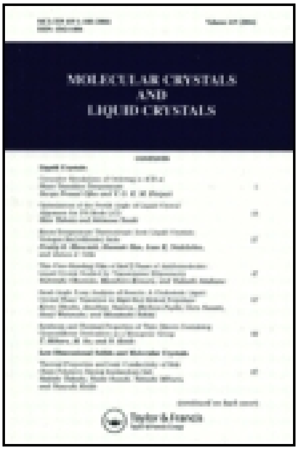

Molecular Crystals and Liquid Crystals

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Effect of Temperature on the Mechanoluminescence of Fluorescent and Phosphorescent Molecular Crystals

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Effect of Temperature on the Mechanoluminescence of Fluorescent and Phosphorescent Molecular Crystals

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The present paper reports the effect of temperature on the mechanoluminescence (ML) intensity of certain fluorescent and phosphorescent molecular crystals. The ML intensity decreases with temperature and follows the relation $I_T = I_T^0 (1 - T/T_c)^n$. The value of n lies between 0.90 and 1.10 for the piezoelectric crystals. Generally the ML of piezoelectric crystals ceases near their melting point, however, it disappears in non-piezoelectric crystals much below their melting points.

It is shown that the decrease of ML efficiency with temperature should involve both, the change in crystal properties with temperature and the usual decrease in quantum yield caused by increased radiationless transition.

Keywords: mechanoluminescence, triboluminescence, fluorescence, phosphorescence, molecular crystals

INTRODUCTION

The luminescence induced during mechanical deformation of solids is known as mechanoluminescence (ML) or triboluminescence. Since the light emitted during the mechanical deformation is not attributed to friction, the nomenclature ML is mostly preferred in the recent literatures.[1-5] The studies on temperature dependence of mechanoluminescence (ML) has been interesting and meaningful from very beginning. Many workers[6-8] have measured the effect of temperature on the ML of certain crystals and have found that the ML intensity decreases with the increasing temperature. Longchambon[9] and Stranski *et al.*[10] have concluded that the recombination of atoms or ions is the primary reason for decrease of ML intensity with increasing temperature of the substances. Wick[11] has reported the effect of temperature on the ML of fluorite crystals. She has concluded that the centres which are affected by a change in temperature are completely deactivated at higher temperatures, however, the ML due to the electrical discharge in air is not modified by a change in the temperature of the crystals. Wick[12] has also reported an emission of light at the instant when there was sudden change in the temperature of the crystals. Metz *et al.*[13] have reported that the ML in X-irradiated KBr, NaCl and LiF crystals increases when their temperature is varied from 10° to 30°C. Chandra *et al.*[14] have found that the ML intensity of X-irradiated KBr, KCl, NaCl and LiF crystals increases, however, the ML intensity of X-irradiated KI crystals decreases with temperature (the temperature range studied was from 35 to 100°C). The decrease in the ML intensity of NaCl crystals has been investigated by Frohlich and Seifert.[15]

We have been interested in studying the effect of various parameters on the intensity and the time dependence of ML. The time dependence, impact velocity dependence, and crystal size dependence of the ML of crystals have been reported previously.[16,17] The present paper reports the effect of temperature on the ML of certain fluorescent crystals like phenanthrene, resorcinol and triphenylamine, and some phosphorescent crystals like $(Et_4N)_2MnBr_4$, $(Ph_3PO)_2MnBr_2$ and benzil. The phenanthrene, resorcinol, triphenylamine and benzil crystals are piezoelectric, however, the crystals of $(Et_4N)_2MnBr_4$ and $(Ph_3PO)_2MnBr_2$ are non-piezoelectric.

EXPERIMENTAL

The single crystals of resorcinol, triphenylamine and benzil were grown by slow evaporation of solution in acetone. The crystals of hexaphenyl carbodisphosphorane were grown following the method reported in an earlier investigation.[18] The $(Ph_3PO)_2MnBr_2$ were synthesized by mixing the solution of $MnBr_2$ and $(Ph_3PO)_2$ in ethanol. The $(Ph_3PO)_2MnBr_2$ compound so obtained was dissolved again in a large volume of ethanol. The solution, kept in beaker, was then allowed to evaporate slowly. The crystals of $(Ph_3PO)_2MnBr_2$ were obtained after the evaporation of ethanol. The complex $(Ph_3PO)_2MnBr_4$ was prepared by mixing Ph_3PO_4 and $MnBr_2$ solutions in ethanol. Good crystals were obtained from the slow evaporation of solution in methanol. The size of $(Et_4N)_2MnBr_4$ and $(Ph_3PO)_2MnBr_2$ crystals used was 2.5 × 2.5 × 2.5 mm and it was 1.5 × 1.5 × 1.5 mm for rest of the crystals.

