Spectral characteristics of doped CdS phosphors

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ABSTRACT

Samples of CdS with different activators i.e. Cu, Mn, Ag and Au are prepared with the activator concentration 4×10^{-3} gm/gram of CdS, NaCl was used as co activators. The heat treatments of these phosphors have been carried out in an atmosphere of purified nitrogen, at 900^0 C for 45 minutes. The photoluminescent and mechanoluminescent characteristic of these phosphors have been studied. One emission bands (at 760nm, 750nm, 747 nm, and 760 nm) have been observed for CdS: Au, CdS: Mn, CdS:Ag, and CdS: Cu phosphors respectively. An ML spectrum of doped CdS is compared with that of their PL spectra.

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INTRODUCTION

To understand the mechanism of luminescent process the photoluminescence of ZnS: Cu, ZnS: Ag have been studied by several investigators. ZnS: Cu phosphors usually exhibit emission in the blue green region of the visible spectra. The emission bands of Cu, Ag, and Au in ZnS and CdS base phosphors have been investigated extensively [1-5]. The intensity and spectral distribution of CdS:Mn and CdS:Cu crystals luminescence are studied at 4.2 ^{0}K by Protsyuk and Rozhko (1976) [6]. The results are explained on the assumption that the pattern of the impurity arrangement in the crystal depends on the degree of concentration. The quenching effect of the impurity is due to changes in the number of luminescence centres, energy transfer from excitations to the impurity and free carrier trapping in the impurity. N. Neukirch (1990) [7] studied the luminescence of heavily doped, highly excited CdS; in crystals, which exhibits a broad luminescent band in the region of the band gap energy. This band shifts to higher energy side with increasing indium concentration. The nature of recombination centres in AgCl doped CdS phosphor was studied by Krustok et al (1990). The intensity of photoluminescence emission bands in CdS: Ag, Cl depends on the added Ag ($10^{16} - 10^{20}$ cm^{-3}) and Cl ($10^{16} - 10^{19}$ cm^{-3}) concentration. It was shown that the intensity of photoluminescence bands is a power function of the silver and chlorine concentration and the partial pressure of components. The comparative

study of experimental and theoretical curves helps to determine the nature of the radiative and non radiative recombination centres of Ag and Cl in CdS: Ag: Cl phosphors.

The spectral distribution of the emitted light as a function of energy (presented here as a function of the wave length of the emitted light) is similar in samples which demonstrate both ML and PL. Although ML and PL occur at the same energies, there exists some difference in the relative intensities of the vibronic bands in the spectra. Koda et al. [8] have shown that large changes in the Franck – Condon factors can be induced by high pressure on the emitting molecules in ZnS phosphors. These changes account for the differences observed in the ML and PL spectra of molecules in mechanoluminescence during under stress. Mechanoluminescence [ML] is the phenomenon of light emission induced by elastic deformation and fracture of special class of solids [9, 10]. As a rough guide about 50% of inorganic salts and organic molecular solids can exhibits ML. The effective use of this phenomenon can be employed to detect mechanical stress remotely converting mechanical energy into visible light [11, 12].

In the present paper details of the preparation and the spectral characteristics of different impurity doped CdS phosphor system are reported. ML spectra are compared with PL spectra of doped CdS phosphors.

MATERIALS AND METHODS

(I) Phosphor Preparation:

Luminescent grade CdS obtained from BDH England was used as base matrix, for the preparation of doped CdS phosphors, Mn activator was added in the form of magnous chloride, Cu activator was used in the form of cupric chloride, Ag activator was added in the form of silver nitrate, while the gold activator was added in the form of chloro auric acid. For preparing CdS doped phosphors the dopant was taken in proper proportion by weight of the CdS along with requisite amount of flux i.e. 4% NaCl and was mixed thoroughly in an agate pestle and mortor for about half an hour.
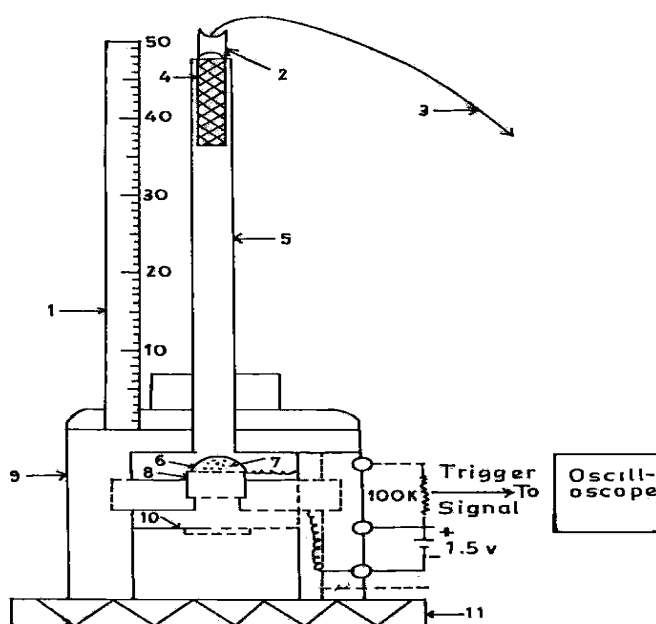

FIG. 1 Scematic diagram of the experimental arrangement for measuring the time dependence of ml in phosphors, (1) scale in cms , (2) pulley, (3) metallic wire, (4) load, (5) guiding cylinder, (6) aluminium foil, (7) sample, (8) transparent, lucite plate, (9) wooden block, (10) photomultiplier tube, (11) iron base mounted on a table

This mixture was transferred in a porcelain crucible with lid. This crucible was kept in a larger refractory crucible surrounded by activated charcoal. This mixture was fired in a tubular furnace for forty five minutes in an atmosphere of nitrogen at 900^0 C. CdS: Mn, CdS: Au, CdS: Cu and CdS: Ag phosphors were prepared in the similar manner.

(II) (a) Mechanoluminescent Spectra:

The weak ML intensity and the short duration of the ML ruled out the use of conventional spectrographs for recording the ML spectra. Here we used the impulsive excitation device. Lucite plate was used as a base for crushing the phosphors since it does not show ML in any region of deformation. The phosphor (approx 20 mg) was placed on the Lucite plate of the device (Fig 1). The thickness of the Lucite plate was so chosen that the absorption of ML emission was as small as possible and it was sufficiently strong to endure the impulse of the load applied. The phosphor was covered with the adhesive tape which eliminates the errors in the ML intensity measurements due to the scattering of the fragments during the impact of the load on to the phosphors. The ML in the phosphors of a given mass attains a saturation value for a height of 50 cm when dropped by a load of 400 gms. Therefore ML in the phosphor was excited impulsively using a load of 400 gms from a height of 50cm. When a specimen of small cross – sectional area as compared to the light sensitive area of the photomultiplier tube was scanned by the photomultiplier tube (RCA 7102) which in turn was fed to the digital storage oscilloscope. Thus the ML intensity per gram mole can be determined relatively from the ML intensity for a given mass of the phosphor. As the position of the phosphor and the photomultiplier tube are fixed, the relative ML intensity is independent of the geometry. For spectroscopic studies a provision was made to insert the optical filters in between the Lucite and the photomultiplier tube. The ML intensity was normalized with respect to the mass of the phosphors and different transmission coefficients of the filters. ML studies were carried out at Physical Research Laboratory, Ahmedabad.

(II) (b) Photoluminescence Spectra:

The photoluminescence spectra of cadmium sulphide doped phosphors were done by "Hitachi Fluorescence Spectrometer" model 650- 10 having a photomultiplier tube RCA 372 F whose response is in the range 220 – 730 nm and has an expansible range from 220 – 830 nm. The illuminating source was a 150 W Xenon lamp. PL studies were carried out at Central Electro Chemical Research Institute, Karaikudi, Tamilnadu.

