CHAPTER - I
INTRODUCTION

1.1 THE PHENOMENON OF LUMINESCEENCE:

The electromagnetic radiation emitted from the substances has been classified, broadly as 'Hot' and 'Cold' radiations. The hot radiation has been thoroughly studied and it is a phenomenon in which the temperature of the body is explicitly involved. This type of radiation can be presented by the Stephen's Law of Radiation \( Q = \sigma T^4 \) Which is approximately true for all the bodies. The quality profile of hot radiation is temperature dependent and is governed by wien's displacement law.

The radiation other than hot radiation, resulting from the change in electronic state of substance is called 'Luminescence', (Curie 1963, Leverenz 1950). As per the usage of the term, it relates to only those electromagnetic radiations which are in the infrared, visible and ultraviolet ranges. It is governed only implicitly by the temperature of the body. The luminescence has been further classified in different categories depending upon the response and duration of radiation which takes place due to change in the electronic states of the substances namely the phenomenon of phosphorscence, fluorescence, Rayleigh scattering and Raman scattering. They are differentiated with respect to their duration of emission. Fluorescence is obtained only during the first \( 10^{-8} \) sec. of excitation and phosphorscence only after \( 10^{-8} \) sec., after the ceasional of excitation (Leverenz
The distinction between the fluorescence and phosphorscence is also made on the basis of the variation of the luminescence decay with temperature. The decay of fluorescence is little dependent on the temperature but the decay of phosphorscence is strongly temperature-dependent (Curie 1963). Luminescence is not the thermal radiation as it does not follow the Kirchoff's law. On the basis of the time delay in emission, it can not be explained by Raman and Compton effects also. In the case of luminescence the time delay after excitation is greater than $10^{-9}$ sec. whereas Raman and Compton effects are completed in an interval of about $10^{-14}$ sec., (Leverenz 1949, 1950).

In luminescence the emission is triggered by providing the necessary energy which changes the electronic status of the substance, which is, generally speaking, unstable and results in parastable states. When substance acquires its original state resulting by radiative emission, it is luminescence. The types of energies by which the electronic change can take place are, thermal, electrical, photo and mechanical energies. It is conventional to prefix the nature of energy to the term luminescence to identify it i.e. the Thermoluminescence (TL) is due to thermal energy, Electroluminescence (EL) is due to electrical energy, Chemi-luminescence (CL) is due to chemical energy and Mechanoluminescence is due to mechanical energy. It has also been reported that two different types of energies may also produce luminescence and accordingly named as electro-photo
luminescence, Thermo-mechano luminescence, mechanothermo luminescence etc. The first prefix in such luminescence denotes the controlling and the second denotes its source of power that stimulates it.

1.2 MECHANOLUMINESCENCE:

The phenomenon of Mechanoluminescence (ML) is the emission of radiation produced by the mechanical energy provided by the different types of mechanical processes like grinding, crushing, rubbing, fracturing, deformation in elastic and plastic regions etc. Though this phenomenon was reported by fransis Bacon in 1605, but it remained an isolated event till recent time. Robert Boyle in 1644 found that a particular diamond when pressed on one spot with a steel bodkin produced "a very vivid but exceedingly short lived splendour". He also noticed that hard sugar being nimbly scraped with a knife would afford a "sparking light".

In 1753, Father Giamathista Baccaria advised that "you may when in dark, frighten simple people only by chewing lumps of sugar and in the mean time keeping your mouth open, which will appear to them as full of fire". Now it has been well known that certain substances in the form of crystals or phosphors and organic compounds, emit radiation due to the deformation, which results in the electronic changes. This phenomenon was earlier named as "Triboluminescence", but now has been more correctly named as "Mechanoluminescence", (ML), or Deformation Luminescence (DL). The term
"Triboluminescence" was coined by Wiedmann (1888). In Greek "tribein" means to rub. Heinrich (1820) had suggested the German name "tronnungslickt" meaning separation or shearing, Wiedmann and Schmidt (1895) interpreted the term 'Triboluminescence' as the emission of light during the mechanical force of solids.

The recent experiments which were carried out just to elucidate the excited state origins of the luminescence and to determine the mechanisms by which those states are populated, showed clearly that the emission of light during the mechanical deformation of solids is not attributed generally to friction. Hence the nomenclature "Mechanoluminescence" a more general term for phenomenon, is preferred in some recent Literatures, (Chandra & Shrivastava 1978, Sodomka 1978, Chandra et al 1980, Karauya et al 1981, Molotaski 1983, M.Elyas 1984, Deshmukh, N.G. 1985). The nomenclature "Mechanoluminescence", (ML) has also been preferred in this thesis.

In recent findings on elementary mechanism of light emission and relation with other crystalline properties, we are faced with the necessity of subjecting the classical phenomenological definition to a critical investigation. A large number of physical processes may occur within very short intervals, which excite or stimulate the process of photon emission. Among these are: (i) Elastic and plastic deformation (ii) Fracture processes, (iii) Local and extremely high pressure and temperature peaks, (iv) Short
period exposures of extremely clean surfaces and the development of free radicals; (v) Electric processes e.g. the development of electric potential differences and gaseous discharge, due to contact potential differences, by the development of electrically charged fracture planes or by the movement of charged dislocations. In addition, the crystal can not be considered separately and specially the kind and pressure of gas must be included in the system.

