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Temperature dependence of electroluminescent emission from (ZnS-Cu)H double band phosphors

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Temperature dependence of electroluminescent (EL) emission from (ZnS–Cu)H double band phosphor has been studied separately for both the bands —blue and green— under varied operating field conditions within the range −100°C to +100°C. The permanent type of EL cells were mounted on copper platform, cooled with liquid air and the light output was measured through a microammeter and photomultiplier assembly. The EL emission shows a maximum on temperature scale which depends on the conditions of excitation such as frequency, voltage and spectral range of light emission. The temperature peaks of blue and green bands occur in different range and possess different shape and area. A shift in peak position is observed on temperature scale due to change in field frequency or voltage and both the peaks behave differently in this respect. The transfer of energy from green to blue centres with respect to change in field frequency and temperature is also studied. The results have been explained on the basis of thermal excitation of the electrons from the donor centres.

1. INTRODUCTION

The temperature dependence study of electroluminescence (EL) is interesting not only because it modifies the EL emission, but it yields information to understand the nature of the phosphor. Destriau (1947) was probably the first who studied the temperature dependence of (ZnS–ZnO) phosphors and observed that the threshold voltage of excitation falls as the temperature is lowered. Later on, various workers in the field carried out investigations on temperature dependence of EL emission for a variety of systems and under different operating parameters. Mention may be made of the works done by (Roberts 1952; Halsted 1954; Mattler 1956; Haake 1957) in this field.

As the temperature dependence of double band phosphors had been relatively less studied and mechanism of energy transfer between the two types of centres is not very clear, a (ZnS–Cu)H double band phosphor was selected for study. In the present communication we give an account of our studies in the light of existing theories.

It may be remarked here that the EL capacitor is a hetrogeneous system and average characteristics depend upon, time, coordinate, particle size and binder etc. which leads sometimes to inconsistent results. Mention may be made of the works by Ghukova (1972) and Maxia (1973) who have tried to discuss the various aspects of temperature dependence of EL emission both for single band and double band phosphors.

2. Experimental

The measurements were carried out with permanent type of EL cells. The phosphor material was sandwiched between two parallel plates of a capacitor as dielectric. Firstly, conducting mica sheets (thickness 0·04 mm) were prepared by spraying $SnCl_4$ solution at a temperature of 600°C on one of its surfaces (This forms a thin and transparent layer of SnO_2). Over the non-conducting surface, i.e., on the other side, phosphor material was sprayed (suspended in araldite) and dried to form a thin layer. The second electrode was provided by colloidal silver layer painted over the phosphor surface.

Such a cell (size 1″ × 1″) was mounted over a copper sheet platform fitted at the end of a copper rod of about 10″ length and 1″ diameter. The desired temperature was achieved by cooling the rod with liquid air contained in a Dewar flask or by heating the rod with a replacable cylindrical heater. The temperature was measured with the help of a copper-constantan thermocouple and the calibration was checked from time to time with standard freezing mixtures. In order to avoid the condensation of water vapour over the cell surface, an air (dry) blower was employed which otherwise reduces the intensity of light. A piece of thick (0·5 cm) glass sheet was kept over the cell surface. In order to keep its temperature unaffected by the air blow (figure 1).

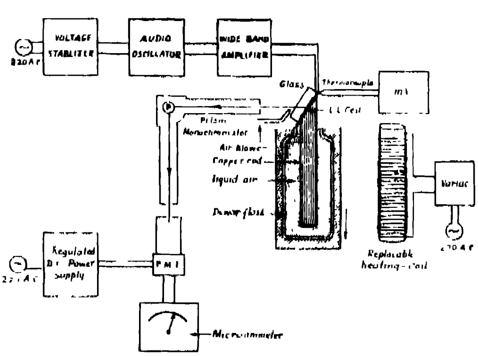

Fig. 1. Schematic representation of experimental set up for studying temperature dependence of EL out put.

The cell was excited at different voltages and frequencies with the help of an audio-oscillator cum wide-band amplifier unit, which could give undistorted sinusoidal voltages up to 600 V in the frequency range 50 c/s to 10 Kc/s. The light output of the cell was measured (In arbitrary units) with an ultrasensitive dc microammeter (RCA WV-84 C) and photomultiplier (RCA 6217) assembly. The two peaks of emission blue and green. were isolated by employing suitable interference filters/prism monochromator. All the observations were corrected for the spectral sensitivity of photomultiplier. The peak intensities were normalized (put to same level) while plotting the graphs.

