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Electroluminescence of $CaSO_4$: Sm phosphors

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Abstract. $CaSO_4$ phosphors activated with Sm^{3+} impurity in varying concentrations have been prepared and their electroluminescence systematically studied. The voltage and frequency dependence of brightness is discussed and conclusions are drawn regarding the possible mechanism involved in the process.

Keywords. Electroluminescence; calcium sulphate phosphors; samarium.

1. Introduction

Studies on the electroluminescence (EL) behaviour of various phosphors have been a subject of interest in many fields of light engineering (Pankove 1977; Shashi Bhushan 1979). Literature survey shows that EL studies of oxygen-dominated lattices have received less attention although they exhibit other luminescence properties such as photo- and thermoluminescence. The growing importance of high bandgap semiconductors have induced the authors to study the EL behaviour of alkaline earth sulphate phosphors. In the present paper the results of voltage and frequency dependence of brightness are reported to understand the mechanism of EL in $CaSO_4$ phosphors.

2. Experimental

Calcium sulphate phosphors doped with Sm as an activator were prepared from gypsum (Sabnis and Pawar 1977). The concentration of Sm was varied from 0 to 0·375 wt%. Studies on EL in oxygen dominated lattices are usually made with dry powder pressed between the conducting cell. The EL set-up in the present investigation consisted mainly of electroluminescent cell, electronic excitation source and the brightness measuring system. The EL cell consisted of a thin phosphor layer sandwiched between two electrodes, one of which was a conducting glass plate and the other an aluminium plate. Different dielectric media such as castor oil, polystyrene, chlorinated rubber, etc suggested in the literature were tried and it was found that the EL intensity was less. As a result, a phosphor layer without any binder was used. The excitation unit consisted of a high power audio-frequency oscillator (Philips-GM 2308) and a wide band amplifier (0 to 5 kV, Telmex Electronics, India). The mains supply to audio frequency oscillator and wide band amplifier was given through stabilizer. The source of voltage is frequency-oscillator, the output of which is further amplified by wide band amplifier. The output of the wide band amplifier was fed to an EL cell. The brightness measuring system includes IP 21 photomultiplier (PM) tube, power supply and nanometer (Aplab Type TFM 13). The alternating voltage applied to the phosphor was varied upto 1500 volts rms keeping the frequency constant. The EL emission was measured in terms of PM tube current in arbitrary units. The observations were taken at room temperature.

3. Results and discussion

The EL spectra were recorded for a series of $CaSO_4$:Sm phosphors and found to give the spectral lines peaking at about 4886, 5500, 5836 and 6180 Å. These emissions are respectively attributed to the spectral transitions

$$^4G_{7/2} \to {^6H_{5/2}},\ {^4F_{3/2}} \to {^6H_{5/2}},\ {^4F_{3/2}} \to {^6H_{7/2}} \text{ and } {^4F_{3/2}} \to {^6H_{9/2}}$$

of Sm^{3+} ions. This agrees with the results reported by Nambi *et al* (1974). The emission at 5836 Å was relatively more intense than others. The voltage (V) and its frequency (F) on the spectral lines were studied and no appreciable change was noticed n the spectral positions. However, their intensities change with both V and F.

3.1 *Voltage dependence of brightness*

In order to study the dependence of brightness on voltage the EL output of $CaSO_4$: Sm phosphors was measured in the voltage range 0 to 1500 volts (rms) at different frequencies. The brightness-voltage curves for typical phosphors at a fixed frequency (800 c/s) (figure 1) show that there is a threshold voltage V_{th} for EL. Above this threshold, the brightness increases with increase in exciting voltage, indicating that initially the number of particles in which EL takes place is small, but on increasing the voltage more and more active regions are exposed to voltage gradient above threshold level, increasing the brightness. Figure 1 shows that brightness increases with the activator concentration if all other parameters are kept constant. The enhancement of brightness with increase in concentration of activator may be attributed to the increase of luminescence centres in the present phosphor system.

The B-V measurements reveal the mechanism of excitation of charge carriers. Franz (1952) calculated for a large-band-gap material the probability per unit time P_i, for ionization from the valence band in the field V,

$$P_i = (ea/h)\, V \exp\left\{-\frac{\pi(2m^*)^{1/2}}{4\,\hbar e}\,\frac{E_g}{V}\right\}, \tag{1}$$

where E_g is the band gap, a the lattice parameter, m^* the effective mass and e, h, $\hbar$, have their usual meanings. The probability, P_i, of transfer of electron from valence band to conduction band, which causes excitation and in turn the emission of light

