

Mechanoluminescence excitation in alkali halide crystals and colouration decay in microcrystalline powders

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Abstract. The mechanoluminescence (ML) of NaCl, NaBr, NaF, LiCl and LiF crystals ceases at 105, 58, 170, 151 and 175°C respectively. Both the temperature T_c at which ML disappears and the temperature T_i required to induce a particular percentage of colouration decay in a given time, decreases with increasing nearest neighbour distance in alkali halide crystals. This perhaps suggests that similar processes cause the disappearance of ML in alkali halide crystals and the colouration decay in their microcrystalline powders. It is shown that mobile dislocations may cause the leakage of surface charge and the decay of colouration in microcrystalline powders.

Keywords. Mechanoluminescence; triboluminescence; colour centres; dislocations; alkali halides.

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1. Introduction

Mechanoluminescence (ML), produced during mechanical deformation of solids, has been studied in many molecular crystals. It has been generally found that piezo-electric crystals exhibit ML whereas non-piezoelectric crystals do not (Chandra 1981), thus supporting the piezoelectric origin of ML. We have found that several non-piezoelectric inorganic crystals also exhibit ML which compares in intensity with that of piezoelectric crystals. This suggests that besides piezoelectrification, there should be some other mechanism for ML excitation in inorganic crystals. The mechanism of ML excitation in non-piezoelectric inorganic crystals is least understood. Limited studies have been made on the ML of centrosymmetric inorganic crystals, particularly on the ML of non-irradiated alkali halide crystals (Meyer *et al* 1970). The present investigation attempts to study the mechanism of ML excitation in centrosymmetric inorganic crystals. It should be noted that the ML of coloured alkali halide crystals is of different origin where ML appears in elastic, plastic and fracture regions of the crystals. The colour centres and mobile dislocations cause ML excitation in coloured alkali halide crystals (Chandra *et al* 1981).

There is yet another phenomenon associated with dislocation motions, viz reduced stability of excess electron centres in alkali halide powders. It is known that stable colour centres can be produced in alkali halide crystals by using various methods

(Compton and Schulman 1962). Coloured crystals can be stored for several years at room temperature, in dark, without any appreciable loss of colouration. However, the colouration of microcrystalline powders of some alkali halides decay at room temperature in darkness (Moharil and Deshmukh 1978). It was shown that the decay was due to mobile dislocations which strip off the charges from colour centres (Moharil *et al* 1979; Pode *et al* 1982; Moharil 1980). It was considered that the correlated study of quenching of ML and loss of colouration would be interesting as both processes might be related to dislocation motions. Such correlations are indeed found and the results are reported in this paper. This has helped in analysing and pinpointing the mechanism of ML excitation in non-irradiated alkali halide crystals.

2. Experimental

The crystals used were supplied by Harshaw Chemical Company, USA. Some of the crystals were grown in laboratory by Czochalski method. G.R. grade powders were used without further purification for crystal growth. The ML vs compression and the force vs compression curves were determined using an Instron testing machine (Chandra and Zink 1980). The ML was excited by a piston moving at a velocity of 312 cm/sec. The total ML intensity was monitored by an IP28 photomultiplier tube in terms of the deflection of a ballistic galvanometer. Lucite or quartz plates (for higher temperature) were used as crystal holders. The crystals were heated to a desired temperature by a cylindrical heater. The crystal temperature was measured by a copper-constantan thermocouple. The ML spectra were recorded by 0.5 m Bausch and Lomb monochromator and EMI9558Q photomultiplier tubes following the technique described by Hardy and Zink (1976).

To measure the colouration decay, single crystals of NaCl, NaBr, KCl, KBr, KI and RbI were cleaved to required size and coloured electrolytically (Deshmukh and Soman 1976). The crystals were heated to a temperature of the order of 600°C, and an electric field (100 V/cm) was applied using flat anode and pointed cathode.

