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Effect of Temperature on the Ml of Mn Doped (Zn, Cd) S Mixed Phosphors

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Abstract

An investigation is made on temperature dependence of the ML intensity in Mn doped (Zn, Cd)S mixed phosphors. The Mn doped (Zn, Cd) S mixed phosphors exhibits intense ML. For this the Mn doped (Zn, Cd) S mixed phosphors were prepared by heating a mixture of ZnS and CdS, with proper proportion of activators and co – activators at 1100^0C for one hour. The measurements are made at temperature between 300 K and 365 K.

It has been found that the peaks corresponding to the ML intensity versus time curve in (Zn, Cd) S: Mn phosphors decreases and shift towards smaller values of time with increasing temperature of the phosphors. It has been observed that there is no change in the slope of the log I versus time curve with increasing temperature, while the total ML intensity decreases with temperature and finally disappear beyond a particular temperature Tc, which is much less than as compared to the melting point of the phosphor. An attempt has been made to explain in the decrease in ML intensity with temperature in Mn doped (Zn, Cd) S mixed phosphors.

Keywords: Luminescence, Mechanoluminescence, Effect of temperature in II – VI Semiconductors, Alkali halide crystals.

Introduction

Mechanoluminescence (ML), the phenomenon of cold light emission induced during mechanical deformation of solids, links the mechanical, spectroscopic, electrical, structural and other properties of solids. A large number of organic and inorganic crystals and amorphous solids exhibit the ML phenomenon (Longchambon 1925; Walton 1977; Zink 1978; Chandra 1985) [14, 15, 16, and 11]. On the basis of the deformation in solids needed for producing ML, we can classify ML into three types, viz. fracto-induced ML, plastico induced ML and elastico-induced ML. It has been found that in the substances showing luminescence at room temperature, the luminescence is quenched at some higher temperature. On the other hand, many substances which are not luminescent at room temperature, show luminescence at low temperature. Therefore, studies on the temperature dependence of luminescence are very interesting, sometimes yielding information to understand the nature of the crystals and to determine the effective trap depth (Leverenz 1950; Curie 1963; Chandra *et al* 1983) [13, 12, and 9]. However, comparison of temperature dependence of luminescence efficiency and decay rates gives information about the location of dissipative transition and permits the calculation of activation energies and frequency factors for these transitions in certain cases. The present paper reports the effect of temperature on the ML of Mn doped (Zn, Cd) S mixed phosphors.

The effect of temperature on the ML has been widely studied by Garlick 1949 [6], Leverenz 1950, Curie 1963 [5], Goldberg 1966 [7], Das and Chandra 1974 [10], Chandra and Deshmukh 1982 [8], Chandra et al 1983 [9]. Temperature studies give information about the location of dissipative transition and for certain cases it permits the calculation of activation energies and frequency factors. It is expected that temperature studies may be helpful in understanding the phenomenon of ML.

The temperature dependence of ML of γ - irradiated KBr, KCl, LiF and NaCl crystals during the application and release of a uniaxial pressure was studied by Chandra et al (1983 b) [3]. It was found that the ML intensity of γ - irradiated KI crystals decrease with temperature, while the ML intensity of γ - irradiated KBr, KCl, LiF and NaCl was found to increase with temperature.

It has been found that the ML of the phosphor disappears much below their melting points. The area of newly created surface of these phosphors should not change considerably at the temperature for which ML disappear. These facts suggest that the decrease in the ML intensity of phosphors with temperature should be related to the decrease in the charge density of the newly created surfaces.

It is known that the decrease of ML intensity with temperature of the phosphor, follows the relation $I_T = I_T (1 - T / Tc)^n$, where 'Tc' is the temperature at which ML disappears. The value of n lies between 0.90 and 1.10. The higher values of n for the phosphor suggest that the decrease in both the mechanically induced electro field and the luminescence efficiency should be responsible for the temperature dependence of the ML of the phosphors.