In fact, the Mechanoluminescence (ML) is a representation of mechano-induced luminescence. Comparing ML with photo luminescence (PL), we are faced with difficulties which indicates the complicated process of the mechanical light excitation. In PL, a direct excitation of the phosphor by the irradiated light takes place. In ML, the mechanical energy added to phosphor would have to be transferred directly to the atoms of solid, e.g. by modified lattice vibrations and excite the atoms to luminescence. This mechanism is conceivable, it is true, but it has never been identified to date. The mechanical energy is rather transferred into other forms of energies which then constitute the last stage of excitation. Thus, in reality, the "Mechanoluminescence" is a "Mechano-induced luminescence". This word fits well with the nomenclature of other types of luminescence where the prefix to luminescence stands for the process of induction or stimulation of the luminescence, for example in thermoluminescence, crystalloluminescence etc.
The response of mechanical energy to produce ML is varied. Some substances have very weak emission and they are known as weak Mechanoluminescent substances. Dr. M. Elyas (1984) reported that colour alkali halides are highly Mechanoluminescent in all the regions of deformation i.e. elastic, plastic and fracture regions. Other categories of substances which are highly Mechanoluminescent are impurity doped phosphors. The luminescent properties also depend on modes of transfer of mechanical energy.

1.3.1 SUMMARY OF EARLIER WORK ON CRYSTALS AND OTHER SUBSTANCES.

The ML of many substances including quartz, diamond and ruby has been observed (Wedgwood 1792). It was found that fracture was necessary in order to observe the emission. Burke (1898) observed the ML spectrum of sugar through a spectroscope and he found that the emission was at wavelengths shorter than 480 nm. This observation was considered to be an evidence against Wedgwood's proposed "particle mechanism". Dewar (1901) observed the ML in uranyl nitrate during placing or removing the crystals from liquid helium. This fact was against Heinrich's "frictional electrification mechanism".

In the early part of this century a series of papers appeared, which were essentially a compilation of previously reported and newly discovered Mechanoluminescent crystals. Tachugaeff (1901) gave a list in which out of 400 organic crystals, 121 were Mechanoluminescent and only 6 out of 110 in
inorganic crystals were Mechanoluminescent. Trautz (1905, 1910) gave a list of 260 Mechanoluminescent materials. Gérnez (1905) listed 82 inorganic salts, Lindener (1910) reported 110 minerals, and Imhof (1917) reported 40 inorganic crystals, which exhibit ML.

Later the attention turned to the spectroscopic investigation of ML. The spectral characteristics of ML of NaCl and As₂O₃ crystals was reported by Weiser (1918) using a series of filters. The ML spectra of sugar using a spectrometer equipped with a photographic plate was published by Long-chambon (1922). He tried to explain the ML excitation on the basis of the piezo electricity of the crystals. He concluded that most of the mechanoluminescent crystals were non centro symmetric and proposed that piezo-electric charging of the crystal caused the dielectric breakdown of the air around it. To justify piezo electric mechanism, he reported that the single crystals of sugar and tartaric acid did not show ML when cleaved parallel to their piezoelectric axis, though they were intensely mechanoluminescent when cleaved in all other directions.

Wick (1937) studied the ML of 12 different fluorite samples and in all samples he found that ML matched the photoluminescence spectra. These findings were similar to the Longchambon's result with other mechanoluminescent materials. Further studies were made by Wick (1937) and it was found that ML spectra of certain minerals were similar to the thermoluminescence spectra (Wick 1937, 1940). To verify
whether ML was the result of thermoluminescence due to local heating, the sample was tested at red heat for over thirty minutes to exhaust any thermoluminescence and then checked for the ML. The ML was observed both in the hot material and in the sample after cooling to room temperature. Curie (1946) proposed an electroluminescent origin of the ML emission in this crystal.

Wolf et al (1952) gave a list of 154 inorganic, 188 organic and 16 minerals mechanoluminescent substances. Wolf et al (1954) also investigated the ML and exoemission of ZnS crystals. Remarkable studies have been made by Stranški and his coworkers (1955) on the ML of As₂O₃.

Belyaev et al (1963) examined the ML intensity as a function of uniaxial strain on LiF, NaCl, KCl, CaI and TI doped KI crystals. They found that no emission was observed during elastic or plastic deformation of the unirradiated crystals. The ML produced by fracture was identified as a nitrogen gas discharge spectra (Belyaev and Martyshev 1969). It was also observed that the ML occurred during the growth of cracks in the alkali halide crystals. This is supported by the fact that the light intensity increased as the rate of uniaxial strain was increased. The ML during fracture did not occur continuously. It appeared in short pulses ranging 20-29 nano secs. (Belyaev and Nabatov 1963). It was concluded that the crack propagates in a stepwise manner and the ML is produced at a few special parts of the crack.
ML during fracture of LiF crystals was observed by Belyaev et al (1966), caused by ruby laser pulse at 694 nm. They found that the emission produced in this manner was 100 times more intense than the normal thermoluminescence.

It was concluded that electrical discharge was the major component of ML in LiF by observing a sharp change in the potential differences across the crystal surface during the fracture and subsequent light emission. (Belyaev and Martyshev 1964, 1969), Meyer and Polly (1965) Polly et al (1967) investigated the ML in unirradiated LiF, KCl, NaCl, and KI crystals. In these studies the ML was excited by impulse or scratching from a Sapphire or steel needle. It was concluded that the potential difference due to the motion of charged jogs and kinks during plastic deformations are responsible for the ML excitation. It was proposed that on impact with the needle, dislocations of opposite charges are created, which then move in opposite directions under strain and produce a potential difference across the crystal.

