

## Photoluminescence of gold-doped (Zn, Cd)S mixed phosphors

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**Abstract.** (Zn, Cd)S: Au, Cl mixed phosphors were prepared in nitrogen atmosphere with various concentrations of impurities. Photoluminescence (PL) spectra were obtained. The peak of the PL spectrum shifts towards longer-wavelength values with increasing replacement of zinc by cadmium in the host lattice. The PL efficiency was found to decrease with increasing CdS content whereas lattice constants increased with increasing CdS concentration.

**Keywords.** Photoluminescence; mixed phosphors; PL spectra; X-ray diffraction; II–VI compounds; optoelectronic materials.

### 1. Introduction

Recent developments in the field of optoelectronic devices have created requirements for high-purity semiconductor materials like II–VI compounds and their alloys. The need for high-quality materials has led to the development of novel semiconductor growth and processing technologies. Characterization techniques, mainly photoluminescence (PL) spectroscopy (Dean 1973; White 1979), have been considerably improved in sensitivity and versatility over the years. The PL technique provides a contactless, nondestructive means for the analysis of semiconductors. Considerable progress has been made in understanding the photoluminescence phenomenon in ZnS, CdS phosphors activated with copper (Froelich 1952; Piper and Williams 1952; Mater and Cera 1962) and silver (Bube 1953; Mater 1957; Gurvich 1966), but to date the least attention has been paid to the investigation of photoluminescence in gold-doped (Zn, Cd)S mixed phosphors. There is still considerable use for sulphide phosphors in cathode ray tube screens for televisions and electroluminescent devices (Elmanharawy and Abdel Kader 1980; Abdel Kader and Bryant 1986). Therefore characteristics of the gold-activated series are of practical interest. The present paper reports preparation, photoluminescent properties and crystallographic studies of gold-doped (Zn, Cd)S mixed phosphors.

### 2. Experimental

The gold-doped (Zn, Cd)S mixed phosphors were prepared by firing a mixture of luminescent grade ZnS and CdS (Fluka, Switzerland), auric chloride ( $\text{AuCl}_3$ ) and sodium chloride in appropriate proportions. The activator concentration was varied from 0 to 10,000 ppm and CdS content was varied from 0 to 40 per cent. The charge was placed in a silica crucible. The firing was done in a silica tubular furnace

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maintained at 1100°C and 800°C in the inert atmosphere of flowing nitrogen gas. After the firing was complete, the charge was taken out of the furnace and immediately crushed and finely powdered to have a uniform particle size. Although defects are produced during grinding but better repetitive results are obtained in case of ground phosphors as compared to that in unground phosphors.

For photoluminescence studies a 365 nm (UV) filter was placed between the 600 W tungsten-halogen lamp and the phosphor, so that PL excitation may take place at 365 nm and PL emission spectra can be obtained in the visible region. The absorption spectra of (Zn, Cd)S phosphors had a peak around 365 nm. The PL spectra was recorded by placing phosphor adhered on glass plate using toluene near the entrance slit of the grating monochromator. Near the exit slit of the monochromator, an EMI-6199 photomultiplier tube was placed, whose output was connected to a digital picoammeter. The variation of PL intensity with the activator concentration was determined by plotting a curve between the total PL intensity i.e. the area below the PL intensity vs wavelength, and activator concentration.

Crystal structures of the various phosphors were identified and X-ray powder pattern taken by the Philips X-ray diffractometer and an 11.48 cm diameter camera using nickel filtered  $\text{CuK}_\alpha$  radiation of wavelength 1.54175 Å. All X-ray powder patterns were obtained in terms of the intensity of the diffracted X-ray beam as a function of the diffraction angle  $2\theta$ . The interplanar spacings were measured to an accuracy of 0.001 Å near  $2\theta$  equal to 64°. The lattice parameters  $a$  and  $c$  of the unit cell were calculated by the following procedure (Kaelbe 1967).

