

Mechanoluminescence and high pressure photoluminescence of (Zn, Cd) S phosphors

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Abstract. The mechanoluminescence spectra of (Zn, Cd)S phosphors shift towards shorter wavelength side as compared to the photoluminescence spectra, 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 mechanoluminescence excitation. The decay of mechanoluminescence after the deformation (Zn, Cd)S phosphors may be controlled by the recombination rate of holes and electrons, i.e. by the finite times required for the liberation of the electrons from the traps and for the electron transport, and consequently the decay of mechanoluminescence may be similar to the decay of photoluminescence.

Keywords. Mechanoluminescence; high pressure phenomena; phosphors; luminescence.

1. Introduction

Mechanoluminescence (ML) or triboluminescence is a type of luminescence produced during mechanical deformation of solids. It is surprising that certain phosphors exhibit ML continuously during grinding. A large variety of phosphors reveal that the activated (Zn, Cd)S phosphors exhibit intense ML. According to the mechanism of its excitation, the ML may be classified into the following types: piezo-induced ML, tribo-induced ML, dislocation-induced ML, cleavage-induced ML, chemi-induced ML, absorption-induced ML, transition-induced ML, etc. It is not clear whether the ML in inorganic phosphors is piezo-induced or dislocation-induced (Meyer *et al* 1970; Alzetta *et al* 1970; Scarmozzino 1971; Zink 1978; Chandra *et al* 1980, 1982). The present paper reports the ML and high pressure photoluminescence (PL) of (Zn, Cd)S phosphors and discusses the possible mechanism of the mechanical population of the excited states.

2. Experimental

Figure 1 shows the schematic diagram of the instrument used for recording ML spectra. Phosphors are ground with a stainless steel rod in a pyrex vial positioned in an aluminium cell with a slit. The emission passes through two collimating lenses and is focussed on to a 2 mm entrance slit of a Bausch and Lomb $\frac{1}{2}$ m grating monochromator. A quartz plate (50 × 50 × 3 mm) placed at a 45° angle to the beam.

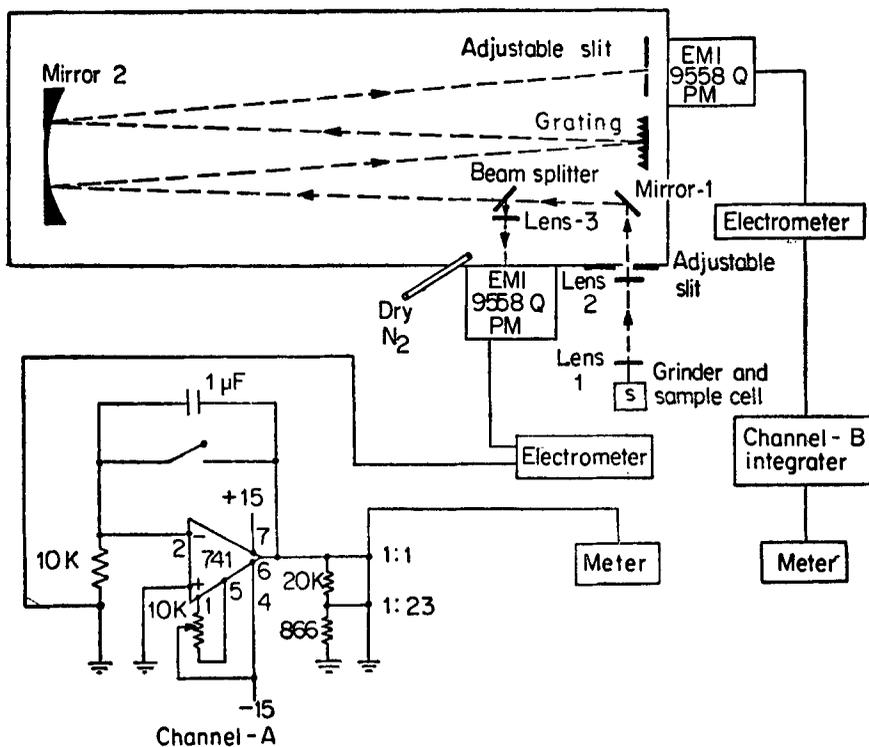


Figure 1. Schematic diagram of the instrument used for recording the mechanoluminescence spectra.

