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CHAPTER IV

EFFECT OF TEMPERATURE ON THE MECHANOLUMINESCENCE
OF FLUORESCENT AND PHOSPHORESCENT MOLECULAR
CRYSTALS

4-1. INTRODUCTION

The studies on temperature dependence of ML has been
interesting and meaningful from very beginning. Trautz (1909),
Van Eck (1911) and Imhof (1917) have measured the effect of
temperature on the ML of certain crystals and have found
that the ML intensity decreases with the increasing temp­
erature. Longchambon (1925) and Strasenki et al (1955) 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 (1937) has reported the
effect of temperature of the ML of fluorite crystals. She
has concluded that the centres which are affected by a change
in temperature are completely deactivated at higher temper­
atures, however, the ML due to the electrical discharge in
air is not modified by a change in the temperature of the
crystals. Wick (1940) has reported an emission of light at
the instant when there was sudden change in the temperature
of the crystals. Metz et al (1957) 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 (1983)
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 certain organic and inorganic crystals has been investigated by Meyer et al (1970), Frohlich and Seifert (1971), Das and Chandra (1974) and by Verma (1983).

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 in Chapter III. In the present chapter, the effect of temperature on the ML of some phosphorescent and fluorescent molecular crystals is reported.

4-2. EXPERIMENTAL

The crystals were grown using the technique described in Chapter III. The dimensions of the crystals were similar to that reported in Chapter III. Transparent lucite and quartz plates were used as base for crushing the crystals at lower and higher temperatures 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. It is shown in Chapter III, that 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 systronic 515 D oscilloscope having CRTP/ phosphorescent screen. The triggering and measurements of \( I_m \), \( t_m \) and \( I_T \) were carried out following the method described in chapter III. For heating the crystal, a heater coil was wound round a ceramic cylinders. 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. The temperature of the crystals was measured by a copper-constantan thermocouple. 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.

4.3. RESULTS

Figure 4-1 shows that the peak corresponding to the ML intensity versus time curve of phenanthrene crystals decrease and shifts towards smaller time values with increasing temperature of the crystals. Figure 4-2 shows the
plot of log I versus t for phenanthrene crystals. It is seen 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 4-3 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, triphenylamine and cinchonine sulphate dihydrate crystals. Figure 4-3 shows that the ML intensity tends to cease near the melting point of crystals. The melting points of phenanthrene, resorcinol and triphenylamine are 99.5, 108.5, and 126°C respectively.

The effect of temperature on the time dependence of ML intensity of (Et₄N)₂Mn Br₄ crystals is shown in Figure-4-4. The peak Iₘ of the ML intensity versus times curve and the total intensity Iₜ of ML decreases with the increasing temperature. The time tₘ corresponding to the peak of the ML intensity versus time curve decreases slightly with increasing temperature of the crystals. Figures 4-5 shows that the ML decays faster with the increasing temperature of the crystals. It is seen from Figure 4-6 that the ML disappears at 160 and 200°C in (Et₄N)₂ Mn Br₄ and (Ph₃PO)₂ Mn Br₂ crystals respectively. The temperature at which ML disappears is much less as compared to the melting point of the crystals. The melting points of (Et₄N)₂Mn Br₄ and
\((\text{Ph}_3\text{PO})_2\text{MnBr}_2\) crystals are 300 and 243\(^\circ\)C respectively. Figure 4-7a,b show the effect of temperature on \(I_m\) and \(t_m\) of \((\text{Et}_4\text{N})_2\text{MnBr}_4\) and \((\text{Ph}_3\text{PO})_2\text{MnBr}_2\) crystals. Figure 4-8 illustrates the decrease of the ML decay time \(\tau\) with the increasing temperature of the crystals. Figure 4-9 shows that the plot of \(\log \tau\) versus \(1/T\) is a straight line with a negative slope. This plot suggests the relation.

\[
\tau = \tau_0 \exp \left(\frac{E_a}{kT}\right) \quad (4-1)
\]

where \(\tau_0\) is a constant, \(k\) is Boltzmann constant and \(E_a\) is the activation energy. The value of \(E_a\) is found to be 0.009 and 0.0115 eV for \((\text{Et}_4\text{N})_2\text{MnBr}_4\) and \((\text{Ph}_3\text{PO})_2\text{MnBr}_2\) crystals respectively.