Transparent lucite and quartz plates were used as base for crushing the crystals at lower and higher temperature respectively. Lucite plate does not show ML in any region of deformation and the quartz plates do not show ML before their fracture. For the measurements of ML at different temperatures, the crystals were fractured impulsively by dropping a load of 800 gm from a fixed height of 50 cm. The ML in the crystals of a given size attains a saturation value for this height of crushing. The ML intensity was monitored by an IP21 photomultiplier tube connected to a storage oscilloscope. The triggering and measurements of I_m and I_T were carried out following the method described previously.[16,17] For heating the crystal, a heater coil was wound around a ceramic cylinder. Some circular sheets of asbestos were placed between the wooden platform and the cylindrical heater. This avoids the excessive heating of the wooden platform. The photomultiplier was placed below the platform only during the measurements. The temperature range studied was from room temperature to 180°C. By changing the voltage, the crystals could be heated to any desired temperature. The ML measurements were carried out when the device had attained a steady state temperature. Because of this, the copper-constanton thermocouple used to measure directly the temperature of the crystal could be taken out before the deformation of the crystal. To avoid the heating of the photomultiplier tube, a thick rubber sheet with a hole at its centre was placed between the lucite or quartz plate and photomultiplier housing. Four crystals were studied at each temperature. As the positions of the crystals and the photomultiplier tube are fixed, the relative ML intensity is independent of the geometry. The error found in the ML intensity measurements was ±6%.

RESULTS

Figure 1 shows that the peak corresponding to the ML intensity versus time curve of phenanthrene crystals, decreases and shifts towards smaller time values with increasing temperature of the crystals. Figure 2 shows the plot of log I versus t for phenanthrene crystals. It is seen

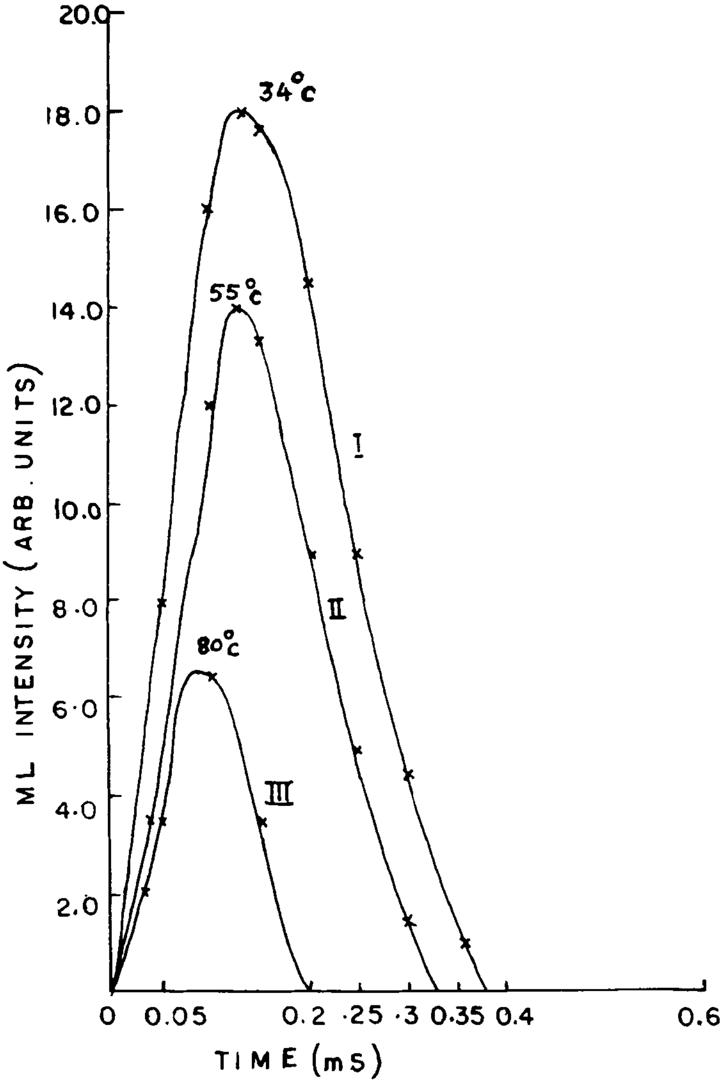

FIGURE 1 Effect of temperature on the ML intensity of phenanthrene crystals.

that the slope of log I versus *t* curve, both for the rising and decaying portion of ML with time increases with increasing temperature of the crystals.

Figures 3 a,b,c show the effect of temperature on the total intensity of ML, peak of the ML intensity versus time curve, and on the time corresponding to the peak of ML intensity versus the time curves of phenanthrene, resorcinol and triphenylamine crystals. Figure 3 shows