(a) Indexing pattern of cubic system:

For cubic crystals, lattice spacing is given by

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}. \quad (1)$$

The values of interplanar distance of the corresponding diffraction peaks were calculated using Bragg's law,

$$2d_{hkl} \sin \theta = \frac{hc}{E_{hkl}} = \lambda. \quad (2)$$

From (1) and (2),

$$\sin^2 \theta / (h^2 + k^2 + l^2) = \frac{\lambda^2}{4a^2} = \text{constant}. \quad (3)$$

The lattice parameter  $a$  for cubic crystallites was estimated from (3).

(b) Indexing pattern of hexagonal system:

For hexagonal crystals, lattice spacing is given by

$$\frac{1}{d^2} = (4/3a^2)(h^2 + hk + k^2) + l^2/c^2. \quad (4)$$

Combination of Bragg's law and plane spacing equation for hexagonal yields the relation

$$\sin^2 \theta = A(h^2 + hk + k^2) + cl^2, \quad (5)$$

where

$$A = \lambda^2/3a^2, \text{ and } c = \lambda^2/4c^2. \tag{6}$$

For  $l = 0$ , (5) gives

$$\sin^2 \theta = A(h^2 + hk + k^2), \tag{7}$$

where possible values of  $(h^2 + k^2 + l^2)$  are 1, 3, 4, 7, etc. The values of lattice parameters  $a$  and  $c$  were estimated using (5), (6) and (7).

### 3. Results

The PL spectra of gold-doped (Zn,Cd)S mixed phosphors for given activator concentration (1000 ppm) are shown in figure 1. It is observed from the figure that the peak of the PL spectrum shifts towards longer-wavelength side with increasing CdS content.

Figure 2 illustrates the variation of  $\lambda_m$ , the wavelength corresponding to the peak PL intensity, with CdS content for these phosphors. It is found that  $\lambda_m$  varies from 476 nm to 588 nm for CdS variation from 0 to 40 per cent in hexagonal (Zn, Cd)S: Au, Cl mixed phosphors. It is observed from figure 3 that for a given activator concentration (1000 ppm), the PL intensity decreases with increasing CdS content in gold-doped (Zn, Cd)S hexagonal phosphors.

Figure 4 shows the dependence of PL intensity on activator concentration in (Zn, Cd)S: Au, Cl phosphors. It is seen that the PL intensity is maximum for a particular

