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A study of the white electroluminescence in ZnS:Cu,Pr,Cl phosphors

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Abstract. The method of preparation of ZnS phosphors doped with praseodymium and copper is given. The electroluminescence (EL) spectrum of ZnS:Pr,Cl has two broad bands at 470 and 570 nm. ZnS:Cu,Pr,Cl gives white emission with spectral peaks at 470, 520, 570 and 640 nm. The EL spectra of both types of phosphor exhibit a conspicuous colour shift as the frequency of the excitation voltage is varied. Detailed investigations show that the relative intensities of spectral peaks are strongly dependent on the frequency of the excitation voltage. The colour shift is explained on the basis of the Schön–Klasens model.

1. Introduction

ZnS doped with rare earth ions forms a very important class of phosphors for the fabrication of electroluminescent (EL) devices. The host lattice here plays a vital role in excitation of rare earth luminescence by energy transport through hole–electron motion. Such phosphors activated with metal ions produce emission in practically the entire visible range (Bube 1953). The properties of ZnS phosphors doped with rare earth ions have been discussed extensively in the literature (Chase *et al* 1969, Kingsley *et al* 1965, Kobayashi *et al* 1985). However, not much attention seems to have been devoted to a systematic study of the dependence of EL emission on dopant concentration or on excitation frequencies, especially in the case of praseodymium-doped ZnS phosphors. Chase *et al* (1969) have reported thin film devices consisting of co-evaporated ZnS and PrF₃ having emission mainly in blue and red regions.

In this paper the method of preparation and emission characteristics of ZnS:Pr,Cl having spectral peaks at 470 and 570 nm are outlined. The dependence of 470 and 570 nm bands on excitation frequencies and on Pr doping concentrations is also investigated in detail. Similar studies have also been carried out in the case of copper-co-activated ZnS:Pr,Cu,Cl phosphors. The observed shift in emission colour with excitation frequency is explained on the basis of the model proposed by Schön and Klasens.

2. Sample preparation and experimental set-up

The electroluminescent phosphors were prepared by mixing a weighed amount of ZnS (luminescent grade)

with known percentages of praseodymium chloride (99.99% pure) and NH₄Cl which acts as a flux. A slurry of the mixture was prepared in an aqueous medium and this was slowly heated and dried. The resulting solid mass was crushed and mixed with an equal amount of sulphur and introduced into the high-temperature zone of a horizontal furnace maintained at 1050 °C. One end of the furnace was closed while the other end was fitted with a small-bore stopper to allow the gases evolved during the solid state reaction to escape. Firing was done at the said temperature for 90 minutes. The white-emitting phosphors were prepared by adding cupric acetate solution containing 0.5 wt% copper and PrCl₃ solution containing 0.5 wt% Pr to the weighed amount of ZnS along with 5 wt% NH₄Cl added as a flux. This slurry was dried and fired in the same manner as described above.

The investigations were carried out by using an experimental electroluminescent powder cell, made by sandwiching a thin layer of the phosphor powder dispersed in castor oil in between two electrodes. The front electrode was a tin-oxide-coated glass plate prepared by spraying an appropriate solution of SnCl₄·5H₂O in alcohol on a glass substrate kept at 450 °C. Introduction of a thin mica sheet between the phosphor layer and one of the electrodes eliminates electrical breakdown.

A variable-frequency high-voltage sine/square wave generator was used to excite the cell. The EL spectrum was recorded using a 0.5 m Jarrel–Ash scanning spectrophotometer coupled to an EMI 9683 KQB photomultiplier tube (PMT) with an S-20 cathode. The PMT anode current was amplified using a low-noise high-gain pre-