3. Results and Discussion

The phosphor sample studied here shows two EL peaks, around 4600 Å and 5200 Å for normal field excitation. As the frequency of excitation is increased, unlike Chlorine coactivation, the peaks do not show any shift towards lower wavelengths, but a sort of sea-saw action (exchange of intensities) is observed as regards the relative evolution of the two peaks (Prakash & Mohan 1969). The behaviour of the two peaks as regards the temperature dependence was studied individually.

3.1. *Frequency effect*

Average brightness versus temperature curves were recorded for the different values of the applied field (240 V) frequency within the range −100°C to +100°C At low temperature, the electrons captured in traps, in the low field region, have relatively lower chance of escape and therefore the number of electrons taking part in the radiative transition is relatively small and hence the brightness level. As the temperature is increased, the number of excited as well as recombining electrons in the available frequency interval increases and hence the brightness. If the temperature is further raised, because of thermal quenching, the intensity falls down (Curie 1963). Thus with rise in temperature, the brightness increases slowly, attains a maximum value and then falls down. There lies also the possibility of secondary maxima, if the phosphor contains deeper traps, because under the increased thermal action, they would begin to release their electrons discernabily(Haake 1957). Such a possibility is there only in case of blue band at 10 Kc/s excitation. As the secondary peak appears on the lower temperature side (70°C) to that of the primary (110°C), this effect seems not because of thermal ionization of deeper traps but due to some sort of trapping action of the electrons which could not follow the rapidly changing electric field.

On increasing the field frequency, the brightness peaks shift towards higher values on the temperature scale. A change of frequency from 100 c/s to 10 Kc/s causes the green peak to shift from 50°C to 75°C on the temperature scale (figure 2), while for the blue peak this shift is from 15°C to 110°C (figure 3). Such a shift towards higher temperature is observed because due to an increase in frequency the available time for the exhaustion of the trapped electrons is decreased and therefore higher thermal energy is required to get these traps emptied within the limitted time interval. Since on increasing the frequency it is the blue transition that prevails over the green, we find that the blue peak is more frequency dependent on temperature scale than the green one. The band width is noticed to reduce for green band and increase for the blue band with the fre-

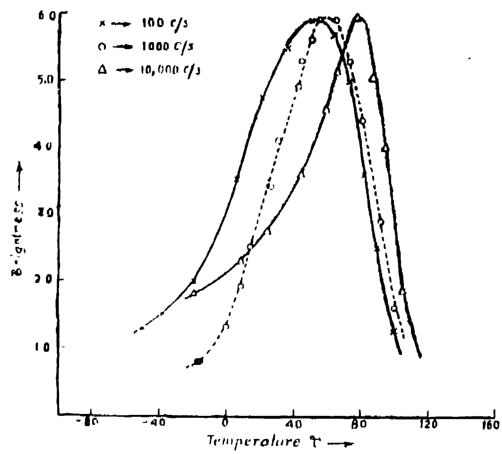

Fig. 2. Temperature dependence of EL out put at different field frequencies for the green peak of a (ZnS-Cu)H double band electroluminophor (Peak intensities normalized and voltage is kept fixed at 240 V).

quency. This effect is probably due to the fact that with increasing frequency of excitation the green emission is transformed into blue. This would increase

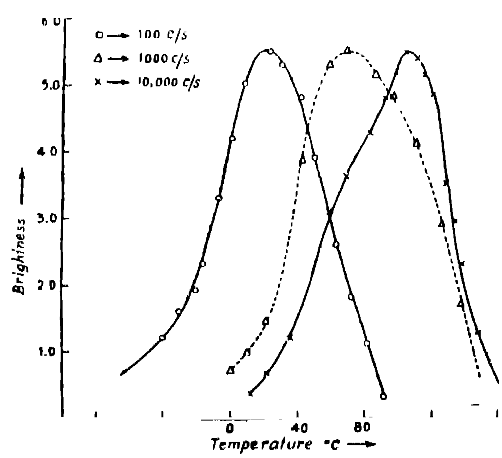

Fig. 3. Temperature dependence of EL out put at different field frequencies for the blue peak of a (ZnS-Cu)H double band electroluminophor (Peak intensities normalized and voltage is kept fixed at 240 V).

the population of electrons, taking part in blue transitions at the cost of green and hence the band width.

3.2 *Voltage effect*

As regards the effect of voltage on temperature dependence of EL there are different views. Haake (1957) and Mattler (1956) have independently reported that on increasing the applied voltage, the peak of output versus the temperature curves shifts towards lower temperature side. Alfrey (1956) in his experiments found peak positions to be independent of voltage applied, while Morehead (1958) reported that the peaks of these curves shift towards higher temperatures with the increasing voltage In any way, a shift towards lower temperature is indicative of a decrease in trap depth or of direct release of electrons from the traps by the field. In our experiments with increasing voltage the blue band shows a shift towards lower temperature side (from 70°C to 20°C). (figure 4) while for green band, the reverse is observed (from 60°C to 110°C), (figure 5).

