oscilloscope having phosphorescent screen. The oscilloscope was operated in the normal triggering mode. In a dark room, the trace appeared on the screen of oscilloscope was visible for about thirty seconds.Atleast four crystals were studied for each set of the observations. For measuring the impact velocity dependence of ML, the piston was dropped from different heights so the velocity of the piston could be changed from. 99 cm/sec. to 300 cm/sec. The errors found were ± 5%. For measuring the size dependence of the ML intensity, the crystals were deformed impulsively for different sizes of the crystals.

III. RESULT

Fig. 1 shows the time dependence of the ML intensity of mannitol crystals. It is seen that the ML intensity initially increases with the time, attains a peak value and then decreases with time, and finally disappears. The same figure also represents the time dependence of the ML intensity of mannitol crystal for different impact velocities of the piston. Similarly Fig. 2 shows the time dependence of the ML intensity of cinconinesulphate crystals. The ML intensities I_m corresponding to the peak in the ML intensity versus time curve, increases with increasing impact velocity of the piston. The time t_m (i.e. time corresponding to the ML) shifts towards shorter time values with increases in the impact velocity.

$$I = I_m \exp\left(-\frac{(t - t_m)}{\tau}\right) \qquad .....(2.2)$$

where τ is the decay time of ML.

Fig 3&4 shows the dependence of the time t_m corresponding to the peak in the ML intensity versus time curve on the impact velocity for Mannitol&cinconine sulphate crystals. It is seen that t_m decreases with increasing impact velocity of the crystal.

Fig. 5 shows the velocity dependence of the peak intensities I_m in the ML intensities versus time curve for mannitol and cinchonine sulphate crystals. It is clear from the figures that I_m linearly increases with increasing value of the impact velocity.

Fig 6 shows the dependence of the total ML intensity I_T (i.e. the area below the ML intensity versus time curve) on the impact velocity for mannitol and cinchonine sulphate crystals. It is seen from the figure that I_T initially increasing with increasing impact velocity or strain rate and then it tends to attain a saturation value for higher value of the impact velocity.

Fig. 7 shows that t_m increases linearly with thickness of mannitol and cinchonine sulphate crystals.

Fig. 8 shows the dependence of total ML intensity I_T on the volume of mannitol and cinchonine sulphate crystals. It is seen from figure that I_T increases linearly with volume of mannitol and cinchonine sulphate crystals.

It is to be noted when mannitol crystals are exposed to atmosphere for long time, then there ML disappears.

IV. DISCUSSION

Mannitol and cinchonine sulphate crystals are piezoelectric because they belong to noncentrosymmetric $P2_12_12_1$ (15) and P1 space groups (15) respectively. Thus, there ML is caused by the creation of charged surfaces during the impact a piston on to the crystals. The ML intensity increases with time (Fig. 1 and 2) because the rate of creation of new surfaces increases with time. The ML intensity gets attains maximum value because the rate of creation of new surfaces is maximum and then intensity decreases with time because the rate of creation of new surfaces decreases.

It is seen from Fig. 3 and 4 show that t_m decreases with increase in the impact velocity. This shows that the deformation rate of the crystal is fast at high velocities.

Fig. 5 show that I_m linearly increases with the impact velocity v_o. Thus, it seems that the rate of creation of new surfaces is directly proportional to the impact velocity v_o of the piston used to deform the crystals.It is seen from Fig. 6 that the total ML intensity I_T initially increases with the impact velocity v_o and later on it tends to attains a saturation value. This result indicates that the total area of newly created surfaces initially increases with the impact velocity and then it tends to attain a saturation value, because beyond a particular level, it becomes difficult to create new surfaces in the crystals.

It has been found that the ML intensity of mannitol and cinchonine sulphate crystals decreases with increasing temperature and tends to disappears beyond a particular temperature of the crystals (16). This may primarily value to decrease in ML efficiency as well as in the change density of the crystals.

The ML spectra of mannitol crystals are similar to the gas discharge spectra and the ML spectra of cinchonine sulphate crystals consist of the gas discharge and fluorescence spectra (17).

