

## Electroluminescence in (ZnS–ZnSe)Cu, H systems

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**Abstract.** A series of copper doped sulpho-selenide binary solid solutions, giving electroluminescent emission, right from green to red, has been prepared using ZnS and ZnSe in varying proportions. The behaviour of such polycrystalline samples was studied by usual methods in audio-frequency range. While the hydrogen ion acted as the main donor impurity in the entire series, its comparative study was made with chlorine coactivated samples. As regards the electroluminescent emission, while in the case of hydrogen coactivation, it is the transition from donor levels to the copper level that predominates, Cl-coactivation favoured direct transition from conduction band to same fundamental copper level. On frequency variation while the samples with ZnS–ZnSe composition showed marked peak shifts in their respective emission bands, no such effect could be observed in samples with single base.

**Keywords.** Electroluminescence; (ZnS–ZnSe) systems.

### 1. Introduction

While the study of blue-green emitting electroluminescent (EL) solids with single base lattice composition has been the subject of more or less countless investigations, the phosphors based on binary or ternary solid solutions of semiconducting materials and giving EL emission in different colours are relatively less studied. The first attempt in this direction using ZnSe as one of the constituents was probably made by Roberts (1952), who synthesized blue and green EL phosphors of the type (ZnS–ZnSe)Cu. A more comprehensive study, later on, was made by Hegyi *et al* (1957), who studied similar sulpho-selenide systems coactivated with different halogens. Kazankin *et al* (1959), prepared chlorine coactivated (ZnS–ZnSe) phosphors in the static atmosphere of a mixture of hydrogen chloride gases. A number of similar phosphors were also reported by Singh and Mohan (1968 *a* and *b*). For comparative study of such systems, the work done by Lehmann (1963, 1966) may be referred. In the present communication we have given an account of our studies of H-coactivation in zinc sulpho-selenide electroluminescent phosphors in conjunction with chlorine coactivation.

### 2. Experimental

The phosphor samples were prepared by heat treatment technique as described in the earlier communications (Prakash and Mohan 1969). The various propor-

tions of luminescent grade (impurity within  $10^{-4}\%$ ) ZnS and ZnSe mixed with copper (1%) were fired in quartz tubes at  $950^\circ\text{C}$  in the atmosphere of flowing hydrogen for 30 minutes. The unreacted copper and zinc oxide were washed with hypo and acetic acid.

The uniformity of solid solution was checked through photoluminescence. A uniform colour in UV suggests the homogeneous compound structure, otherwise one would have observed green and red spots due to ZnS and ZnSe respectively.

The EL panels were prepared by pressing the phosphor material in castor oil dielectric, between the two electrodes in the form of a sandwich. Such cells were excited at different voltages and frequencies employing an audio oscillator-cum-wide band amplifier unit. RCA 6217 and 7102 photomultipliers coupled with a battery operated ultrasensitive microammeter were used for measuring the EL output. For photoluminescence (pL)  $3650\text{ \AA}$  UV lamp was used. The spectral analysis was carried out using a prism monochromator, which utilizes a drum with L.C. of  $10\text{ \AA}$  and has a dispersion of about 50 wavelengths/mm of slit width. All the observations were later on corrected for spectral sensitivity of the photomultiplier and the intensity curves were normalized.

### 3. Results and discussion

#### 3.1. Spectral distribution

The spectral distribution curves of EL output at 100 Hz and 400 V excitation depict that as the percentage of ZnSe in the phosphor lattice is increased, the peak emission shifts from green ( $5200\text{ \AA}$ ) to red ( $6300\text{ \AA}$ ) (figure 1). The forbidden band width for ZnS being  $3.64\text{ eV}$  and for ZnSe  $2.6\text{ eV}$  on forming a solid solution of the two components a resultant compound lattice is formed which causes the emission to shift towards the higher wavelength side (Lehmann, 1967). Such a variation is observed to be almost linear beyond 20% ZnSe (figure 3). In figure 2 is shown the pL of  $(6\text{ZnS}-4\text{ZnSe})\text{Cu}$ , X (X=H, Cl) samples under  $3650\text{ \AA}$  UV excitation. The emission from H-coactivation has its peak at  $5500\text{ \AA}$ , while that of the Cl, at  $5450\text{ \AA}$ .

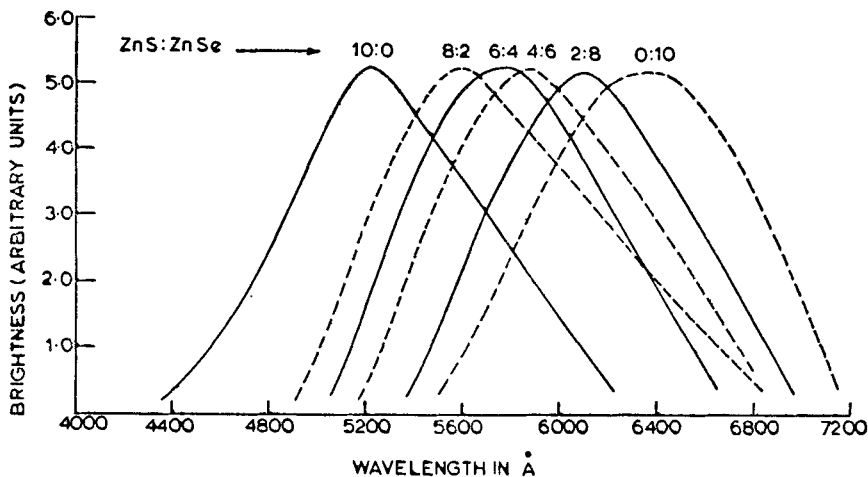


Figure 1. Spectral distribution of EL output from various samples of  $(\text{ZnS-ZnSe})\text{Cu}$ , H system at 100 Hz and 400 volts.