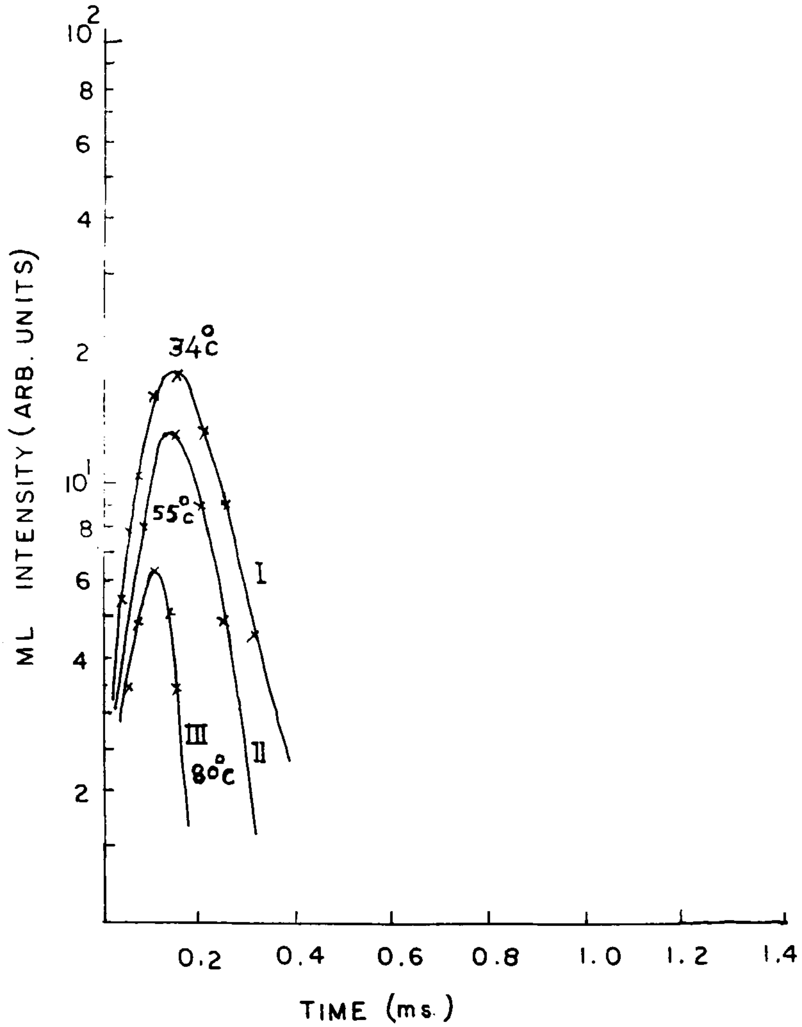

FIGURE 2 Plot of logI versus *t* for different temperatures of phenanthrene crystals.

that the ML intensity tends to cease near the melting point of crystals. The melting points of phenanthrene, resorcinol and triphenylamine crystals are 99.5°, 108.5°, and 126°C respectively.

The effect of temperature on the time dependence of ML intensity of $(Et_4N)_2MnBr_4$ crystals is shown in Figure 4. For a single crystal, the ML intensity varies smoothly as shown in Figure 4. However, for polycrystalline crystals, many unwanted peaks are found which are difficult to repeat. Thus, the accurate measurements of the time de-

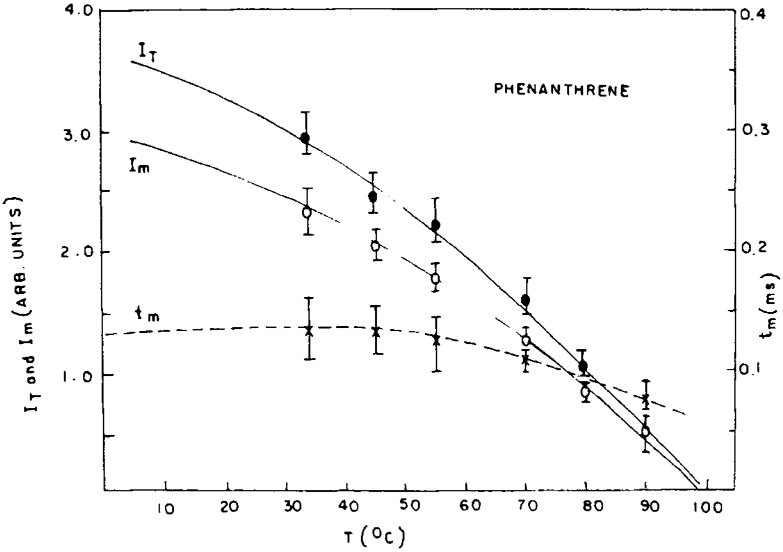

FIGURE 3a I_T, I_m and t_m for different temperatures of phenanthrene crystals.

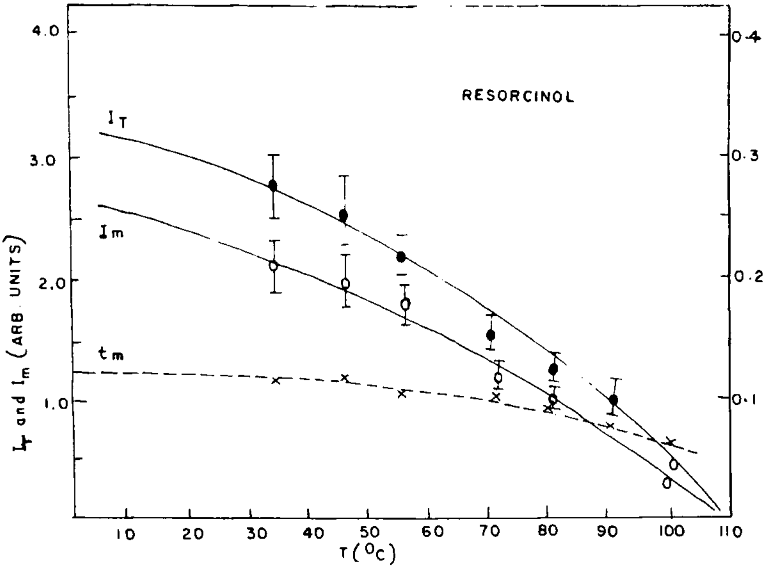

FIGURE 3b I_T, I_m and t_m for different temperatures of resorcinol crystals.

