CHAPTER 1

INTRODUCTION

1-1. LUMINESCENCE

Although luminescence is one of the oldest known scientific phenomena, its systematic study started in the middle of the nineteenth century. The term 'luminescence' was introduced by Wiedemann in 1838. He defined the phenomena (though not very accurately) as "the excess emission over and above the thermal emission of light which is not purely thermal in origin. Luminescence is the general term for the emission of visible or invisible radiation (ultraviolet and infrared) from a substance during or following the absorption of energy from many of the varied sources such as ultraviolet, X-ray or high energy particles or simply from the applied electric field (Wiedemann 1838, Kendal and Wilkins 1945, Carlick 1949). The luminescence is often called "cold light" as it is not due to incandescence. The thermal radiation follows Kirchhoff's law whereas luminescence does not. In the case of luminescence, the time delay after excitation is greater than $10^{-9}$ sec, whereas as Raman and Compton effects are completed in an interval of about $10^{-14}$ sec (Leverenz 1949, 1950).

Fluorescence and phosphorescence are two special aspects of luminescence. In the case of fluorescence, when the source of excitation is removed, there is invariably an exponential afterglow, whose decay rate is
independent of excitation intensity and temperature. There is an additional component of this afterglow which decays more slowly and with more complex kinetics dependent of temperature. This component is known as phosphorescence. According to Leversen, fluorescence is obtained only during the first $10^{-6}$ sec of excitation and pure phosphorescence is obtained only after $10^{-6}$ sec after the cessation of excitation (Leversen 1940). Garlick defines fluorescence as the emission during the excitation and phosphorescence as the emission during the excitation and phosphorescence as that which persists after the excitation has ceased (Garlick 1949). The demarcation between the two phenomena may be fixed at $10^{-8}$ sec after the cessation of excitation, because this is the time of relaxation of an ionized gas atom in the excited state. On the basis of physical processes taking place during fluorescence and phosphorescence, Perrin (1929) has given the following definition. The phenomenon is fluorescence, if the emission takes place by one or more spontaneous transitions. On the contrary, if the emission occurs with the intervention of a metastable state followed by return to the excited state due to the addition of energy, then this is phosphorescence. The distinction between the two processes is also made on the basis of the variation of luminescence decay with temperature. The decay of fluorescence is little dependent on the temperature, but the decay of phosphorescence is strongly temperature dependent (Curie 1963).

On the basis of the modes of excitation, the luminescence has been classified into the following types:

**Photoluminescence** - It is produced by absorption of photons of energies from a few to several electron volts for example, from ultraviolet radiations.
Cathodoluminescence: It is produced by energetic electron or cathode rays.

Electroluminescence: It is produced by voltage applied to the luminescent substances.

Mechanoluminescence or Triboluminescence: It is produced during the mechanical deformation of solids.

Chemiluminescence: It is produced due to the energy released by chemical reactions.

Thermoluminescence: It is produced when a substance is heated to a moderate temperature which releases the previously absorbed radiation.

Radioluminescence: It is excited by any or all radioactive disintegration products.

Phosphoroluminescence: It is a specific case of radioluminescence produced by X-rays.

Sonoluminescence: It is produced by ultrasonic waves.

Bioluminescence: It is produced by the energy from biochemical reactions.

Crystalloluminescence: It is produced during growth of the crystals from solution.

Lyoluminescence: It is produced during dissolution of certain coloured crystals (by high energy radiations) in aqueous solution.
Electroluminescence or Voltageluminescence: It is a luminescence phenomenon accompanying the passage of electric current through aqueous solutions.

There are further subclassifications of the luminescence such as: photo-electroluminescence, electro-photoluminescence, mechanic-thermoluminescence, thermal-chemiluminescence etc. The first prefix in such luminescence denotes the controlling and the second denotes the source of power that stimulates it. In certain types of luminescence like photoluminescence, cathodoluminescence, electro luminescence, chemiluminescence, thermluminescence, radionluminescence, roentgenoluminescence, bioluminescence, and geloluminescence, the energy related to the prefix in the luminescence, directly populates the excited states of the molecules or atoms comprising the luminescent materials. In the other types of luminescence, like sensiluminescence, mechanicluminescence, scintilloluminescence and crystalloluminescence, the action related to the prefix in the luminescence induces some other process which populates the excited states.

