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ML SPECTRA OF GOLD DOPED (Zn, Cd) S MIXED PHOSPHORS

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The present paper reports that the ML spectral distribution of Au doped (Zn, Cd) S mixed phosphors. The measurements were made at room temperature between 4000 3and $7000A^0$. The ML spectra was recorded on the oscilloscope using a series of filters with different transmission coefficients while the spectral emission curves of the sample were measured at room temperature, between 4000 Å and 7000Å on the Hitachi spectrometers using long wavelength ultraviolet excitation provided by 150 watt xenon lamp. Since the excitation process depend on mechanical deformation, which is slower than the absorption of photon, the rate of ML will be different from that of PL & EL. ML and PL are examined by comparing their energy relationship. The spectral distribution is found to be similar in ML and PL. Since the PL of phosphors is well known, it is expected that the comparative study of ML with PL will be helpful to understand the process of ML excitation in (Zn, Cd) S mixed phosphors.

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1. Introduction

Mechanoluminescence (ML) is the phenomenon of light emission from a solid as a response to the mechanical stimulus given to it. The light emission induced by elastic deformation, plastic deformation and fracture of solids is known as elastico ML, plastico ML and fracto ML, respectively. The ML induced by rubbing of solids or separation of two solids in contact is known as tribo ML or triboluminescence [1]. In the recent past, several materials have been investigated, which emit intense ML during their elastic deformation, plastic deformation, and fracture. These materials have been reported to be useful in stress sensor [2, 3], fracture sensor [4, 5], damage sensor [6], and in the fuse-system for army warhead [7]. The ML has also been reported to be useful in the online monitoring of grinding in milling machines [8], and in radiation dosimetry [1].

For the determination of emitting states in ML, it is useful to compare the ML emission properties with those of other known emission such as Photoluminescence (PL), Electroluminescence (EL) etc.

It is observed that at the room temperature the PL spectra & EL spectra correspond closely to that obtained from ML. It indicates that the identical excited electronic states are being populated in ML, PL & EL, but with different mechanism. ML and PL are examined by comparing their energy relationship. The spectral distribution is found to be similar in ML, PL & EL.

Studies on II – VI phosphors have shown that large changes in the Frank-Condon factors can be induced by high pressures on the emitting molecule (Koda et al 1966) [11]. These changes could account for the differences observed in ML & PL spectra. Five kinds of typical luminescence have been observed in II – VI compounds.

We have chosen the mixed phosphors with Au as activator to study the ML spectra and PL spectra with variation in percentage of CdS in ZnS. We have studied & observed the effect of CdS

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concentration on the wave length corresponding to peak PL Intensity, effect of CdS content on PL intensity of Au doped mixed phosphors and effect of activator concentration on PL intensity of Au doped (Zn, Cd) S mixed phosphors. ML spectra are compared with PL spectra.

2. Experimental

(A) Determination of ML spectra of Au Doped (Zn, Cd) S mixed phosphors.

Samples were prepared by mixing of ZnS and CdS in proper proportion using Au as activator in the form of Chloro Auric acid. Firing time was one hour. The amount of flux (NaCl) is taken as 4 percent of the base material the phosphor preparation was done in tubular furnace in N_2 atmosphere.

The ML spectra were determined using a series of optical filters having different transmission wavelength. 10 mg of phosphor was placed on the Lucite plate and was excited by deforming the phosphor by dropping a load of 800 gm from a height of 20 cm. In these measurements, an RCA 6199 photomultiplier tube fig (1.1a) & fig (1.1b) was used for monitoring the ML intensity. To obtain the complete profile of the ML spectra a number of filters in the visible region of the violet side were used. The filters were of the different absorption coefficients. The average intensity was standardized taking into account the absorption coefficient. After finding out the mean intensity, a grass profile was prepared by drawing graph between the intensity and wavelength for all the filters used.

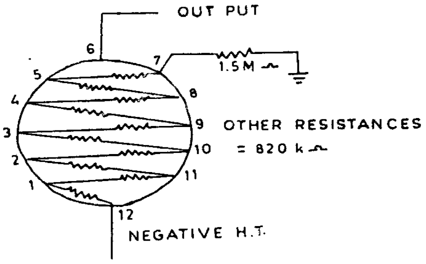

Fig 1.1 (a) Biasing circuit of the photomultiplier tube R C A 6199.