In the ML of Alkali halide crystal by scratching with a needle, it was found that the light intensity was proportional to the amount of new surface area created and, just rubbing the crystal surface with a smooth miller did not produce ML. Thus mere contact potential difference were not sufficient, and fracture was necessary, (Obrikat et al 1967). A thermal mechanism is proposed where the emission is correlated to black body radiations of the order of $10^4$ K. According to Meyer et al (1970), this temperature is produced at the tip of
the propagating crack.

Initially it was believed that the ML appears only during fracture of crystals, but the investigations made revealed that impurity doped zinc sulphide and coloured alkali halide crystals exhibit ML in their elastic and plastic regions as well as during their fracture. (Alzetta et al, 1970, Butler 1966, Chandra et al 1982). Crystals of certain rare earth oxides exhibit ML both in their plastic and fracture regions (William and Turner 1979). ML is observed in certain variety of rubber during their plastic deformation (Grabec 1974, 1975). Most of the inorganic compounds and a quarter to one third of all organic compounds are mechanoluminescent to varying degrees. Coloured alkali halide crystals, manganese doped zinc sulphide, uranyl nitrate hexahydrate and sucrose are examples of intense mechanoluminescent crystals.

Chandra and Elyas (1982) have proposed that the dislocations are responsible for the ML in X - irradiated alkali halide crystals. A linear relation is found between the ML intensity and the newly created dislocations. They concluded that the ML excitation involve the process related to both the colour centres and the movement of dislocations. Chandra and Majumdar (1983) have reported the temporary mechanoluminescence of certain organic and inorganic crystals. ML is found to be different for different crystals and it increases with the temperature of the crystals. It is concluded that the phase transformation may be responsible for the temporary mechanoluminescence.
Chapman and Walton (1983) have reported the room temperature mechano-luminescent spectra of single crystals of CaF$_2$ : 1% Tb, CaF$_2$ : 1% Dy, CaF$_2$ : 1% Sm and CaF$_2$ : 1% Eu using high gain image intensifier spectrograph. The spectra obtained as the crystals were cut with a diamond impregnated Circular saw, show more structure than that recorded in the room temperature photoluminescent spectra. It is suggested that the observed splitting of the lines, attributable to the triply ionised rare earth dopants is due to the rapidly changing crystal fields within the vicinity of a growing crack.

The effect of temperature on the ML intensity of certain fluorescent and phosphorescent molecular crystals have been reported by Chandra et al (1986). They found that the ML intensity decreases with temperature and follows the relation $I_T = I_{T0} (1- T/T_C)^n$. The value of $n$ lies between 0.9 and 1.10 for the piezoelectric crystals. The ML of non piezoelectric crystals disappear much before their melting points. 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 has been shown.

ML in tetrahedral manganese (II) complexes has been found an intense and unique type. This was observed by Chandra et al (1987). By the impact of a piston onto the crystal, during the excitation of ML, initially the ML intensity increased with time and after attaining a certain
maximum value, it decreased. The decay rate of ML is found to be faster during crystal deformation. However, its value decreased after cessation of the deformation and became equal to the decay rate of phosphorscence. The ML disappeared much below the melting point of the crystal. It is proposed that since the crystals of tetrahedral manganese (II) complexes are centro-symmetric, the local non centro-symmetric sites near the defects are attributed to be responsible for the ML excitation.

1.3.2 REPORT OF EARLIER WORK DONE ON ML OF PHOSPHORS

The phenomenon was named "trennungslicht" by Heinrich (1820). He suggested that ML might be due to a cracking of rough places on the crystals. Burke (1898) made a serious attempt on measuring the ML spectrum of sugar but he was unable to photograph the spectrum (because of "the rapid rate at which the sugar wore out"). On viewing it directly through the spectroscope, he found that it was confined to the more refrangible end of the spectrum, which lay at wave length below 486 nm. This finding was considered to be an evidence against Wadewoods proposed "red hot" particle mechanism.

1.3.2(A) WORK ON ML OF pure ZnS PHOSPHORS

During this century a systematic study of ML produced from natural and synthetic Zinc sulphides has been made. The rubbing of the surface of minerals sphalerite (ZnS) shows the visible trails of light, however this fact has been known long back. Karl (1907,a,b) observed visually the relative ML intensities of new solids e.g. manganese oxides, tin or
sodium.

Sodomka (1963), Chaudacek and Sodomka 1963, Sodomka 1964, Chaudacek 1965, 1966, 1967, Sodomka 1968 made vast investigations on the ML in crystals and phosphors. In luminescent zinc sulphide powder, ML was observed by Sodomka (1963) by applying different pressure on zinc sulphide powder. It was shown in the experiments that the ML appears only when there is a time change in the applied pressure.

The ML excitation in ZnS phosphors occur in two stages, the plastic elastic deformation and the fracture stage, Chaudacek (1967). The mechanical stress affects the local electric field which ionises the luminescence centres in the first stage. While in the second stage the bonds between the luminophor atoms are torn, give rise to a large number of free electrons in the region between the fractured surfaces. The luminophor is disturbed to a certain depth below the fracture space at the moment of fracture. This supports the conclusion that at the instance of fracture some electrons and holes are created in the conduction and valence bands in the regions below the fractured surfaces. In this way space charges are produced which in turn give rise to ML.