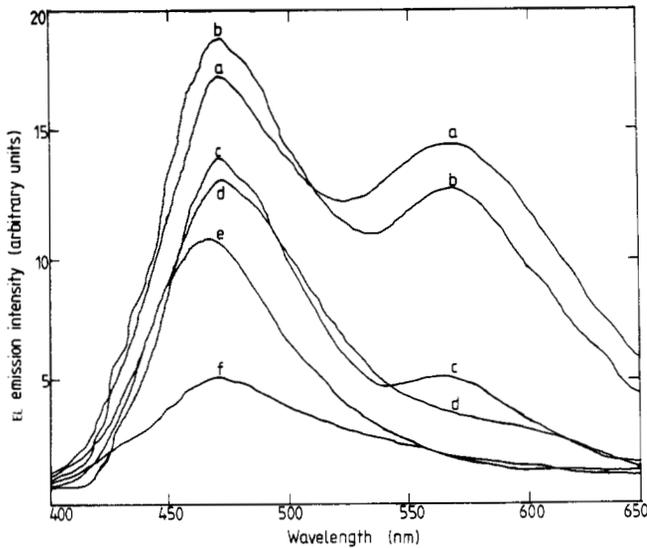


Figure 1. EL spectra of ZnS:Pr,Cl phosphors containing various concentrations of Pr. a, b, c, d, e and f are phosphors containing 1.0, 0.5, 0.25, 0.1, 0.02 and 0.01 wt% of Pr respectively in the pre-fired mixture under 1 kHz excitation frequency and 400 V peak-to-peak.

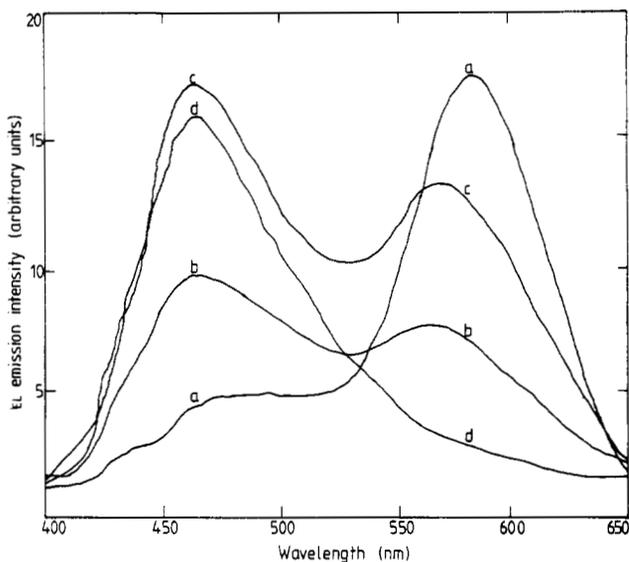


Figure 2. EL emission spectra of ZnS:Pr,Cl (Pr 0.5 wt%) at various excitation frequencies under 400 V peak-to-peak. a, 100 Hz; b, 400 Hz; c, 1 kHz and d, 4 kHz.

amplifier (Pillai *et al* 1982) and recorded with a strip chart recorder. No correction due to PMT spectral response was applied to the recorded EL spectra.

3. Results and discussion

The EL spectrum of ZnS:Pr,Cl phosphors consists of two bands. One appears at 470 nm and the other at 570 nm (figure 1). The emission intensities of these bands are found to depend on activator (praseodymium) concentration as well as on the frequency of the excitation voltage (figure 2). An important feature of the experimental results obtained here is that EL emission shows a colour shift towards the blue in a

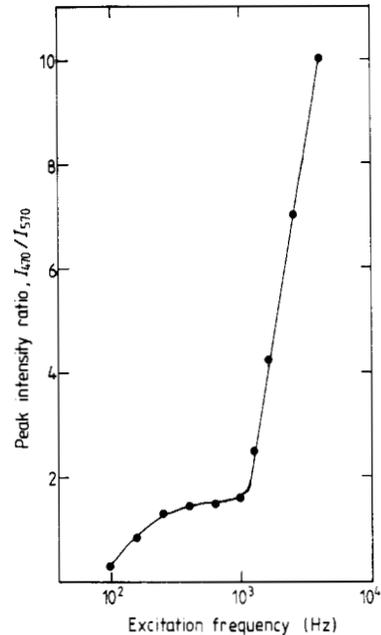


Figure 3. Variation of ratio of peak intensities of 470 and 570 nm bands with frequency of excitation voltage. Note that from 0.5 to 1.5 kHz the intensity remains virtually constant which is in accordance with Schön-Klasens model.