reflects 12% of the polychromatic light to a lens focussed on to a photomultiplier tube (EMI 9558Q) placed inside a refrigerated housing. The remaining 88% of the light passed through the monochromator to a 2 mm exit slit where the monochromatic light intensity is measured by a second refrigerated photomultiplier tube. The two intensity readings (labelled I_T and I_λ , for polychromatic and monochromatic intensities, respectively) were amplified and integrated over a large number of individual flashes. The ratio I_λ/I_T , removed any fluctuations in intensity caused by variations in the applied mechanical energy, crystal size, etc. At least 4 ratio readings were taken at each wavelength and the average ML intensity is plotted with error bars of one plus or minus standard deviation. The decay of PL was determined using a pulsed xenon lamp and a dual beam 564 storage oscilloscope.

The high pressure PL spectra were measured using a cell similar to the one suggested by Drickamer type I high pressure optical cell (Nicol *et al* 1972) as shown in figure 2. The cell has three sodium chloride windows, two of which are pictured. The third window lies in a direction perpendicular to the plane of paper. Each window which has an outer diameter of 6.3 mm is slowly reduced to around 1 mm for the inner diameter. The phosphor was packed into the cylindrical chamber within the cell as follows. A thin tungsten piston was placed adjacent to the large piston A and followed by a 3 mm diameter disc of sodium chloride. These two layers elevated the sample so that its placement was in front of the windows. A small amount of phosphor was powdered in an agate mortar and pestle along with an equal amount of sodium chloride. Due to mixing of the phosphor in this manner, the applied pres-

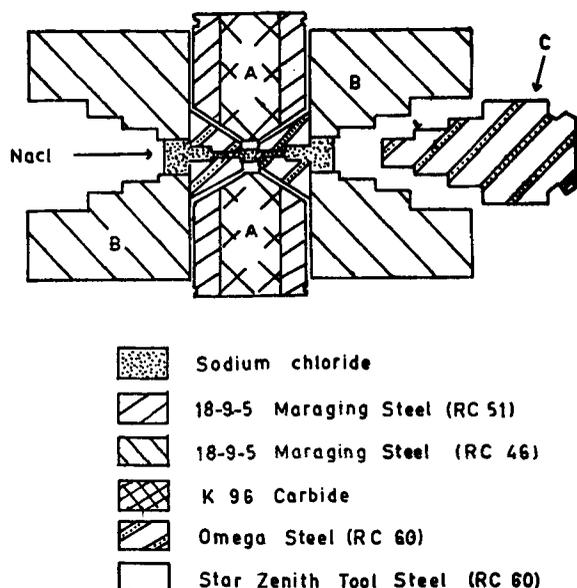


Figure 2. Schematic diagram of the high pressure cell.

sure becomes more hydrostatic. The phosphor NaCl mixture was placed tightly into a half-moon shaped piece of salt about 1.5 mm thick. The other half of the sample chamber was filled with a solid half disc of NaCl of the same thickness. It was necessary for the packing to be done in this manner due to the tendency of solids to absorb and emit at their surface. The displacement of the cell by trial and error helps in proper alignment of the luminescence emission with the exit window. Another 3 mm diameter salt disk was placed on top of the packed sample followed by a thicker tungsten piston. The sample was then closed off by the large piston A. Filtered ultraviolet excitation light from a 100 W Hg lamp was focussed by a lens through one of the windows. Emission from the sample was focussed by a lens and monitored at right angles to the excitation. Pressure was applied to the sample by means of a hydraulic press which pushed the outer piston labelled A. These pistons in turn transferred the force to the small tungsten pistons and finally to the sample. The pressure was measured by a strain gauge connected to a load cell in the hydraulic press. The gauge was calibrated by ruby emission to read 50 strain units for each 3 kbar of pressure. After each increase in pressure it was necessary for the pressure to equilibrate throughout the system. Emission signals passed through a chopper which was coupled to a lock-in amplifier. The emission then entered the monochromator to be scanned over the peak maximum. The signal was detected by an IP 28 photomultiplier tube and was recorded on a strip chart recorder.

