

Preparation and characterization of gold doped (Zn, Cd)S mixed phosphors for mechano-optical transducers

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Abstract. When mechanically excited, initially the ML intensity increases, attains a maximum value and then decreases with time. The total ML intensity I_T initially increases with the impact velocity V_0 of piston and attains a saturation value for higher values of V_0 and follows the relation $I_T = I_T^0 \exp(-V_c/V_0)$ where I_T^0 and V_c are constants. The ML intensity is maximum for 20% CdS contents in the (Zn, Cd)S phosphors due to increase in hardness which may in turn increase the fracture stress and subsequently the piezoelectric field strength. The wavelength corresponding to the peak of both the ML and PL spectra shift towards longer wavelength with increasing CdS contents. Some models are discussed and it is concluded that the impulsive deformation of these phosphors may be due to piezoelectrification of newly created surfaces. The similarity of ML spectra with EL and PL spectra suggests that although the excitation processes are different, emission process is governed by the states of similar nature.

Keywords. Mechanoluminescence; mixed phosphors; ML spectra; piezoelectrification; electroluminescence; photoluminescence.

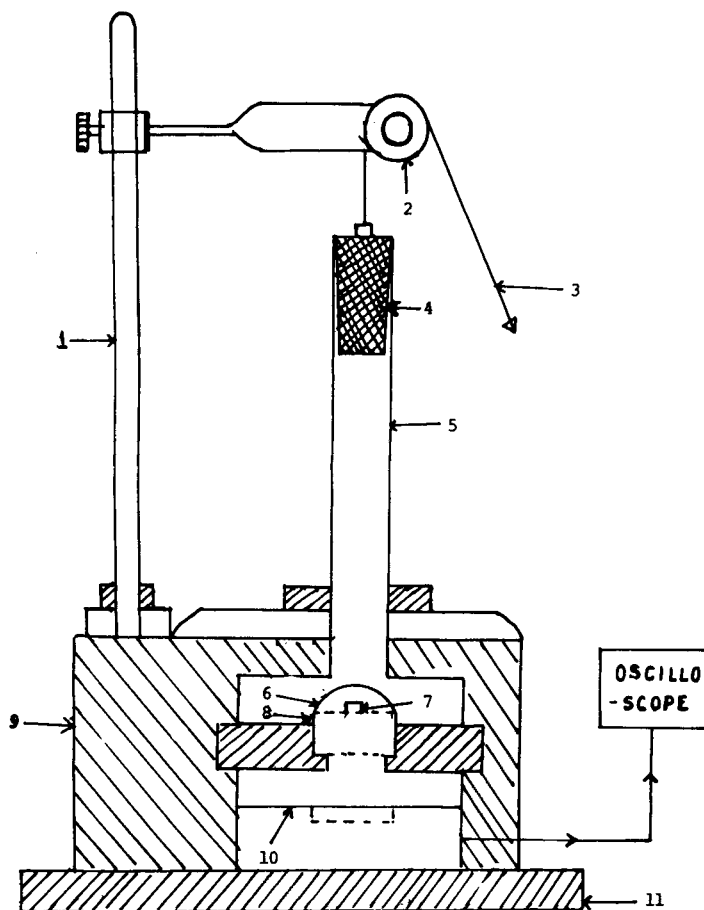
1. Introduction

The last two decades have witnessed a phenomenal growth in research and application of mechanoluminescence for the following reasons: the phenomenon of ML provides an ultrasensitive micro-probe for the investigation of cracks in solids and the highly efficient ML materials may be used for various applications such as mechano-optical transducers where the users will be able to excite display by simply pressing the solid. The present paper reports the preparation and characterization of efficient mechanoluminophors of gold doped (Zn, Cd)S and discusses the possible mechanism of ML excitation.

2. Experimental

The preparation of phosphors was carried out following the conventional technique reported earlier (Tiwari *et al* 1994). The (Zn, Cd)S: Au, Cl phosphors (hexagonal) and (Zn, Cd)S: Au, Cl phosphors (cubic) were prepared by firing for 1 h in nitrogen atmosphere at 1100°C and 900°C respectively. The activator concentration was varied from 0 to 10,000 ppm and concentration of CdS was varied from 0 to 40 mol%.

The schematic diagram of the device used for measuring the ML activity is shown in figure 1. For measuring the ML activity, 5 mg phosphor was placed on a transparent lucite plate below the guiding cylinder. An RCA 931 photomultiplier tube was used for monitoring the luminescence from below the lucite plate. The phosphor was covered



1—Stand; 2—Pully; 3—Metallic Wire; 4—load; 5—Guiding cylinder; 6—Aluminium foil; 7—sample; 8—Transparent lucite plate; 9—Wooden block; 10—Photomultiplier tube; 11—Iron base mounted on a table.