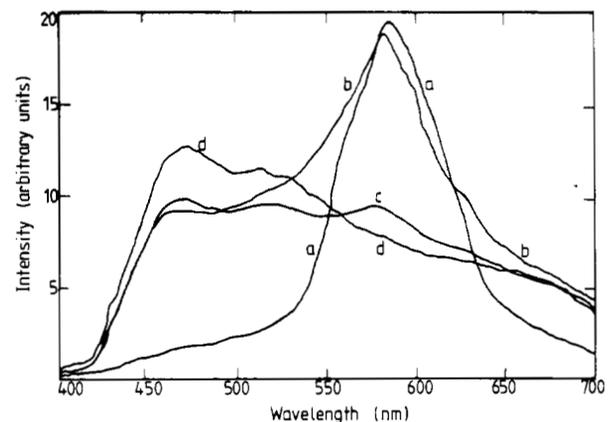


Figure 4. EL spectra of ZnS:Cu,Pr,Cl (Cu 0.5 and Pr 0.5 wt%) phosphors at various excitation frequencies 400 V peak-to-peak. a, 100 Hz; b, 500 Hz; c, 1 kHz and d, 2 kHz.

striking manner as frequency of excitation is increased. This is apparently caused by a change in relative intensities of bands rather than by a major shift in emission wavelengths. Figure 3 gives the variation in ratio of intensities (I_{470}/I_{570}) with excitation frequency. In the case of the EL spectrum of ZnS:Cu,Pr,Cl it has been found that emission peaks occur at 470, 520 and 570 nm in addition to a shoulder peak at 640 nm. These phosphors also exhibit a shift in overall emission colour as the frequency of excitation is varied (figure 4). Keeping the doping concentration of Pr at 0.5 wt%, when the Cu concentration is increased, the emission intensities of all the bands are found to increase. For a concentration of 0.5 wt% of Cu at an applied voltage frequency of 1 kHz, the emission bands have more or less equal intensities and the emission has an overall white appearance (figure 5).

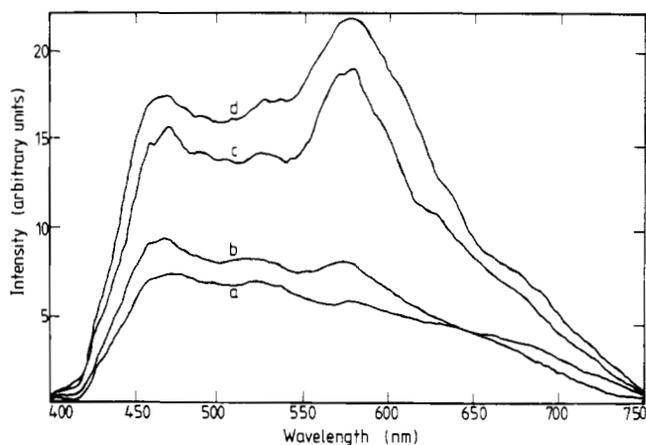


Figure 5. EL spectra of ZnS:Cu,Pr,Cl phosphors at 1 kHz excitation frequency. a, 400 V; b, 500 V; c, 600 V and d, 800 V peak-to-peak.

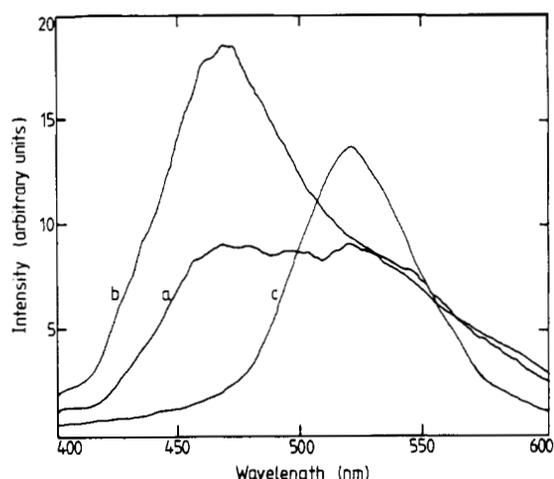


Figure 6. EL emission spectra of ZnS phosphors without any activators at various excitation frequencies under 400 V peak-to-peak. a, 100 Hz; b, 2.5 kHz and c, EL spectrum of ZnS:Ag,Pr,Cl (Ag 0.5 wt%, Pr 0.5 wt%) under 1 kHz excitation frequency 400 V peak-to-peak (c recorded at much reduced gain).