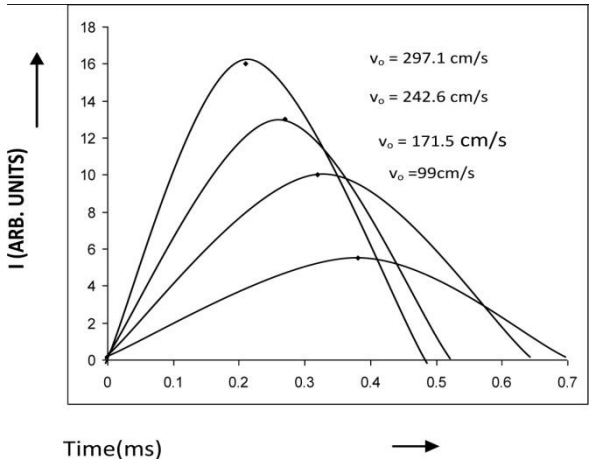

Fig.1: Time dependence of the ML intensity of mannitol crystals fordifferent impact velocities (size of crystals = 1.5 x 1.25 x 0.65 mm)

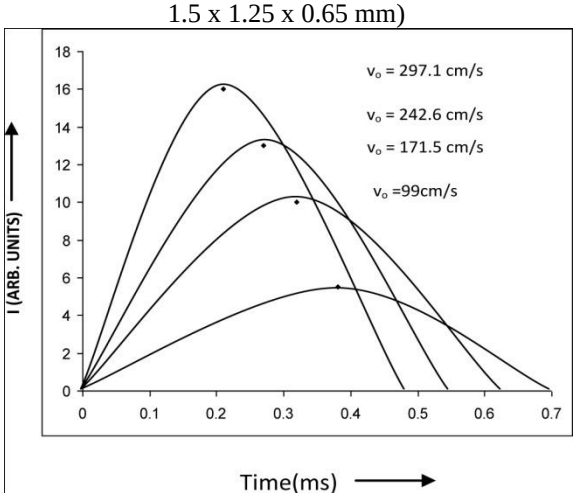

Fig. 2: Time dependence of the ML intensity of cinchonine sulphate crystals for differentimpact velocities (size of crystals = 1.5 x 1.25 x 0.65 mm^3

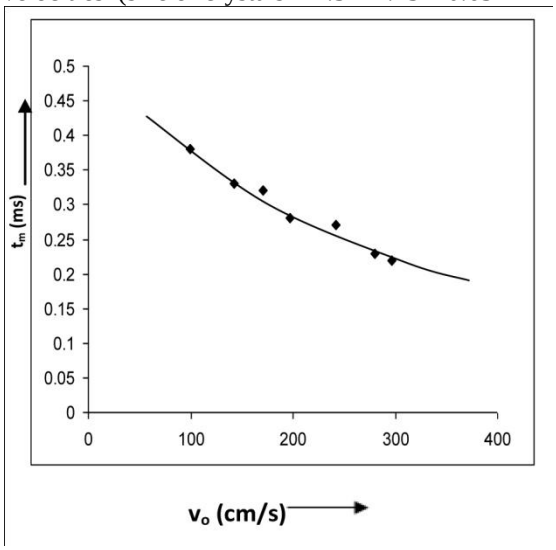

Fig. 3 Dependence of t_m on impact velocity for mannitol crystals (size of crystals = 1.5 x 1.25 x 0.65 mm^3)

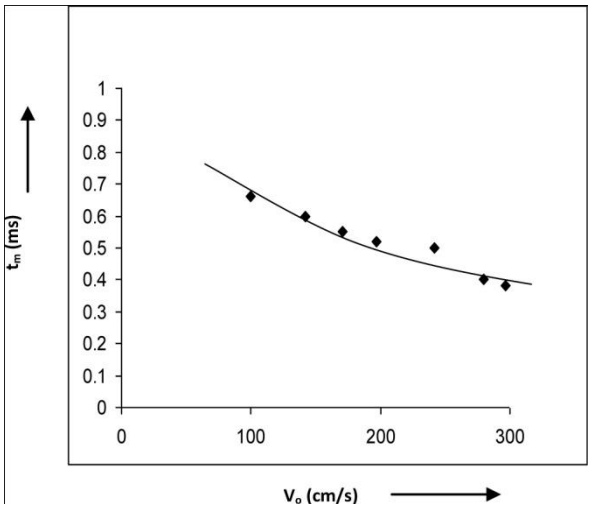

Fig. 4 Dependence of t_m on impact velocity for cinchonine sulphate crystals (size of crystals = 1.5 x 1.25 x 0.65 mm^3).