Experimental

To study the effect of temperature on the ML of doped mixed phosphors, the Mn activated hexagonal phosphors having activators concentration 4×10^{-3} (by weight of 1 gm. Of matrix, 10% CdS) were chosen as they exhibit intense ML among the phosphors prepared with different concentration.

For studying temperature effect on the ML, the phosphors were placed on a transparent Lucite plate, which was heated using the heating filaments fitted on the thin aluminium and asbestos sheets and was fixed closed to the Lucite plate, with the help of variac, different temperature starting from room temperature to 100^0C were achieved by feeding voltages to the heating filaments. The device used for measuring ML intensity at different temperature was shown in fig. (1.2). Heating arrangement with PMT housing is shown in fig. (1.1). The temperature was measured using a calibrated chromel alumel thermocouple. Fig (1.3) shows that peak corresponding to ML intensity versus time curve of (Zn, Cd) S: Mn phosphor decrease and shift towards smaller values of time with increasing temperature of the phosphors. Fig (1.4) shows that the plot of log I versus time‘t’ curves for (Zn, Cd) S: Mn phosphors. It is seen that there is no considerable change in the slope of curves for both the rising and decaying portion of ML with time. Fig (1.5) shows the effect of temperature on the total ML intensity I_T. It is found that I_T decreases with temperature and finally disappears beyond a particular temperature Tc. Fig (1.6) shows that the plot of log I_T versus log (I – T / Tc) is a straight line with positive slope, which follows the relation

$$I_T = I^0_T (I - T / Tc)^n \qquad (1)$$

Where I^0_T is a constant, Tc is the temperature at which ML disappear and n is the slope of log I_T versus log (I – T / Tc) plot, which lies between .09 and 1.10.

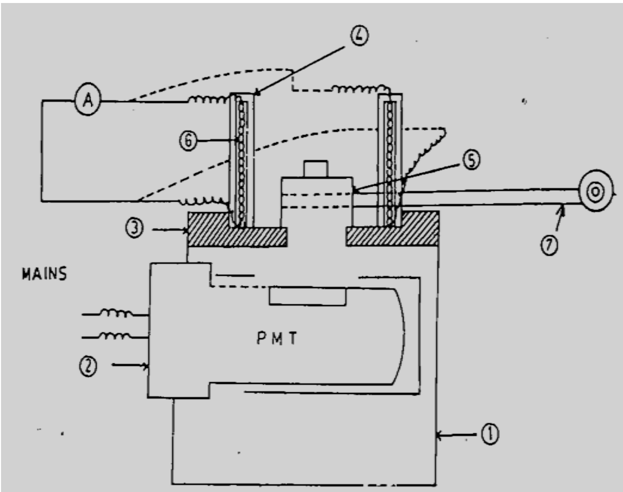

Fig 1.1 ML measuring device at different temperatures. PMT housing (2) Photomultiplier tube (3) Rubber sheet (4) Asbestos sheet and Al sheet (5) Lucite plate (6) Heating filament (7) Thermocouple (8) Variac

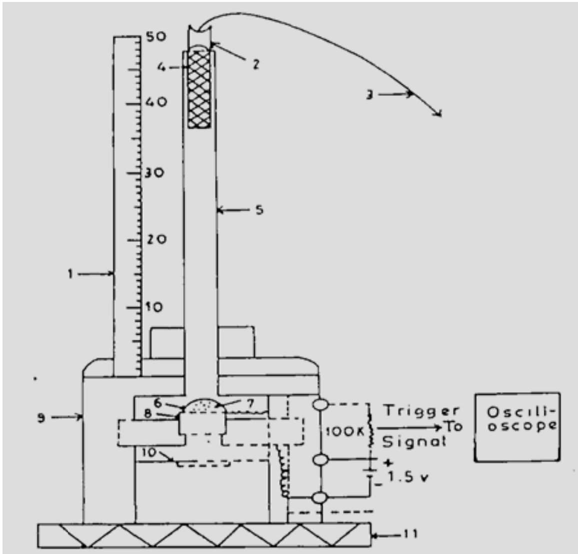

Fig 1.2 Schematic diagram of the experimental. Arrangement used for measuring the time dependence Of ML phosphors Scale in CMS, (2) Pulley, (3) Mettalic Wire (4) Load, (5) Guiding cylinder (6) Alluminium foil (7) Sample, (8) transparent Lucite plate, (9) Wooden block, (10) photomultiplier tube (11) Iron base mounted a table