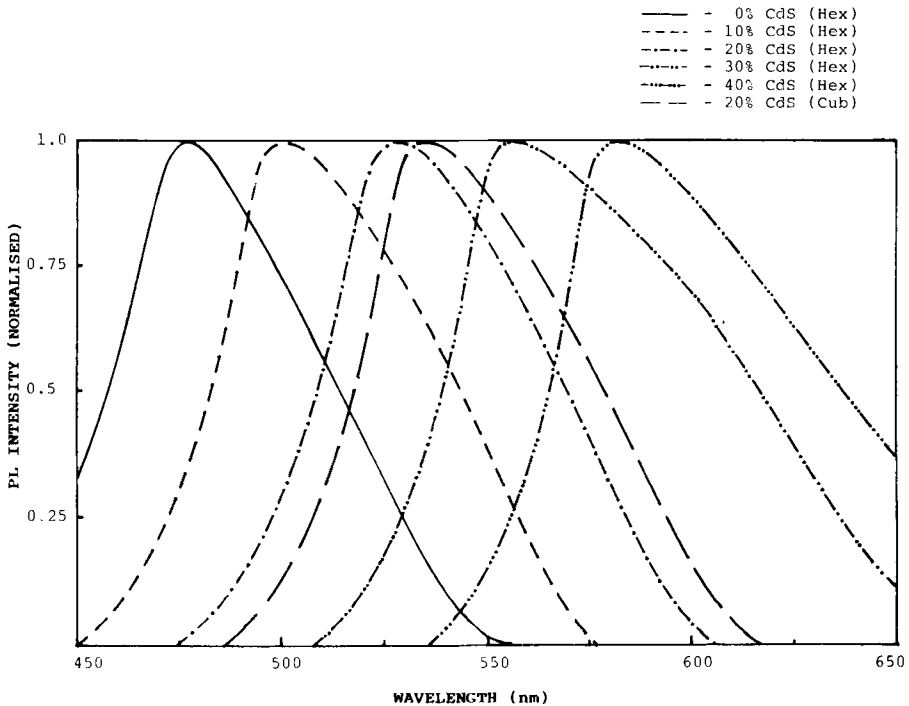


Figure 1. PL spectra of (Zn, Cd)S: Au, Cl mixed phosphors.

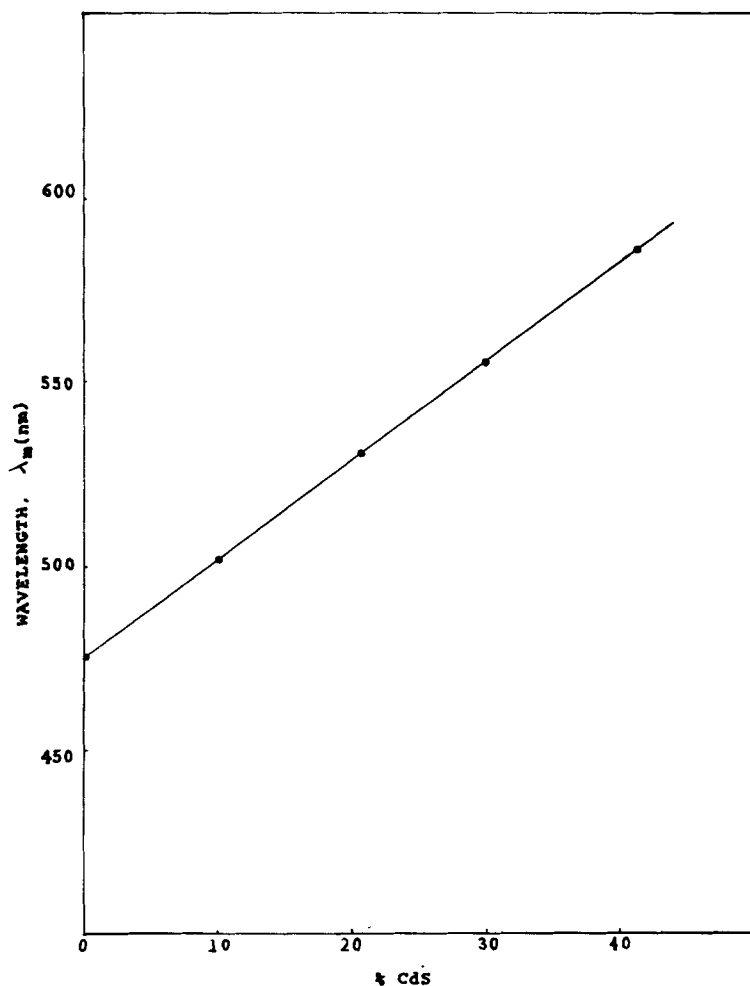
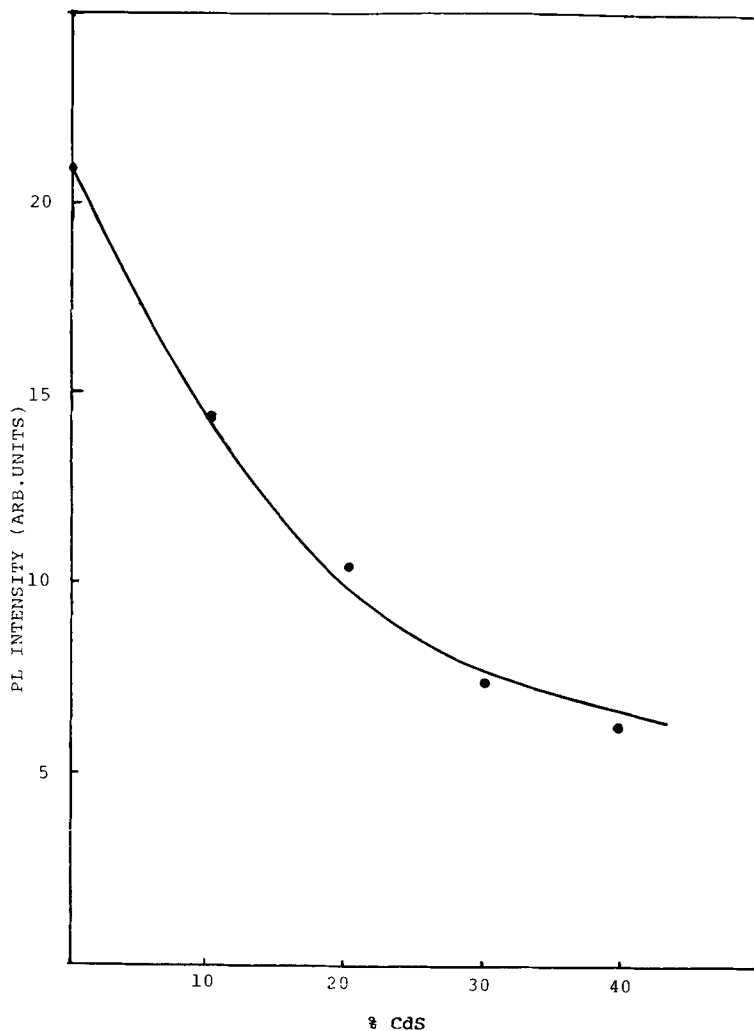