Phosphors are the substances which emit cold radiations. They are also named as luminifer or the light-bearer. Generally phosphors are crystalline insulators and are very sensitive to structural changes. They are strongly influenced by the chemical composition of the base compound, physical condition of preparation, and the presence of traces of impurities, known as activators. The main constituent of a phosphor, the crystalline material itself is known as host material or matrix. An efficient phosphor is that which
converts a large portion of the absorbed excitation energy into luminescence emission with negligible energy losses by increase in lattice vibration or electron emission or chemical or structural changes (Leverenz 1958). The phosphors may be classified into the following two types: (i) the impurity activated phosphor in which luminescence is due to the addition of an activator in the form of traces of impurity, and (ii) the so-called "self activated" phosphor, which exhibit luminescence in the pure form in which the luminescence is apparently due to the specific atomic groups or atoms (Hendall 1939).

Luminescence occurs efficiently in materials where there are atomic or molecular sites at which the absorbed energy can be re-emitted optically by means of electron transitions. In solids, these are called "luminescence centres". The spectral distribution of the emission of phosphors is determined by the nature of luminescence centres. Here, in the luminescence centre, the probability of radiative transition is much greater than that for the non-radiative transition. If the probability of non-radiative transition is zero, the centre is called a "killer centre" and the impurities producing it are known as "poisons" (Adrain 1956).

In the phosphors, traps are the metastable levels, which are capable of capturing electrons or holes within them and making them immobile. These trapped electrons can be released later by supplying an optimum amount of thermal or optical energy (Bube 1960, Garlick 1960). An electron thus released from a trap can either combine with a luminescence centre or can be trapped in another trap. The trap provides
the mechanism of energy storage in most of the electronically-active solid including phosphors and are responsible for the phenomena of phosphorescence and thermoluminescence (Spurr 1943). The trapping levels owe their origin to impurity atoms, preparative conditions and imperfections in the crystal lattice (Kroger 1948). A donor level is a normally occupied electron trap whereas an "acceptor level" is a normally occupied hole trap.

It is called optical stimulation when the emission intensity of a phosphor is increased by irradiating it with a long wave-length, visible or infrared radiation. On the other hand, if intensity decreases by irradiation, it is called optical quenching. Both, stimulation and quenching, effects can also be observed when a phosphor excited with ultraviolet radiation, is subjected to an electric field. Lomer et al (1939) have studied these effects in the phosphor of alkaline earth sulphides with infrared radiation. In the case of stimulation, the radiation releases trapped electrons, which can not make transition to the dominant activator centres due to insufficient quantum energy. However, in the case of quenching, the excitation releases positive holes from empty emission centres which then migrate to trap and capture electrons in non-radiative transition.

Luminescence spectra differ from the atomic spectra in two respects: (i) Bands (of the order of hundreds of angstrom wide) rather than lines are generally obtained and (ii) the emission band is displaced to the low energy
side of the absorption band by as much as electron volt or more. Phosphors can produce both line and band emission spectra separately or simultaneously. Line spectra are obtained when radiative transitions take place between discrete highly localized energy levels. Such discrete levels often occur when well ionized impurity ions with incomplete inner cells, form luminescence centres. The band emission is attributed to the outer valence electrons making transitions between levels having different principal and angular momentum quantum numbers. The luminescence processes are explained with a configuration coordinate model (von Hippel 1934, Seitz 1939) and with an energy band model (Schott and Schoen 1939, Schoen 1948). The configuration coordinate model ignores energy transport while the band theory ignores atomic rearrangements. Continuous dielectric model has also been proposed by many workers (Nuss and Rhye 1950, Lax 1952, Meyer 1934, Lax and Burstein 1954). Three important models for luminescence centres in photoconducting phosphors involving transfer of charge have been suggested (Schoen 1942, Klasens 1959, Lambe 1955, Lambe and Klick 1956, Williams 1960, Williams and Freiser 1956). These models are known as: Schoen-Klasens Model, Lambe-Klick model, and William-Freiser model. Cascade mechanism, resonance mechanism, and exciton migration have been shown to be responsible for the luminescence involving energy transfer with no movement of charge (Schoen 1940, Dexter 1958, Freiser 1950, Balkanski 1958, Clifford et al 1957).
The kinetics of luminescence has been discussed on the basis of first order and second order kinetics of fluorescence and phosphorescence (Boesewald 1967, Urbach et al 1948, Garlick 1944, Carle 1963). Many workers have explained the luminescence decay in terms of a “superposition scheme”, where the physical constants (e.g. trap depth) involved may have suitable distribution of their values (Garlick 1949, Hopkins and Jesty 1946, Williams and Byrnes 1947, Dube 1960).