Figure 1. Schematic diagram of the experimental arrangement used for measuring the time dependence of ML in phosphors.

with a thin aluminium foil and fixed with an adhesive tape. This arrangement was made to eliminate the error in the measurement of ML intensity due to scattering of crystallite fragment during the impact of load onto the crystal. The ML was excited impulsively by dropping a hollow cylinder of 800 g (2 cm dia) from different heights through a guiding hollow cylinder. The output of the PMT was connected to Scientific HM 307 oscilloscope having P7 phosphorescent screen capable of sustaining a trace in dark for more than a minute. The ML vs time curve was determined by recording the trace onto the oscilloscope screen and total ML intensity was determined by measuring the area below this curve. The error in the measurement of ML intensity was found to be $\pm 6\%$. No correction in ML intensity was made for spectral response of the photomultiplier tube.

For measuring the effect of temperature on the ML of phosphors, the phosphors were placed onto a lucite plate which was heated by two heating filaments. The

ML measurements were carried out when the device had attained a steady state temperature.

The ML spectra were recorded with the help of a series of optical filters. The electroluminescence (EL) and photoluminescence (PL) spectra were recorded using grating monochromator as described earlier (Chandra *et al* 1991).

3. Results

The time dependence of the ML of (Zn,Cd)S: Au, Cl (1000 ppm Au, 20% CdS) phosphors for different impact velocities of a load of 800 g is shown in figure 2. The ML intensity increases with time, attains a maximum value and then decreases with time.

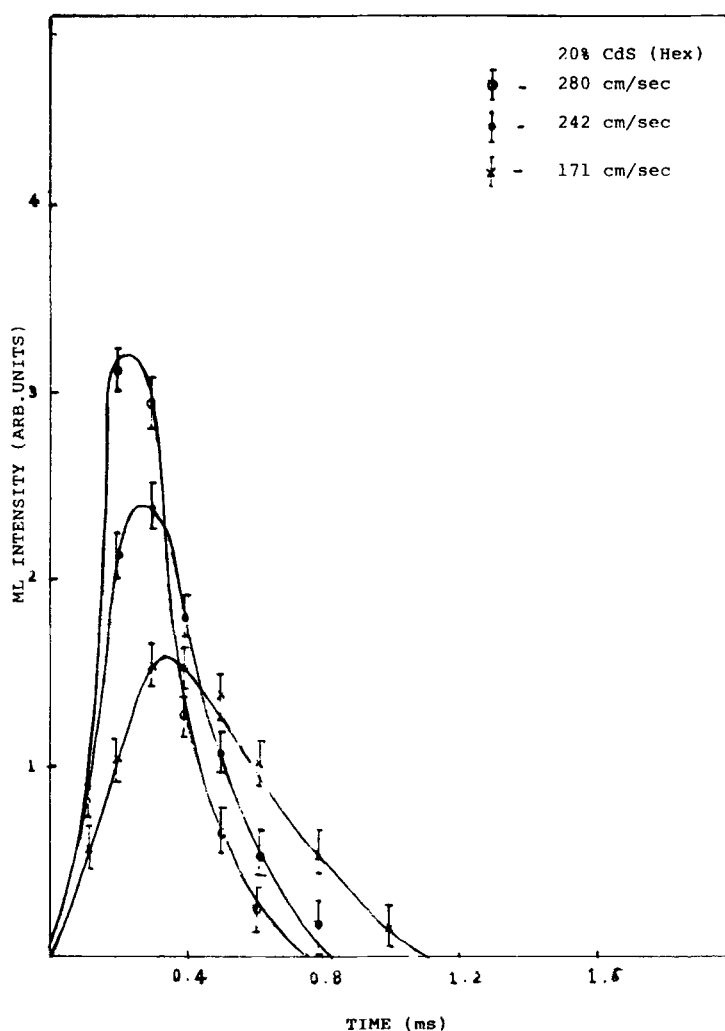


Figure 2. Time dependence of mechanoluminescence intensity of (Zn, Cd)S: Au, Cl phosphors for different impact velocities.