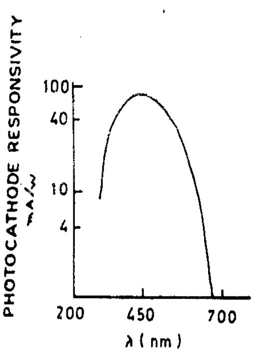

Fig.1.1 (b) Spectral response of the photomultiplier tube RCA 6199

B) Determination of PL spectra

The photoluminescence measurements of different impurity dopped (Zn, Cd) S mixed phosphors were done at central electrochemical Research Institute, Karaikudi (T.N.). The experiments were carried out at 300 K using Hitachi 650-10 fluorescence spectrophotometer equipped with 150 watt xenon lamp & Hamma Matsu R- 928 F photomultiplier. The output emission was recorded by X-Y Recorder. A gross profile of PL spectra was obtained by drawing graph between standerdised intensity and wave length.

The relative PL intensity of the phosphors could be compared by measuring the area below the intensity versus wavelength curve of the PL spectra. Thus the effect of concentration quenching of activator and CdS content could be investigated.

3. Results

The ML spectra & PL spectra of Au dopped (Zn, Cd) S mixed phosphor is shown in Fig. (1.2) & Fig (1.3) respectively. It is seen from Fig. (1.2) & Fig (1.3) that the peaks λm of ML and PL spectra shift towards longer wavelength values with increasing CdS content for given activator concentration.

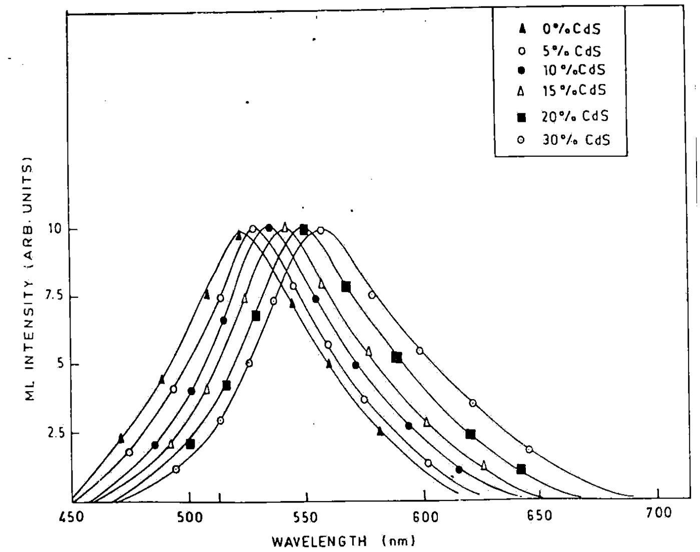

Fig 1.2 ML spectra of (Zn, Cd)S: Au, Cl phosphor

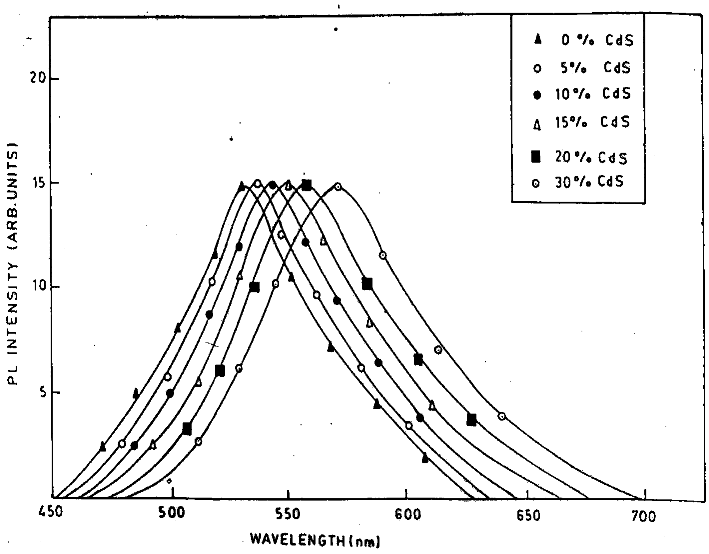

Fig 1.3 PL spectra of (Zn, Cd)S: Au, Cl phosphor

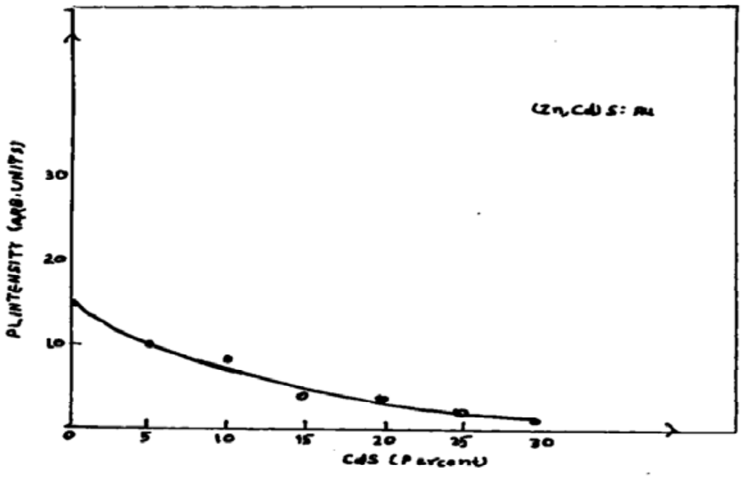

Fig 1.4 Effect of CdS concentration on the wavelength on PL of doped mixed Phosphor