RESULTS AND DISCUSSION

A systematic comparison of spectral data of ML and PL is shown in Fig 2 to Fig 5, Fig 3 shows that the ML spectrum shifts towards longer wavelength as compared to their PL spectrum. Whereas Fig 2, 4, 5 shows that the PL spectrum shifts towards longer wavelengths as compared to their ML ones. The PL spectra of CdS: Au, CdS: Mn, CdS: Ag and CdS: Cu phosphors have peak centered at 760nm, 750nm, 747nm and 760nm respectively, when excited at 250 nm at an activator concentration 4×10^{-3}. The activator concentration for which the PL intensity attains an optimum value is 1×10^{-3}, and the ML intensity attains an optimum value for 4×10^{-3} concentration. It is found that for a given phosphor the critical activator concentration for which the PL intensity attains an optimum value is always greater than that for ML intensity. It has been observed that the ML intensity is more for CdS: Au and decreases in the following order, CdS: Mn, CdS: Ag: CdS:Cu. It was also found that the ML spectra shift towards longer wavelengths with increasing firing temperature and dopant concentration.
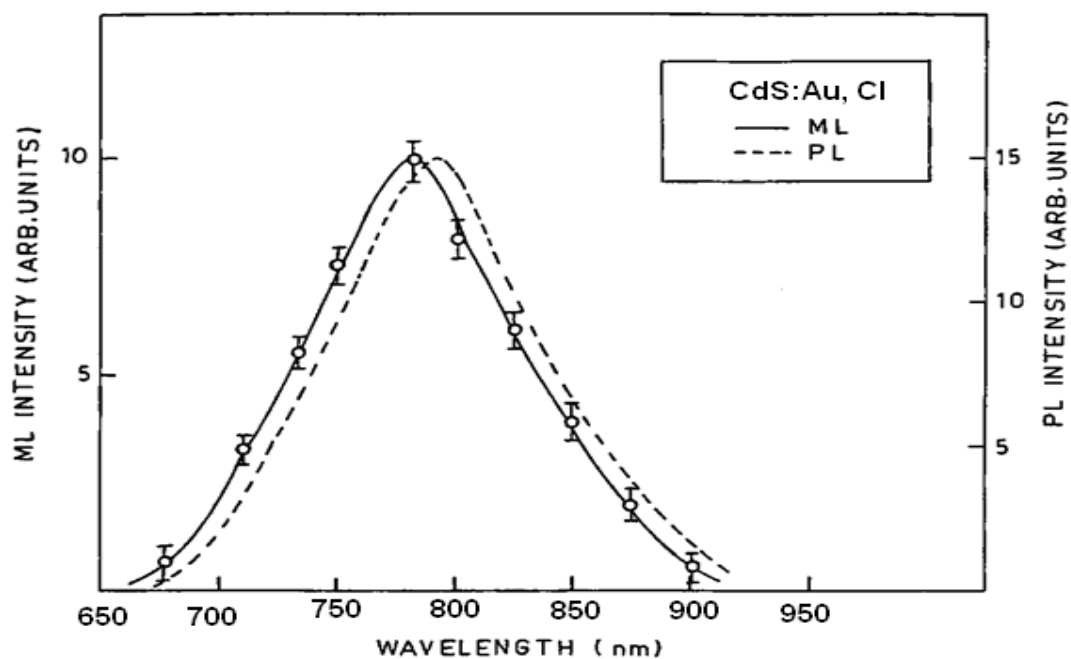
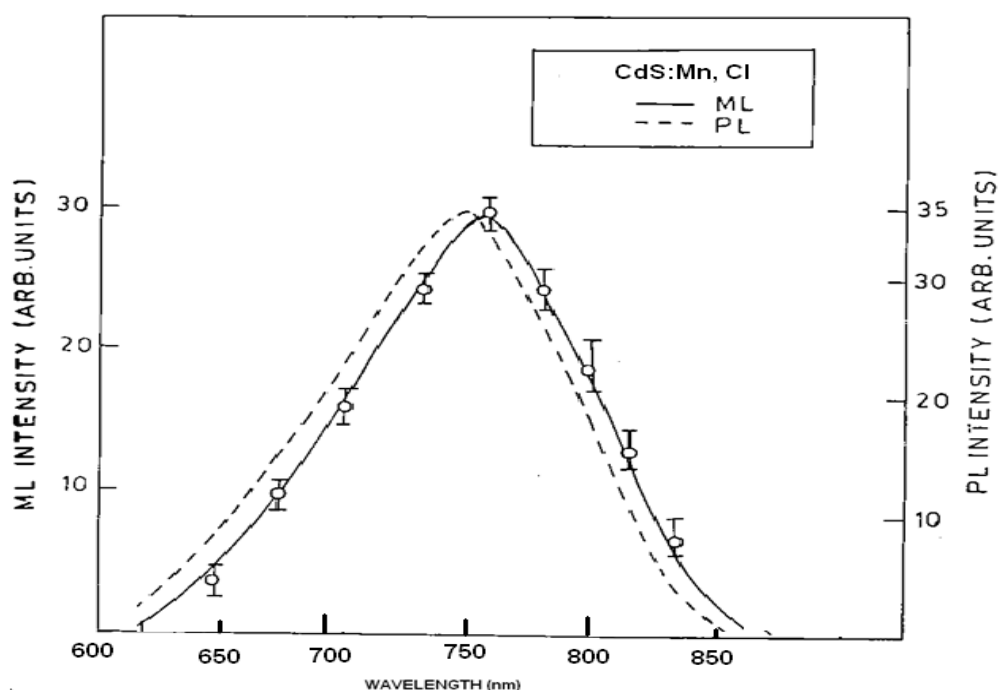**Fig2 ML and PL spectra of CdS:Au, Cl Phosphors**