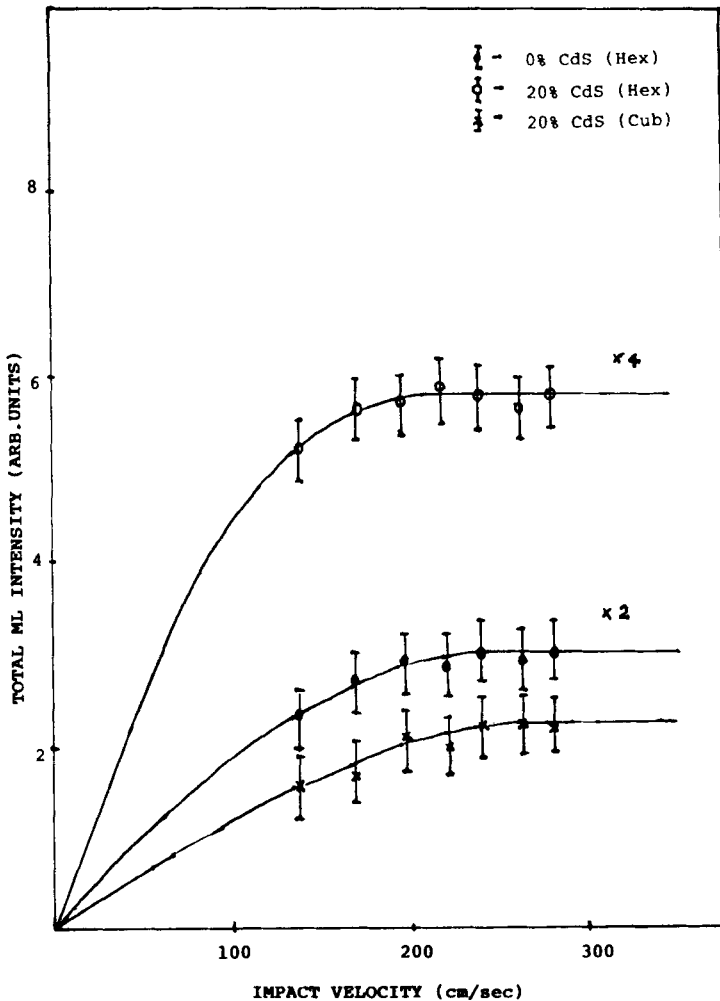


Figure 3. Dependence of total ML intensity I_T of (Zn, Cd)S: Au, Cl phosphors on the impact velocity V_0 .

Figure 3 shows the total ML intensity I_T vs time curve. It initially increases with the impact velocity V_0 and then attains a saturated value of the impact velocity. Figure 4 shows that the plot of $\log I_T$ vs $1000/V_0$, is a straight line with negative slope, following the relation

$$I_T = I_T^0 \exp[-V_c/V_0], \quad (1)$$

where I_T^0 and V_c are constants.

Figure 5 shows that for a given activator concentration (1000 ppm), the ML intensity is maximum for a particular CdS content i.e. for 20% of CdS in (Zn, Cd)S: Au, Cl phosphors. Figure 6 shows the ML spectra of cubic and hexagonal (Zn, Cd)S: Au, Cl phosphors, respectively for 1000 ppm activator concentration and for different contents of CdS in the phosphors. It is seen from these figures that the peaks of the ML spectra shift towards longer wavelength values with increasing CdS contents.

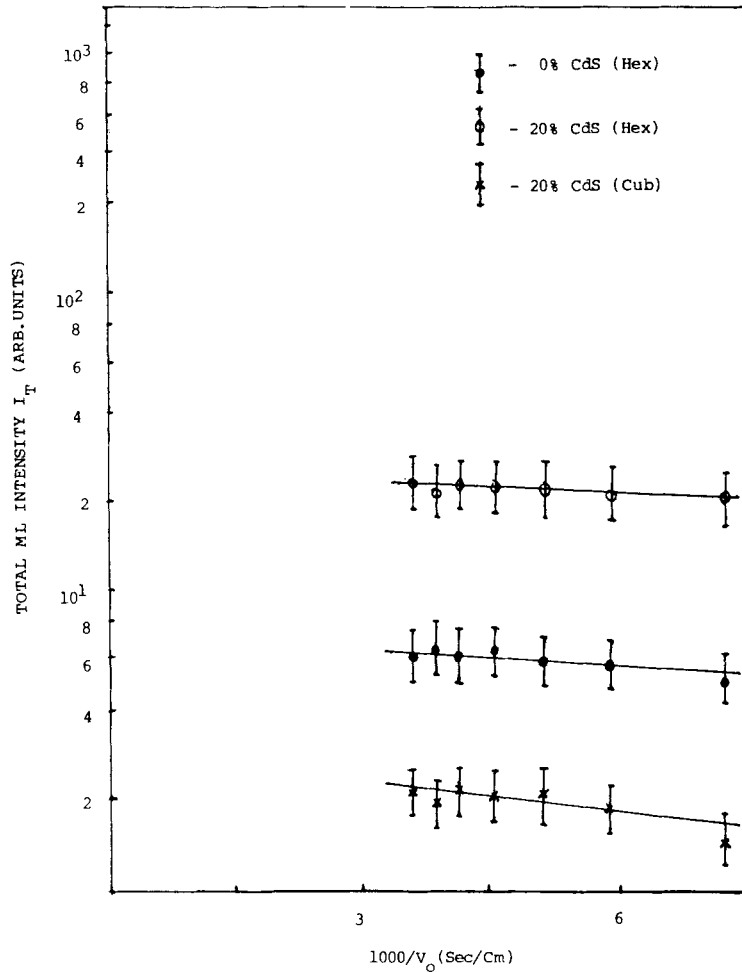


Figure 4. Plot of the logarithm of total ML intensity I_T vs $1000/V_0$ for (Zn, Cd)S: Au, Cl phosphors.