Curie and Prost (1946) has made the suggestion that EL might be responsible for ML of ZnS. A similar conclusion was made by Meyer and Obrikat (1969) on the basis of resemblance found in the ML and EL spectrum of ZnS phosphors.
ML can be produced by elastic plastic and fracture deformation. This was proved after studying the ML of ZnS single crystal, Sodomka (1972). During the deformation of ZnS crystal, mechano electron may be produced with high energies up to 10 kev. It is also reported that the strongest ML can be interpreted by the stimulating part of radiations.

The detailed investigations of ML of ZnS single crystals have been carried out by Bredikhin and Shmurak (1974). They found the emission of short pulses during the deformation of the crystals. After studying the spectral and temperature characteristics, they concluded that ML is produced by a dislocation mechanism. Bredikhin and Shmurak (1976) observed the deformation induced electroluminescence peaks produced by ZnS single crystals.

Bredikhin and Shmurak (1977) in their further investigation studied the ML and electrical characteristics of ZnS crystals. They reported that the charged dislocations which move during the deformation, bring charge out to the surface of the sample and this charge induces surface electroluminescence.

1.32.(B) WORK ON ML OF SINGLE IMPURITY DOPED PHOSPHORS:

The ML spectra of sphateriate was roughly measured by Levison (1904) (ZnS:Mn). The ML was excited by allowing a rotating disc suspended in glue, on which the powdered material was pasted. He observed by naked eyes that the ML
spectrum was extended from 550 nm to about 650 nm. The ML spectra of different samples of ZnS:Mn was measured by Waggoner (1916) and he compared them with the phosphorscent spectra produced under X-ray excitation. He found the maximum intensity at a mean value of 557±5 nm of the ML spectra of all samples. Comparing with the phosphorscent spectrum, the mean value of maximum intensity has been found 552 ± 3 nm, which can be compared well with the ML spectra. This fact showed the similarity between the mechanoluminescence and photoluminescence spectroscopy.

Experiments with Cu doped ZnS was carried out by Chaudracek and Sodomka (1963). A conclusion was made by these experiments that the instantaneous change of pressure and the ML does not occur until a certain minimum pressure $P_{\text{min}}$ is attained, ML in luminescent ZnS:Mn and ZnS:Cu powder are recorded by Sodomka (1964) during impact on the samples. The powder was placed in solid binding matter, 1mm thick in layer in a weight ratio of two parts of binding matter to one part of luminescent powder having a mean grain size of 20 microns. It showed that when the pressure pulse decreased the luminescent pulse was produced, and it had maximum value when the pressure Pulse was minimum. Thus Sodomka concluded that at the impact on luminescent powder the luminescent brightness was caused by elastic or plastic deformation. It could not be confirmed whether ML was produced only by elastic or plastic deformation or by the influence of both together.
By taking the photograph of ML spectra of four natural sphalerite samples and one commercially produced ZnS:Mn powder, it was found that the maximum phosphorescent intensity (excited by mercury arc) occurred virtually at the same wavelength i.e. around 590 nm and 575 nm respectively.

The gas discharge component in the ML spectra of ZnS:Mn has been reported by Chaudacek (1967). Obrikat et al (1967), Meyer and Obrikat (1969) and Theissen (1970) has made the investigation for verifying whether the mechanism of ML resembles with that of electroluminescence (EL) or photoluminescence (PL). They observed the ML spectra of ZnS phosphors with different activators and co-activators and found that the ML spectra was closely identical as EL spectra.

Some other observations were also made to correlate ML with EL such as the ML intensity was shown to have the same functional dependence on force, as the electroluminescence intensity has on voltage. The temperature dependence and time decay characteristics in both ML and EL were found to be of similar nature (Meyer et al 1970 b). They proposed that the ML of doped ZnS phosphors is due to the deformation induced electroluminescence. A burst of light was emitted at both the instances of rise and fall of compressional pulse when a 'top hot' compressional pulse is applied to Mn doped ZnS powder suspended in oil in a pressure cell (Alzetta et al (1962). The pressure pulse in the cell was monitored with the help of a piezoelectric transducer and the ML output was also recorded by Alzetta et al (1967). They applied a voltage pulse.
similar to the pressure pulse, to a cell containing an identical suspension of ZnS:Mn powder and observed the EL output. They found that the ML pulse closely resembled the EL pulse created after applying the voltage pulse to the EL cell. By applying a periodic sinusoidal varying pressure to a thin layer of ZnS:Mn powder, through a piston connected to an electromagnetic vibrator, they found that the frequency of ML pulse was twice the frequency of applied varying force. This fact also showed some kind of resemblance between ML and EL phenomenon.

Detailed investigations on the pressure dependence of ML and voltage dependence of EL were carried out by Meyer et al (1970). Different doped ZnS samples were prepared in the form of 1 mm thick layers and a pressure pulse and a voltage pulse were applied to each sample separately. A transient stress was applied by dropping a fixed weight onto the sample kept at the top of hard glass plate. The nature of the stress curve was measured by a piezoelectric disc placed beneath the sample.

The maximum value of ML intensity (I) for ZnS:Cu,Cl, ZnS:Mn and ZnS:Cu, varies with the maximum value of compressive force as \( I = I_0 \exp \left( -\frac{b}{K^2} \right) \), where \( I_0 \) and \( b \) are constants, different for each phosphor, have been reported by Meyer et al (1970). But at that time other workers could not yet the results obeying this relationship. Alzetta et al (1962) found that the total quantity of ML intensity I after subjecting a ZnS:Mn powder to hydrostatic pressure step of
magnitude $P$ varies as $I \propto \exp(Kp^2)$, where $K$ is a constant.