The origin of the 470 and 570 nm bands can be attributed to ${}^3P_0 \rightarrow {}^3H_4$ and ${}^3P_0 \rightarrow {}^3H_5$ transitions of Pr^{3+} ions on the basis of the assignment made by Magno and Deike (1962) and Chase *et al* (1969). Recombination of conduction band electrons with Cu^{2+} and Cu^+ ions may also give rise to emission in these regions. But the observed proportionate increase of intensity of 470 and 570 nm bands with Pr concentration clearly indicates that these bands originate essentially from the transitions occurring in Pr^{3+} ions.

Figure 6 shows the EL emission spectra of ZnS phosphor prepared without any dopants but within 5 wt% of NH_4Cl with the same firing conditions as for the above phosphors. The emission spectrum of this phosphor is found to be a broad band centred around 500 nm, which though very weak also shows a frequency-dependent emission profile. The atomic absorption analysis shows that the luminescent-grade ZnS used as a starting material contains about 80 ppm by weight of copper. Hence the emission in this

phosphor apparently arises from the presence of levels due to Cu centres in the ZnS band gap. The emission colour of ZnS:Cu,Cl phosphors depends on the amount of copper and chlorine present in the sample (Thornton 1960). Also, it is possible to identify three different types of centres, namely Cu^{2+} , Cu^+ and Cl^- , introduced into the ZnS lattice as a result of the firing process (Godlewski *et al* 1982). It has been shown that the recombination of conduction electrons with Cu^{2+} gives rise to a 460 nm emission and with Cu^+ gives rise to a 520 nm emission (Pillai and Vallabhan 1983).

In ZnS phosphors containing copper and chlorine the relative concentration of Cu^{2+} , Cu^+ and Cl^- ions in the phosphor has been found to depend on the amount of chlorine in the initial mixture (Pillai and Vallabhan 1983). Therefore in ZnS:Pr,Cl phosphors, as the amount of $PrCl_3$, which is the starting material for Pr doping, is increased there is a good possibility of having more Cu^+ centres since the original luminescent-grade ZnS powder has been found to contain copper. Also, because the tendency for all lanthanides in ZnS:Cu,Ln is to emit from levels near 20000 cm^{-1} , sensitisation may involve energy transfer from Cu defects at or slightly above 20000 cm^{-1} (Kingsley *et al* 1965). In the present case the ${}^3P_0 \rightarrow {}^3H_4$ and ${}^3P_0 \rightarrow {}^3H_5$ transitions can thus be considered to be excited by the resonant energy transfer from Cu^{2+} and Cu^+ levels respectively. As observed earlier (Pillai and Vallabhan 1983), when the concentration of chlorine in the starting material becomes higher due to the addition of more $PrCl_3$, the number of Cu^+ centres may also increase. Thus the intensity of the 570 nm band increases at higher Pr concentrations owing to the possibility that this band is excited via the Cu^+ level due to the ${}^3P_0 \rightarrow {}^3H_5$ transition of Pr^{3+} ions. The energy transfer from Cu to Pr is resonant, and this can be further demonstrated by substituting Ag instead of Cu as the sensitising impurity. ZnS:Ag,Pr,Cl phosphors prepared along the same lines as indicated previously do not give the 470 and 570 nm emissions; instead they give only a broad band emission centred at 520 nm (figure 6). Thus the 3H_4 and 3H_5 levels are not now excited by energy transfer processes. Also it has been noted that the emission spectrum of silver-co-activated phosphor is independent of the excitation frequency of the applied voltage (Jayaraj and Vallabhan 1989).