Fig3 ML and PL spectra of CdS:Mn , Cl phosphor

The results of the present investigations indicate that the ML profiles of the different doped phosphors of Cadmium Sulphide are the same qualitatively. The similarity of ML spectra to the PL spectra and the appearance of ML during plastic deformation of the phosphors suggested that an intense electric field created during the mechanical deformation of a phosphor can not be simply assigned to a unique mechanism. The complex energy band structure of imperfect crystals allows a multitude of excitation and relaxation process. However, it appears the ML emission is comparable to other well documented and better understood luminescence phenomenon. The difference is in the process of excitation of electrons while relaxation with emission involves the same optical transition centres as in other types of luminescence.

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Also the position of the emission bands in these phosphors depends both on the conditions of preparation and on the dopant concentration. Similar results were obtained by Bryant and Cox [14] and G.G.Patil and T. Woods [15] for photoluminescence bands in CdS:Cu crystals.
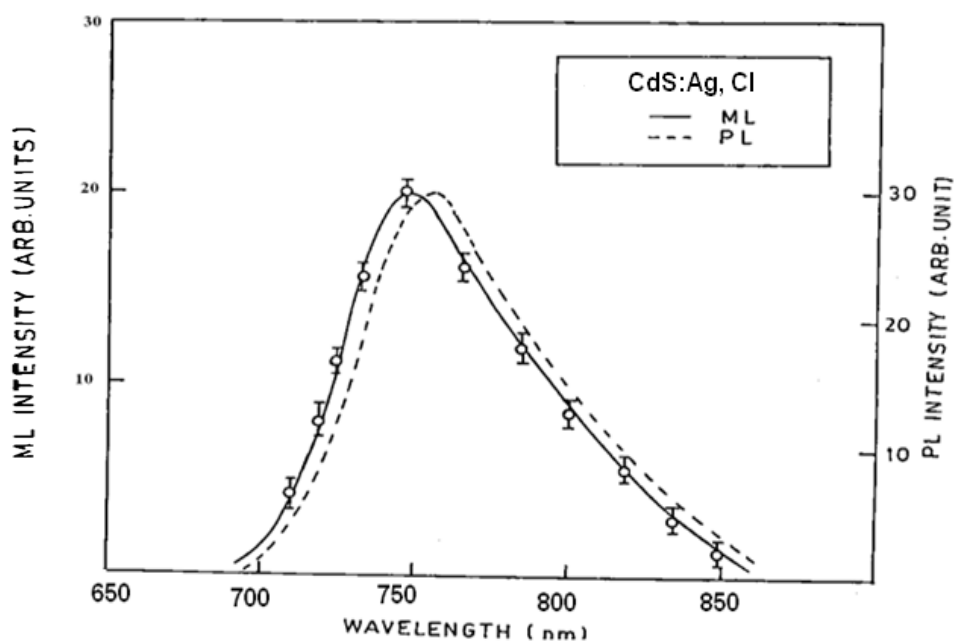