An investigation of ML as a function of strain was made by Alzetta et al (1970). Results on ZnS:Mn phosphor indicated that in the elastic region 5% of the emitted light was observed, 80% observed during plastic deformation and the remaining 15% at fracture. It was found that no light was emitted in the elastic or plastic regions on the second application of strain until the magnitude of the previous applied strain was passed. This was observed in the activated alkali halides as well as in doped ZnS samples. They also observed the dependence of ML intensity on the strain rate.

If ML were the result of piezoelectrically induced electroluminescence then it should be observed under hydrostatic pressure. Dislocation are not mobile under pure hydrostatic pressure and 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 a sufficient electric field piezoelectrically and observed the electroluminescence. There was no ML emission and so he suggested that moving dislocations were responsible for ML in these crystals and disprove the piezoelectric origin of EL field. A change in the number of ML pulses occur by the electric field which depends upon the polarity of electric field, Bredikhin and Shmurak (1975). Investigation on the effect of light on the ML of doped ZnS phosphors was made by Bredikhin et al (1975) and they found that illumination of the sample in the absorption band ($\lambda \sim 340$ nm)
increases the number of ML pulses per unit time.

Sodomka (1978) has given the quantum mechanical interpretation of ML. Detailed studies have been carried out on the ML excitation in Mn doped ZnS and on the possibilities of X-ray emission from the highly mechanically overstrained solids. It is shown that the condensed matter may induce broad electromagnetic waves extending up to X-ray frequency, when the time dependent pressure is applied to the condensed matter. A difference of 15 nm has been observed in ML and photopeaks of Dupont D screen (ZnS:Ag). Djordjevic made a conclusion that ML caused by the mechanical deformation of a solid can not be simply assigned to a unique mechanism. The complex energy band structure of imperfect crystals may allow a multitude of excitation and relaxation processes.

Lin (1980) proposed a theoretical model for the mechanoexcitation mechanism due to the electric field and pressure effects. He has investigated a technique for determining the external factors affecting the ML phenomenon by analysing the ML spectra. Sodomka (1980) measured simultaneously the ML emission and acoustic emission in an experiment. These emissions are produced during the mechanical deformation of organic compounds, glass, steel and copper covered with the mechano-luminescent layers prepared by mixing the mechanoluminescent ZnS powder dispersed in solidified lack. For the deformation stimulated ML and acoustic emissions, the same sources are responsible.
1.32(C) WORK ON ML OF DOUBLE IMPURITY DOPED PHOSPHORS:

In an experiment ML was excited mechanically by means of a magnetic vibrator having a frequency of 50 cycles; The ZnS:Mn (Cu, A⁹) was scattered in the form of a suspension in different solids. Choudacek (1965) proved that periodic ML can be excited by periodically supplying deformation energy to ZnS luminophor. The exciting mechanical frequency and the frequency of the periodic ML impulses were the same. It was also found by Chaudacek that at lower pressure the ML exhibits periodicity, which is limited in time and the periodicity of ML disappears at an exciting pressure of 700 KP/Cm². In the ideal ZnS lattice recombination centre of the Cu⁺, -S⁻, has "local" piezoelectric properties. This was explained theoretically by Chaudacek (1966), and he made an attempt to explain the ML excitation.

Myazdrikov et al (1966) dropped a steel ball onto a ZnS:Mn, Cu electroluminescent panel from different heights and found that the amplitude of the ML pulse was proportional to the impact energy of the ball.

Recently some work on ML of one host matrix with two impurities has been done in our laboratory by R.S.Gupta (1990). It was found that when the ML is excited impulsively by impact of a moving piston on to the phosphors, the ML intensity increases with time, attains a maximum value and then it decreases. Total ML intensity increases linearly with the mass of the phosphors for higher impact velocities. The
ML spectra of ZnS:Cu, Mn, Cl (Cubic) and ZnS:Cu,Mn,Cl (hexagonal) phosphors have peaks centred at 545 and 540 nm respectively.

1.32(D) WORK ON MIXED PHOSPHORS:

Temperature dependence of the photoluminescence intensity of zinc cadmium sulphide was observed by I. Soudek (1957, 58). The PL intensity studied, in the range 10°-370°C, was found to vary non-monotonically with temperature and to display hysteresis. Although the nonmonotonic nature of the variation and the change in colour with temperature can be explained by the existence of two types of luminescence centre, this does not account for the hysteresis. The latter is explained by the occurrence of red centres at higher temperature and the increase in their concentration with temperature. Zn, CdS were excited by long wavelength U.V and their light output measured at a single wavelength in each experiment during temperature cycle to about 200°C. Some heating and cooling curves coincided but often on cooling the original output was regained more slowly. This hysteresis effect was attributed to traces of copper in phosphors. Excessive heating produced permanent losses in the fluorescence. The temperature dependence varied for different emission wavelengths in the same phosphors showing the presence of subsidiary bands.

The dependence of the spectral composition of the luminescence of zinc-cadmium sulphides on the excitation intensity was observed by I. Soudek (1958). He found a shift
of the emission bands to longer wavelengths for an increase in the excitation intensity. This phenomenon was explained by the migration of holes on the assumption of statistical dispersion between the energy levels of the luminescent centres.