The instrument used for the excitation of ML at different impact velocities is based on an air-driven steel piston. Figure 3 illustrates the design of the instrument. The air pressure is variable upto 27 Pa. A velocity transducer (Hewlett-Packard Model No. LVSYNLVI) is connected to the piston to measure its velocity. The calibration constant of the velocity transducer was $0.238 \text{ V cm}^{-1} \text{ sec}$. Below the piston, there is a vertically adjustable sample holder. The crystal is placed on a lucite plate inside the sample holder. The luminescence is monitored from below the transparent plate

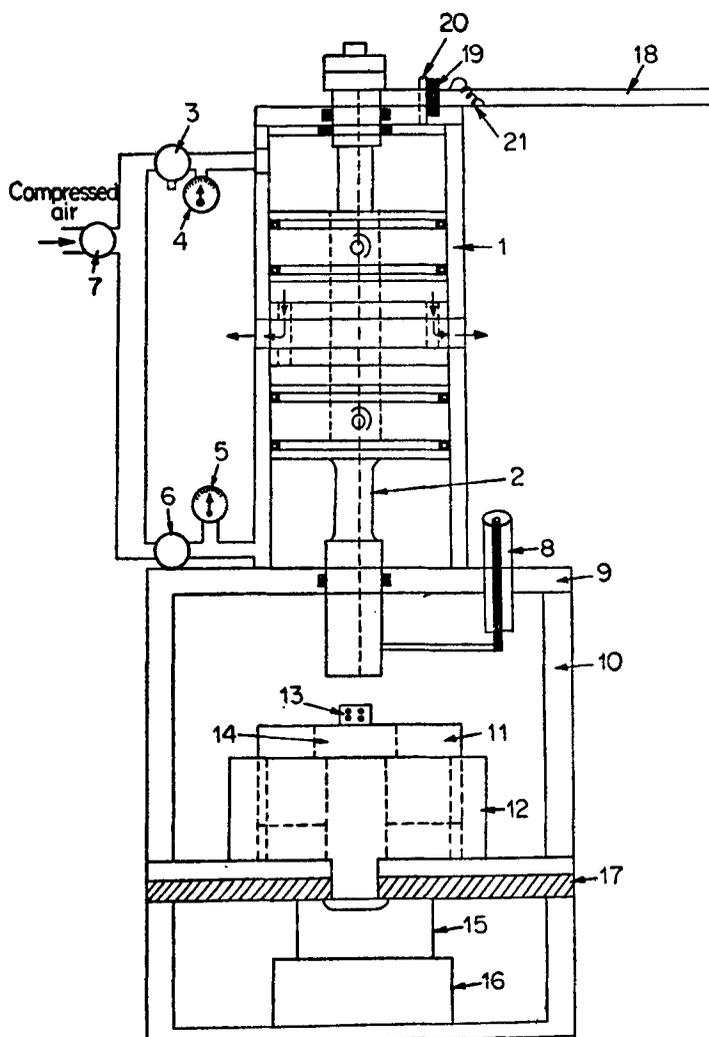


Figure 3. Schematic diagram of the instrument used for the excitation of mechanoluminescence at different impact velocities (1. cylinder, 2. piston rod, 3. three way valve, 4 & 5. gauges, 6 & 7. regulators, 8. velocity transducer, 9. piston guiding plate, 10. spacers, 11. sample holder, 12. sample holder housing, 13. crystal, 14. lucite plate, 15. photomultiplier tube with housing, 16. photomultiplier housing platform, 17. rubber ring, 18. trigger handle, 19. pin stop, 20. centre pin axis and 21. spring).