The ML in benzil crystals also disappears at their melting point, that is, at 94\(^\circ\)C. The temperature dependence of ML of the hexaphenylcarbodiphosphorane crystals could not be studied because these crystals are unstable when they are kept in the atmosphere for a long time. Because of the limited quantity of cinchonine sulphate dihydrate, the studies of temperature effect on its ML could not be done.

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 4-10 and 4-11 show that the plot of \(\log I\) versus \(\log (1 - T/\tau_m)\) is a straight line with a positive slope. The value of slope
lies between 0.5 and 0.6 for \((\text{Et}_4 \text{N})_2 \text{Mn Br}_4\) and \((\text{Ph}_3 \text{PO})_2 \text{Mn Br}_2\) crystals and it lies between 0.9 and 1.05 for phenanthrene, resorcinol, triphenylamine, sphenamine sulphate dihydrate and benzil crystals. Thus the decrease of ML intensity with temperature follows the relation

\[
I_T = I_T^0 \left(1 - \frac{T}{T_c}\right)^n \quad (4-2)
\]

where \(I_T^0\) is a constant and \(n\) is the slope of \(\ln I_T\) versus \(\ln \left(1 - \frac{T}{T_c}\right)\) plot. Figure 4-12 a,b show that the PL intensity of phenanthrene, resorcinol, triphenylamine, sphenamine sulphate dihydrate, \((\text{Et}_4 \text{N})_2 \text{Mn Br}_4\), \((\text{Ph}_3 \text{PO})_2 \text{Mn Br}_2\) and benzil crystals also decreases with the increasing temperature.

4-4. DISCUSSION

The ML intensity will depend strongly on the charge density and the charge distribution on the fracture surfaces 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 $T < T_{\text{melt}}$, which supports the factor (1) 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 required bonds and the disappearance of piezoelectricity near the melting point. For the crystals whose structure changes before the melting point, a different type of the temperature effect on the ML is expected (Chandra and Shrivastava 1979). Since the probability of the ML excitation depends on many physical properties of the crystals like piezoelectric constants, fracture stress, charge leakage, rate of radiative recombination etc., it is not yet possible to approach quantitatively the effect of temperature of the ML of crystals.

The discussion of the temperature effects on the ML of centrosymmetric crystals like $(\text{Et}_4\text{N})_2\text{MnBr}_4$ and $(\text{Ph}_3\text{PO})\text{MnBr}_2$ needs the knowledge of the mechanism of ML excitation in these crystals. The quantitative and qualitative nature of the temperature effects on the ML of crystals will be discussed in detail in Chapter VI after collecting some more information about the ML in subsequent chapters.
$t_m, I_T$ and $I_m$ (ARB. UNITS)

Phenanthrene
Fig. 4-6. Dependence of Mn intensity on the temperature of $(Et_4N)_2MnBr_4$ crystals
Fig. 4-5. Plot of $\log T$ versus $T$ for different temperatures of $(\text{Et}_4\text{N})_2\text{MnBr}_4$ crystals.
Fig. 1. Plot of \log \text{activity} versus 1000/T.
Fig. 4-10. Plot of log I versus log \( \left(1 - \frac{T}{T_c}\right) \) for fluorescent crystals.
Fig. 4-11 Plot of log $I$ versus log $(1-T/T_c)$ for phosphorescent crystals.

$\left(\text{Ph}_3\text{PO}\right)_2\text{MnBr}_2$

$\left(\text{Et}_4\text{N}\right)_2\text{MnBr}_2$
REFERENCES