In fluorides, accurate conditions are necessary for electrolytic colouration. In these cases, the powders were coloured by ionizing radiations (γ -rays) or electrodeless discharge. Three slices (0.5–0.1 mm) were cleaved from the central, uniformly coloured portion of the single crystals for optical absorption measurements. Weakly coloured, or non-uniformly coloured portions of the crystals were cleaved out and rejected. The remaining uniformly coloured pieces were then crushed to powders and sieved to the required fineness. The reflecting surfaces were prepared from these powders, and the reflectance spectra were scanned on Carl Zeiss spectrophotometer VSU2P with 45/0 reflectance arrangement. For recording the decay, reflectance at F band maximum was measured at suitable intervals. Complete spectra were scanned at longer intervals (\sim 2 hr). The decay was recorded at elevated temperatures by storing the samples in an oven, removed at intervals and quickly cooled to room temperature. Reflectance at the F band maximum was measured and samples were replaced carefully at the same marked position in the oven (to avoid errors due to temperature inhomogeneity in the oven if any). The entire procedure took only a couple of minutes. If readings were taken at longer intervals (\sim 2 hr), complete spectra were recorded in 5–7 min during which time the samples remained at room temperature and before they could be returned to the oven. In the case of KI, readings were taken below room temperature by adopting a

similar procedure and storing the samples in various compartments of a refrigerator. All optical measurements were carried out at room temperature. The particle size used was between 124 and 140 μ .

3. Results and discussion

Figure 1 shows ML versus compression and force versus compression curves of a non-irradiated crystal of NaF. The steps in the force versus compression curve correspond to the movement of cracks in the crystal. It is seen that ML occurs only during the movement of cracks in the crystal. However, the movement of all the cracks is not followed by the ML emission. Figure 2 shows that ML disappears in NaCl, NaBr, NaF, LiCl and LiF crystals at 105, 58, 170, 151 and 175°C respectively. These temperatures are much lower when compared with the melting point of the crystals. The melting point of NaCl, NaBr, NaF, LiCl, and LiF crystals are 800.4, 743, 993, 605, and 845°C respectively. Figure 3 shows that the plot of $\log I$ versus $\log (1 - T/T_c)$ is a straight line with a positive slope between 0.5 and 0.6, where T_c is the temperature at which ML disappears. This suggests the relation $I = I_0 (1 - T/T_c)^n$, where I_0 and n are constants and n lies between 0.5 and 0.6. Figure 4 shows that the ML spectra of NaCl crystals are similar to the discharge spectra of nitrogen gases. The ML spectra of NaBr, NaF, LiCl and LiF crystals are also similar to that for NaCl crystals. The incandescent emission reported by Meyer *et al* (1970) could not be found presumably because our experiment was performed at atmospheric pressure.

The isothermal decay of F centres for different samples recorded at various temperatures is shown in figure 5. The Kubelka-Munk function normalized in terms of initial values is plotted as a function of time (Kubelka-Munk function $F(R) = (1 - R)^2/2R$, where R is the reflectance in fraction). It is seen that potassium halide

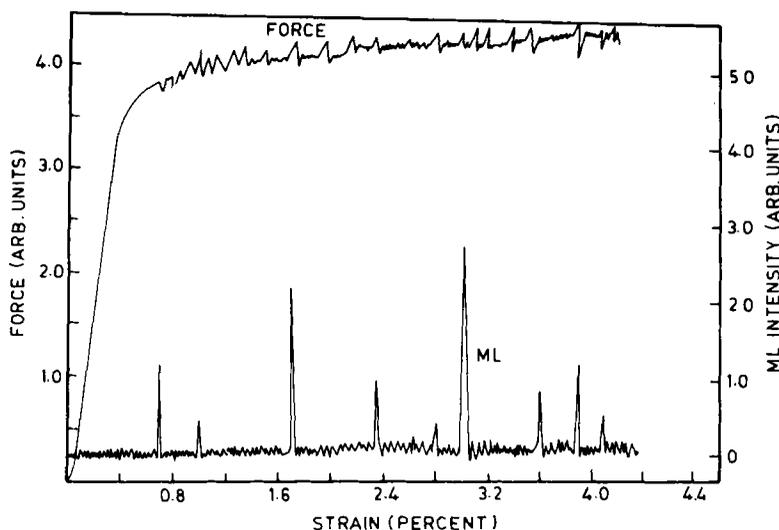


Figure 1. ML versus compression and force versus compression curves of a $4 \times 4 \times 10$ mm NaF crystal (compression rate 8.5×10^{-3} mm/sec).