using the photomultiplier tube (response time 7μ sec) connected to a dual beam storage oscilloscope (Tektronix 564). To start the experiment, the piston is released and moved under the forces of the compressed gas. By changing the pressure, the impact velocity of the piston can be changed from very low values to 500 cm/sec. To trigger the oscilloscope, the crystal is covered with a thin aluminium foil which is connected to one terminal of a 1.5 V battery through a resistance. The other terminal of the battery is connected to the piston. When the piston touches the aluminium foil on the crystal, the pulse which appears across the resistance triggers the oscilloscope. The rise and decay of the luminescence and the velocity of the piston are recorded simultaneously. The total intensity of ML is determined from the area

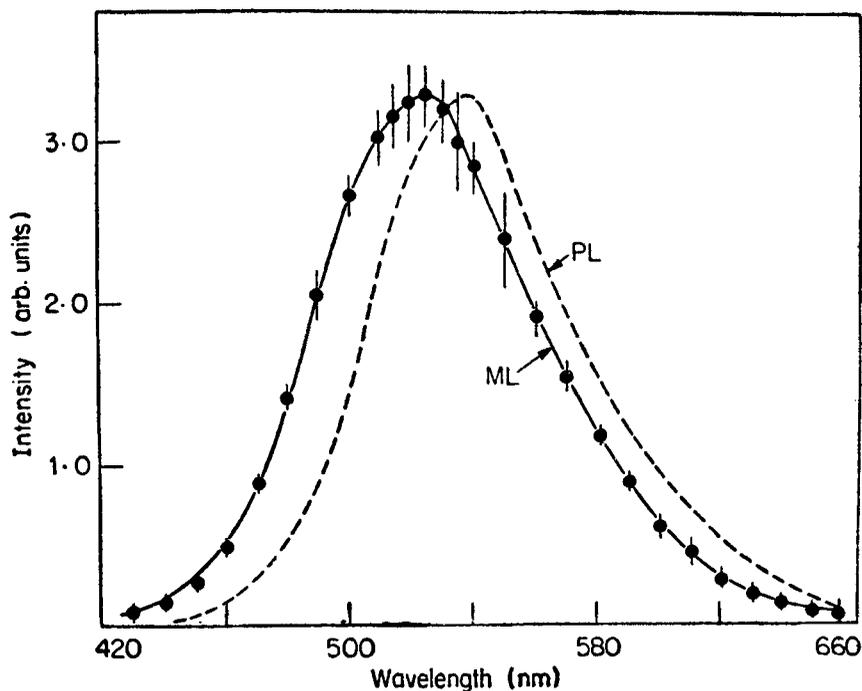


Figure 4. Mechanoluminescence and photoluminescence spectra of (Zn, Cd)S DuPont 1200 phosphors.

below the ML intensity versus time curve which is measured with a planimeter. The compression of the impact instrument was 0.32, 0.52, 0.63 and 0.76 mm for the impact velocity of 63, 210, 315, and 378 cm/sec, respectively. The (Zn, Cd)S used were DuPont 1200 phosphors which were crystallites of an average grain size 5 microns.

3. Results

Figure 4 shows the ML and PL spectra of the (Zn, Cd) S phosphors. It is seen that the ML spectra shift towards shorter wavelength side as compared to the PL spectra. The ML spectra do not contain any nitrogen emission. Figure 5 shows the effect of hydrostatic pressure on the energy, E_{\max} , corresponding to the peak of the PL spectra. It is seen that the E_{\max} increases with increasing pressure on the phosphors. The pressure coefficient for the increase in E_{\max} is found to be $44 \text{ cm}^{-1}/\text{kbar}$.

