

## Electroluminescence and electrical properties of CaS : Zn phosphors

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**Abstract :** CaS phosphors activated with varying concentrations of  $Zn^{+2}$  have been prepared and their electroluminescence and electrical properties have been studied. The dependence of electroluminescence brightness on voltage and device current is discussed. The I-V characteristics have been used to infer the existence of Mott-Schottky type exhaustion barriers. An attempt has been made to infer the mechanism and the kinetics involved in EL process.

**Keywords :** Opto-electrical properties, electroluminescence, electrical properties.

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### 1. Introduction

CaS is a versatile phosphor host material and according to Lehmann (1972) CaS phosphors of good quality can be obtained to replace other commercial phosphors. Studies on CaS phosphors doped with one or more impurity elements have been reported (Gour 1970, Pawar *et al* 1971, Lehman and Ryan 1972, Patil and Lawangar 1981 and Pipiny's *et al* 1986). However, these have been largely confined to the interpretation of fluorescence and phosphorescence spectra and to the determination of trap depths and investigation of their opto-electrical properties is lacking. Electroluminescence (EL) studies have been reported (Lehmann 1958, Sharma and Bhushan 1971, Lawangar *et al* 1977, Tanaka *et al* 1986) but the mechanism of EL and the kinetics involved is not clear. The present work reports electroluminescence and electrical characteristics of CaS phosphors activated with varying concentrations of  $Zn^{+2}$ . The EL-brightness has been measured as a function of applied voltage and device current. The possible relationship between applied voltage and device current has also been studied. An attempt has been made to infer the mechanism of EL-process and the kinetics involved.

### 2. Experimental

CaS phosphors doped with varying concentrations of  $Zn^{+2}$  and added with flux  $Na_2SO_4$  (5% by weight of  $CaSO_4 \cdot 2H_2O$ ) were prepared by the thermal reduction

of calcium sulphate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , AR, BDH) as described elsewhere (Patil and Lawangar 1981). Out of the principal impurities in the base material labelled by manufacturer, chlorine and lead may give "nominally unactivated" luminescence (Lehmann 1972). The concentration of  $\text{Zn}^{+2}$  is varied from zero to 2% by weight of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The average grain size of phosphors determined by SEM is about 1.5  $\mu\text{m}$ . The details of the samples prepared are given in Table 1.

**Table 1.** Concentration of  $\text{Zn}^{+2}$  and value of  $n$ .

Sample No.	Concentration of $\text{Zn}^{+2}$ (wt.%, of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )	value of $n$ (1 kHz)
P <sub>1</sub>	0.0	2.36
P <sub>2</sub>	0.2	3.16
P <sub>3</sub>	0.4	2.94
P <sub>4</sub>	0.6	2.39
P <sub>5</sub>	0.8	3.04
P <sub>6</sub>	1.0	3.75
P <sub>7</sub>	1.2	4.48
P <sub>8</sub>	1.4	4.05
P <sub>9</sub>	1.6	4.85
P <sub>10</sub>	1.8	3.10
P <sub>11</sub>	2.0	3.25

Sandwich type EL-cell with silicone grease as dielectric medium was used to study the EL-behaviour of phosphors. The thickness of phosphor layer was about 0.2 mm. The EL-cell was excited by applying a.c. electric field obtained from an audio frequency generator (Philips GM 2308/90) having maximum output of 90 V. As this voltage was not sufficient to excite the phosphors, a wide band amplifier (Telmax SP100) was used in conjunction with the frequency generator. The maximum voltage thus available was upto 1.5  $\text{kv}_{\text{rms}}$  in the frequency range of 50 Hz to 2 kHz.

The brightness measuring system consisted of a photo-multiplier tube (RCA 931A). The tube was operated at 900 V obtained from a well stabilized d.c. power supply. The output of the PM-tube was measured by a d.c. microvoltmeter (Philips PP-9004).

### 3. Results and discussion

#### 3.1. Voltage dependence of EL-brightness :

The various functional relationships between EL-brightness (B) and voltage (V) are examined by plotting different graphs. It is found that the plot  $\log B$  against  $\log V$  (Figure 1) is almost linear over a wide range of voltages. The linearity

between  $\log B$  and  $\log V$  suggests that the brightness and voltage follow the power law relation of the form (Harman and Raybold 1956)

$$B = A(V - V_0)^n$$

with  $V_0 = 0$ ;  $A$  and  $n$  are constants. The constant  $n$  is indicative of the rate of change of brightness with voltage. The value of  $n$  is evaluated by the method of least squares (Hoel 1954) and is found to vary from 2.36 to 4.85 (see Table 1).