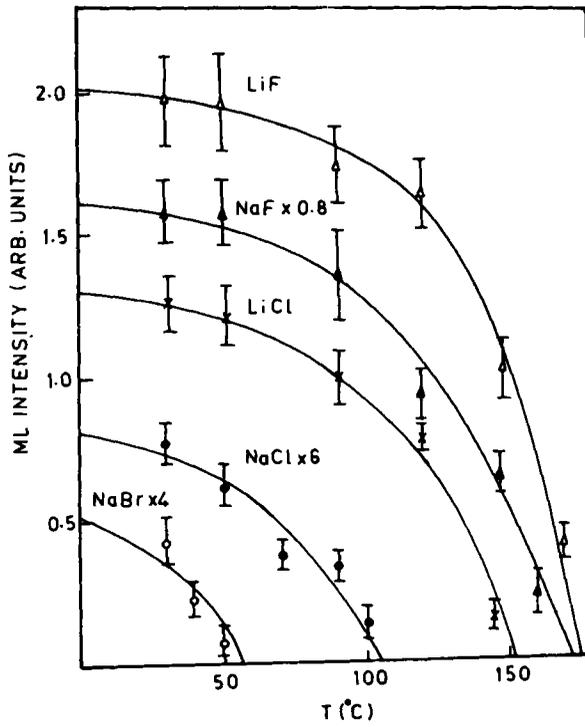


Figure 2. Effect of temperature on the ML intensity of alkali halide crystals.

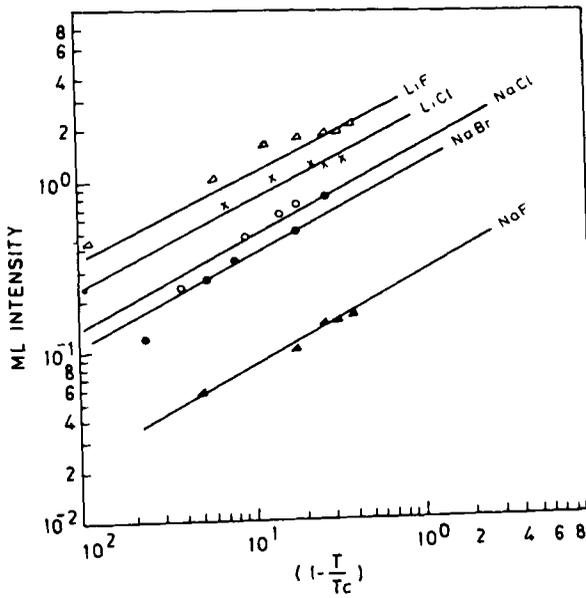


Figure 3. Dependence of log of ML intensity I on $(1 - T/T_c)$.