The time dependence of the ML after the impact of a moving piston is shown in figure 6a. The ML appears during the impact of the piston. The intensity of ML increases with time and attains a maximum value after a particular time and then it decreases with time. Figure 6a also illustrates the time dependence of the velocity of air-driven piston. The ML appears even after the piston has stopped. It is seen that the nature of time dependence of ML changes at the time the piston attains a zero velocity. Figure 6b shows that the intensity, I_m , corresponding to ML intensity versus time curve, and the total intensity of the ML (*i.e.* the area below ML intensity

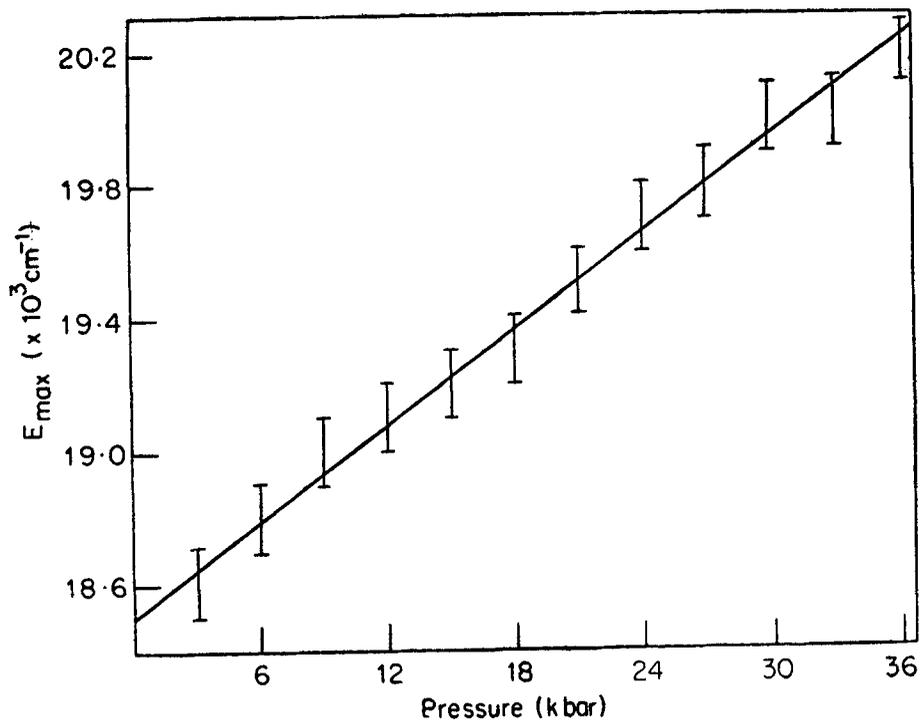


Figure 5. Effect of hydrostatic pressure on the energy, E_{\max} corresponding to the peak of the photoluminescence spectra of (Zn, Cd)S Du Pont 1200 phosphors.

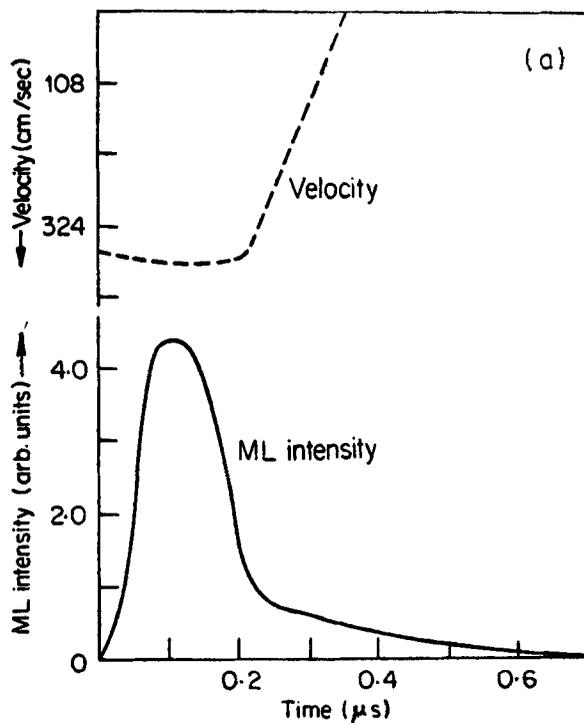


Figure 6(a). Time dependence of the mechanoluminescence intensity (bottom) and the velocity of piston (top), for (Zn, Cd)S phosphors.

