

Effect of Temperature on the Mechanoluminescence of Coumarin Crystals

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The mechanoluminescence of coumarin crystals is studied. It is found that mechanoluminescence decreases sharply with temperature near the melting point and that it may be a useful probe for studying the behaviour of crystals near the melting points.

The luminescence produced during mechanical deformation of solids is known as mechanoluminescence (ML) or triboluminescence. Nearly half of the inorganic compounds and from one-fourth to one third of the organic compounds exhibit ML. Spectroscopically, the mechanoluminescent substances can be divided into three types [1-3]: (i) substances, the ML spectra of which resemble their luminescence spectra; (ii) substances, the ML

spectra of which resemble the spectra of the surrounding gases, and (iii) substances, the ML spectra of which consist of both the luminescence spectra and the molecular spectra of the gases surrounding the crystals. The correlation of ML to the crystal-structure and the memory-effects related to plastic deformation may be very interesting [4-6]. ML studies have been found to be a suitable probe for studying the fracture dynamics of the crystals [7]. The object of the present investigation is to check whether the ML may be helpful in understanding the behaviour of a crystal near its melting point. The present paper reports the effects of temperature on the ML of coumarin crystals.

The effect of the impact velocity on the time dependence of the ML of coumarin crystals has been reported in an earlier investigation [8]. It is found that the peak in the ML intensity versus time curve increases and shifts towards shorter times with increasing impact velocities. It is found that the maximum in the ML intensity versus time curve decreases and shifts towards smaller time values with increasing temperature. Figure 1 shows the effect of temperature on the peak intensity I_m , the total ML intensity I_T (i.e. the area below the ML intensity versus time curve), and the time t_m corresponding to the peak of the ML intensity versus time curve.

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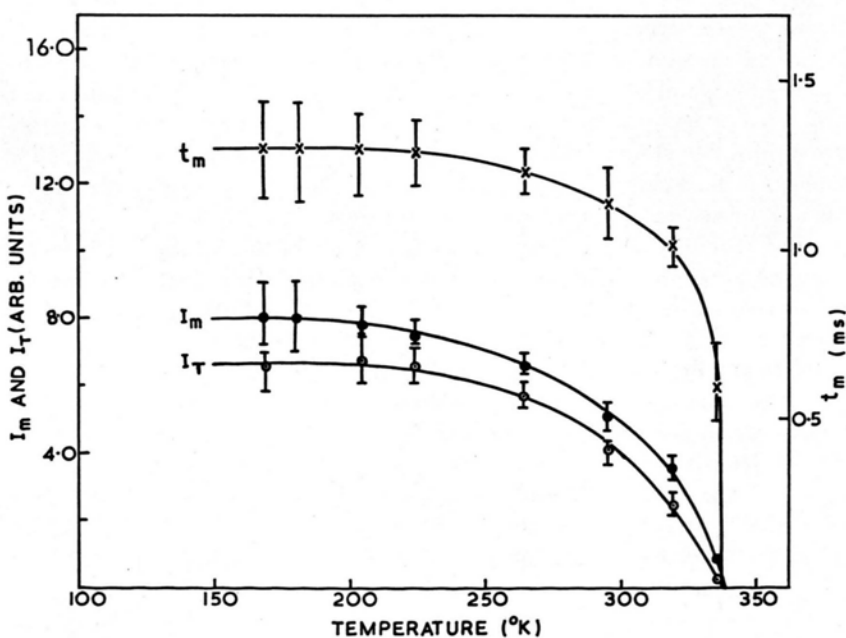


Fig. 1. Temperature dependence of I_m , I_T and t_m of coumarin crystals (observation taken for the impact velocity 378 cm/sec of the piston).