Cu concentration is high in the case of ZnS:Cu,Pr,Cl phosphors, and in addition to the transitions of Pr^{3+} ions the chlorine centres below the conduction band get field-ionised. These electrons either form a raised conduction band or they can recombine with a nearby Cu^+ centre with emission at 640 nm. In addition recombination of conduction electrons with Cu^+ and Cu^{2+} centres gives emissions at 520 and 460 nm (Pillai and Vallabhan 1983) respectively. This makes the EL emission white in appearance.

The apparent colour shift in the emission from these EL phosphors can be accounted for within the framework of the Schön-Klasens theory concerning tem-

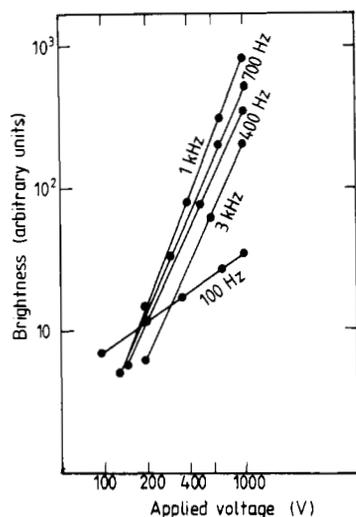


Figure 7. Plot of $\log B$ against $\log V$ for a typical ZnS:Pr,Cl EL cell excited at different frequencies.

perature quenching of luminescence, which was adopted by Waymouth *et al* to explain the field-induced colour shift in electroluminescent ZnS phosphors (Klasens 1953, Schön 1942, Waymouth and Bitter 1956). The presence of copper in the present case creates two energy levels within the band of ZnS due to Cu^{2+} and Cu^+ centres below the conduction band. An empty low-lying centre will be filled by an electron from a filled higher centre, if sufficient time and activation energies are available. Thus for the applied voltage at lower excitation frequencies, time is available to transfer the electron from a higher centre, and hence more frequent recombinations take place at a higher centre so that emission at longer wavelengths predominates. At higher excitation frequencies the case is different and there will be no rapid transfer of electrons from a higher centre to a lower centre; this favours shorter-wavelength emission. But in the case of ZnS:Pr,Cl and ZnS:Cu,Pr,Cl phosphors the emissions are mainly due to internal transitions: $^3\text{P}_0 \rightarrow ^3\text{H}_4$ and $^3\text{P}_0 \rightarrow ^3\text{H}_5$ occurring in Pr^{3+} ions. However, these levels, which have energies closely matching those of Cu^{2+} and Cu^+ , can now be excited due to resonant energy transfer from the Cu defects to Pr^{3+} levels. Since the excitation of Cu levels is a frequency-dependent process the energy transfer from Cu to Pr^{3+} ions thus also becomes frequency dependent. This evidently explains the phenomenon of frequency-dependent emission colour in ZnS:Pr,Cl and ZnS:Cu,Pr,Cl phosphors.

The plot of $\log B$ against $\log V$ (figure 7) shows that the brightness-voltage relation follows $B = bv^n$, where b and n are constants. This can be considered as a special case of the Destriau relation (Destriau and Ivey 1955) given by $B = B_0V^n \exp(-b/V)$. Such characteristics arise when carrier acceleration occurs at a Mott-Schottky barrier. A Mott-Schottky barrier often exists at the electrode-phosphor interface giving rise

to a high-field region, where carriers are accelerated to energies necessary for the ionisation of luminescent centres. The width of the barrier is normally proportional to \sqrt{V} . But if the width of the barrier becomes equal to the length of the crystal, then barrier width cannot increase any more due to the field, and the brightness changes are now proportional to V^n where n is a positive number. Such a transition has been interpreted by many workers in terms of size of the particles or length of the comets (Lehman 1958, Fisher 1962).

4. Conclusion

Pr^{3+} -doped ZnS EL phosphors were prepared. It was found that copper-co-activated ZnS:Pr,Cl phosphors give white emission at an excitation frequency of 1 kHz. The EL emission colour can be shifted by varying the frequency of the applied voltage. The shift in colour of EL emission can be explained on the basis of the Schön-Klasens model. The $\log B$ versus $\log V$ plots of the EL cell have been observed to be straight lines indicating that carrier acceleration occurs across a Mott-Schottky type barrier.

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