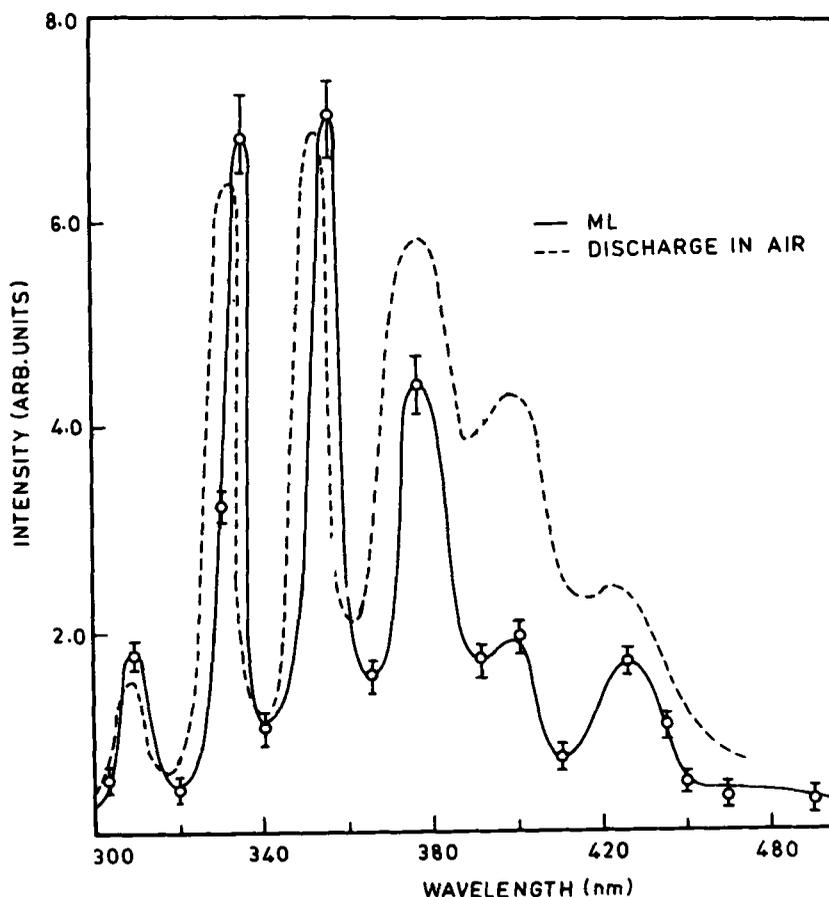


Figure 4. Spectra of ML of NaCl crystals and gas discharge in air.

powders are not stable even at room temperature and there is rapid isothermal decay of colouration. It was found that when colouration decays over the entire wavelength region, there was no conversion of F and F -aggregate centres.

The alkali halide powders with lattice parameters smaller than that of KCl were found to retain colouration for a longer time when stored at room temperature. NaCl powder stored at an increased temperature upto 80°C showed no appreciable decay of colouration. Conversion of F to F -aggregate and colloids was observed when the temperature was 50 – 80°C . Above 100°C , the aggregates and colloids already formed disperse upon storing and one can observe a rise in F centre concentration. Above this temperature a genuine colouration decay is observed without any conversion.

The LiF and NaF crystals can be electrolytically coloured only under exacting conditions (Coilins *et al* 1974). These powders were therefore coloured in an electrodeless discharge (Moharil and Deshmukh 1977). When NaF was held at 175°C , conversion of F to F -aggregate and colloids could be observed. A similar conversion is seen when LiF powder was held at 400°C . This shows that genuine F centre decay does not commence atleast upto 175°C in NaF and upto 400°C in LiF. Genuine decay could

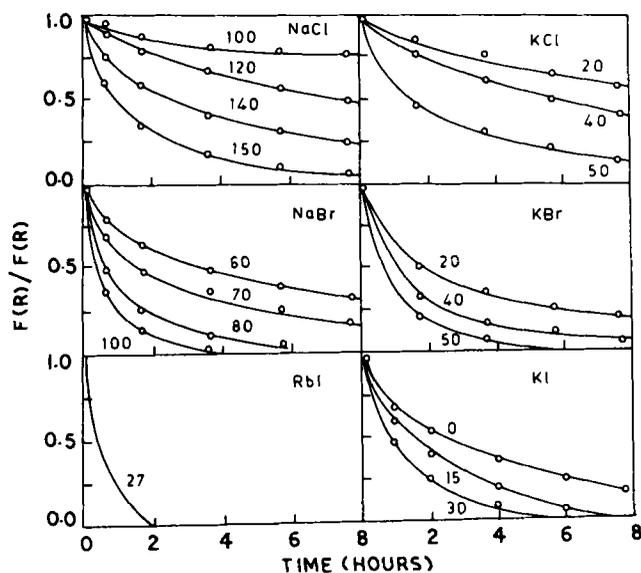


Figure 5. Isothermal decay of F centres in microcrystalline powders ($124\text{--}140\ \mu$) of various alkali halides at different temperatures (numbers on the curves) (Kubelka-Munk function, normalized in terms of initial values of F band maximum, is plotted as a function of storage time).

be observed in NaCl powder only above 100°C , and an appreciable decay occurs only above 120°C (Deshmukh *et al* 1983).