G.Wendel (1960) studied the field enhancement in ZnS, CdS:Mn phosphors. These phosphors, not containing Au, when made into cell like those used in EL show an increase of up to 10 times in their X-ray luminescence by simultaneous exposure to an a.c. field. At constant frequency this enhancement factor rises with the applied voltage to a flat maximum near 300V. At constant voltage the factor falls steadily as frequency increases from 0.1 to 10K c/s. Enhancement also occurs with UV, cathode rays or X-particles instead of X-rays. H.Winkler (1961) observed the field enhancement in ZnS. CdS:Mn phosphor under X-ray excitation.

The emission spectrum of the mixed crystal phosphors (Zn,Cd)S activated by Cu and Ag or selfactivated, was measured for stimulation by UV.. light wavelength 3650A°, H.Ortmann and H.Treptow (1961). It was found that the band displacement produced at different composition of the mixed crystals were comparable but not exactly similar for the different activators. The influence of the crystal habit (hexagonal or cubic) on the position of the band maxima was also measured.

Drozd and V.L.Leveshin (1961) studied the spectral distribution of radiation from non activated ZnS, CdS
phosphors as a function of temperature. The luminescence spectra of ZnS - CdS- NaCl 2% phosphor were investigated as the composition is varied from 100% ZnS to 100% CdS and the temperature was varied from 195°C to +180°C. Three emission bands were found. The first was observed over the entire range of temperature and composition. Second was observed at temp. below -120°C for CdS concentrations ranging from 5 to 95%. The third band appears at 35% CdS and become more intense as the CdS concentration increases. All the bands shifted towards longer wavelengths as the cadmium concentration is increased. A slight shift in the same direction is observed for the first band when the temperature is lowered.

Determination of the trapping centre concentration, binding energies and recombination constants from the luminescence of ZnCdS phosphor were studied by H.Eder 1962, (German)

1.32(E) **WORK ON ML OF MIXED PHOSPHORS:**

Djordjevic (1978) of the US Army Armament Research and Development Command, Blallistic Research Laboratory, maryland, measured the ML spectrum and Roetgen luminescence. (X-ray excitation) spectrum of samples ZnCdS phosphor. Both the spectra peak are found at 540 nm.

Glass et al (1975,1977) in an experiment tested the ML of five inorganic ML materials i.e. ZnF₂:Mn ZnS:Ag, ZnS:Mn, CaF₂O₇:Dy and ZnCdS, ZnCdS produced highest ML light emission.
They used this finding in a prototype design of wireless fuse system for army warheads.

The ML spectra and high pressure spectra of (Zn,Cd)S phosphors are recorded by Chandra (1982). It has been observed that the ML spectra shifted towards shorter wavelength side as compared to PL spectra. It has been seen that PL spectra shifted towards longer wavelength side, when the pressure is increased. This finding has eliminated the thermal population mechanism and thus suggested the electrical excitation. Majumdar (1984) has made an elementary survey of ML intensity in different phosphors.

Recently some work on ML of (Zn,Cd)S mixed phosphors with Cu as activator has been reported by Anjali Bhatnagar (1990).

1.4 RECENT APPROACHES TO ML STUDIES OF PHOSPHORS:

It had been known for centuries that visible trails of light are emitted on rubbing the surface of the mineral sphalarite (ZnS) with one's finger nails, until this century no systematic study was made on the ML produced from natural and synthetic zinc sulphide.

Scarmozzino (1971) reported an experiment by which he disproved the piezoelectric origin of EL field. The experiment consisted in looking for ML as a single crystal of ZnS:Cu was subjected to hydrostatic compression. On the basis of the known properties of hexagonal ZnS, he calculated that a
hydrostatic pressure $10^7$ Pa is sufficient to produce a polarization field of $10^7 V m^{-1}$ in the crystal to a rapidly changing hydrostatic pressure up to $10^9$ Pa (with a rise time of 3 ms) and ML was detected. It may simply be that the (unstated) level of copper doping was such that the ML was too low to be detected (as it is known that the ML intensity of ZnS:Cu can be as small as 1/400 of ZnS:Mn). Earlier work by Scarmozino, Alzetta et al (1970) had shown that such a quasi state bending deformation does produce ML in ZnS crystals. The null result was taken by Scarmozino as supporting a model in which ML is produced solely as a result of unpinning of dislocations from luminescence centres; under pure hydrostatic pressure dislocations will not move and so there should be no ML.

Djordjevic (1978) investigated the following five inorganic ML materials, zinc fluoride, manganese activated (ZnS: Mn) calcium pyrophosphate:dysprausm activated (CaP$_2$O$_4$: Dy) and zinc cadmium sulphide (Zn,Cd)S. It was determined that (Zn,Cd)S produced the highest ML out of the five inorganic materials tested. The overall purpose of this work was to apply the ML concept to a wireless fuse system for army warheads. The concept was tested in several prototype 60 nm low warheads and proved successful, (Glass et al 1977). He further made efforts to determine the light output of the ML of (Zn,Cd)S phosphor as a function of (i) bonding resin (ii) thickness of phosphor (iii) substrate material (steel and aluminium) (iv) impact pressure (projective velocity) and (v) temperature.
Chandra and Zink (1980 c) have carried out the qualitative investigation of the spectroscopy and dynamics of the ML of 45 common inorganic metal sulphates. It is found that the all non centro symmetric crystal donot exhibit ML.

Chandra and Majumdar (1983) have reported the temporary Mechanoluminescence of certain organic and inorganic crystals. The rate constant of the decrease in ML is found to be different for different crystals and it increases with the temperature of the crystals. It is concluded that the phase transformation may be responsible for the temporary mechanoluminescence in the crystals.