Figure 7 shows the EL spectra of (Zn, Cd)S: Au, Cl phosphors. It is observed that the peaks of the EL spectra shifts towards higher wavelength values with increasing CdS contents in the phosphors.

Figure 8 shows the PL spectra of gold doped (Zn, Cd)S mixed phosphors. It is seen that the peak of PL spectra shifts with increasing CdS percentage.

Figure 9 shows the effect of temperature on the total ML intensity I_T . It is observed that the I_T decreases with temperature and finally disappears beyond a particular temperature T_c which is much less than the melting point of the phosphor. The decrease of the ML intensity with temperature shown in figure 10 follows the relation

$$I_T = I_T^0 (1 - T/T_c)^n, \quad (2)$$

where I_T^0 is constant, n the slope of $\log I_T$ vs $(1 - T/T_c)$ plot and its value lies between 0.90 and 1.10 for the (Zn, Cd)S phosphors. T_c is the temperature at which ML disappears. The value of T_c for 20% of CdS content in (Zn, Cd)S: Au, Cl is 130°C and

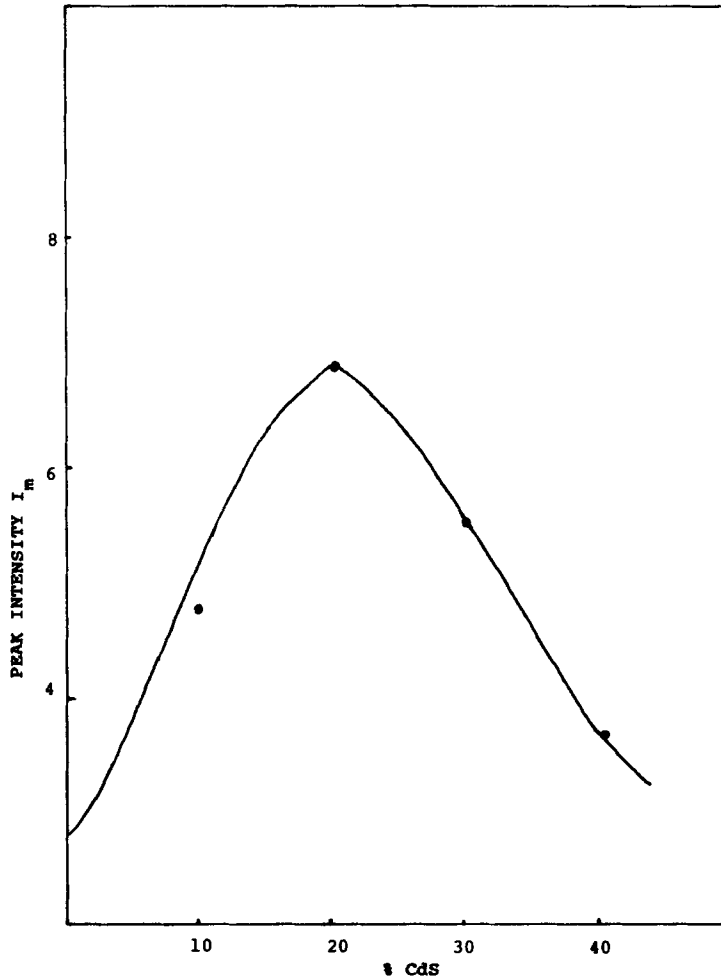


Figure 5. Effect of CdS concentration on peak ML intensity I_m in hexagonal (Zn, Cd)S: Au, Cl phosphors.

140°C in cubic and hexagonal phosphors, respectively and 136°C for hexagonal phosphors without CdS content.

4. Discussion

The ML in gold doped (Zn, Cd)S phosphors may be discussed with respect to three main features: (i) mechanical characteristics of ML, (ii) mechanism of ML and (iii) effect of temperature on the ML.

4.1 Mechanical characteristics of ML

It is known that II–IV compounds exhibit ML during their elastic, plastic and fracture deformations (Zhang and Bryant 1981; Chandra 1985). Since the ML was excited