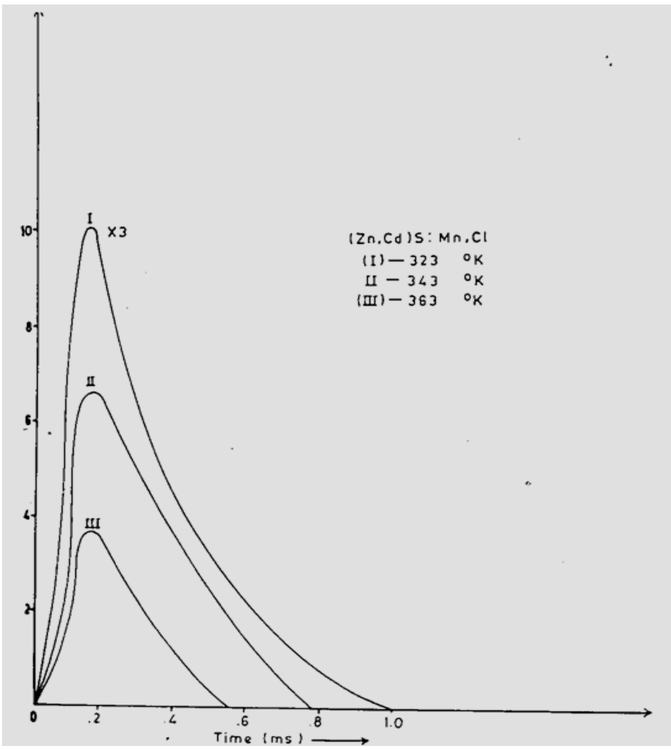

Fig 1.3 Time dependence of ML intensity of (Zn, Cd) S:Mn, Cl phosphors for different temperatures

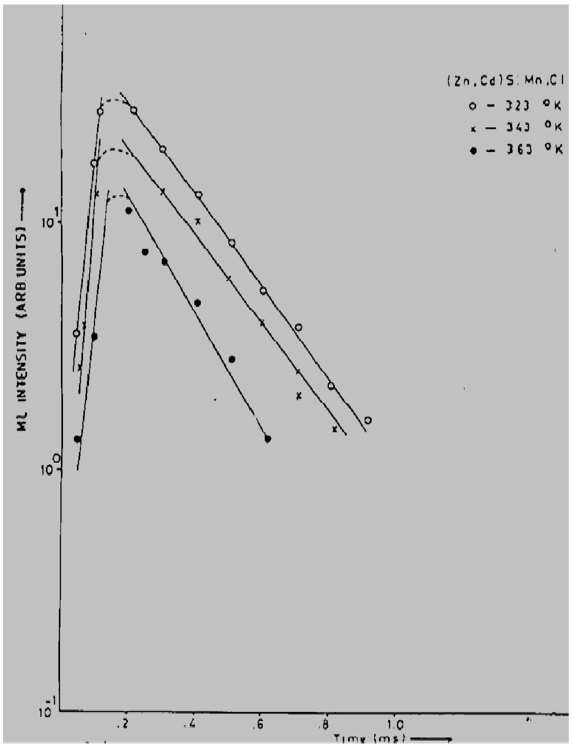

Fig 1.4 Plot of log I versus t, for (Zn,Cd) S:Mn, Clphosphors at different temperatures