The colouration of single crystals of alkali halides is stable. The colouration of powders, on the other hand, is more prone to bleaching when stored in dark at suitable temperatures. The stability of colouration keeps decreasing as one proceeds along alkali halide series of increasing lattice parameters. For a more quantitative measure of this property, we have plotted T_s , the temperature required to induce 50% decay in 2 hours, as a function of "nearest neighbour distance" d (figure 6). It is seen that the stability decreases rapidly as the d values increase. Figure 6 shows that the temperature T_c at which the ML intensity decreases to zero, also decreases with increasing value of d . It is seen that ML activity also decreases with increasing value of d . The arrows at LiF and NaF points in the T_s curve indicate the estimated lower values of T_s .

The increase of both T_s and T_c with increasing nearest neighbour distance d suggests that similar physical processes might cause the colouration decay in crystalline powders and the disappearance of ML with temperature. The decay of colouration in crystalline powders has been attributed to the sweeping-up of charges from colour centres by moving dislocations (Deshmukh *et al* 1983; Janszky *et al* 1980; Weilke 1981; Hersh and Cocco 1967).

In microcrystalline powders one can expect dislocations to be present in far greater abundance than in single crystals. The observed loss of colouration may be due to interaction of moving dislocations with colour centres. Plastic deformation, which among other things results in dislocation motions, is known to cause bleaching of colour centres (Hawkins 1971). During the interaction, dislocation makes the colour centres deprived of charges. This idea was supported by results on doped crystal

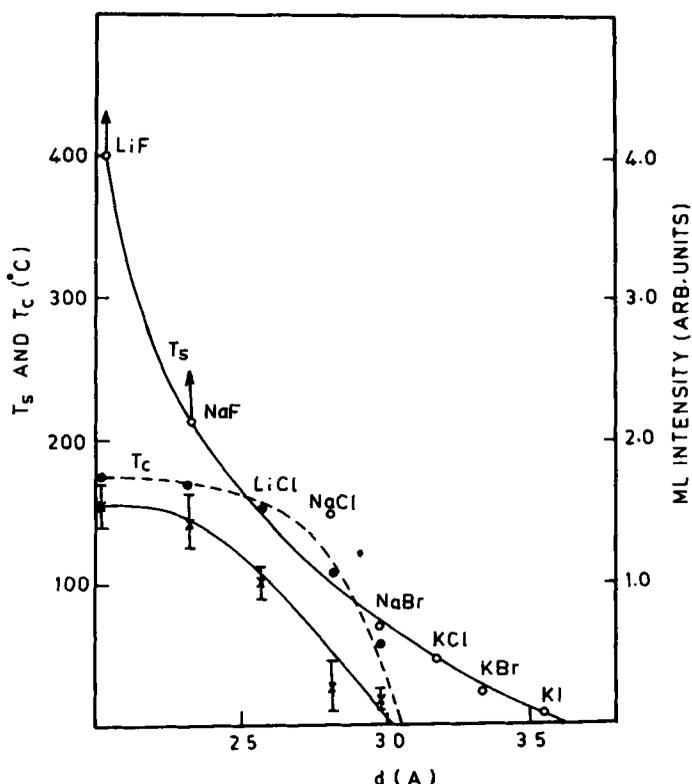


Figure 6. T_s , T_c and ML activity as a function of nearest neighbour distance d (in the case of LiF and NaF, estimated lower values of T_c have been taken) (— ML activity).

powders. It was observed that impurities inhibit the decay (Wakde *et al* 1979), and the extent to which this happens is proportional to the 'misfit'. This is consistent with the idea that the decay observed is due to the interaction between colour centres and dislocation. The impurities are expected to pin the dislocations and thus inhibit the decay. Impurities differing most in size from host ions are expected to be effective in pinning the dislocations.