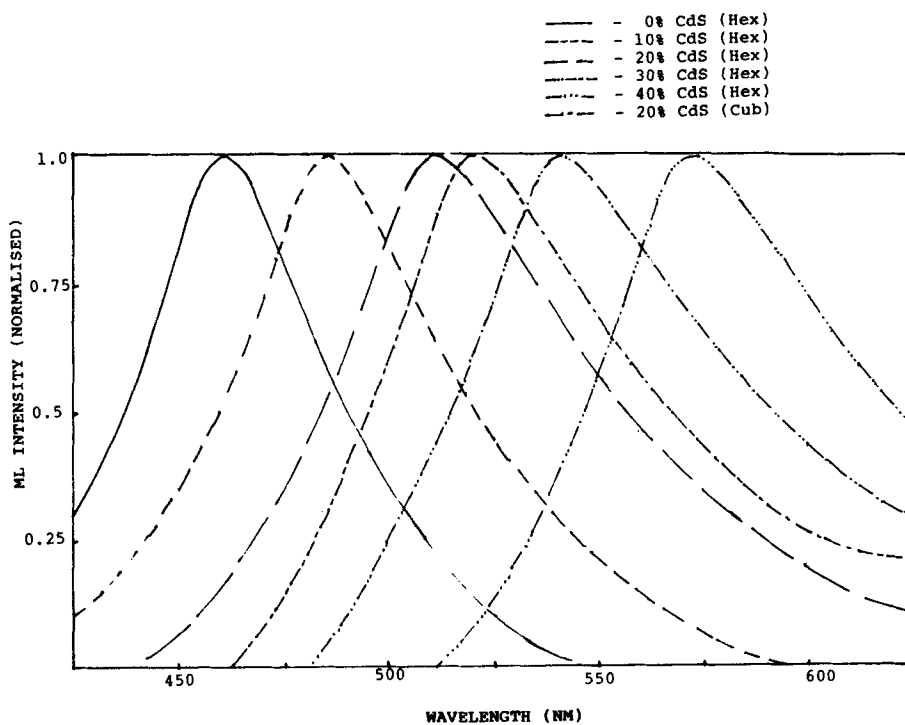


Figure 6. ML spectra of (Zn, Cd)S: Au, Cl phosphors for different CdS concentrations.

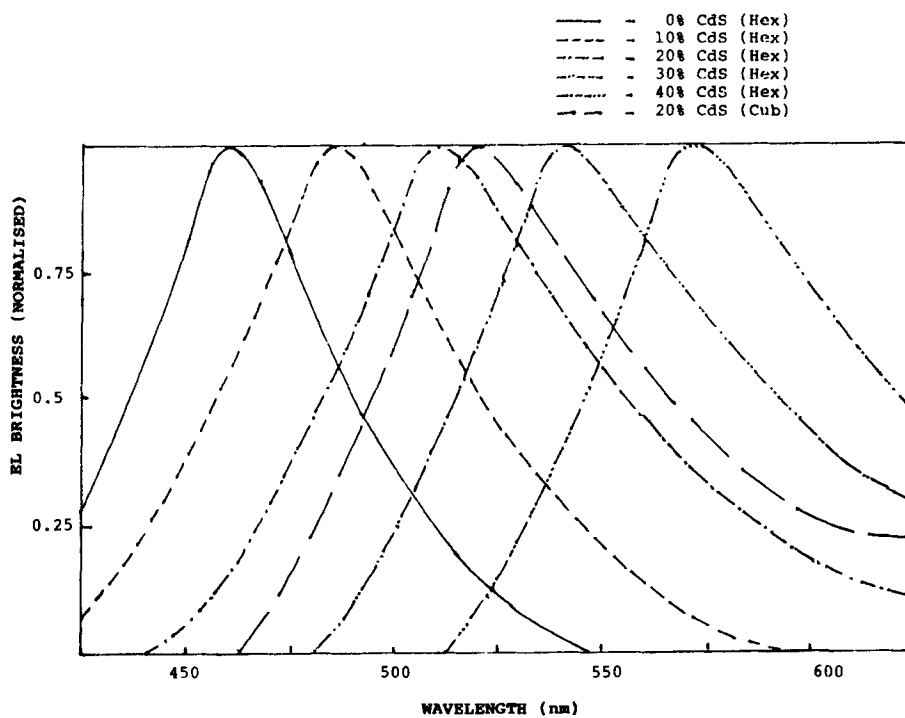


Figure 7. EL spectra of (Zn, Cd)S: Au, Cl phosphors.

