

EFFECT OF CHLORINE CONCENTRATION ON THE SPECTRAL CHARACTERISTICS OF ELECTROLUMINESCENCE IN ZnS: Cu: Cl PHOSPHOR

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ZnS: Cu: Cl phosphor prepared under a vacuum firing process is found to give blue electroluminescence with emission peak at 460 nm which remains unaltered with the frequency of the excitation voltage. Addition of excess chlorine in the phosphor gives blue, green and red emission at 460, 520 and 640 nm. The intensity of the blue band decreases and it finally disappears as chlorine concentration is increased. A scheme involving three energy levels attributed to Cu^{2+} , Cu^+ and Cl^- centres in ZnS explains the experimental results completely.

1. INTRODUCTION

THE PROPERTIES of copper doped ZnS phosphors giving blue, green or red electroluminescence (EL) have been discussed extensively in the literature. Among them the blue and green emitting ones are the most efficient and well investigated phosphors. However it appears that there is no guiding physical principles for the preparation of such phosphors with different emission colour, and the various procedures given in this context seem to arise purely from the past experience of the worker involved and from reasons of convenience [1]. Thornton has reported that the emission colour of this kind of phosphors depends on the amount of copper and chlorine present in the sample [2]. Generally these phosphors show a change in emission colour as the frequency of excitation is changed. Different models have been suggested to explain the occurrence of the two emission bands and their frequency dependence [3, 4]. But these models do not furnish a satisfactory explanation for all the observations on these phosphors. Moreover these models do not take into account the red emission from this phosphor. Also a ZnS based EL phosphor (ZnS: Ag: Cu: Cl) giving only the blue emission band which is independent of the excitation frequency has been reported recently [5]. Thus there are compelling reasons for making further investigations on this phosphor directed towards clarifying the various physical processes involved in its EL emission. In this communication we report the results of our experiments which shed some light on the above aspects of EL in such phosphors. The method of preparation and the emission characteristics of a blue emitting ZnS: Cu: Cl phosphor with the wave length of emission peak independent of the excitation frequency are outlined. Also the spectral

characteristics and its dependence on the frequency of the excitation voltage of another set of phosphors prepared by adding an excess amount of chlorine are investigated in detail. The experimental results obtained are found to be fully consistent with a system having three energy levels occurring between the valence and conduction bands of ZnS.

2. EXPERIMENTAL

For preparing blue emitting EL phosphor a weighed amount of ZnS (luminescent grade) was mixed with cupric acetate solution containing 0.5 wt. % Cu and 5 wt. % NH_4Cl added as flux and the mixture was slowly heated and dried. The black powder thus obtained was fired at 1050°C for 90 min. in a vacuum furnace at 10^{-2} torr. A second set of phosphors was prepared with the same concentration of copper but with varying amount of chlorine by adding specific quantities of HCl in the primary mixture and firing it in a stagnant sulphur atmosphere, at 1050°C . The EL cell was fabricated by sandwiching the phosphor powder layer, dispersed in castor oil, in between a conducting glass plate and an aluminium block which acts as the second electrode. A thin mica sheet introduced within the cell and kept adjacent to one of the electrodes prevents electrical breakdown.

A variable frequency high voltage (500–1500 V r.m.s.) sine wave generator was used to excite the cell. The spectra were recorded with a 0.5 M Jarrel Ash scanning spectrometer having an EMI 9683 KQB PMT with S-20 cathode as detector along with a highly stabilized power supply (EMI Model PM 28B).

3. RESULTS AND DISCUSSION

Figure 1 shows the EL spectra of the vacuum fired

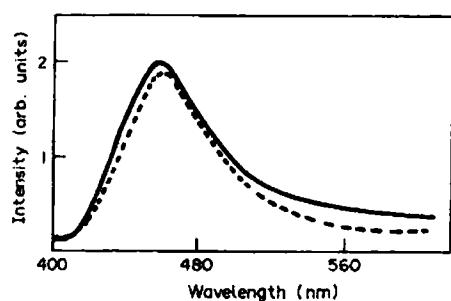


Fig. 1. The EL spectra of the blue emitting ZnS: Cu: Cl phosphor excited with sine wave voltage at 50 Hz (broken line) and 10 kHz (solid line).

ZnS: Cu: Cl phosphor recorded at 50 and 10 kHz excitations. It can be seen that the emission spectrum consists of a single band with its maximum at 460 nm which is independent of the frequency of excitation. Thus the present ZnS: Cu: Cl phosphor has virtually the same spectral characteristics as those reported in the case of ZnS: Ag: Cu: Cl phosphor [5] though the former does not contain any silver.

Unlike the blue emitting phosphor the second set of ZnS: Cu: Cl samples having excess chlorine shows three distinct bands in its emission spectrum with the maxima at 460, 520 and 640 nm respectively. Figure 2 gives the normalized EL spectra recorded in the case of phosphors containing different concentrations of chlorine. It is observed that a higher chlorine content increases the relative intensity of the red band while the blue band is reduced in its intensity. Beyond a certain chlorine concentration the blue band is completely suppressed and only green and red bands are observed.