1-2. THE PHENOMENON OF MECHANOLUMINESCENCE

When certain solids are subjected to stress beyond a particular level, light emission follows their deformation. This physical process of light emission is known as mechanoluminescence or triboluminescence. Among the two, the word mechanoluminescence is preferred by most of the recent workers (Chandra and Shrivastava, 1978, Alok 1978, Chandra et al 1980, Koota et al 1981), because the light emission during the mechanical deformation is not attributed to friction. The word mechanoluminescence has also been used in the thesis. The research Degree Committee of Savishankar University, Aipur (M.P.) has accepted this nomenclature. Since mechanical energy can not directly populate the excited states of the molecules comprising the crystals, some other process should be responsible for the ML excitation. In fact, the mechanoluminescence (ML) is a representation of mechano-induced luminescence. The ML is considered to be a complex phenomenon due to several reasons. The elastic and plastic deformation as well as fracture may take place during the action of a stress on a solid. The fracture process involves crack initiation, propagation, stab...
amplification and in some instances the production of high electric fields. In the following, a summary of the previous studies on NL is given with emphasis on the important results and discussions.

1.2 REVIEW OF THE WORKS ON MECHANOLUMINESCENCE

The first recorded observation of NL was by Sir Francis Bacon (1605). He observed that light emission took place when lumps of sugar were broken. In 1664, Waller reported NL from sugar, rock salt, agate and jasper and concluded that these materials were able to "hold the light which they receive" which could be released by fracture.

The NL of many minerals and pottery materials has been reported by the end of 1700 (Harvey 1987). Woodward (1792) reported the NL of quartz, diamond, ruby and many other substances. He found that fracture was necessary to observe the emission. He noticed that sparks from stones were sufficiently hot to ignite gunpowder, therefore, he attributed the light to be due to the surface particles becoming red hot or white hot as a result of the friction. The phenomenon was named "Krannungslicht" (light of shearing) by Heinrich (1920). Heinrich thought, that the emission was a short of electric discharge caused by friction or by chemical decomposition as a result of electricity. The denomination 'triboluminescence' was proposed by Klenkova (1896) (light of rubbing). Burke (1900) studied the NL spectrum of sugar and found that the emission was of the wavelengths shorter than 480 nm. This finding was considered against
Wadsum's proposed "red hot" particle mechanism. Dowar (1901) found that ML is observed in uranyl nitrate when placing or removing the crystal from liquid helium. This finding gave a clue to the Meinrich's theory of electrification mechanism.

A number of papers in the early part of this century were published which were essentially compilations of previously reported as well as newly discovered mechanoluminescent crystals. Tschupaff (1901) published a list in which 121 out of 400 organic crystals, and only 6 out of 110 inorganic crystals are mechanismuminescent materials. Gernes (1905) investigated 81 inorganic salts, Lindemer (1910) listed 110 minerals and Ihnof (1917) reported 40 inorganic crystals which exhibit the phenomenon of ML.

Waiss (1918) made the spectroscopic study of ML and reported the spectral characteristics of ML of NaCl and As₂S₃ crystals using a series of filters. Longchambon (1922) published the ML spectra of sugar using spectrometer equipped with photographic plate. He identified the spectrum as the electrical discharge of molecular nitrogen and recorded similar spectra for a variety of other mechanismuminescent materials including copper sulphate, barium chloride and amiline hydrochloride (Longchambon 1925). He tried to explain the ML excitation on the basis of the piezoelectricity of the crystals. He showed that majority of the mechanismuminescent crystals were non-centrosymmetric and proposed that piezoelectric charging of the crystal caused the dielectric breakdown of the air around it. In some samples, such as uranyl nitrate etc., where he observed the emission in addition to the nitrogen discharge, he suggested that they were the result of
photoluminescence excited by ultraviolet gas discharge. In
support of his piezoelectric mechanism of ML, Longchamps
(1928) reported that the single crystals of sugar and tan-
taric acid did not show ML when cleaved parallel to their
pyroelectric axis, though they exhibit intense ML when
cleaved in all other directions.

ML spectra of 12 different fluoride samples were
studied by Wick (1937) through spectroscope. In all samples,
she found that ML spectra matched with photoluminescent
spectra. These findings were similar to the longchamp's
results with other mechanoluminescent materials. Wick(1937)
demonstrated that ML spectra of certain minerals were simi-
lar to their thermoluminescence spectra (Wick 1937, 1946).