The appearance of ML only during fracture and similarity of the ML spectra to the gas discharge suggest the creation of charged surfaces during the crystal fracture. There are several possible mechanisms of creating charged surfaces during crystal fracture: the motion of charged dislocations, frictional electrification caused by rubbing together of two dissimilar materials, internal electrification at cleavage or shear planes in the crystals, and electrifications caused by separation of crystal regions of microscopically disturbed electrical equilibrium due to chemical defects. Some of the possible mechanisms may be eliminated on the basis of experimental results. Since alkali halide crystals are centrosymmetric, ML excitation may not be due to piezo-electrification. Since ML intensity increases at low temperatures where the movement of dislocations is blocked, ML excitation may not be due to the motion of charged dislocations. Also, since ML intensity does not depend on the materials used for crushing the crystals, ML excitation may not be due to frictional electrification between the crushing implements

and the crystals. The ML activity does not very much depend on the purity of the chemicals used for crystallization; hence there seems to be no ground to accept that ML excitation due to electrification is caused by separation of crystal regions of microscopically disturbed electrical equilibrium as a result of chemical defects. This model is also not in accord with the results of quenching experiment for NaCl and LiF crystals in which the defects are frozen, but the ML intensity decreases.

The systematic dependence of ML intensity on the lattice constants of alkali halides suggests that ML excitation should be the inherent property of the crystals. ML excitation may be due to cleavage electrification of the crystals. It is known that cleavage along charged direction, that is, along [111] direction can create charged surfaces. This cleavage along charged directions requires more energy than cleavage along an unchanged direction. Thus, a crack normally propagates along uncharged direction. Defects in crystals create misoriented regions atleast at microscopic levels. If the crack propagating along uncharged direction reaches the misoriented region where a charged direction lies along the direction of propagating crack, and if the crack has sufficient energy to pass through the misoriented regions, then local charging of the region will occur and this may excite ML.

The temperature dependence of decay of colouration in microcrystalline powders of alkali halides suggests that at room temperature less dislocations are mobile in LiF and NaF crystals and more dislocations are mobile in KCl, KBr and KI crystals. The movement of charged dislocations may decrease the charge density of the newly created surfaces and in turn may decrease the intensity of the electric field responsible for ML excitation. This model supports the existence of intense ML in LiF and NaF crystals, medium intensity ML in NaCl and NaBr crystals and non-existence of ML in KBr, KCl and KI crystals. We have found that ML disappears in LiF, LiCl, NaF, NaCl and in NaBr crystals at 175, 151, 170, 105 and 58°C respectively. This finding is also in accord with the leakage of surface charge due to the movement of charged dislocations. The present investigation rules out the mechanism proposed by Balyaev and Martyshev (1964) and by Meyer and Polly (1965), who suggest that the motion of electrically charged dislocations is responsible for ML excitation. It may be concluded that cleavage electrification is the major process for ML excitation in non-irradiated alkali halide crystals. Since fewer dislocations are mobile in LiF and NaF crystals, the charge density of these newly created surfaces will be greater and consequently, they should exhibit intense ML. On the other hand, greater dislocations are mobile in NaCl and NaBr crystals, hence, they should exhibit lesser ML as compared to that in LiF and NaF crystals. This agrees with the experimental observations illustrated in figure 6.

From the dependence of other physical properties on the critical temperature, and moreover, from the linear relation between ML intensity I and $(1 - T/T_c)^n$, it may be concluded that T_c should be related to the energy required for the diffusion of charged dislocations to the newly created surfaces of the crystals. Thus, ML measurements suggest that higher energy is needed in LiF and NaF crystals for the diffusion of charged dislocations towards the surface as compared to that in NaCl and NaBr crystals.

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