Figure 2. Effect of CdS concentration on wavelength corresponding to peak PL intensity ( $\lambda_m$ ) of hexagonal (Zn,Cd)S: Au, Cl phosphors.

activator concentration. Furthermore, the activator concentration for which PL intensity attains maximum value increases with increasing CdS content.

The diffraction patterns for gold-doped (Zn,Cd)S phosphors for given activator concentration (1000 ppm) and CdS content from 0 to 40 per cent are illustrated in figure 5, a-e. The diffraction patterns show sharp lines indicating a high degree of crystallinity. It is important because crystalline phosphors exhibit an efficient emission when they have a high degree of crystallinity (Leverenz 1968; Chandra and Majumdar 1983). Indexing of the diffractograms was done as described earlier from which it has been found that phosphor films are of hexagonal (wurtzite) structure as CdS content is increased. The occurrence of the single phase shows that ZnS and CdS are completely soluble in each other (Burton and Hence 1976; Vankar *et al* 1978).

Figure 6 shows the variation of the lattice constants with CdS content. It is found that lattice constants  $a$  and  $c$  increase monotonically with increasing CdS content.



**Figure 3.** Effect of CdS concentration on PL intensity of (Zn,Cd)S: Au,Cl phosphors with 1000 ppm Au.

#### 4. Discussion

In view of its importance for practical applications, a great deal of effort has been spent in the investigation of the well-known (Cu, Ag, Au) activated luminescence in ZnS phosphors (Shionoya *et al* 1964, 1965a, b; Kingsley *et al* 1965; Tripathi *et al* 1980, 1981). When a part of zinc in ZnS is replaced by cadmium, the fundamental absorption edge and the emission maximum of fluorescence band shift to the long-wavelength side, the separation between the activator level and full band remaining unchanged. The incorporation of Cd has two effects: in the right place, the Zn and Cd ions interact thoroughly, forming the fixed conduction band; in the second place, the lattice constant is increased, resulting in a decrease of the electrostatic