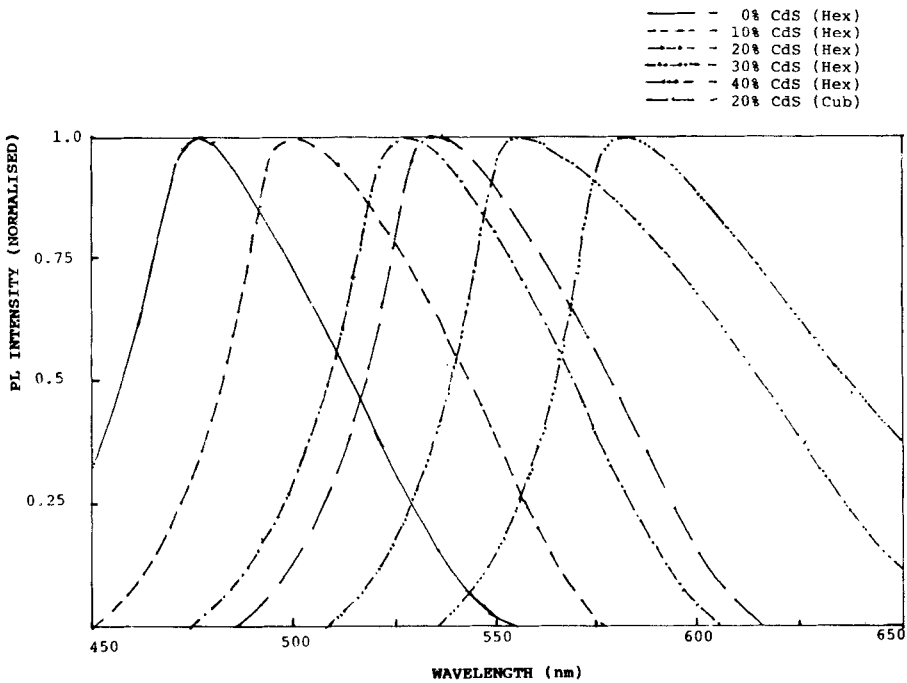


Figure 8. PL spectra of (Zn,Cd)S: Au, Cl phosphors.

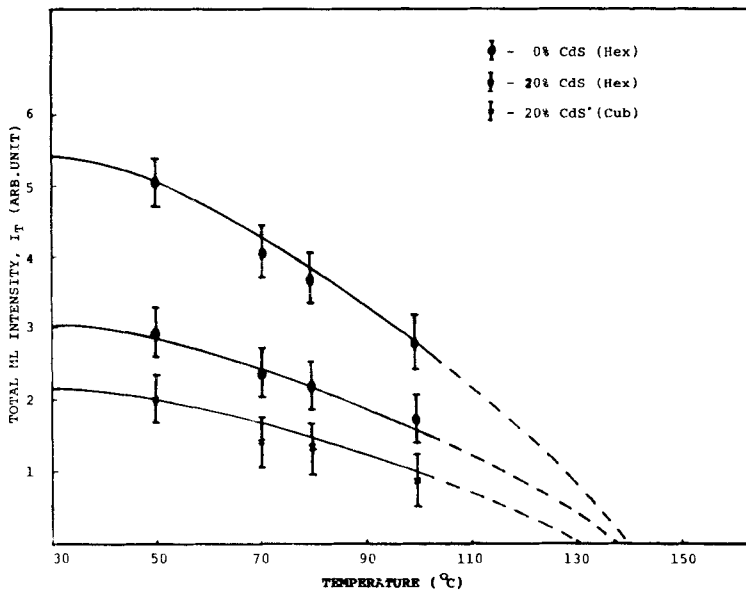


Figure 9. Effect of temperature on total ML intensity I_T of (Zn,Cd)S: Au, Cl phosphors.

impulsively, the fracture of phosphor crystallites was the major factor responsible for the ML emission.

4.1a *Time dependence of mechanoluminescence:* In the impulsive excitation of ML,

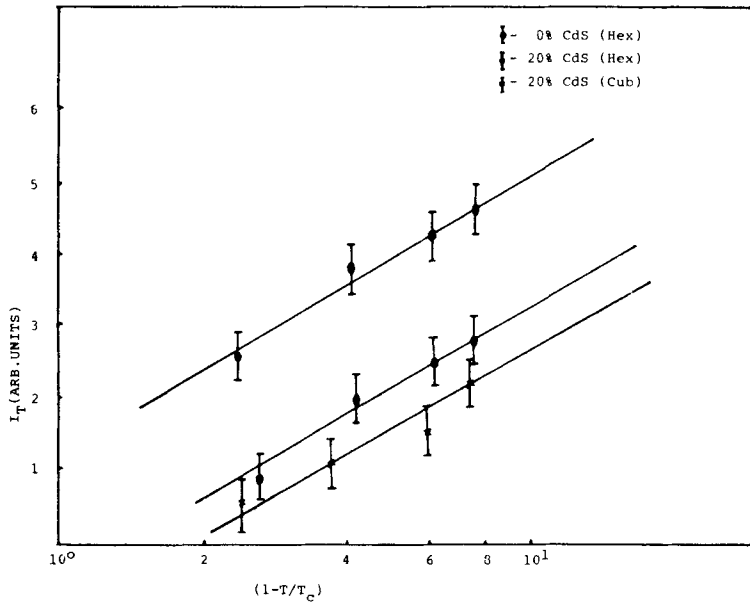


Figure 10. Plot of logarithm of I_T vs $(1 - T/T_c)$ for (Zn, Cd)S: Au, Cl phosphors.

the ML intensity is found to be directly proportional to the total area of newly created surfaces in the crystals (Zink 1978; Chandra *et al* 1983). Therefore there is a possibility to describe phenomenologically the time dependence of the ML produced during impact of a piston on the crystal in terms of newly created surfaces. Considering the phosphors as a collection of crystallites, the equation of the ML may be expressed as (Chandra *et al* 1986)

$$I = \frac{2\eta V^{2/3} (M_0)^{1/3} \alpha^{2/3}}{h} V_0 \exp(-\beta_1 V_0 t) \left\{ \exp \frac{\alpha}{h_1 \beta_1} [1 - \exp(-\beta_1 V_0 t)] - 1 \right\}^{1/3} \quad (3)$$

where η is the normalization constant which takes into account the ML produced during creation of a unit surface area of the crystal, i.e. η is related to the ML efficiency of the phosphors, V the volume of the crystal, $M_0 = \beta/\alpha$, where β and α are constants, h_1 the thickness of the crystal, V_0 the initial velocity of the load, and t the time.