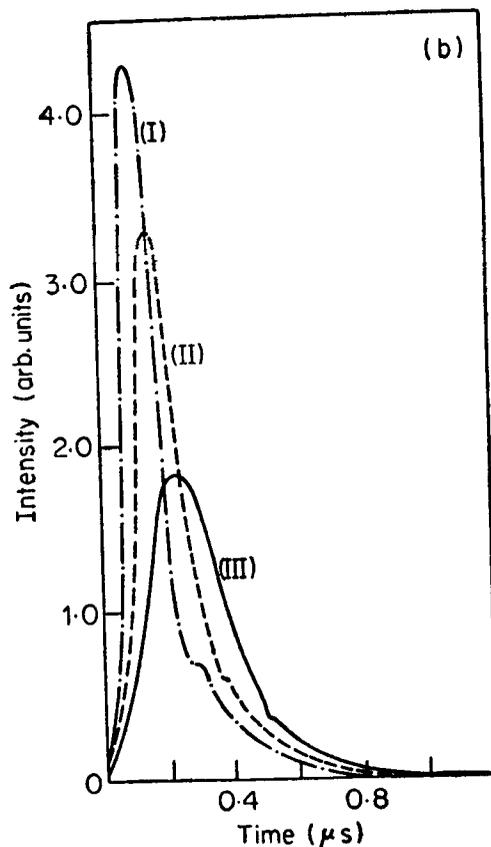


Figure 6(b). Time dependence of mechanoluminescence of (Zn, Cd)S phosphors at impact velocities of (I) 378 cm/sec. (II) 287 cm/sec. and (III) 155 cm/sec.

versus time curve) increases with the impact velocity of the piston. The time corresponding to the peak of the ML intensity versus time curve decreases with the impact velocity.

Figure 7 shows the plot of the logarithm of ML intensity I versus time t . The dotted portion corresponds to the ML decay between the peak of the ML versus time curve, and the time at which the moving piston stops. The solid line represents the decay after the piston has stopped. The slope of the dotted curve decreases with the increasing values of the impact velocity. However, the slope of the solid line is independent of the value of the impact velocity. It is nearly equal to the slope of the PL decay. The slope of the dotted lines is higher than that of the solid lines.

4. Discussion

The results on ML and PL spectroscopy suggest two main possibilities of the mechanical-induced excitation of the luminescence centres; first, the thermal population of the excited state at high pressure and, second, the electrical excitation of the luminescence centres.

If the ground and the excited states respond differently to the medium, the appli-