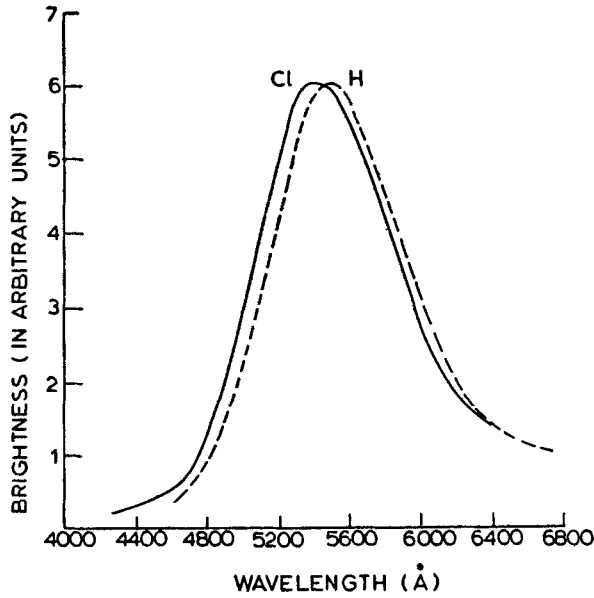


Figure 2. Spectral distribution of PL from  $(6\text{ZnS}-4\text{ZnSe})\text{Cu}, \text{X}$  ( $\text{X} = \text{H}, \text{Cl}$ ) samples.

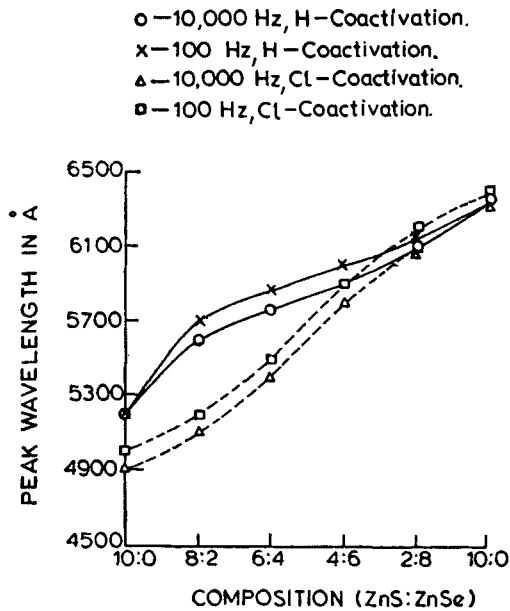


Figure 3. Variation of peak emission with frequency at different fixed compositions.

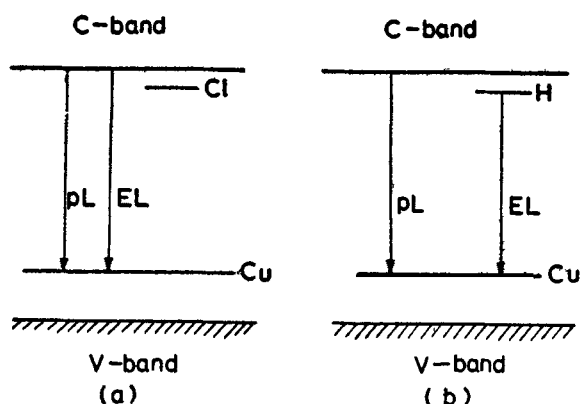


Figure 4. Energy level diagram showing transitions for (a) Chlorine (b) Hydrogen coactivated samples.

### 3.2. Transitions

The EL studies of (6ZnS-4ZnSe)Cu, Cl sample show its peak emission at 5450 Å in contrast with the H-coactivation at 5800 Å, of similar composition. This means for Cl-coactivation both the pL and EL transitions are between the same levels, *i.e.*, from the conduction band to Cu-level. Whereas for H-coactivation pL may be due to a transition from conduction band to Cu-level while EL due to transitions from H-donor levels to same fundamental Cu-level (figure 4). Meaning thereby that for Cl-coactivation the transitions from donor levels are less probable.

The same effect is noticed by figure 3. The EL peaks due to Cl-coactivation are always found to lie at lower wavelengths as compared to similarly processed H-coactivated samples. It is also noticed that this difference of wavelength goes on reducing with the increasing proportion of ZnSe, and ultimately vanished for samples with more than 80% ZnSe. This effect is due to the fact that by successive increase of ZnSe into the base matrix the depth of donor levels below the conduction band is gradually decreased along with the reduction in total energy band gap (Zalm 1956).

### 3.3. Frequency dependence

Figure 3 shows a shift of the order of 100 Å in the EL peaks towards the lower wavelengths as the excitation frequency is increased from 100 Hz to 10 kHz (keeping the voltage fixed at 400 V) except for 100% ZnS and 100% ZnSe samples coactivated with hydrogen.

For H-coactivated samples this effect may be due to a narrow distribution of donor levels which has been found to be a characteristic feature of these systems (Prakash and Mohan 1969). So even on increasing the applied frequency the transitions take place practically from the same narrow range of the donor levels. In the case of mixed lattice structure, the narrowness of the donor distribution is rather broadened, and that is why a peak shift is observed.

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