The above experimental observations can be satisfactorily explained on the basis of an energy level scheme shown in Fig. 3. Based on the method of preparation of these phosphors, it is possible to identify [6] three different centres viz., Cu^{2+} , Cu^+ and Cl^- introduced into the ZnS lattice as a result of the firing process. It is evident that the vacuum fired phosphor contains predominantly the Cu^{2+} centres giving rise to the 460 nm transition which remains unaffected by the change in excitation frequency. The addition of dilute HCl in the mixture converts a portion of the cupric salt into cuprous chloride, thus producing Cu^+ and Cl^- ions. The relative concentration of Cu^{2+} , Cu^+ and Cl^- centres should depend entirely on the amount of chlorine added in the form of HCl in the initial mixture. So the relative intensities of the green and red band should increase as the chlorine concentration is increased and the blue emission should be completely suppressed at a sufficiently high concentration of HCl. This in fact is observed experimentally (Fig. 2, Curve c).

Detailed measurements show that the brightness vs

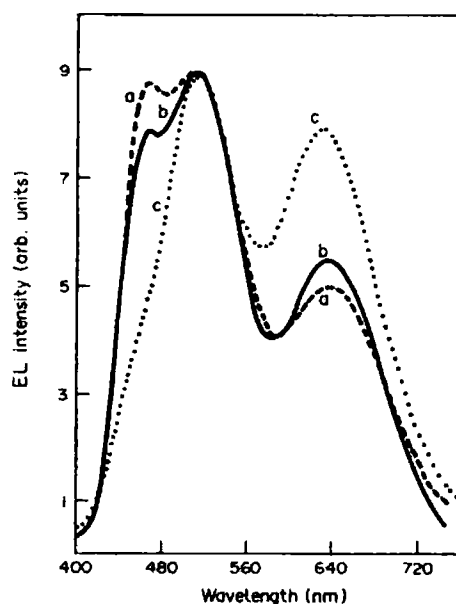


Fig. 2 Normalized EL emission spectra recorded at 2.5 kHz for three phosphor samples a, b, c containing chlorine in the ratio 1:2:5 in the prefixed mixture.

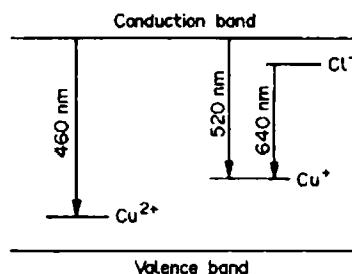


Fig. 3. The proposed energy level scheme for ZnS: Cu: Cl phosphor giving blue, green and red EL emission.

excitation voltage obeys the customary exponential relation, $\log B \propto 1/\sqrt{V}$ indicating the occurrence of acceleration collision mechanism involved in the EL emission. But it is to be noted that the relative intensities of the various bands in the emission spectrum remain unaltered for any change in the excitation voltage. In this phosphor the initial electrons required for the acceleration and collision excitation of the luminescent centres arise mainly from the field ionization of the chlorine (donor) levels which are equivalent to deep traps. These electrons are either raised to the conduction bands or they recombine with a nearby Cu^+ centre giving rise to red emission. The green band can be attributed to the recombination of Cu^+ centres with the conduction band electrons. According to the present energy level scheme the red band should show the smallest rate of increase of

intensity with the increase of the frequency of excitation voltage since it evidently arises from donor acceptor recombination which relatively is a slow process [3, 7]. Such an effect does indeed take place as can be seen from Fig. 4. Here an increase in the frequency of excitation clearly increases the intensity of the blue and green bands but the red band is virtually unaffected indicating saturation. On the basis of the present energy level scheme the position of the Cl^- donor can be calculated and is found to be 0.46 eV below the bottom of the conduction band. This is in good agreement with the

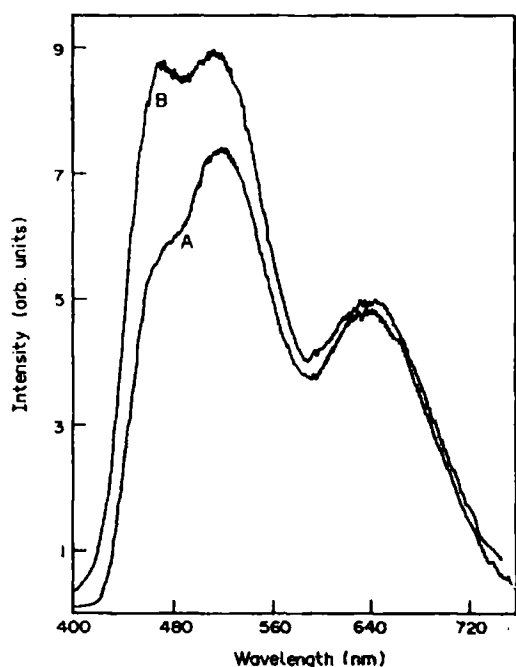


Fig. 4. The EL spectra recorded for the sample (a) at two different excitation frequencies: (A) 1 kHz, (B) 2.5 kHz.

result obtained from thermoluminescence experiments [8].

4. CONCLUSION

In conclusion, experimental results show that addition of excess chlorine in the form of HCl in the prefired mixture gives green and red EL emission from ZnS: Cu: Cl phosphor apparently due to the creation of additional Cu^+ and Cl^- centres, the concentrations of which are strongly dependent on the amount of excess chlorine added. A detailed study of the EL emission characteristics indicates the occurrence of three different energy levels attributed to Cu^{2+} , Cu^+ and Cl^- centres in ZnS.

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