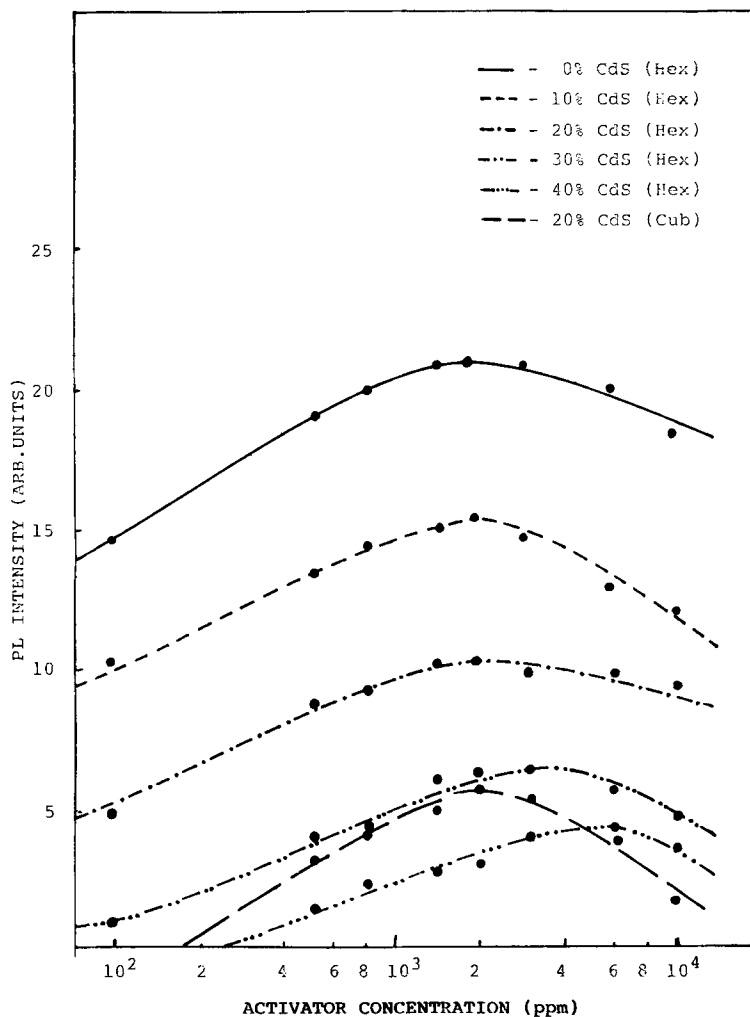
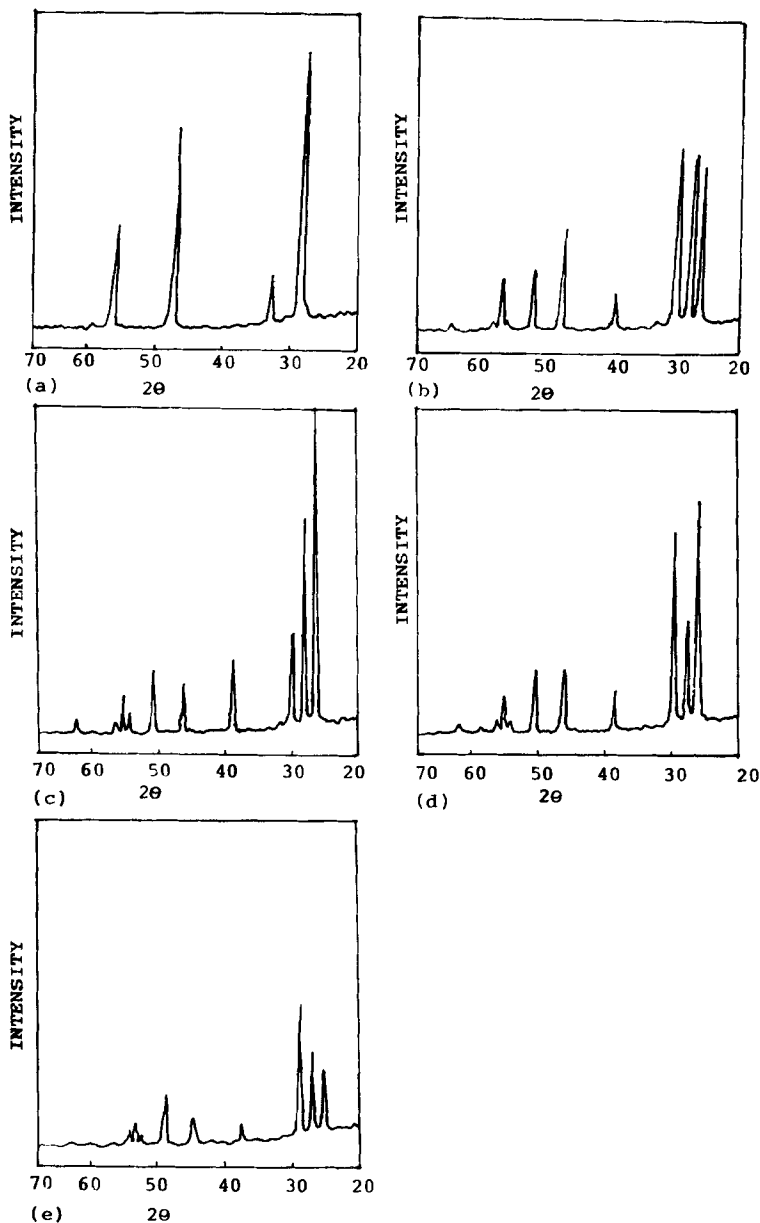