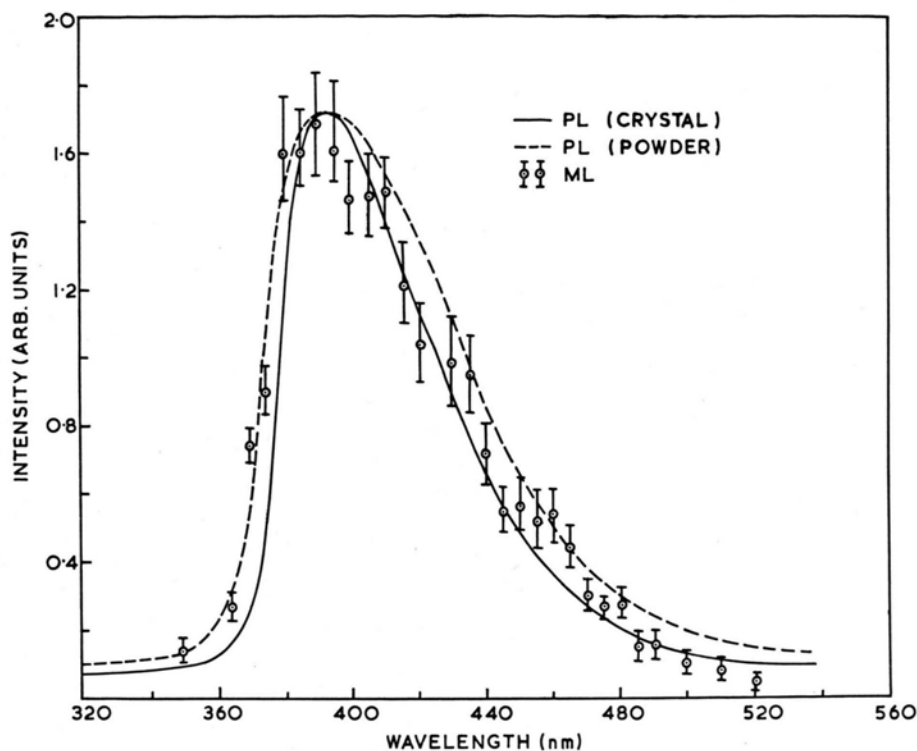


Fig. 2. Mechanoluminescence and photoluminescence spectra of coumarin crystals.

It is seen from Fig. 2 that the ML spectra of coumarin crystals are similar to their photoluminescence spectra. The simultaneous measurements of the ML versus strain and the force versus strain suggest that the ML appears only during the movement of cracks in the crystals. The melting point of coumarin is 70°C .

The crystals of coumarin were grown by slow evaporation of the solution in acetone. For the study of the time-dependence of ML an air driven steel piston was used [7]. The ML is excited by crushing the crystal with a piston velocity several m/sec. The rise and decay time of the ML was monitored by an 1P28 photomultiplier tube connected to a storage oscilloscope. The crystals were heated to any desired temperature by a cylindrical heater. For the measurement of ML below room temperature, a spiral tubing was connected to a cylinder of dry nitrogen filled with liquid nitrogen. One end of the spiral tubing was connected to a cylinder of dry nitrogen and the cooled gas coming out from the other end of the copper tubing cooled the crystals placed on a lucite plate. By changing the velocity of the nitrogen gas, the crystal could be cooled to different temperatures. The temperature of the crystal was

measured by a copper-constantan thermocouple. For the determination of the temperature effects on the ML, the crystals were fractured by an impact velocity of 378 cm/sec. The size of the crystals was $1.7 \times 1.6 \times 1.2$ mm. The ML spectra were determined by using EMI 9558 Q photomultiplier tubes and a Bausch and Lomb $\frac{1}{2}$ m grating monochromator, following the technique described previously [7]. The photoluminescence spectra were recorded by a spex spectrofluorometer.

The coumarin crystals belong to the $\text{Pca}2_1$ space group [9], and are piezo-electric. Thus, the ML in coumarin crystals may be due to the piezoelectrification during the creation of the new surfaces [1]. As a matter of fact, the ML intensity should depend primarily on the intensity of the field produced during the piezoelectrification of the newly created surfaces [10]. The intensity of the electric field will depend on the piezo-electric constant and the stress near the tip of the mobile cracks. The increase in the ML intensity with the impact velocity may be due to the creation of more new surfaces at higher velocities. The temperature may affect the piezo-electric constant, the stress near the tip of the mobile cracks and the area of the newly-created surfaces.

Since the diffusion process dominates near the melting point of the crystals, the decrease in the ML intensity may chiefly be attributed to a decrease in newly-created surfaces at higher temperatures. At the melting point, it is difficult to create new surfaces by deforming the crystals; hence the ML vanishes at the melting point of the crystals. Thus

the ML may be a useful probe for studying the behaviour of crystals near their melting point.

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