In order to test whether ML was the result of thermolumines-
ence due to local heating, she treated the sample at red hot
for over thirty minutes to exhaust any thermoluminescence and
then checked for the ML. The ML emission was observed both
in the hot material and in the samples after cooling to room
temperature. Curie (1948) proposed an electroluminescent
origin for the ML emission in these crystals.

Wolff et al (1952) gave a most up to date list of mech-
oluminescent substances, which contained inorganic, organic
as well as many minerals. The ML and emission studies of
ZnS crystals were also carried out by them (Wolff et al 1954).
Stranski and his co-workers made the spectral study of the ML
of arsenic trioxide. The results revealed that the spectrum
contained both nitrogen discharge-lines and a broad band cent-
ered at 425 nm, which correspond to the photoluminescence (St-
ranski et al 1955). Stranski et al (1951) reported that the ML
intensity of newly formed As$_2$O$_3$ crystals diminished if the crystal.
were stored for any length of time. This experiment thereby confirmed the earlier results of Kaiser (1916). After studying the decrease in intensity as a function of time, storage temperature and conditions of crystallization, it was concluded that only the arsenolite form was mechanoluminescent (Gross et al, 1955). It is known that $\text{As}_2\text{O}_3$ exists in two polymorphic forms: first Claudelite and second arsenolite.

The investigation of ML in the crystals and phosphors of $\text{ZnS}$ was carried out by Andeska and Chudacek (Andeska 1963, Chudacek and Andeska 1965, Chudacek 1965, Andeska 1968). It was shown theoretically by Chudacek (1964) that a recombination centre of the type $\text{Cu}^+ (\text{S}^+) \text{has "local" piezoelectric properties in the ideal ZnS lattice. On the basis of this logic, an attempt was made by Chudacek (1967) to explain the mechanism of ML in ZnS phosphors, according to which, the ML excitation takes place in two stages. In the very first stage, the mechanical stress during the plastic-elastic deformation, affects the local electric field which ionizes the luminescence centres. In the second stage, the fracture takes place, during which the bonds between the luminespher atoms are torn, thus giving rise to a large number of free electrons in the region between the fractured surfaces. As soon as the fracture occurs, the luminespher is disturbed to a certain depth below the fracture surface. Thus a certain density of electrons and holes are created in the conduction and valence bands, in the region below the fractured surface, at the moment of fracture. The surface states created are filled with the charges present and a space charge is produced at the fracture surface. This may be responsible for the second stage of ML emission.
An electroluminescent origin of ML in ZnS crystal was suggested by Meyer and Ohikek (1969) and Meyer et al (1970). It was found that in Mn doped ZnS, the ML, electroluminescence and the photoluminescence spectra were all identical. Theissen and Meyer (1970) reported that in Mn doped with Cu, the ML spectra differed significantly from its photoluminescence spectra produced by an electric field of frequency 13 kHz. Meyer et al (1970) reported that in Cu doped (Zn, Cd)S sample, the ML spectra resembled very closely the corresponding electroluminescence spectra, but in every case a slight blue shift was observed, which was suggested to be due to the contraction of the crystal lattice under high stress. Theissen and Meyer (1970) showed that the dependence of ML intensity on force was similar to the dependence of electroluminescence intensity on voltage. Both the phenomena of ML and electroluminescence had the similar temperature dependence and the temporal decay characteristics. It was found that ML was observed at both the instances of rise and fall of the compression pulse when a compression pulse waveform was applied to crystals of Mn doped ZnS (Azet al et al 1962). This is analogous to the observation of electroluminescence during both the rise and fall of the applied electric field. The ML pulses were found to occur at twice the frequency of the applied force under a sinusoidal compression. Azetta et al (1967) also found that the ML and ML appeared identical in shape when pressure or voltage of the same applied pulse shape was applied to ZnS doped with Mn.
Aucet et al (1970) investigated the ML during elastic and plastic deformation and fracture of NaCl and coloured alkali halide crystals. In both the cases of activated alkali halides and doped NaCl samples, the ML "memory" effect was obtained. Experiments where the strain was recycled showed that no light was emitted in the elastic or plastic regions of the second application of strain until the magnitude of the previous applied strain was passed. The dependence of ML intensity on the strain rate of crystals was found which suggested that the unpinning of dislocations under stress is responsible for the ML excitation. This mechanism was tested by Scarmozzino (1971) on Cu doped NaCl. 