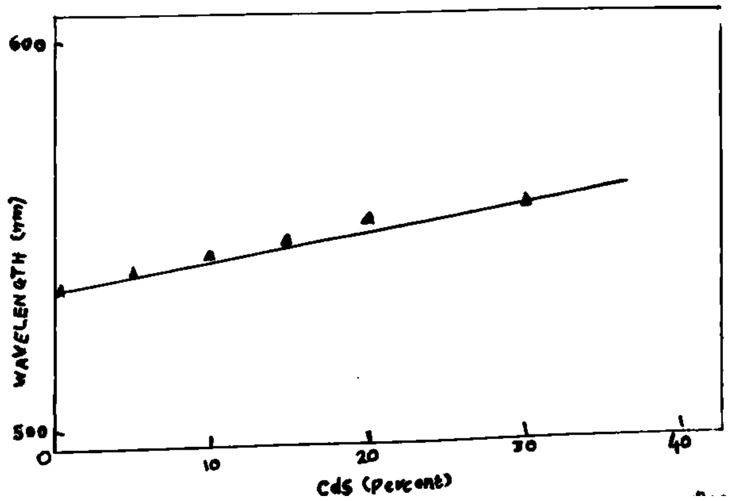

Fig 1.5 Effect of CdS content Corresponding in peak PL intensity of (Zn, Cd)S: Au_.

Fig.1.4 shows the variation of λm, the wave length corresponding to the peak PL intensity with CdS content for (Zn, Cd) S: Au mixed phosphors. Fig (1.5) shows the PL intensity decreases with increasing content of CdS in dopped (Zn, Cd) S mixed phosphors, Fig. (1.6) shows the dependence of PL intensity on the activator concentration in Au doped (Zn, Cd) S mixed phosphors. It is seen that the PL intensity is maximum for a particular concentration. Furthermore, the activator concentration, for which the PL intensity attains maximum value, decreases with CdS content.

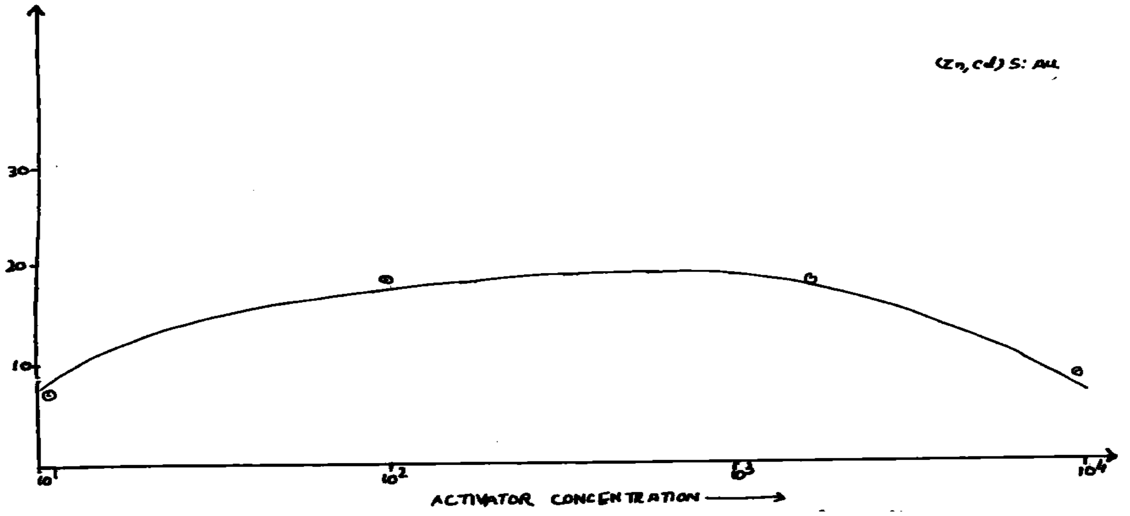

Fig 1.6 Effect of Activator Concentration on PL Intensity of Doped (Zn, Cd) S: Au Phosphor