Equation (3) shows that the ML intensity is zero for $t = 0$, as well as for $t = \infty$. Thus the ML intensity should be maximum for a particular value of t . For smaller value of t , (3) may be written as

$$I = \frac{2\eta V^{2/3} M_0^{1/3} \alpha^{2/3}}{h_1} V_0 \exp(-\beta_1 V_0 t) \left\{ \exp \frac{\alpha V_0 t}{h_1} - 1 \right\}^{1/3} \quad (4)$$

Since α/h_1 is much greater than 1 the first term inside the curly bracket in the above equation will be much greater than 1 after same value of $V_0 t$. Thus (4) may be

approximated as

$$I = \frac{2\eta V^{2/3} M_0^{1/3} \alpha^{2/3}}{h_1} V_0 \exp \left[\left(\frac{\alpha}{3h_1} - \beta_1 \right) V_0 t \right], \quad (5)$$

which shows the exponential increase of I with t , which has been determined experimentally also.

For higher values of t , (3) may be written as

$$I = \frac{2\eta V^{2/3} (M_0)^{1/3} \alpha^{2/3}}{h_1} V_0 \exp(-\beta_1 V_0 t) \cdot \{e^{\alpha/\beta_1 h_1} - 1\}^{1/3}, \quad (6)$$

which shows the exponential decreases of I with t and matches with experimental observations. The ML intensity goes to zero at infinite time.

4.1b *Total intensity of mechanoluminescence:* The total intensity of ML is given by (Chandra et al 1986)

$$I_T = 6\eta V^{2/3} M_0^{1/3} \alpha^{-1/3} \exp \left(\frac{\alpha}{3h_1 \beta_1} \right). \quad (7)$$

The value of $1/\beta_1$ is related to the maximum compression at a particular velocity (Mott 1952). The compression attains a saturation value due to work hardening in the crystal, which can be raised with great difficulty by raising the value of external stress on the crystal (Taylor 1934; Kochendorfer 1950; Mott 1952). On the basis of this fact, let us assume that the variation of $1/\beta_1$ with the impact velocity V_0 may be given by the compression

$$1/\beta_1 = 1/\beta_0 \exp(V_d/V_0), \quad (8)$$

where $1/\beta_0$ is the maximum compression of the crystals for higher values of V_0 and V_d is a constant. From (7) and (8), I_T may be written as

$$I_T = 6\eta V^{2/3} M_0^{1/3} \alpha^{-1/3} \exp \frac{\alpha}{3h_1 \beta_0} \exp \left(\frac{V_d}{V_0} \right). \quad (9)$$

For higher values of the impact velocity, V_0 will be much greater than V_d and (9) may be written as

$$I_T^S = 6\eta V^{2/3} M_0^{1/3} \alpha^{-1/3} \exp \left(\frac{\alpha}{3h_1 \beta_0} \right). \quad (10)$$

The above equation shows that for higher values of the impact velocity, the total intensity I_T of ML will attain a saturation value I_T^S . Such results have been found experimentally.

4.1c *Effect of CdS contents on the ML of (Zn, Cd)S: Au, Cl phosphors:* For a given activator concentration, the ML intensity is found to be maximum for a particular content of CdS in (Zn, Cd)S: Au, Cl phosphors. From the reports on the microhardness of mixed crystals, it seems that the microhardness of the mixed crystals attains

a maximum value for a particular CdS content in (Zn, Cd)S crystals (Ghadkar and Deshmukh 1982). This fact helps in developing a higher fracture stress and which, in turn, produces higher piezoelectrification near the newly created surfaces. Therefore the ML intensity is higher for a particular content of CdS in (Zn, Cd)S: Au, Cl phosphors. Since the band gap decreases with the CdS content the peaks of the ML spectra shift towards larger wavelength side with increasing CdS contents in (Zn, Cd)S: Au, Cl phosphors.

4.2 Mechanism of mechanoluminescence

The mechanism of ML excitation in activated II–VI compounds is explained on the basis of mainly two models: (a) charged dislocation model and (b) Langevin's piezoelectrification model.

4.2a Charged dislocation model: Bredikhin and Shmurak (1979) reported that the onset of ML in ZnS and CdS crystals can be explained by taking into consideration the presence of electric fields around the moving charged dislocations. It is known that dislocation 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. Thus, the dislocations cannot move in the phosphors of very small grain size and at low temperatures. Since the crystals of ZnCdS have partly the ionic and covalent behaviour (Van Bueren 1968), the brittle fracture of the grains of these materials may be expected. Thus the ML excitation in these phosphors may not be explained by the charged dislocation model.