The ML should be observed under hydrostatic pressure if it is due to piezoelectrically induced electroluminescence. It is known that under pure hydrostatic pressure, since the dislocations are not mobile, the ML excited by this mechanism would not be observed. Scarmozzino (1971) applied rapid pulses of hydrostatic pressure 100 times greater than that necessary to produce piezoelectrically induced electric field and subsequent electroluminescence in NaCl doped Cu crystals, but no emission was detected. This established the idea that moving dislocations were responsible for ML excitation in these systems.

The ML emission during the mechanical deformation of irradiated alkali halide crystals were reported for the first time by Urbach (1930). Trinks (1938) found the increase in ML of NaCl and KCl crystals with irradiation doses, thickness of the crystal and with the pressure. Vicker (1939) also reported the ML emission during deformation of coloured alkali halide crystals. The linear
dependence of light emission on the strain rate in X-irradiated KBr, NaCl and LiF crystals was reported by Mets et al (1957) and by Alseta et al (1970). The decrease in PL with increasing rate of compression was reported by Pirog and Sukov (1968). It was proposed by many workers that the phenomena of PL occurs, in most of the cases, due to the recombination of free electrons with the luminescence centres (Mets et al 1957, Leider 1964, Semchukov and Shurak 1970). Kuglov et al (1966) have reported that in irradiated KCl crystal, the PL is due to the impact of moving dislocations with luminescent centres. Shurak and Klinesberg (1947) have shown that the PL excitation in irradiated KCl crystals is actually due to unpinning of dislocations from luminescent centres whereas Alseta et al (1970), Semchukov and Shurak (1970) have suggested that the PL in γ-irradiated alkali halide crystals is due to the interaction of dislocation with the colour centres. It was found by Shurak (1949) that the total number of photons emitted from irradiated KCl is directly related to the area swept out by the dislocation lines. Ueta et al (1962) reported that the decay curve of the electric current produced during plastic deformation of non-irradiated KCl crystals and the decay curve of the PL produced during deformation of the irradiated crystals were of the same form. The dependence of PL and thermoluminescence on the strain of γ-irradiated KCl crystals has been studied by Guerrero and Alvaro Rivas (1978). Butler (1966) has reported that the PL spectra of γ-irradiated alkali halide crystals are similar to the luminescence spectra excited by high energy radiation.
and they have found that the in situ detectors are one of
several phenomena contributing to the uneven distribution of
activity of active foreshock and after shocks, recognizably

deeply into the crust at a depth, and at a distance very

remote from the epicenter of the earthquake of December 1, 1968,
and December 3 (1969), November, December 28 (1969), and
January 1 (1970). The RT1 detectors during the earthquake

cataclysmic. Moreover, the results of 1968 (1970) and November 28
(1969) have shown

that the strike-slip, or the earth's surface movement, has been
reported in 1968 (1970) while, as reported in 1970 (1970),
and December 28 (1969), the detectors

and copper plates and the detectors at the surface

during the mechanical deformation of the elastic glass
seer the phenomena of the earth at a normal level for the

earth and copper plates and the detectors at the surface

it is not clear whether some components have been


the interactions of charged dislocations with luminescent centres. Graber (1975) has investigated ML during plastic deformation of rubbers. It has been concluded that the ML measurements may provide useful information about the mechanical states of the sample.

Ohman (1976) has found the effects of polarization in the thermal emission of glowing TCM flakes. Polarization of a kind similar to that appearing during the thermal emission from narrow filament was also found in flakes of small sizes. In addition to this, a sudden flashes of light also appear in the thermal emission from flakes produced in a grinding wheel, which splits up into two parts and the origin of which is suggested as due to triboluminescence.

Kodama (1976) has given a quantum mechanical explanation of ML in Mn doped ZnS and it was proposed that X-ray emission may take place from highly mechanically overstressed solids. Furthermore, it is shown that the time dependence pressure applied to the condensed matter may induce broad electromagnetic spectra spreading from low electromagnetic frequency to X-ray frequency. Recently, Lin et al (1980) has developed a theoretical model for the mechanism of excitation mechanism due to the electric field effect and the pressure effect. They have shown how to analyse the ML spectra to determine the external factors that effect or induce the ML.