Chandra et al (1983) in spectral study of (Zn,Cd)S mixed phosphors reported that the ML spectra of (Zn,Cd)S shifted towards shorter wave length side as compared to the photoluminescence, however the photoluminescence spectra shift towards shorter wavelength side with increasing pressure with less pressure coefficient. This finding eliminates the thermal population mechanism and suggests the electrical excitation mechanism for the ML excitation. The decay of ML after the deformation of (Zn,Cd)S phosphors may be controlled by the recombination rate of holes and electrons, i.e. by the finite time required for the liberation of the electrons from the traps and for the electron transport, and consequently the decay of ML may be similar to the decay of photoluminescence (Chandra 1982).

Majumdar (1984) has suggested the existence of ML in several phosphors. He prepared several phosphors of Zns, ZnO, Zn Se and Cds:Te. From the comparative study of the ML intensity it has been reported that the Zns:Mn phosphor is
intense mechanoluminescent. It has been shown that on the basis of ML spectroscopy the phosphors can be grouped into two classes (i) phosphors, the ML spectra of which resembles other type of luminescence spectra, and (ii) phosphors, the ML spectra of which consist of other type of luminescence spectra and the discharge of surrounding gases.

The theory of ML excitation has been studied by Valiev (1986). It has been shown that the steady luminescence of plastically deformed ZnS crystals with Cu activator is of dislocation origin. He has studied the dependence of ML intensity of a wide class of parameters such as the temperature of crystal, the velocity of the moving dislocation, dislocation charge density and the depth of electron centres.

Chandra et al. (1986) reported the mechanoluminescence (ML) and electroluminescence of heavily doped ZnS : Mn phosphors. The heavily doped ZnS : Mn phosphors exhibit intense ML. The ML spectra of ZnS : Mn phosphors are similar to EL spectra of ZnS phosphor. No nitrogen emission is found in the ML of ZnS phosphors. It is concluded that the ML in ZnS : Mn phosphor is deformation induced EL. It is surprising that why the ML emission of most of intense mechanoluminescent phosphors does not contain emission from the surrounding gases.

Majumdar et al. 1988 reported the effect of impact velocity on the kinetics of ML in CdS:Te and (Zn,Cd):Ag phosphors. It is found that ML intensity first increases
with time, reaches its maximum value in a few tenths of a millisecond after the impact and then it decays. The peak in the ML intensity versus time curve increases and shift towards shorter time value with increasing impact velocity in CdS:Te phosphor.

Anjali Bhatnagar (1990) reported, that ML is optimum for a particular content of CdS in (Zn,Cd) S:Cu, Cl phosphor. This is due to the fact that microhardness is maximum for a particular percentage of the constituent material in a mixed phosphor. It is expected that ML will be optimum for a particular content of CdS in (Zn,Cd)S:Cu,Cl phosphor.

B.P. Chandra and Yuvraj Rahangdale (1990) reported the results of some theoretical approach. It is found that the ML intensity depends on three major factors, the ML efficiency, damping factor, and elastic compliance. It was concluded that the non viscous solids with high elastic compliance possessing luminescence centres with appropriate efficiency may exhibit intense ML. It is shown that the ML emission should take place only during the time at which there will be change of applied pressure with time. There should be a phase difference between the applied pressure and the emitted ML signal.
1.5 OUTLINE OF THE PROPOSED STUDIES OF ML IN DOPED (Zn,Cd)S MIXED PHOSPHOR.

The ML has been an active and interesting field of scientific research during the present century. ML has been studied by physicists, chemists, geologists and material scientists. Most of the organic and inorganic crystals exhibits ML only during their fracture. The crystals of impurity doped zinc sulphides and coloured alkali halides exhibit ML in their elastic, plastic and fracture regions. ML is also observed in the crystals of certain rare earth oxides in their plastic and fracture regions. Intense ML has been observed in the crystals of sucrose tartaric acid (Zn,Cd)S Cu, ZnS:Mn, and phenanthescence. It has been reported that the ML excitation in piezoelectric organic and inorganic crystals is due to the piezoelectrification during the mechanical deformation.

It has been shown that the ML has many potentially important applications. ML can be used as convenient self probe for the investigation of fracture of solids. The emission of light observed when a solid is deformed provides a self indicating method of monitoring the microscopic and macroscopic process occuring in the solid during deformation. Many properties of cracks may satisfactorily be understood with the help of the ML investigation. It may be useful technique to study the dislocation dynamics of crystals. Crystals which exhibit intense ML in their elastic and plastic regions may be of
great importance in the mechanooptico transducers.

Recently the fibre glasses are being used for the communication purpose. The breaking of fibre glasses give rise to ML and changes the message. The ML of thermoluminescent crystals like CaF$_2$, alkali halides and Na$_2$B$_4$O$_7$ and Li$_2$B$_4$O$_7$ glasses have been studied in detail and it has been found that the ML intensity increases linearly with the radiation dose given to the crystals. This open the possibility of ML dosimetry.

It is known that II-VI compounds exhibit many types of luminescence. The ML in II-VI compounds has been investigated in detail, the understanding of its ML is still doubtful. Meyer and Sodomka have reported that the piezoelectrification is responsible for ML excitation in ZnS. While Bredikhin and Alzetta have shown that the movement of dislocations during mechanical deformation is responsible for ML excitation in ZnS. The doubt has not been cleared satisfactorily till now. Thus the mechanism related to ML excitation in II-VI compounds need further investigation.