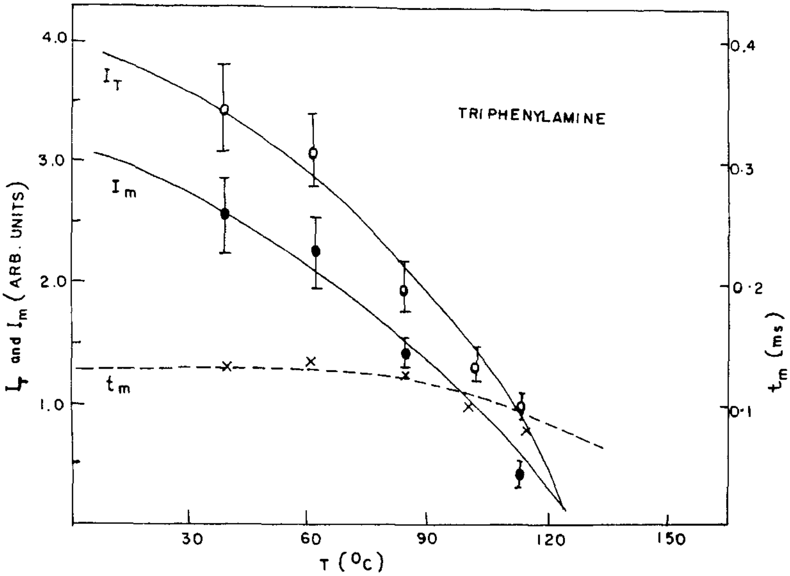

FIGURE 3c I_T, I_m and t_m for different temperatures of triphenylamine crystals.

pendence of ML intensity requires single crystals of considerably good shape. The peak I_m of the ML intensity versus times curve and the total intensity I_T of ML decreases with the increasing temperature. The t_m, corresponding to the peak of the ML intensity versus time curve decreases slightly with increasing temperature of the crystals. Figure 5 shows that the ML decays faster with the increasing temperature of the crystals. It is seen from Figure 6 that the ML disappears at 160°C and 200°C in $(Et_4N)_2MnBr_4$ and $(Ph_3PO)_2$ $MnBr_2$ crystals respectively. The temperature at which ML disappears is much less as compared to the melting point of the crystals. The melting points of $(Et_4N)_2MnBr_4$ and $(Ph_3PO)_2MnBr_2$ crystals are 300°C and 243°C respectively. Figures 7 a,b show the effect of temperature on I_m and t_m of $(Et_4N)_2MnBr_4$ and $(Ph_3PO)_2MnBr_2$ crystals. Figure 8 illustrates the decrease of the ML decay time, τ with the increasing temperature of the crystals. Figure 9 shows that the plot of log τ versus $1/T$ is a straight line with a negative slope. This plot suggests the relation

$$\tau = \tau_0 \exp (E_a/kT) \qquad (1)$$

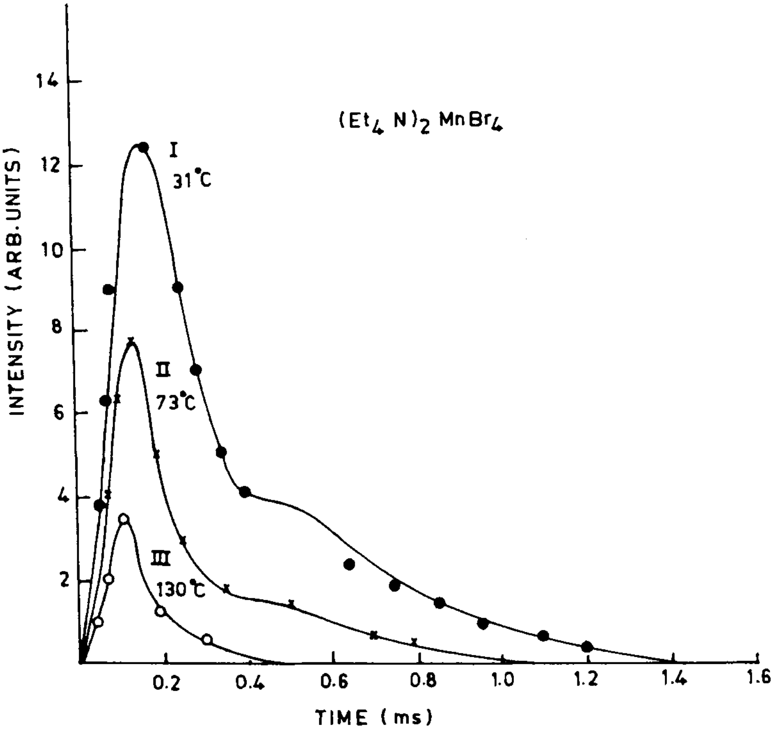

FIGURE 4 Dependence of ML intensity on the temperature of $(Et_4N)_2MnBr_4$ crystals.

where τ_0 is a constant, k is Boltzmann constant and E_a is the activation energy. The value of E_a is found to be 0.099 and 0.115 eV for $(Et_4N)_2MnBr_4$ and $(Ph_3PO)_2MnBr_2$ crystals respectively. The ML in phosphorescent benzil crystals also disappears at their melting point, that is, at 94°C.