Figure 4. Effect of activator concentration on PL intensity of (Zn, Cd)S: Au, Cl phosphors.

forces and therefore in lowering of the levels of electrons at positive ions and a rise of the levels of electrons at negative ions (Leverenz 1968; Chandra *et al* 1981).

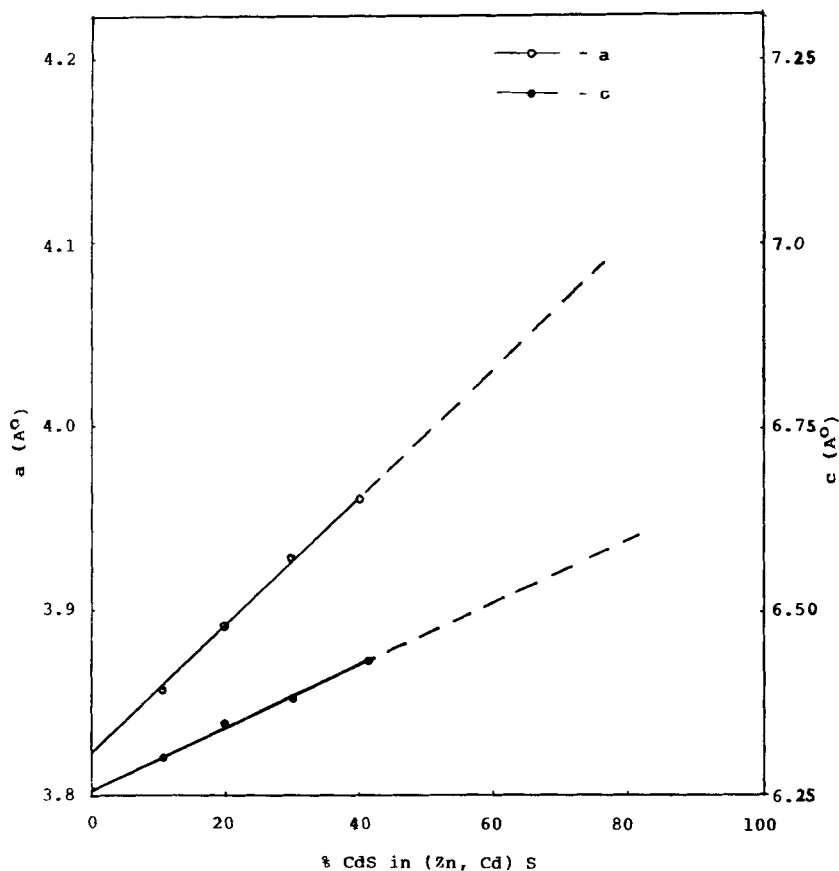
When the amounts of activator gold and co-activator chloride are of the same order, the long-wavelength band dominates. If, on the other hand, the activator concentration is much higher than that of the co-activator, then the short-wavelength band dominates. It has been shown in ZnS containing Au with Cl that although the incorporation of the activator ions is governed by the principle of charge compensation resulting in the formation of solid solution of ZnS–AuCl, the metal ion and halogen need not necessarily occupy neighbouring sites in the lattice. Therefore, there are still three possibilities for the fluorescence, viz. (i) the activator  $A^+$  with its neighbours, (ii) the halogen  $X^-$  with its neighbours, and (iii)  $A^+X^-$  with neighbours.