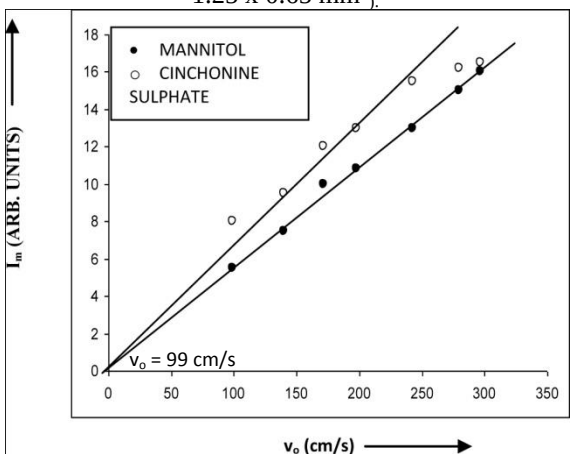

Fig.5. Dependence of peak intensity I_m of mannitol and cinchonine sulphate crystals on differenent impact velocities (size of crystals = 1.5 x 1.25 x 0.65 mm^3)

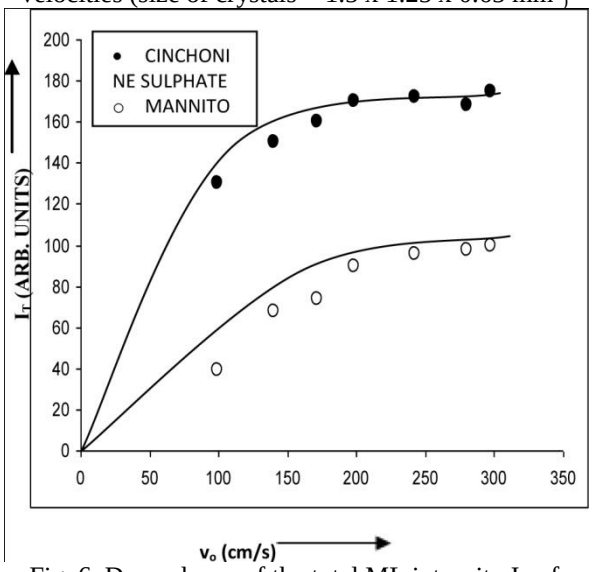

Fig. 6. Dependence of the total ML intensity I_T of mannitol and cinchonine sulphate crystals on different impact velocities (size of crystals = 1.5 x 1.25 x 0.65 mm^3

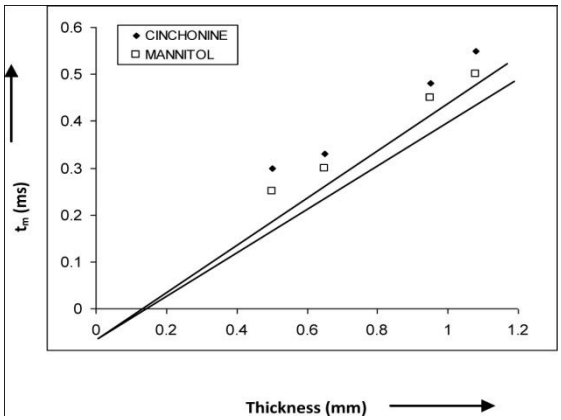

Fig. 7. Dependence of t_m on thickness of mannitol and cinchonine sulphate crystals

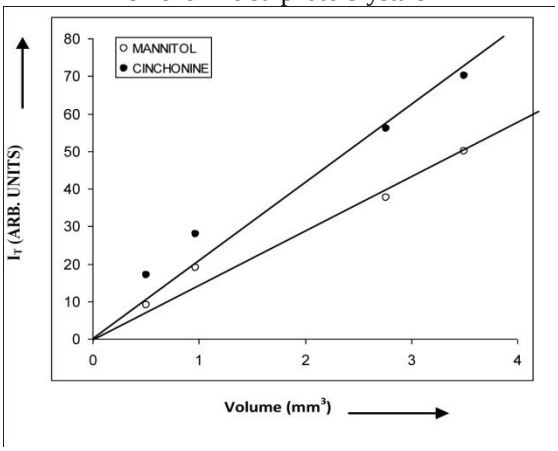

Fig.8. Dependence of total ML intensity I_T on the volume of mannitol and chinonine sulphate crystals.

V. CONCLUSION:

The important conclusions drawn from the ML produced during impulsive deformation of mannitol and cinchonine sulphate crystals are as given below :

(i) When the crystals are deformed impulsively by the impact of a moving piston onto the crystals, initially the ML intensity increases with time, attain a maximum value and then it decreases with further increase in the value of time.

(ii) In impulsive excitation of ML, the time tm corresponding to the peak of the ML intensity versus time curve, for mannitol and cinchonine sulphate crystals, decreases with increasing impact velocities.

(iii) The intensity I¬m of the ML peak increases linearly with the increasing value of impact velocity and the total ML intensity IT initially increases with increasing impact velocity and then it tends to attain a saturation value for higher values of the impact velocity of the piston.

(iv) The total ML intensity IT increases linearly with volume of mannitol and cinchonie sulphate crystal.

(vi) The time tm increases linearlywith the thickness of mannitol and cinchonine sulphate crystals.

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