Krause et al (1981) have investigated the laws governing the destruction of a unidirectionally reinforced glass fiber plastic when stretched in the direction of reinforcement. They have detected the initial stage of
destruction of tubular fiber glass specimens in the plane stressed stage by means of ML. Kryukov and Smirnov (1981) have made an investigation of the radiation flashes resulting from internal focusing of CO₂ laser pulses in samples of commercial grade NaCl, KCl and KBr crystals. The flashes were attributed to ML due to cracks formed under the action of thermoelectric stresses near absorbing inhomogeneities heated by laser radiation to temperatures \( \gtrsim 1000^\circ \text{K} \). Recently, emission of photons during fracture of aluminium oxide and its application to fracture mechanical investigation has been reported by Krall (1982). It is shown that the ML intensity increases with the hardness of the tested specimen, but it does not depend on the macroscopic fracture strength.

The spectroscopic investigation of ML and PL of many organic and inorganic crystals have been carried out by Zink and his coworkers (Zink 1978, Hardy et al 1977, Chandra and Zink 1981). Eight origins of ML have been proposed, such as crystal fluorescence, crystal phosphorescence, luminescence from nitrogen or other gases, metal centered luminescence, luminescence from charge transfer complexes, luminescence from free radicals, black body radiation and conduction band to surface band transition. It was found that only one or the combinations of several of above origins should contribute to the ML of crystal. The ML was correlated satisfactorily to the crystal-structure of the molecular crystals (Hardy et al 1978, 1981, Chandra and Zink 1981). Chandra and Zink (1980 a,b) have reported mechanical characteristics of ML exhibiting gas discharge ML and the molecular emission ML.
in the presence of high concentrations of DTPA, and the equilibrium constants for the formation of the complex between the metal and DTPA at various pH levels were determined. These results suggest that the metal complex formation is favored at higher pH conditions. The stability constants were calculated using the least squares method and are listed in Table 1. The presence of DTPA in the solution significantly decreases the stability of the metal complexes, indicating the importance of chelation in the binding process.
The spectra of light emitted during the crystallization of ${\text{Ba(ClO}}_4)_2\cdot\text{H}_2\text{O}$, $\text{Al}_2\text{O}_3$, and methyl salicylate have been reported by Nak and Chandra (1981) in which the crystalloluminescence (CRL) spectra have been compared with the ML and PL spectra. It has been found that CRL spectra differ from ML spectra in $\text{Ba(ClO}}_4)_2\cdot\text{H}_2\text{O}$, which showed that the former do not arise from the fracture of the newly formed crystals. The resemblance of ML and CRL spectra in $\text{Al}_2\text{O}_3$ and methyl salicylate crystals suggests the similar origin of both the phenomena.

The research group at Government Science College, Balpur is actively engaged in the studies of ML in a large variety of organic and inorganic crystals for more than a decade. Das et al (1972) and Chandra et al (1977) have reported that the ML is related to the strength and fracture of crystals. From the measurements of kinetics of ML, Chandra (1982, 1983a) has shown that the time dependence of ML of fluorescent and of non-photoluminescent crystals follow the time dependence of the newly created surfaces. It was also found that the two rates of decay are associated with the kinetics of ML of phosphorescent crystals; one being related to the kinetics of the creation of new surfaces where as the other is related to the kinetics of the phosphorescence (Chandra 1982, 1983a).

The ML was also correlated to the crystal-structure and to the piezoelectric charge produced during the deformation of the crystals (Chandra and Shrivastava 1978, Chandra and Elyes 1979, Chandra and Shrivastava 1979, Chandra et al 1980). The ML in many phosphores of $\text{Sn}$, $\text{Cd}$, $\text{Ca}$ and alkali halides has been investigated by
Chandra and Majumdar (1987). The crystalline luminescence, together with ML of certain organic and inorganic crystals has been investigated and an attempt has been made to correlate ML with the kinetics of crystal-activation (Chandra et al. 1982, Chandra and Bhatia 1983a,b).