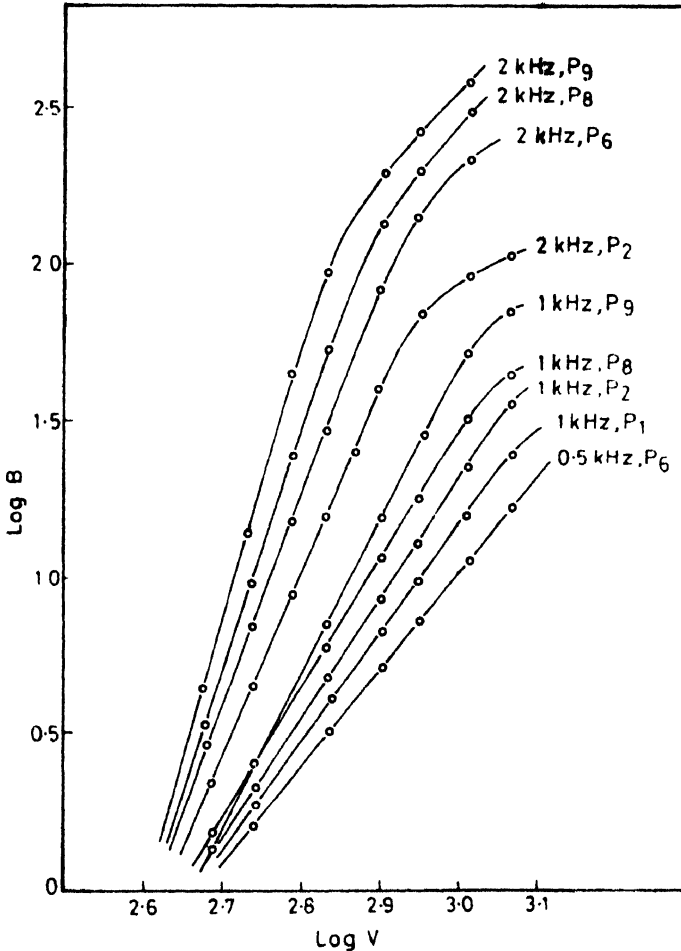


Figure 1. Plots of  $\log B$  against  $\log V$  for CaS phosphors containing different concentrations of  $Zn^{+2}$  and obtained at different frequencies.

The variation in  $n$  value may be attributed to the variation in the population density of the energy states acting as luminescence centres. However, the observed variation is not systematic with respect to the activator concentration. Besides the power law, an exponential relation proposed by Zalm *et al* (1955), viz.

$$B = B_0 \exp(-a/\sqrt{V})$$

is also found applicable over a limited range of voltages, with  $B_0$  and  $a$  as constants. The existence of exponential relation suggests the presence of Mott-Schottky type barriers in the phosphor (Pandey et al 1978). The simultaneous validity of power law and exponential relationship was also suggested by Masoorkar and Ranade (1973); Patil and Lawangar (1981).

The brightness is found to increase slowly with voltage at higher voltages (Figure 1). Lehmand (1958) determined the distribution function for the grain size in an actual sample and have shown that the plot of  $\log B$  against  $\log V$  is a straight line which bends at high voltages.

### 3.2. Electrical characteristics of phosphors :

3.2a. *Brightness-current characteristics* : EL-brightness is studied as a function of device current. It is an increasing function of device current in the initial part, and the curves bend towards the current axis in the later part. In the initial region, the variation can be described by the relation of the form,