4.2b Langevin's piezoelectrification model: The crystals of ZnS and CdS have non-centrosymmetric crystal structure, hence ML excitation in these crystals or phosphors may also be due to the piezoelectrification. It is well known that with few exceptions, generally all the piezoelectric crystals exhibit ML and crystals not exhibiting ML are non-piezoelectric. This result indicates the piezoelectric origin of ML.

According to Langevin (1921) model, when stress is applied to a piezoelectric crystal, one of its surface gets positively charged and the opposite surface negatively charged

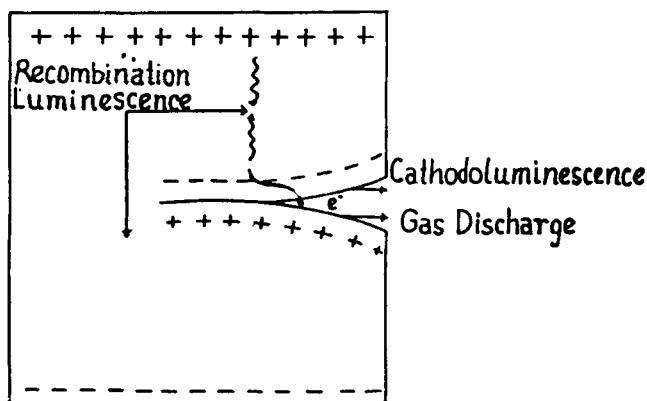


Figure 11. Electric field produced during the movement of a crack in a piezoelectric crystal.

(figure 11). Owing to the movement of a crack in the crystal, new surfaces are created. The newly created surfaces nearer to the positively charged surface of the crystal get negatively charged and those nearer to the negatively charged surface of the crystal get positively charged. Thus, an intense electric field may be produced between the newly created surfaces of the crystal.

The intense piezoelectric field near the tip of the mobile crack may produce electrons and holes due to the dielectric breakdown of solids and, in turn, the recombination of electrons with holes may give rise to luminescence. The powder phosphor of (ZnCd)S are crystallites of micron size where the fracture create charged surface which in turn may give rise to intense electric field. It can be concluded that ML excitation during the impulsive deformation of (Zn,Cd)S: Au, Cl mixed phosphors may be due to the piezoelectrification of the newly created surfaces.

The similarity of ML spectra with EL and PL spectra suggests that although there is difference in the process of excitation of electrons, relaxation with photon emission involves the same optical transition centres as in other types of luminescence.

4.3 Effect of temperature on the mechanoluminescence

The ML intensity in phosphors will depend strongly on the charge density and the charge distribution on the fracture surfaces near the crack tip. For the decrease in ML intensity of phosphors, the following factors may be responsible: (i) considerably less fracture surface is being created at higher temperature, (ii) the charge density is not reaching the same values during fracture as at lower temperature (Tetelman and McEvily 1967; Chandra *et al* 1987). The first point is supported by the fact that at room temperature new surface is created during the fracture, however, near the melting point no new surfaces are created. The second point is supported by the fact that by increasing temperature the conductivity of crystals increases and thereby the charge leakage may cause decrease of surface charge density at higher temperatures. It has been shown by Chandra *et al* (1986) that the total intensity of ML can be expressed by the following equation

$$I_T = 6\eta V^{2/3} N_c M_0^{1/3} \alpha^{-1/3} \exp\left(\frac{\alpha}{3h_1\beta_0}\right),$$

or

$$I_T = 6\eta N_c \gamma^{1/3} \alpha^{-2/3} \exp(\alpha/3h_1\beta_0). \quad (11)$$

The above equation shows that the decrease in the ML intensity with temperature may be due to the temperature dependence of γ and η . For the piezoelectric crystals, where the ML ceases at their melting points, the decrease in the area of newly created surfaces with increasing temperature as well as the decrease in the charge density with increasing temperature of the crystals may be responsible for the decrease of the ML intensity with temperature. The first fact may be related to γ and the second fact may be related to η .

It has been described that the ML of phosphors disappears much below their melting points (Chandra *et al* 1987). The area of newly created surfaces of these phosphors should not change considerably at the temperature for which the ML disappears. This implies that the decrease in the ML activity of phosphors with temperature should be related to the decrease in the charge density of the newly created surfaces.

The result of the present investigation shows that the decrease of the ML intensity with the temperature of the phosphor follows the relation

$$I_T = I_0(1 - T/T_c)^n,$$

where T_c is the temperature at which the ML disappears. The value of n lies between 0.90 and 1.10 for the gold doped (Zn, Cd)S mixed phosphors. The value of n for LiF, NaF and NaCl crystals has been reported to be 0.50, where the decrease of surface charge with temperature is only responsible for the decrease of ML (Verma 1983). The higher value of n suggests that both the mechanically-induced electric field and the luminescence efficiency decreases, with the temperature of the phosphors.

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