CHAPTER I

This chapter starts with the brief introductions of luminescence and mechanoluminescence (ML), and then summarizes the previous works on ML to date. Finally, the plan of the work proposed is stated and it is mentioned, that the chief interests of the present investigations are: (1) to understand the mechanism of ML excitation in organic molecular crystals, and (2) to understand the impact velocity dependence, temperature dependence, crystal size dependence and time dependence (kinetics) of ML in organic molecular crystals.

CHAPTER II

This chapter reports the results of the survey made on the ML of organic molecular crystals. The ML is measured in 56 crystals and it is found that 34 crystals, which are piezoelectric, exhibit the phenomenon of ML. All the 22 crystals not exhibiting ML are non-piezoelectric. Four non-piezoelectric crystals also exhibit ML, whose ML intensity is comparable to that of the piezoelectric crystals. The mechanoluminescent crystals studied in the present investigation exhibit ML only during their fracture and the ML efficiency is different for different crystals. The ML spectra are recorded and it is concluded that on the basis of the ML spectroscopy, the crystals can be grouped into three classes.
(i) crystals, the ML spectra of which resemble other types of luminescence spectra, (ii) crystals, the ML spectra of which resemble the discharge spectra of surrounding gases, and (iii) crystals, the ML spectra of which consist of both the other types of luminescence spectra and the discharge spectra of surrounding gases.

CHAPTER III

This chapter reports the mechanical characteristics of the ML of organic molecular crystals. It is found that during the ML excitation by the impact of a moving piston on to the crystal, initially the ML intensity increases with time, attains a maximum value at a few tenth of a millisecond after the impact and then it decreases. The peak corresponding to 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 decreasing portion follows the relation $I = I_2 \exp (-\lambda_2 t)$, where $I_1$, $I_2$, $\lambda_1$, and $\lambda_2$ are constants. The total intensity $I_T$ of ML defined as the area below the ML intensity versus time curve initially increases with the impact velocity and then attains a saturation value for higher values of the impact velocity. The increasing portion of $I_T$ with $v_o$ follows the relation $I_T = I_{T0} \exp (-v_c/v_o)$, where $v_c$ is a constant for higher values of the impact velocity, the peak of the
ML intensity versus time curve increases linearly with the impact velocity. The time, $t_m$, corresponding to the peak of ML intensity versus time curve decreases with the increasing value of the impact velocity. For higher values of the impact velocity, the plot of $t_m$ versus $1/V_0$ is a straight line with a positive slope.

After a minimum 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. Although the ML efficiency is different for different crystals, the total ML intensity, $I_m$, increases linearly with the area of newly created surfaces. 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.

**CHAPTER IV**

This chapter reports the temperature dependence of the ML of organic molecular crystals. The ML intensity of piezoelectric crystals like p-anisidine, acenaphthene, N-acetylanthranilic acid, $\beta$-rhamnose, and tartaric acid decreases with increasing temperature and the ML disappears near the melting point of the crystals. The ML intensity of triglycerine sulphate crystal ceases at $68^\circ\text{C}$.
which is higher than its ferroelectric phase-transition temperature (49°C), but it is less than its melting point. The temperature dependence of total ML intensity follows the relation, \( I_T = I_T^0 (1 - \frac{T}{T_C})^n \), where \( T_C \) is the temperature at which ML disappears. The value of \( n \) lies between 0.90 and 1.10 for piezoelectric crystals like p-anisidine, acenaphthene, N-acetylanthranilic acid, \( \beta \)-rhamnose and tartaric acid crystals, however, the value of \( n \) is 0.59 for the triglycine sulphate crystals. No significant difference is found between the temperature dependence of the ML resembling photoluminescence emission and the ML resembling the nitrogen emission.

CHAPTER V

This chapter deals with the ML of centrosymmetric organic molecular crystals. The dependence of ML intensity of non-piezoelectric crystals on the impact velocity is similar to that of the piezoelectric crystals, however, the temperature dependence of ML is different for the piezoelectric and non-piezoelectric crystals. Generally, the ML disappears in piezoelectric crystals near their melting points; however, the ML of non-piezoelectric crystals like saccharin, phthalic acid, triphenylphosphine and triphenylarsine disappears at temperatures which are much below the melting point of the crystals. The temperature dependence of non-piezoelectric crystals also follows the equation \( I_T = I_T^0 (1 - \frac{T}{T_C})^n \) where \( n \) lies between 0.45 and 0.60. The ML
in saccharin crystals disappear after their purification. The ML intensity of phthalic acid, triphenylphosphine and triphenylarsine crystals decreases with the number of their recrystallizations. However, the ML intensity of piezoelectric crystal does not change considerably with the number of their recrystallizations.

CHAPTER VI

This chapter correlates the different results obtained in the previous chapters. The mechanisms of ML excitation in organic molecular crystals are discussed and it is shown that the piezoelectrification is responsible for the ML excitation in piezoelectric crystals. Different models are proposed for the ML excitation in non-piezoelectric crystals, which are: (i) triboelectrification model, (ii) phase-transformation model, (iii) space-charge electrification model, (iv) gas adsorption model, (v) chemical reaction model, (vi) thermal population model, (vii) molecular deformation model, (viii) charged dislocation model, (ix) dislocation annihilation model, and (x) defective piezoelectric-phase model. It is concluded that the defective piezoelectric-phase model is more suitable for the ML excitation in non-piezoelectric organic molecular crystals. A theoretical approach is made for the ML of crystals and a master equation is derived which can explain different parameters of ML like the impact velocity dependence and load dependence of ML, the time dependence (kinetics) of ML, temperature dependence of ML, and the crystal size dependence of ML.
It is shown that the decrease in the number of detective piezoelectric phases may be responsible for the decrease of ML intensity with increasing temperature of the non-piezoelectric crystals. However, both the decrease in the charge density and the area of newly created surfaces may be responsible for the decrease in the ML intensity of the piezoelectric crystals. The presence of the non-centrosymmetric phase may be responsible for the ML above ferroelectric phase-transition temperature of triglycine sulphate crystals.

At the end of the chapter, the different conclusions drawn from the studies on the ML of organic molecular crystals are summarized.