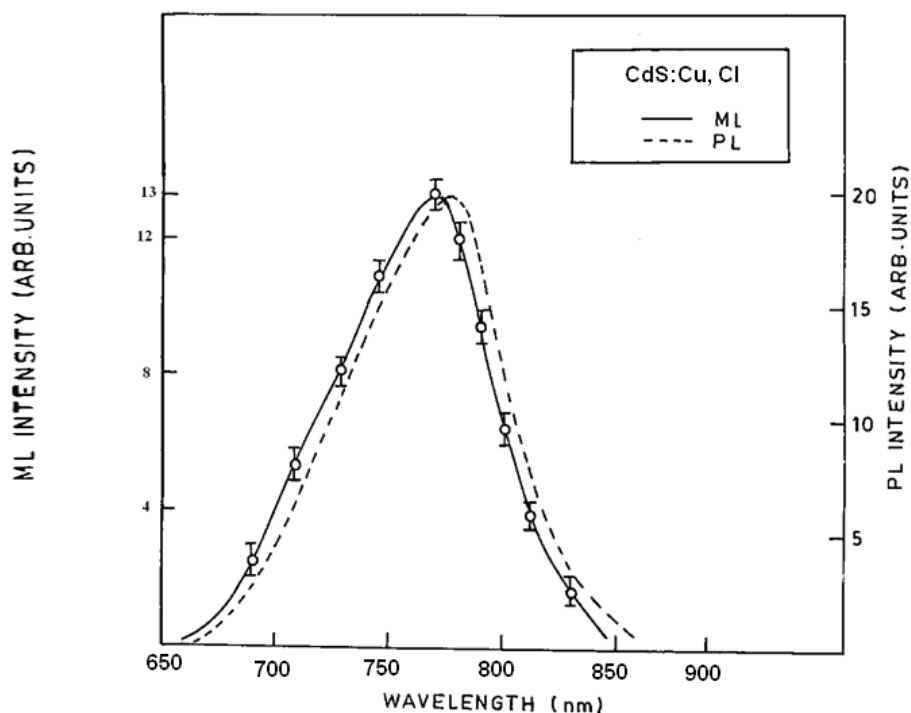**Fig. 4 ML and PL spectra of CdS:Ag , Cl phosphor**

Fig 5 ML and PL spectra of CdS:Cu , Cl phosphor

It is well known that the Mn orange luminescence arises from Mn^{2+} ion which has a $3d^5$ electron configuration at the substitutional site. The energy level of the d^5 system is cubic crystal field has been given by Tanabe and Sugano (1954) [16], on the basis of crystal field theory. According to this theory each energy level is generally expressed in terms of the crystals field strength 100 g and of Racah's parameters B and C, all of which depend on the ligand configuration. Koda et al

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[8], have studied in detail the red shift in the case of ZnS: Mn and interpreted it to be due to the effect of the change of crystal field parameter for the d – electro system of the Mn^{+2} ion [17].

The phenomenon of concentration quenching can be easily explained by the equation:

$$n = \frac{C(1-c)^z}{C + \gamma(1-c)} \quad \text{------ (1)}$$

Where 'n' is luminescence efficiency, 'C' is activator concentration 'γ' is ratio of capture cross section leading to non radiative de – excitation, 'z' is number od sites producing luminescence.

It seems that the excitation during the impulsive deformation of cadmium sulphide doped phosphors may be due to the piezoelectrification of the newly created surfaces. Since the powder phosphors chosen in the present investigation are crystallites of micron size where the fracture may occur and may cause ML excitation.

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