For the study of temperature effects on the ML of the crystals, the crystals were placed on the lucite or quartz plate which was in a steady state. The time of annealing at this temperature does not have any considerable effect on the ML intensity of the crystals. Figures 10 and 11 show that the plot of log I versus $\log(1 - T/T_c)$ is a straight line with a positive slope. The value of slope lies between 0.5 and 0.6 for $(Et_4N)_2MnBr_4$ and $(Ph_3PO)_2MnBr_2$ crystals and it lies between 0.9 and 1.05 for phenanthrene, resorcinol, triphenylamine, and benzil crystals. Thus the decrease of ML intensity with temperature follows

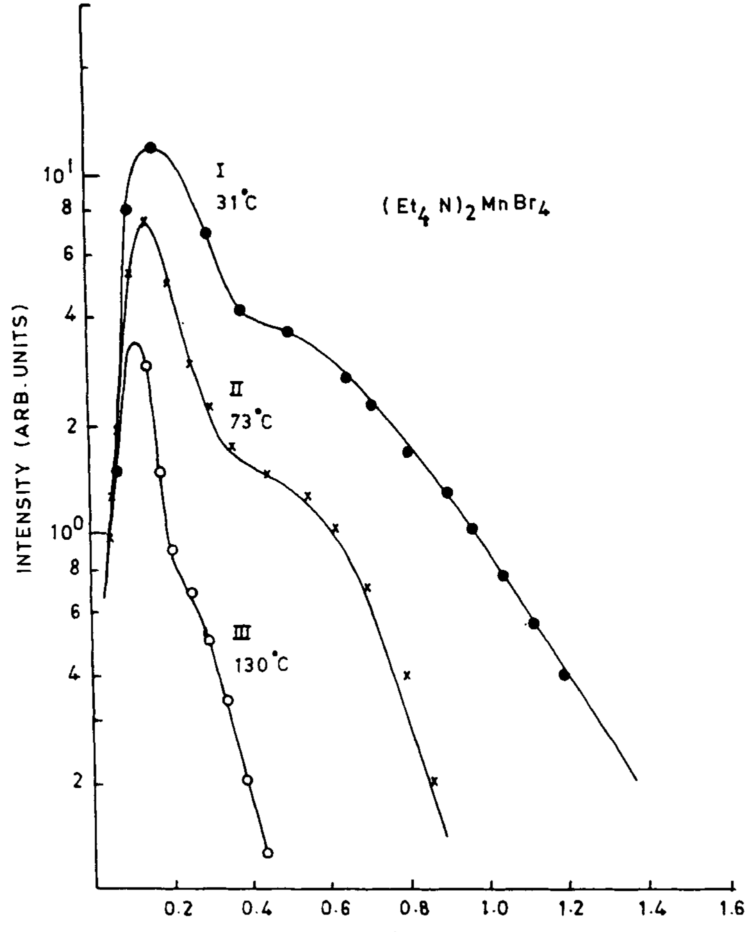

FIGURE 5 Plot of logI versus t for different temperatures of $(Et_4N)_2MnBr_4$ crystals.

the relation

$$I_T = I_T^0(1 - T/T_c)^n \qquad (2)$$

where I_T^0 is a constant and n is the slope of I_T versus $(1 - T/T_c)$ plot.

The effect of temperature on the photoluminescence of crystals is shown in Figure 12 (a,b). It is seen that the photoluminescence intensity of phenanthrene, resorcinol, triphenylamine, $(Et_4N)_2MnBr_4$, $(Ph_3PO)_2MnBr_2$ and benzil crystals also decreases with the increasing temperature.

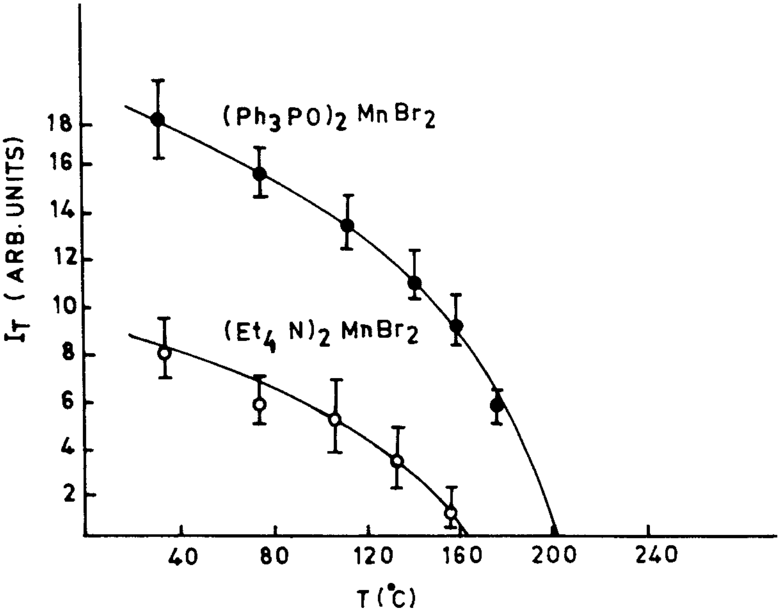

FIGURE 6 Effect of temperature on the total ML intensity of $(Et_4N)_2MnBr_4$ and $(Ph_3PO)_2MnBr_2$ crystals.