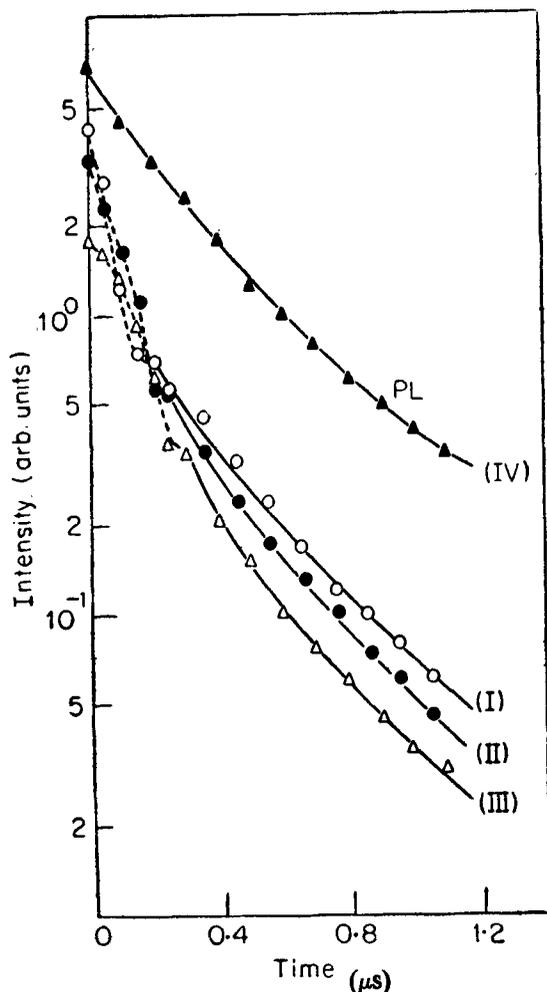


Figure 7. Plots of log of the ML and PL intensity versus time for (Zn, Cd)S phosphors.

cation of pressure can cause a shift in the relative energies and the inter-nuclear coordinates of their minima. Thus, at high pressure, thermal population of the excited states different from the ground state could occur even though the Frank-Condon transition energy is much larger than kT (Hardy and Zink 1976). Release of the pressure from the phosphor could result in the luminescence centres in their excited states at lower pressure. Drickamer *et al* (1972) demonstrated that states which are higher in energy than the ground state at atmospheric pressure can become thermally populated at high pressures. The observed increase in emission energy of (Zn, Cd)S phosphors with increasing pressure (figure 5) does not support the population of the excited states by the mechanism discussed above. Moreover, it is found that the ML spectra of many phosphors like ZnS: Cu, etc. contain nitrogen emission in addition to the luminescence emission. It is difficult to propose an intramolecular pressure mechanism which could explain the emission of absorbed molecular nitrogen.

It seems that the mechanism of excitation of the luminescence centres in (Zn, Cd)S phosphors during their deformation is related to the mechanical-induced electric

field. It is known that the electroluminescence spectra shift towards shorter wavelengths which depend on the magnitude and the frequency of the electric field. Thus, the ML in (Zn, Cd)S phosphors may be the deformation-induced electroluminescence. If the electric field produced during the mechanical deformation of phosphors is of sufficient strength, then the luminescence may also appear due to the tunnelling process. During the mechanical deformation of the phosphors, the electric field may be produced due to the piezo-electrification (Chandra 1981) and also due to the movement of the charged dislocations in crystals. Scarmozzino (1971) applied a hydrostatic pressure on ZnS:Mn phosphors, which was large enough to produce a piezoelectric polarization higher than that required to excite electroluminescence. In this experiment, piezo-electrification large enough to cause ML does occur, but it does not excite ML. This result does not support the ML excitation to be due to the piezo-electrification. Bredikin and Shmurak (1979) have found the ML in ZnS:Cu crystals only during the plastic deformation. Since the existence of charged dislocations is well known in ZnS type crystals (Bredikin and Shmurak 1975), the ML excitation in ZnS and other ZnS type crystals may be due to the electric field produced during the movement of the charged dislocations. In the experiment of Scarmozzino (1971), the ML may not appear because the dislocations may not move during the hydrostatic compression.