It has been found that the ML efficiency of ZnS depends on the concentration of activator present as well as the content of CdS in ZnS. It is anticipated that by changing the percentage of CdS, activator content and the firing temperature, an efficient mechanoluminophor may be synthesised. No systematic approach has been made in this direction. Thus the preparation of efficient mechanoluminescent phosphors need further investigation.
The ML intensity of the phosphor depends on the rate of deformation and on the mass of the phosphor. Thus for the kinetics (time dependence) study of ML with respect to different rates of deformation, different stress and with different mass of phosphor, there is a separate room for investigation.

The study on the effect of temperature on ML generally affects the efficiency of ML. There is not much data related to the temperature dependence of the ML of phosphors. It has to be investigated systematically.

The correlation of ML with EL has been studied, particularly with spectroscopic study. The correlation among the ML and EL of the phosphors with respect to the intensity and temperature dependence has not been made. It is anticipated that the systematic study of the correlation of ML with EL and PL will be able to throw light on the mechanism of the ML excitation and emission in II-VI compounds.

The purpose of this study is to examine the present phosphor system with different concentrations of the dopants such as Cu, Mn, Ag and Au with the following objectives: First, the nature or the excited state origin of ML must be unambiguously determined. Second, the electric chemical or physical properties necessary for the production of ML in phosphors would be enumerated. Finally, a mechanism or model for the ML process would be constructed which would be consistent with all the experimental data.
The following studies are proposed to be done for the present investigation:

1. Spectroscopy of ML in impurity doped (Zn,Cd)S Phosphors.
2. Effect of impact velocity on the ML of phosphors.
3. Effect of temperature on the ML of phosphors.
4. Electroluminescence of intense mechanoluminescent phosphors.
5. Mechanism of the ML excitation in the phosphors.

The studies will be made on hexagonal (Zn,Cd)S mixed phosphors.
1.6 REFERENCES

ALBERS, K., (1959) : Crystalline Phosphors, meeting
Greifswald, P 228 - 35

ALZETTA, G., CHELLA, G. and SANTUCCI, S. (1967) :
Physics Lett. 26, 94.

ALZETTA, G., CHAUDACEK, I. and SCARMUZZINO, R (1970) :
Phys. Stat. sol. (a), 1, 775.

ALZETTA, G., MINNAJA, N., and SANTUCCI, S. (1962) :

BACON, F., (1605) : "The Advancement of Learning",
Book IV, Chapter 3.

Phys. Crystallogr, 9, 96.

Sol., 34, 57.

Crystallogr., 8, 744.

BELYAEV, L. M., NABATOV, V. V., and MARTYSHEV, Yu. N., (1963) :

BELYAEV, L. M., NABATOV, V. V. PISAREVSKII, Yu. V., and SHALDIN,

BHATNAGAR, ANJALI., (1990) : "Studies on mechanoluminescence of
Cu doped (Zn,Cd)S mixed phosphors" Ph.D Thesis, Rani
Durgavati Univ., JBP (M.P)


CHANDRA, B.P and RAHANGDALE, YUVRAJ (1990): 
cryst. Res. Technol. 25, 197-208
Phys. 54, 5961.
Soc. Paris; 223, 1125.
of certain fluorescent and phosphorescent molecular 
crystals", Ph.D thesis, R.S.Univ, Raipur (M.P)
DJORDJEVIC, B.B. (1978):'Triboluminescence',
DROZEL, L. and LEVSHIN, V.L. (1961): Optika,
Spektrosof (USSR), Vol.10, No 6, 773-9.
during application and Release of uniaxial pressure 
in X-irradiated KBr, KCl, KI, LiF and NaCl crystal",
Ph.D thesis, R.S.Univ, Raipur (M.P)
Defects, 2, 239.


GRABEC, I. (1975) : Non destructive Test, 8, 258.


HEIN-RICH, P. (1820) : "Die Phopherescenz der Koper" (Nürnberg), 4 (entitled phosphorcenz durch mechanische Erregung), 425.


LEVERENZ, H.W (1950) : "Introduction to Luminescence of Solid" (John Wiley and Sons, Newyork).

LEVISON, W.G. (1904) : Science; 19, 826.


ORTMAN, H; and TREPTOW H.(1959) : Crystalline Phosphors meeting, Greifswald, P 223-7.
POLLY, F; OBRIKAT, D; and MEYER, K. (1967):
Z. angew. Phys; 22, 516.


SODOMKA, L. (1972): Kristall and Technik, 7, 975.

on Energy Transfer in condensed matter, held
at Prague from June 29 to July 2, 1976 (Charles
Univ; Prague); P. 286.

SODOMKA, L; LEISTNER, M; TESSMAR, H and
KAREL, F (1980): Kristall and Technik, 15, 1101


STRANSKI, I. N., STRASS, E; and WOLFF, G. (1955):

57, 423.


WEDGWOOD, T.(1792) : Phil.Trans.R.Soc. 82, 28


WILLIAM, G.P and TURNER, T.J,(1979) :
Solid State Communications, 29, 201.

WINKLER, H; ROPPISCHER, H. and WENDAL G.(1961) :
Z.Phys. 161, NO.3, 330-8 (Germany)

WOLFF, G; GROSS, G; and STRANSKI, I.N.(1952):
Z.Electro Chem; 56, 420.

WOLFF, G; SCHONEWALD, I. and STRANSKI, I.N, (1954):
Z.Kristall, 106, 146.