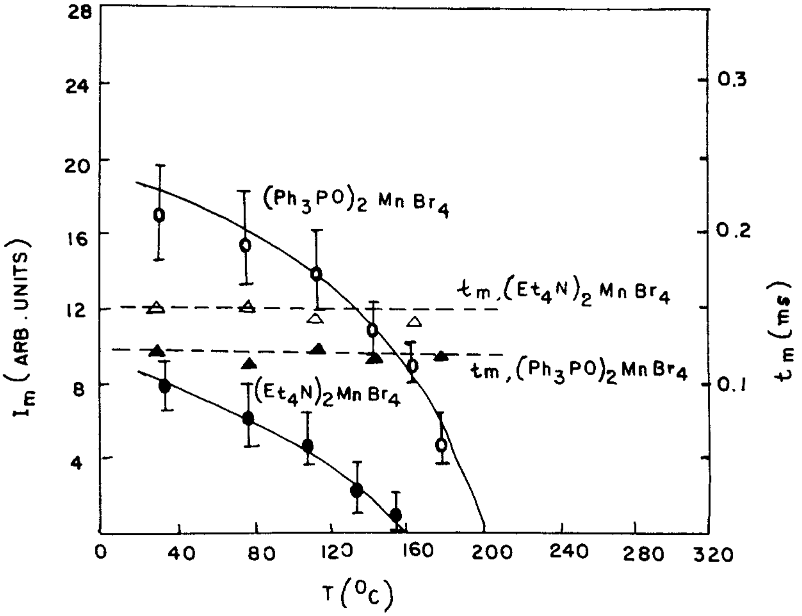

FIGURE 7 Effect of temperature on the I_m and t_m $(Et_4N)_2MnBr_4$ and $(Ph_3PO)_2MnBr_2$ crystals.

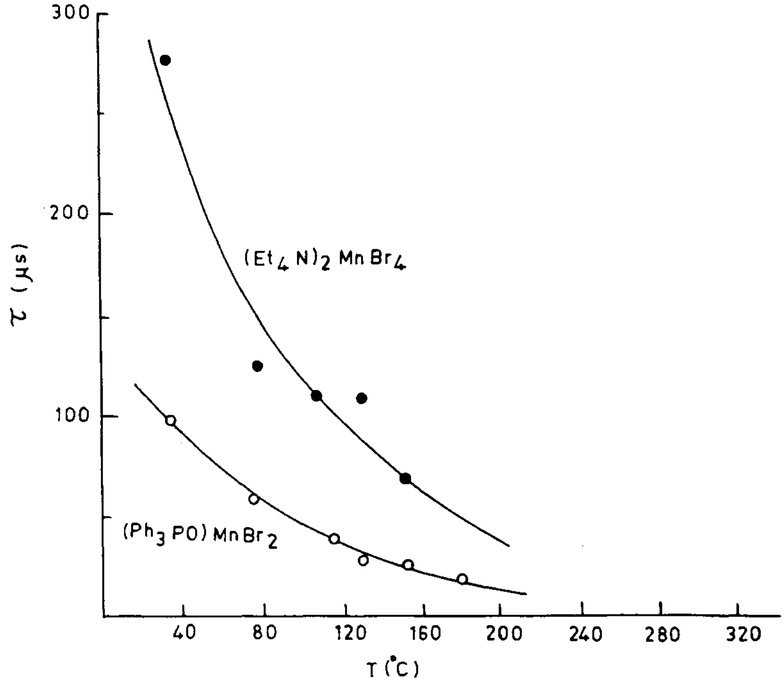

FIGURE 8 Effect of temperature on the decay time of the ML of crystals.

DISCUSSION

The ML intensity will depend strongly on the charge density and the charge distribution on the fracture surface near the crack tip. For the decrease in the ML intensity, the following three speculations can be made: (i) Considerably less fracture surface is being created at higher temperatures, (ii) the charge density is not reaching the same values during fracture as at lower temperature, and (iii) the charge is more rapidly leaking off the fracture surfaces due to the increase in the conductivity at higher temperature. Since the ML excitation takes place instantaneously with the creation of new surfaces, the first two factors may be more responsible rather than the third.

When the crystals of given dimension were crushed by dropping a load of 800 gm from a height of 50 cm, they get crushed into crumbled masses. Thus, the post-mortem examination of the crushed crystals clearly tells that the degree of fragmentation decreases at T_{melt}, which

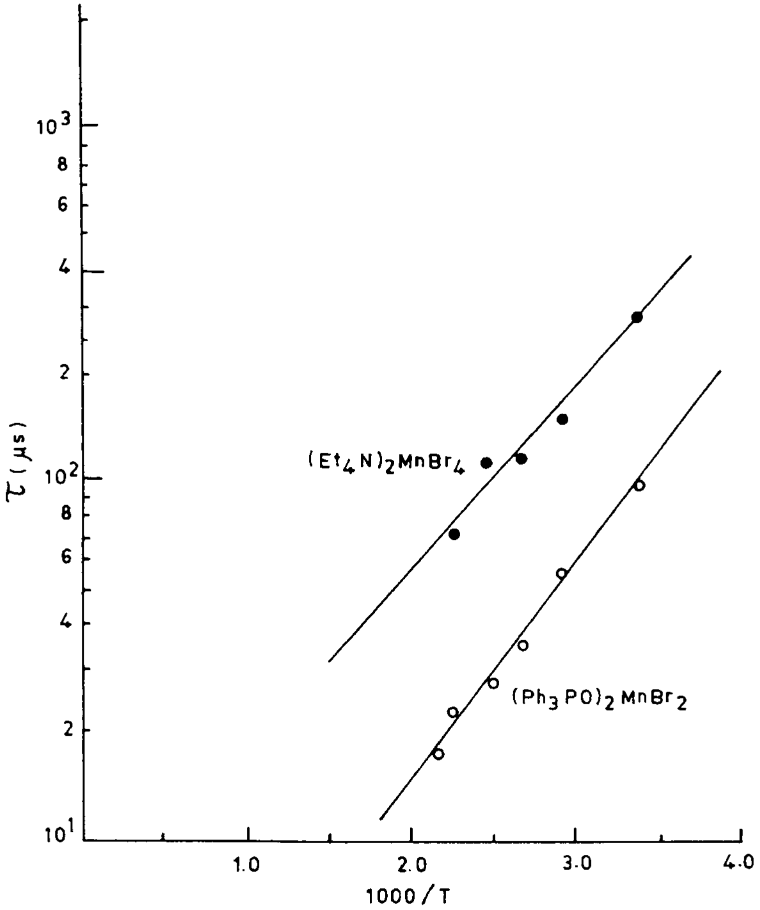

FIGURE 9 Plot of log τ versus 1000/T.