The second possibility is ruled out by the fact that ZnS activated with Au or Zn shows different bands, while on the other hand the peaks of systems containing different halogens do not show the slightest difference (Chandra *et al* 1981). The third



**Figure 5.** X-ray diffraction patterns for (Zn,Cd)S: Au, Cl phosphors with 1000 ppm Au and CdS concentration of (a) 0%, (b) 10%, (c) 20%, (d) 30% and (e) 40%.

possibility can also be discarded: if ions as different as  $\text{Cl}^-$  were to belong to the centre, marked differences should be expected. Therefore, only the first possibility remains open, and it must be concluded that this represents the actual situation where the centres of fluorescence consist of monovalent activator ions surrounded by four surplus ions. The fluorescence caused by Au and Zn is known to be due to an electronic transition between the conduction band or a defect level close to this band (Leverenz 1968).



**Figure 6.** Variation of lattice constants  $a$  and  $c$  with CdS content in hexagonal (Zn, Cd)S: Au, Cl phosphors.

X-ray diffraction data show that the 100% ZnS baked at 1050°C for half an hour is a mixture of blende and wurtzite forms, the blende proportion being the greater. The mixed crystals ZnS + CdS are also mixtures of blende and wurtzite; the wurtzite proportion was found to be greater and increased linearly as the amount of CdS increased.

In addition, the X-ray diffraction study shows that the lattice constants  $a$  and  $c$  increase regularly with increasing CdS content. On the other hand, the ratio  $c/a$  decreases with increasing CdS content. The ionic radii of zinc and cadmium atoms are 0.074 nm and 0.097 nm respectively (Abdel Kader and Elknoly 1990). The increase in the values of the lattice parameters  $a$  and  $c$  with increasing CdS concentration in the hexagonal gold-doped (Zn, Cd)S phosphors is attributed to the larger size of the cadmium ion compared to that of zinc ion.

It has been found that the PL intensity is maximum for a particular concentration of activator in the phosphor. When the activator concentration is increased, initially the number of luminescence centres increases, hence the PL intensity increases. Later, when the activator concentration increases beyond a certain level, concentration



quenching starts and the efficiency of radiation transition decreases. In the gold-doped (Zn, Cd)S mixed phosphors, the lattice parameters increase linearly with Cd ion content resulting in decrease of the band gap. As a matter of fact, the peak of PL spectra shifts towards longer-wavelength side with increasing CdS content in (Zn, Cd)S phosphors.

## 5. Conclusion

The shift in emission band energy due to increasing CdS concentration is very important for industrial applications such as in cathode ray tubes for television and in electroluminescent devices. The desired emission band (colour) can be obtained by adjusting the ZnS/CdS ratio in (Zn, Cd)S: Au, Cl phosphors. The (Zn, Cd)S: Au, Cl phosphors containing appreciable amounts (20%) of CdS are crystallized in the hexagonal structure. In contrast, the lattice constants  $a$  and  $c$  for hexagonal structures are found to increase with increasing CdS concentration.

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