$$B \propto I^m$$

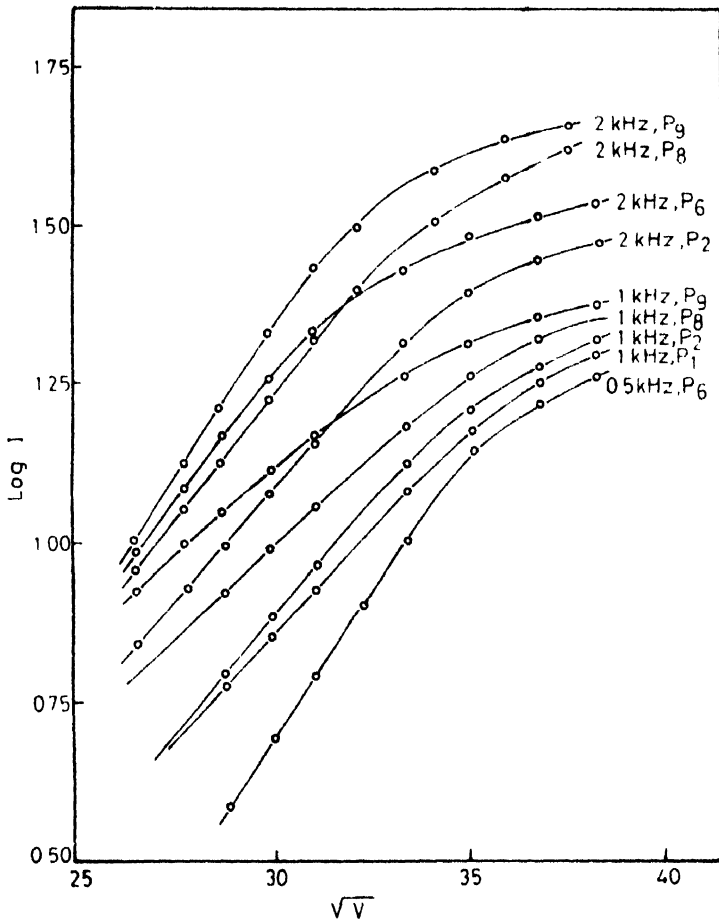
where  $m$  is an exponent whose value depends upon the current region chosen and it is indicative of the rate of change of EL-brightness with current. In the present study, it varies from 3.2 to 4.8. Explanation of variation of  $m$  follows from that of  $n$ . The bending of the plots may be due to heating effect becoming apparent at higher current densities ( $\geq 20$  mA/cm<sup>2</sup>). The power law dependence of brightness on current ( $B \propto I^m$ ) indicates that the mechanism of EL-process is likely to be an acceleration collision (Bhawalkar and Malhotra 1969).

3.2b. *Current-voltage characteristics* : Figure 2 depicts the variation of logarithm of device current with square root of applied voltage. It may be seen that the plots exhibit two distinct regions. The region towards low voltage side closely follows the relation  $I \propto \exp(a\sqrt{V})$  while the other on high voltage side obeys the relation  $I \propto \exp(aV)$ . The change in current-voltage characteristics from  $\exp(a\sqrt{V})$  to  $\exp(aV)$  confirms the existence of exhaustion barriers (Maheshawri and Khan 1975, Sharma and Bhushan 1971).

### 3.3. Mechanism of electroluminescence :

The qualitative test for thermoelectric power in the prepared phosphors indicates that the phosphors are  $n$ -type, and as such, the carrier injection mechanism for exciting the phosphor appears to be improbable. On the other hand, to observe the EI-emission comparatively high fields of the order of  $1.4 \times 10^4$  V/cm are required. The requirement of intense electric field for EL-emission to occur, along with the existence of power law relationship between brightness and voltage suggests that the probable mechanism of excitation, in these phosphors, is likely

to be direct field ionisation of either valence band electrons or impurity centres, where transfer of electrons into the conduction band takes place by a quantum mechanical tunnelling process (Piper and Williams 1955, Gour 1970, Gour 1987). However, existence of the relation  $B = B_0 \exp(-a/\sqrt{V})$ , besides the power law, indicates that the luminescence emission also results from a potential barrier of Mott-Schottky type, where field is proportional to  $\sqrt{V}$ , and the mechanism of exci-



**Figure 2.** Plots of  $\log I$  against  $\sqrt{V}$  for CaS phosphors containing different concentrations of  $Zn^{+2}$  and obtained at different frequencies.

tation is acceleration collision type (Pandey et al 1978, Bhúshan et al 1979). The electrical characteristics such as brightness-current and current-voltage also go in favour of existence of potential barrier of Mott-Schottky type. Thus, it may be concluded that the probable mechanism of electroluminescence in these phosphors is likely to be direct field ionisation of either valence band electrons or impurity centres, where transfer of electrons into the conduction band takes

place by quantum mechanical tunnelling process through the Mott-Schottky type barriers existing at the grain boundaries (Patil and Lawanger 1981). These electrons recombine radiatively at a later stage with impurity centres or holes, created in the valence band giving emission.

#### 3.4. Kinetics involved in electroluminescence process :

The existence of power law relationship between brightness and voltage indicates the possibility of bimolecular process in recombination of electrons (Park and Shin 1977). However, besides the power law, the exponential relation  $B = B_0 \exp(-a/\sqrt{V})$  is also found suitable over a limited range of voltages. Hence, here, it cannot be concluded with a reasonable certainty that the process of recombination of electrons with luminescence centres is bimolecular.

#### 3.5. Effect of activator concentration on EL-behaviour :

The B-V, B-I and I-V characteristics show variation from sample to sample. However, the basic laws obeyed by these characteristics are the same for all the samples studied. Thus it may be concluded that the activator  $Zn^{+2}$  does not affect significantly the basic nature of EL-behaviour of the samples but only the relative EL-brightness.

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