supports the factor (i) mentioned above. It has been mentioned earlier that the ML activity of piezoelectric crystals ceases completely near the melting point of the crystals. This may particularly be due to the absence of ruptured bonds and the disappearance of piezoelectricity near the melting point of the crystals. For the crystals whose structure changes before the melting point, a different type of the temperature effect on the ML is expected.[13] Since the probability of the ML excitation depends on many physical properties of the crystals like piezoelectric constants, fracture stress, charge leakage, rate of radia-

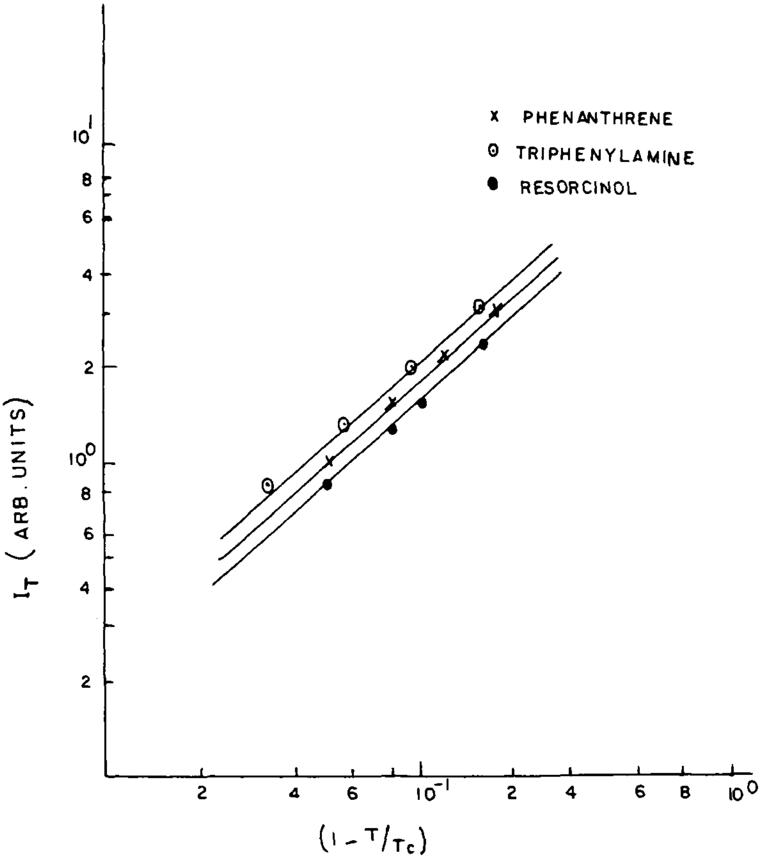

FIGURE 10 Plot of logI versus log $(1 - T/T_c)$ for fluorescent crystals.

tive recombination etc., it is not yet possible to approach quantitatively the effect of temperature on the ML of crystals.

It seems that the ML in the non-piezoelectric crystals of $(Et_4N)_2MnBr_4$ and $(Ph_3PO)_2MnBr_2$ is due to the presence of some defective piezoelectric phase, which produces the microscopically charged surfaces during the passage of cracks in the crystals and the electric field near the charged surfaces excites ML. The decrease of ML with increasing temperature of these crystals may be due to the decrease in the number of defective piezoelectric phase with increasing temperature of the crystals.