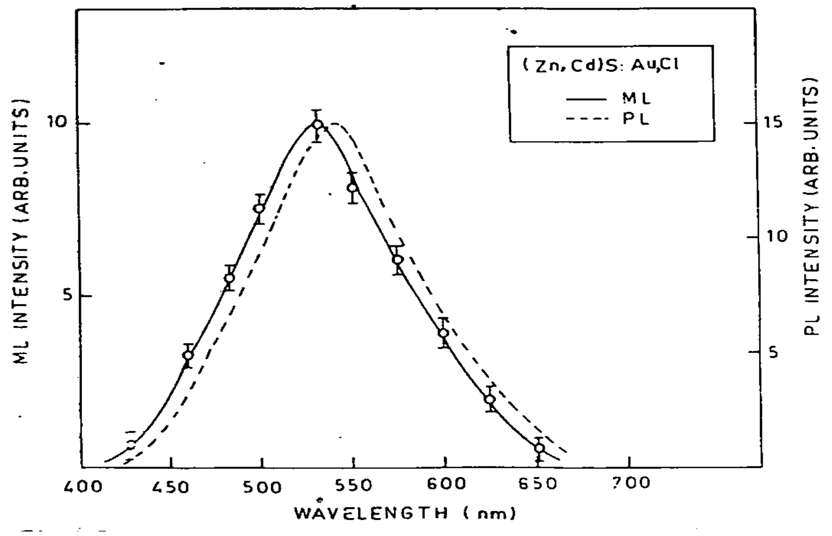

Fig 1.7 Mechano-luminescence and Photo-luminescence spectra (Zn, Cd) S: Au, Cl (4 X 10^{-3}, 10% CdS) Phosphor

Fig. (1.7) shyows the ML & PL spectra of (Zn, Cd) S: Au (with Au concentration 4 X 10^{-3} gm / cc of (Zn, Cd) S, 10% CdS) mixed Phosphors. The photoemission spectrum of (Zn, Cd) S: Au shows a single emission band at 548 nm. It is seen that the ML spectra, apart from the shift of 3 nm towards lower wave length side, is almost similar to the PL spectra. Hence the same emission process may be assumed for the ML emission.

4. Discussion

It is known that ZnS and CdS form a continuous series of solid Solutions having the hexagonal wurtzite structure. If the Zn in ZnS is replaced by Cd, the lattice constant increases with increasing cadmium concentration and the absorption edge shift towards longer wavelength side when cadmium is introduced into ZnS phosphors activated with monovalent ions, there is a gradual shift of the emission spectra to longer wavelength as the cadmium content increases fig. (1.2). The continuous shift in emission with Cd / Zn ratio has led to the suggestion that luminescent centers in this system are associated with sulphide rather than with the specific activator employed (Leverenz 1950) [15]. Klassen (1953) [19] has proposed that the excess negative charge associated with monovalent activator at a Zn^{+2} lattice site perturbs the surrounding S^{-2} ions and give rise to an occupied localized levels above the filled band. The energy necessary to ionize a S^{-2} ion perturbed in this way will be less than that required to excite an electron from the filled band itself. If the absorption edge of the pure crystal corresponds to the transfer of an electron from the filled band to the conduction band, the perturbation of the nearly S^{-2} by the activator will result in the appearance of a new absorption band lying at lower wavelength than the absorption of the host material. Such additional absorption bands associated with the incorporation of the usual cations activators in ZnS have long been known (Gisolf et al 1941).

If the emission process is assumed to be associated with the return of an electron from the conduction band to an ionized perturbed S^{-2} centre, the approximate similarity of emission spectra of all the monovalent activators with in a given host composition seems reasonable. Since the width of the forbidden band decreases regularly as the Cd / Zn ratio increases, the gradual shift of all spectra to longer wavelength with increase in Cd^{+2} content follow naturally. It is observed that the ML spectra also shift towards longer wavelength side with increasing Cadmium content. This phenomenon can be attributed to a change of the lattice constant.

The shift of ML spectra as compared to the PL spectra in the direction of longer wavelengths can be explained by a reduction of the lattice constants. The reduction of the lattice constants results from the strong mechanical treatment of (Zn,Cd) S phosphors, where high pressure exist at the moment of the ML excitation.

It may be concluded that the ML are similar to the PL spectra. The states responsible for PL emission should also be responsible for the ML emission. Both the ML and the PL intensities are found to be optimum for a particular concentration of the activator in (Zn,Cd) S mixed phosphors, although the values of critical activator concentrations are different for the ML and PL emission.

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