ABSTRACT OF THE THESIS

Chapter I

This chapter begins with the definition of mechanoluminescence (ML) and then reviews the recent works on mechanoluminescence. It has been mentioned that the chief interests of the present investigation are: (i) To understand the mechanism of ML excitation in fluorescent and phosphorescent molecular crystals, and (ii) To understand the impact velocity dependence, temperature dependence, crystal size dependence, stress dependence, and time dependence (kinetics) of ML of these crystals.

Chapter II

This chapter reports the ML and photoluminescence spectra of four fluorescent crystals like phenanthrene, resorcinol, triphenylamine and cinchonine sulphate di-hydrate and four phosphorescent crystals like (Ph₃PO)₂MnBr₂, (Et₄N)₂MnBr₄, hexaphenylcarbodiphosphorane and benzil. It is concluded that on the basis of the ML spectroscopy, the fluorescent and phosphorescent crystals can be grouped into two classes: (i) crystals, the ML spectra of which resemble their photoluminescence spectra and (ii) crystals, the ML spectra of which consist of both, the photoluminescence spectra and the discharge spectra of surrounding gases.

Chapter III

This chapter deals with the impulsive excitation of ML in fluorescent and phosphorescent crystals. When the
ABSTRACT OF THE THESIS

Chapter I

This chapter begins with the definition of mechano-luminescence (ML) and then reviews the recent works on mechenoluminescence. It has been mentioned that the chief interests of the present investigation are: (i) To understand the mechanism of ML excitation in fluorescent and phosphorescent molecular crystals, and (ii) To understand the impact velocity dependence, temperature dependence, crystal size dependence, stress dependence, and time dependence (kinetics) of ML of these crystals.

Chapter II

This chapter reports the ML and photoluminescence spectra of four fluorescent crystals like phenanthrene, resorcinol, triphenylamine and cinchonine sulphate di-hydrate and four phosphorescent crystals like \((\text{Ph}_3\text{PO})_2\text{Mn Br}_2\), \((\text{Et}_4\text{N})_2\text{Mn Br}_4\), hexaphenylcarbodiphosphorane and benzil. It is concluded that on the basis of the ML spectroscopy, the fluorescent and phosphorescent crystals can be grouped into two class : (i) crystals, the ML spectra of which resemble their photoluminescence spectra and (ii) crystals, the ML spectra of which consist of both, the photoluminescence spectra and the discharge spectra of surrounding gases.

Chapter III

This chapter deals with the impulsive excitation of ML in fluorescent and phosphorescent crystals. When the
ML is excited by impact of a moving piston on to a crystal, at first the ML intensity increases with time, reaches its maximum intensity a few tenths of millisecond after the impact and then it decays. The peak of the ML intensity versus time curve increases and shifts towards shorter time values with increasing impact velocities. The rising portion of ML intensity with time, follows the relation 
\[ I = I_1 \exp (\lambda_1 t) \] and the decay portion follows the relation 
\[ I = I_2 \exp (-\lambda_2 t), \] where \( I_1, I_2, \lambda_1 \) and \( \lambda_2 \) are constants. In phosphorescent crystals, the ML appears even after the deformation of crystals and the decay time of ML is nearly equal to the decay time of photoluminescence.

The total intensity \( I_T \) of ML defined as the area below the ML intensity versus time curve intensity increases with the impact velocity \( V_0 \) of the piston and then it attains a saturation value for the higher values of the impact velocity. The increasing portion of \( I_T \) with \( V_0 \) follows the relation, 
\[ I_T = I_T^0 \exp \left(-\frac{V_0}{V_0^c}\right). \] The time \( t_m \) corresponding to the peak of ML intensity versus time curve decreases with increasing value of the impact velocity. For higher values of the impact velocities, the plot of \( t_m \) versus \( 1/V_0 \) is a straight line with a positive slope. For higher values of impact velocity, the peak intensity \( I_m \) of the ML intensity versus time curve increases linearly with the impact velocity.

After a minimum size of the crystals, the total ML intensity increases linearly with the volume or mass of
the crystals, and the peak of the ML intensity versus time
curve increases linearly with the area of cross-section of
the crystals. For higher mass of the impacting load, the
total ML intensity attains a saturation value at lower
values of the impact velocity as compared to that obtained
for the lesser mass of the impacting load. The total ML
intensity is directly related to the area of newly created
surfaces (although the ML efficiency is different for
different crystals).