Phosphors are luminescent crystallites whose grain size is generally of the order of few microns. Now, let us discuss whether or not the movement of dislocations is possible in the phosphors. It is well known that the grain size of the phosphors decreases with their grinding or milling (Sodomka 1964; Sekine and Kotera 1976). The expressions for brittle fracture derived by Griffith suggest that the stress required to fracture the solids increases with decreasing dimension of the grains (van Bueren 1968). Since the crystals of zinc sulphide and zinc cadmium sulphide have partly the ionic and covalent behaviours, the brittle fracture of the grains of these materials may be expected (van Bueren 1968; Klasen-Nekljudova and Rozanski 1962). In the beginning of milling, the fracture occurs on the boundary of mosaic blocks of the crystal grains and then the grain size decreases. As soon as the initial crystal grain cracks into coherent regions, the next part of the milling process starts. During the milling of the crystallites, the stresses accumulate and the density of newly created dislocations and other imperfections caused by deformation increases. If the dislocation density reaches the critical value required to attain the critical stress for fracture, the crystallites fracture and then the stress is released. At fracture, the dislocations are partly released; however, their density increases again until there produces another fracture. The process of accumulation of stress and its release at fracture is repeated with attenuation until the grain size is reduced to such a value that for the stress used during milling, the imperfections are no longer maintained in the crystallite so densely that a further fracture could occur. At this stage, imperfections are easily released through the surface. This happens when the grain size is smaller than or equal to the critical dimensions of the 'microcrack' needed for the crystal fracture. Using the x-ray technique, Sodomka (1964) has shown that the density of dislocations in impurity doped ZnS phosphors increases from 1.32×10^9 to 1.555×10^{12} per cm^2 when the grain size is decreased from 30 to 2 microns by ball-milling technique. During deformation of a crystal, new dislocations are created, their movement takes place and then they become stationary. Thus, the density of stationary dislocations increases with deformation. It is thus evident

that dislocations movement is possible in phosphors until their grain size is smaller than or equal to the critical dimension of the microcracks, the expansion of which leads to the crystallite fracture.

It is seen from figure 7 that initially the ML of (Zn, Cd)S phosphors decays faster. The kinetics of decay changes just before the stopping of the motion of the piston used for the deformation, and then the ML decays with a slow rate. Since the ML spectra of (Zn, Cd)S phosphors contain only the solid state luminescence and they do not contain nitrogen emission, the two kinetics should be related only to the earlier emission. Many speculations can be made for the change in the ML kinetics during the stopping of the piston: First, that the moving piston may get rebounded after attaining the zero velocity and if there is ML emission during the release of the pressure, then superposition of the ML produced during the impact and that produced during the release of the pressure may increase the ML intensity. Our independent experiment suggests that, the intensity of ML produced during the release of pressure is much less as compared to the intensity of ML produced during the application of the pressure. Thus, the observed increase in the ML intensity during the stopping of the piston may not be due to the superposition of the ML during the impact and during the release of the pressure. Moreover, this may not explain the absence of ML emission after the stopping of the piston in many crystals exhibiting fluorescence and nitrogen emission ML. It is to be noticed that only the ML of phosphorescent crystals exhibits two kinetics.

The second speculation for the change in the ML kinetics during the stopping of the piston may be the disappearance of the impact generated electric field after the stopping of the piston. Due to the piezo-electrification or due to the movement of the charged dislocations, an electric field resembling the shape of the impact wave may be produced during the impact of a piston on the phosphors. Although the electric field produced during deformation may excite luminescence centres, it may also perturb the ground and excited states of the system and consequently, the decay rate may increase. Thus, the ML may decay at a faster rate, during the impact (after attaining the maximum value) and may decay at a slow rate; that is, with its original rate of PL decay, in the absence of electric field after the stopping of the piston. Figure 7 shows the changes both in the ML intensity and the decay kinetics after the stopping of the piston. This process may be applicable for the phosphorescent molecular crystals where the electric field changes the decay time considerably. The third possibility may be the delayed recombination of electrons with the luminescence centres. After the excitation of the electrons during the mechanical deformation, some of them may be removed away into more remote regions, whereas some of them may recombine radiatively by giving rise to transient ML. The removed electrons, which have dropped into traps may return to the excited region after the disappearance of the electric field and may recombine there with the activator ready for recombination. The decay of ML may be controlled by the time dependence of this recombination rate, that is by the finite times required for the liberation of the electrons from the traps and for the electron transport. Thus, the decay of ML intensity in (Zn, Cd)S phosphors may be similar to decay of their PL.

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