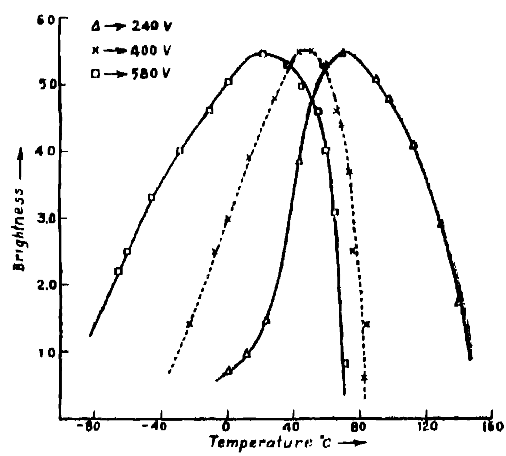

Fig. 4. Temperature dependence of EL out put at different voltages for the blue peak of a (ZnS–Cu)H double band electroluminophor (Peak intensities normalized and field frequency is kept fixed at 1 Kc/s).

Any possibility of modification of average trap depth by increasing field is ruled out here, because the previous studies (Prakash & Mohan 1969) show that field is ineffective in causing any sliding shift of emission peaks on wavelength scale, only the over all intensity is increased. So this effect may be presumably due to modification of recombination rates. A detailed explanation is still awaited.

An increase in band width is noticed for both the bands. This means the number of electrons taking part in recombination is increased with the field for both blue and green transitions.

3.3. *Intensity ratio of the two band peaks*

The intensity ratio of the green and blue band peaks i.e., I_G/I_B is plotted against frequency at different temperatures in (figure 6). The curves show a rapid fall in the beginning, then a slow but rather linear variation with increased frequency. This means at a given temperature the green transitions are being

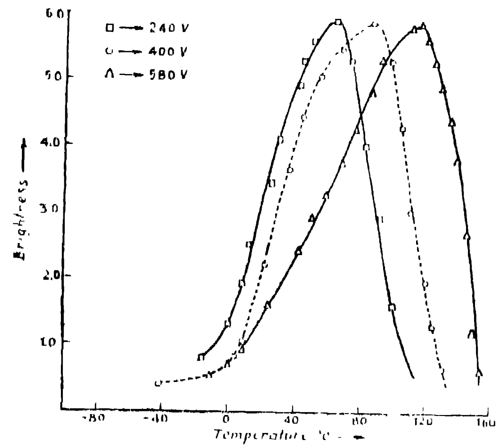

Fig. 5. Temperature dependence of EL out put at different voltages for the green peak of a (ZnS-Cu)H double band electroluminophor (Peak intensities normalized and field frequency is kept fixed at 1 Kc/s).

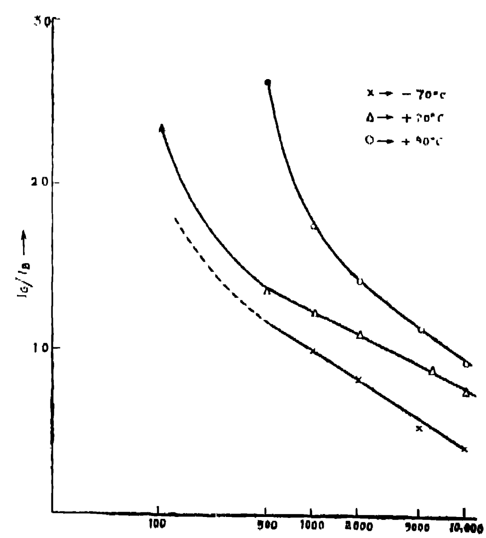

Fig. 6. **Variation of relative evolution of the two peaks (I_G/I_B) of a (ZnS-Cu)H double band** electroluminophor with excitation frequency at different temperatures.

transformed into blue one with the increasing frequency, which is obvious (Ivey 1963).

One also concludes from these curves that at fixed frequencies due to a rise in temperature, the ratio I_G/I_B increases. According to Klasens (1964) as the temperature is increased, the hole migration takes place from empty blue centres to non-ionised green centres or to quencher centres and consequently the green light increases faster than the blue. Thus the ratio I_G/I_B increases at higher temperatures for fixed frequency excitations

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