Chapter IV

In this chapter, the effect of temperature on the
ML intensity of crystals is reported. The ML of phenan-
threne, resorcinol, triphenylamine, cinchonine sulphate
dihydrate and benzil crystals disappears at their melting
points. However, the ML of \((\text{Ph}_3\text{PO})_2\text{Mn Br}_2\) and \((\text{Et}_4\text{N})_2\text{Mn Br}_4\)
crystals disappears at temperatures much below their
melting points. The temperature dependence of total ML
intensity follows the relation \(I_T = I_T^0 (1 - T/T_c)^n\). The
values of \(n\) lies between 0.90 and 1.05 for phenanthrene,
resorcinol, triphenylamine, cinchonine sulphate dihydrate
and benzil crystals, however, it lies between 0.5 and 0.6
for \((\text{Ph}_3\text{PO})_2\text{Mn Br}_2\) and \((\text{Et}_4\text{N})_2\text{Mn Br}_4\) crystals. The decay
time of ML of phosphorescent crystals also decreases with
their temperature. The value of activation energy for the
decrease in ML decay time with temperature is found to be
0.90 and 1.05 eV for \((\text{Ph}_3\text{PO})_2\text{Mn Br}_2\) and \((\text{Et}_4\text{N})_2\text{Mn Br}_4\)
crystals respectively.
Chapter V

In this chapter the correlation of ML with electroluminescence is reported. The crystals of (Ph\textsubscript{3}PO)\textsubscript{2} Mn Br\textsubscript{2} and (Et\textsubscript{4}N)\textsubscript{2}Mn Br\textsubscript{4} exhibit electroluminescence. The ML efficiency of these crystals does not follow the order of their electroluminescence efficiency. The electroluminescence spectra of (Ph\textsubscript{3}PO)\textsubscript{2} Mn Br\textsubscript{2} and (Et\textsubscript{4}N)\textsubscript{2}Mn Br\textsubscript{4} crystals are similar to their ML and photoluminescence spectra. Although the crystals of phenanthrene, resorcinol, triphenylamine, cinchonine, sulphate dihydrate and benzene exhibit intense ML, they do not exhibit electroluminescence. The voltage dependence of electroluminescence brightness at different frequencies for phenanthrene, (Ph\textsubscript{3}PO)\textsubscript{2} Mn Br\textsubscript{2} and (Et\textsubscript{4}N)\textsubscript{2}Mn Br\textsubscript{4} crystals follows the relation $B = B_0 \exp \left(-b/V^{1/2}\right)$. This result indicates that the mechanism of excitation should be of an acceleration, collision type.

Chapter VI

In this chapter, the correlation between the different results obtained in the previous chapters are described. The piezoelectrification is shown to be responsible for the ML excitation in piezoelectric crystals. For the ML excitation in non-piezoelectric crystals, the suitability and unsuitability of different models are analysed. The models proposed are: (i) space charge electrification model, (ii) trielectrification model, (iii) phase transformation model, (iv) gas adsorption model, (v) Chemical
reaction model, (vi) thermal population model, (vii) molecular deformation model, (viii) charge dislocation model, (ix) dislocation annihilation model and (x) defective piezoelectric phase model. It is concluded that the defective piezoelectric phase model may cause the ML excitation in centrosymmetric crystals of \((\text{Ph}_3\text{PO})_2\text{Mn Br}_2\) and \((\text{Et}_4\text{N})_2\text{Mn Br}_4\). On the basis of the dependence of area of newly created surfaces, an equation is derived which can explain all parameters of ML, like the impact velocity and load dependence of ML, the time dependence of ML, temperature dependence of ML crystal size dependence of ML etc.

The decrease in the number of defective piezoelectric phase may be responsible for the decrease in the ML intensity with increasing temperature of \((\text{Ph}_3\text{PO})_2\text{Mn Br}_2\) and \((\text{Et}_4\text{N})_2\text{Mn Br}_4\) crystals. However, both the decrease in the charge density and the area of newly created charged surfaces may be responsible for the decrease in the ML intensity of piezoelectric crystals.

At the end of the chapter, the different conclusions drawn from the studies of ML of fluorescent and phosphorescent crystals are summarized.