Previously it was accepted that the solid state ML resembling in

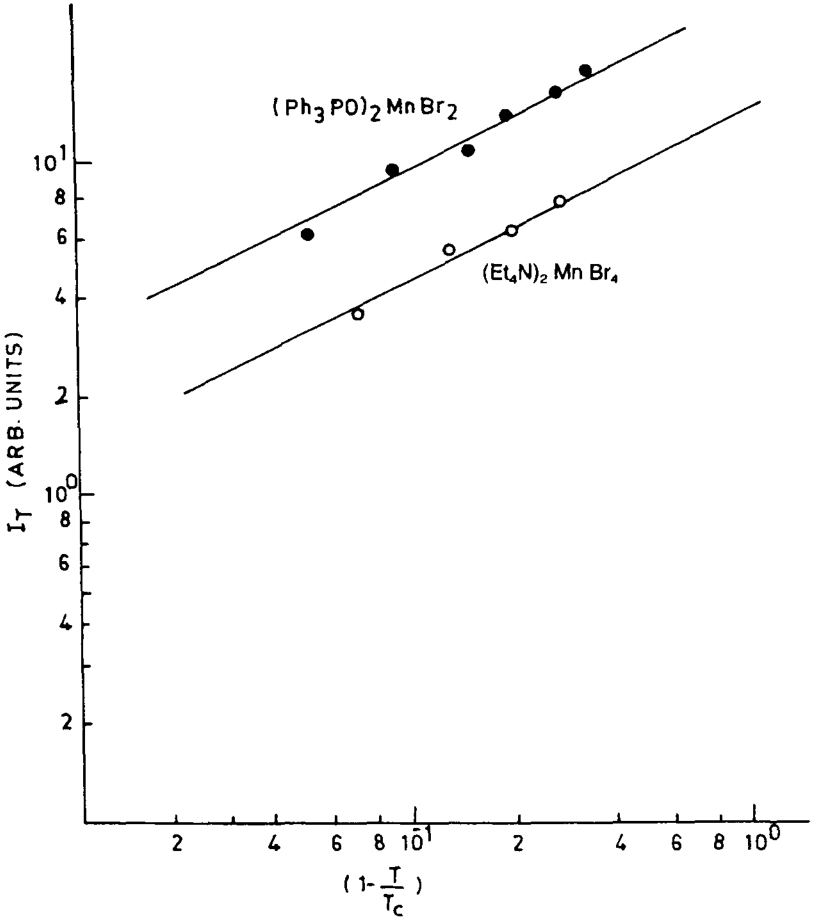

FIGURE 11 Plot of logI versus log $(1 - T/T_c)$ for phosphorescent crystals.

spectra to that of PL was excited by the gas discharge produced during the deformation of the crystals.[9,19] However, when the crystals are crushed inside liquid or in CO_2 atmosphere, then the ML still appears without any considerable loss in the intensity. This fact suggests that ML resembling PL in spectra, has independent and intrinsic origin. Furthermore, no systematic correlation is found between the ML and PL efficiencies of different crystals.

The PL is related to the transition between ground and excited states of the molecules comprising the crystals and the ML is related to the recombination of charge carriers, hence, the ML and PL efficiencies may be controlled by the parameters in different manners.

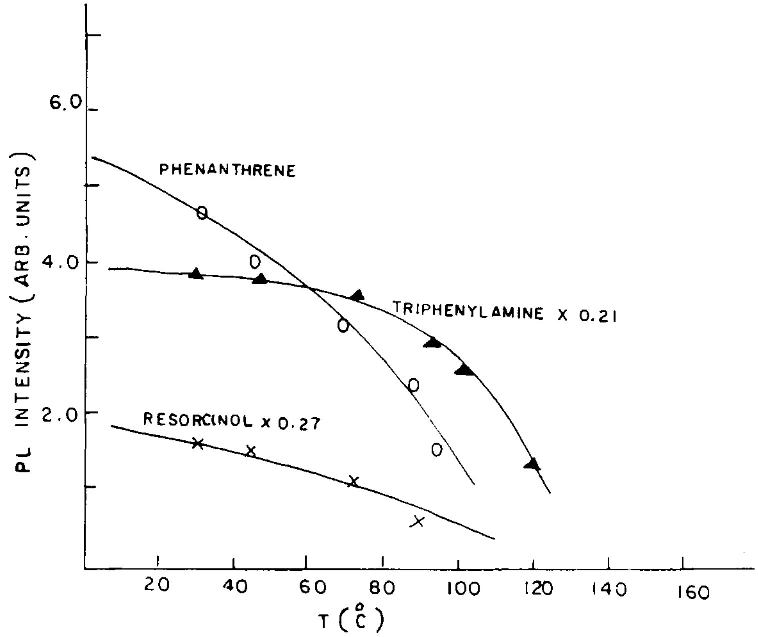

FIGURE 12a Dependence of PL intensity on the temperature of fluorescent crystals.

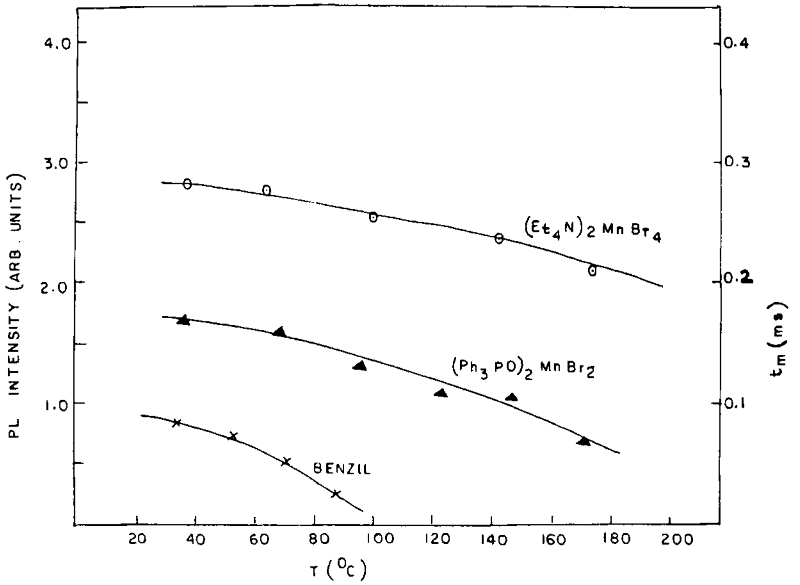

FIGURE 12b Dependence of PL intensity on the temperature of phosphorescent crystals.

Figure 12(a,b) shows that the fluorescent and phosphorescent molecular crystals chosen in the present investigation, exhibit a decrease in the photoluminescence quantum yield with temperature. It is evident from Figures 3, 6 and 12 that the decrease in ML intensity with temperature is faster than that of PL intensity. This fact indicates that the decrease of ML efficiency with temperature should involve both, the change in crystal properties with temperature and the usual decrease in quantum yield caused by increased radiationless deactivation.

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