The ML of coloured alkali halide crystals has been the subject of considerable interest in our research group. Chandra and Alyas (1978) have reported that ML appears in X or γ-irradiated alkali halide crystals, not only during the application of pressure but also during the release of pressure. The peak corresponding to the ML spectra is directly related to the square of the lattice constant of the crystals, and it follows the Malinas-Ivey plot (Alyas and Chandra 1982). The intensity of ML produced during the application and release of a uniaxial pressure, in X or γ-irradiated KBr, KCl, KI, LiF and NaCl crystals decreases with the number of applications and releases of the pressure. The ML intensity of X or γ-irradiated KBr, KCl, LiF and NaCl crystals increases with the temperature (investigated upto 110°C), however, the ML intensity of X or γ-irradiated KI crystals decreases with the increasing temperature. The ratio of the ML intensity during the release of pressure to the ML intensity during the corresponding number of applications of pressure, decreases with the temperature of the crystals. Assuming that the movement of dislocations is responsible for the ML excitation, the pressure and temperature dependence of ML is discussed (Chandra et al. 1982). The activation energy related to the increase in the number of dislocations with the temperature is estimated from the ML measurements and it is found to be
0.33, 0.28, 0.26, and 0.33 eV for γ-irradiated KBr, KCl, LiF and NaCl crystals respectively. Four models, that is, dislocation defect-stripping model, dislocation unpinning model, dislocation interaction model, and dislocation annihilation model, have proposed for the ML excitation in X or γ-irradiated alkali halide crystals (Chandra et al 1982). The dislocation annihilation model is found to be the major process for the ML excitation. According to this model, when dislocations of opposite sign are annihilated, then considerable thermal energy is produced and it excites luminescence exactly like thermoluminescence. It has been found that the acoustic and light emissions occur simultaneously during the deformation of coloured alkali halide crystals (Chandra 1983b). Additively coloured alkali halide crystals do not show ML.

The above review shows that considerable attention has been paid to investigate the phenomenon of ML. From time to time, the works on ML have been reviewed by many workers (Tretia 1905, 1910; Gerné 1908; Langchamon 1929; Lenard et al 1938; Mayer et al 1970; Walton 1977, Sink 1978).

1.4. OUTLINE OF THE PRESENT STUDY

Nearly half of all inorganic compounds and between a quarter and a third of all the organic compounds exhibit the phenomenon of ML. Coloured alkali halides and impurity doped zinc sulphide exhibit ML in their elastic, plastic as well as in fracture regions (Butler 1960, Alueta et al 1970, Chandra et al 1980). The crystals of certain rare earth oxides exhibit ML in their plastic and fracture
regions (Williams and Turner 1979). Certain variety of rubbers exhibit ML only during their plastic deformation (Grabec 1974, 1975). Most of organic and inorganic crystals exhibit ML only during their fracture. Intense ML has been found in sucrose, tartaric acid, uranyl nitrate hexahydrate, acenaphthene, phenanthrene, impurity doped zinc sulphide, impure saccharin and in ditriphenylphosphine oxide manganese bromide crystals. The ML of impurity doped zinc sulphide, impure saccharin and ditriphenylphosphine oxide manganese bromide is so intense that it can be seen in day light by simply pressing the crystals between two glass plates.

So far as the work is concerned, the ML may be regarded as an inter-disciplinary subject of research. It has been studied by physicists, chemists, geologists, material scientists etc. Physicists are interested in the correlation of ML to the physical properties of crystals, chemists are interested in the role of molecular behaviour and structure in the process of ML excitations, geologists are interested in the correlation of ML to the cleavage and crystal structure, material scientists are interested in the correlation of ML to the deformation, fracture, hardness of the crystals etc.

The ML has been studied in many molecular crystals and it has been found that generally the piezoelectric crystals exhibit ML, and the non-piezoelectric crystals do not (Chandra and Niyaz 1979, Chandra et al 1980, Chandra 1981, Hardy et al 1981). This result supports the piezoelectric origin of ML. We found that
several centrosymmetric, that is, non-piezoelectric inorganic crystals also exhibit ML which is comparable in intensity to that of the piezoelectric crystals. This fact suggests that in addition to the piezoelectric mechanism, there should be some other mechanism for the ML excitation in inorganic crystals. The ML in centrosymmetric inorganic crystals has not been studied in detail, and the mechanism of ML excitation in such crystals is least understood.

Only limited studies have been made on the ML of centrosymmetric inorganic crystals. The first systematic investigation of the light emission during fracture of alkali halide crystals was carried out by Kliman and Schmidt (1933). In 1935 Lengchamps was successful in recording the ML spectra of NaCl crystals. The effect of uniaxial strain on ML intensity was studied by Belayaev et al (1963) on LiF, NaCl, KCl, CaI and TI doped KI crystals. They reported that no emission was observed during elastic or plastic deformation of the non-irradiated crystals. The ML produced on fracture was identified as a nitrogen gas discharge (Belayaev and Martyushev 1969). An acoustic signal accompanying each ML pulse was also detected by Belayaev and Martyushev using a ceramic microphone placed next to the crystal under stress. It was possible to detect a 1.5 MHz radio frequency signal simultaneously with the ML in LiF and NaCl crystals by placing an antenna around the sample. The amplitude of radio frequency signals was found to be proportional to the ML intensity.
exceeds by the cross.