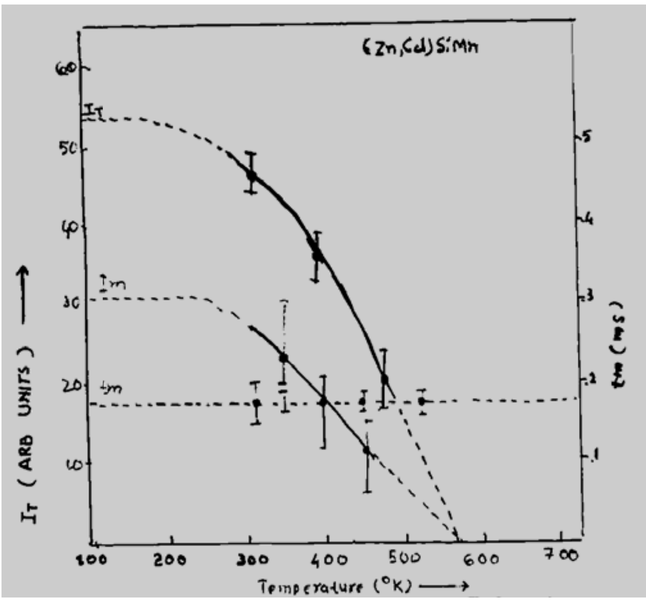

Fig 1.5 Effect of temperature on total ML intensity I_T and I_m for (Zn,Cd) S:Mn phosphors

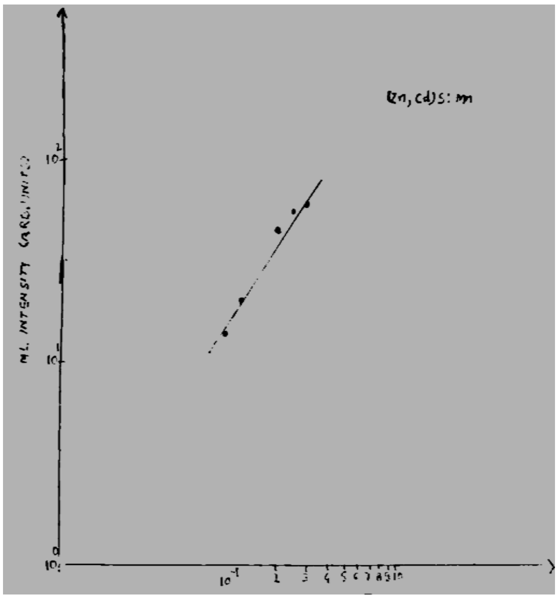

Fig 1.6 Plot of log I_T versus log (t T/Tc) of (Zn, Cd) S:Mn mixed phosphors

Discussion

Fracture of crystallites is primarily responsible for the ML emission as we know that the ML in phosphors is excited impulsively. Hence the ML intensity in phosphors will depends on the charge density and the charge distribution on the fracture surfaces near the crack tip. Following factors may be responsible for the decrease in the ML intensity of phosphors (i) considerably less fracture surface is being created at higher temperature (ii) The charge density is not reaching the same values during fracture as it lower temperature and (iii) the charge is more rapidly leaking off the fracture surfaces due to increase in the conductivity at higher temperature. The first two factors may be more responsible rather than the third one, since the ML excitation takes place instantaneously with the creation of new surfaces.

Chandra et al (1986) [4] have shown that the total intensity I_T, and the ML intensity I_m corresponding to the peak of ML intensity versus time curve may be given by the following equations:

$$I_m = 6\eta\ N_T\ V\ \gamma^{1/3}\ \alpha^{1/3}\ V_0\ \beta_1\ e\ \alpha\ 3h_1\ \beta_1(1 - 3h_1\beta_1) / \alpha$$

And $$I^S_T = 6\eta\ N_T\ V^{2/3}\ M_0\ \alpha^{1/3} e^{\alpha /} 3h_1\beta_0 \quad (2)$$

$$\text{Or } I^S_T = 6\eta\ N_{T\,V}\,\gamma^{1/3}\ \alpha^{-1/3}\ e^{\alpha /} 3h_1\beta_0 \quad (3)$$

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

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