of electricity from the electrode bonded to the extracellular fluid component of the Pt emission produced by the electric current.

high current and low frequency pulses to a second pulse.

of the Pt were recorded under a 10-30 Hz frequency.

in the high current region of the operation, when the Pt

the presence of nitrogen deoxidizing process to be observed.

was measured to be responsible for the potential difference.

mercury 1969, 1969). The advantage of the current density

charge was the major component of Pt in the electrolysis

supplementary data and discussion concerning the electrolysis

was recorded at 3 Hz in which other effects may be observed.

more intense than the normal electrolysis.

is 1968). The emission produced in the manner we studied

and 0.1 Hz, respectively by applying a

the Pt during exposure to the emission current by a

and that Pt is produced at a new potential of the Pt.

also concluded that the effect produced in a separate manner

suppressed by 1.0-2.0 (ref. 210 and reference 197). It was

remaining time of 2-20 ms in duration and other control

continuously during electrolysis, but appeared in short pulses

were increased, they also expected that the Pt did not change

light intensity increased to the same extent and in the

growth of Pt was in agreement with others.

but those of Pt (1968) showed that the concentration of the
The ML in non-irradiated LiF, KCl and KI crystals were investigated by Meyer and Polly (1963) and by Polly et al (1967). In their experiments the ML was excited by impulse or by scratching with a sapphire or steel needle. They proposed that the potential difference due to motion of charged jogs and kinks during plastic deformation are responsible for the ML excitation. This potential difference across the crystal was produced due to dislocations of opposite charge, which are created on impact with the needle. These dislocations move in opposite directions under strain and produce potential difference across the crystal. To support this mechanism, Polly et al (1967) pointed to the observation of light emission upon needle impact with no visible evidence of crystal fracture. It was reported later by Meyer et al (1970) that the potential dropped on impact and then it increased as the needle rebounded. Subsequent discharge was accompanied by sudden drop in potential. Therefore it was concluded that the fractureless emission as observed by Polly et al (1967) was not the true ML but it was actually an electrical discharge between the crystal and the needle, which was caused by the contact potential differences.

Obrikat et al (1967) excited ML in alkali halides by scratching with a needle or by milling the crystal surfaces. They found that the light intensity was proportional to the area of newly created surfaces and that the mere rubbing of the crystal surfaces with smooth miller did not produce ML. This fact showed that the contact potential difference is not sufficient to cause ML excitation. They reported that the fracture was necessary for the ML emission.
A thermal mechanism is proposed for the ML emission which is correlated to black body radiation. According to Meyer et al (1970), the temperature of the order of $10^4 \text{ K}$ may be produced at the tip of the propagating cracks. Such incandescence emissions were detected only when the crystals were fractured in vacuum. Sodium line emissions were also found when NaCl crystals were fractured in vacuum.

An attempt to measure ML in NaCl crystal, down to temperatures of about $20 \text{ K}$ at 1.5 Torr hydrogen atmosphere (gas discharge region of ML) was carried out by Fröhlich and Seifert (1971) and they found that the intensity of ML strongly increased with decreasing temperature. Since the temperature dependence of the potential differences due to the charged dislocation is opposite to that of ML, they concluded that charged dislocations can not be responsible for the creation of the electric field.

The objects of present investigation are: (i) to understand the mechanism of ML excitation in centrosymmetric inorganic crystals, and (ii) to understand the impulsive velocity dependence, temperature dependence, crystal-size dependence and time dependence (kinetics) of ML in centrosymmetric inorganic crystals. To fulfill the objects, the following studies have been made and described in the subsequent chapters:

(i) Survey of ML in inorganic crystals.

(ii) Impulsive excitation of ML in centrosymmetric and non-centrosymmetric crystals.
(iii) Effect of temperature on the PL of centrosymmetric and non-centrosymmetric crystals, and

(iv) Dependence of PL on microhardness and dislocation density in crystals.

Because of the availability of literature, more attention has been paid to the PL studies of non-irradiated alkali halide crystals, which are centrosymmetric. It should be noted that the PL of coloured alkali halide crystals is of different origin, where the PL appears in the elastic, plastic and fracture regions of the crystals. The colour centres and mobile dislocations have been found to be responsible for the PL excitation in coloured alkali halide crystals. The PL of coloured alkali halide crystals is not the subject of the present investigation. It has already been investigated in detail by a member of our research group (Ryaz 1981).
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