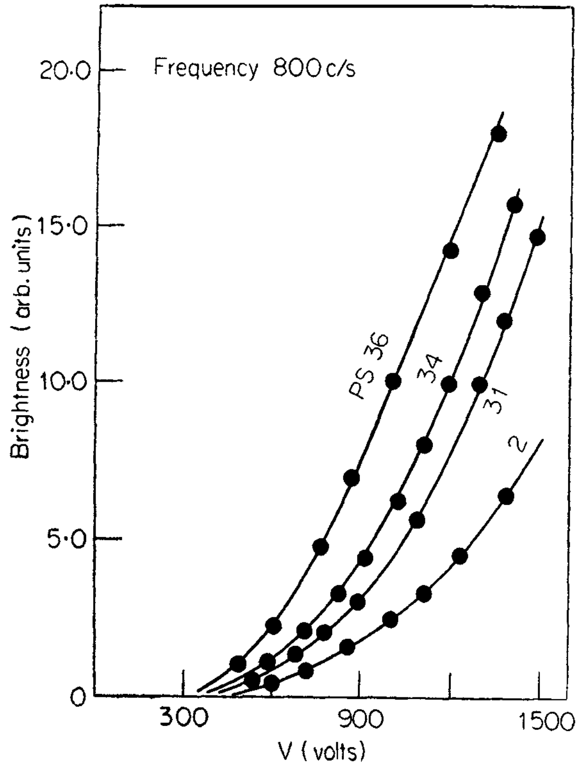

Figure 1. Plots of brightness versus voltage for four different concentrations of Sm wt % in $CaSO_4$. $PS_2(0.037)$, $PS_{31}(0.087)$, $PS_{34}(0.11)$, $PS_{36}(0.37)$.

via luminescence centre is proportional to the brightness B. Hence equation (1) can be modified as

$$B=A\ V\exp(-X/V), \tag{2}$$

where $$X=\frac{\pi(2m^*)^{1/2}E_g}{4\hbar e},$$

and A is a constant involving ea/h.

An attempt has been made to see the validity of this equation by plotting log B/V versus $1/V$. The plots obtained for a typical phosphor (PS 31) are shown in figure 2. The nonlinearity observed, rules out the possibility of excitation of charge carriers by the field ionization of valence electrons. The probability P_t for the field ionization of an impurity ion electron is given by (Goldberg 1966)

$$P_t=17\times10^{12}\,(m^*/m)\,(v/\epsilon^5)^{1/4}\exp\left\{\frac{-7\times10^7\,(m^*/m)}{V}\,E_n^{3/2}\right\}, \tag{3}$$

where ϵ is the dielectric constant.

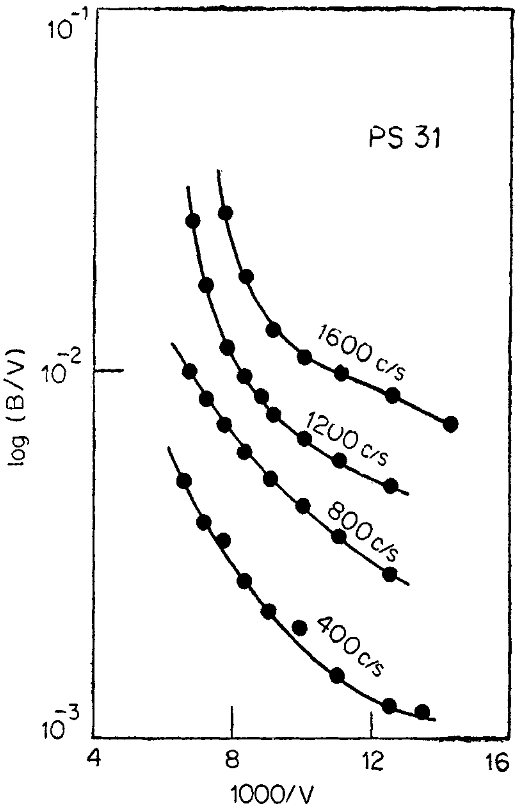

Figure 2. Plots of log (B/V) versus $1000/V$ for PS 31 phosphor.

In the experiment, the field strength applied across EL cell is of the order of 10^4 volts/cm. Therefore, the exponential term in equation (3) has relatively less bearing on P_t, and hence can be ignored without appreciable error. Further, considering B as proportional to P_t, one can write

$$B = A\ V^n, \tag{4}$$

where $A = 17 \times 10^{12} \times (m^*/m)^{1/2}$, and n is a constant depending upon the dielectric constant. This equation is tested for all the phosphors studied by plotting the graphs of log B versus log V and found to be valid. The plots of log B versus log V for a typical phosphor are shown in figure 3. The validity of equation (4) suggests that in the EL of $CaSO_4$:Sm phosphors, the charge carriers are excited by the field ionization of impurity ion electron. A similar observation has been made by Harman and Raybold (1956) for ZnS phosphors. The values of n in equation (4) are deduced from the slopes of log B—log V plots and found to vary between 2·5 and 3 with the frequency of AC field and activator concentration. But the variation is not systematic.

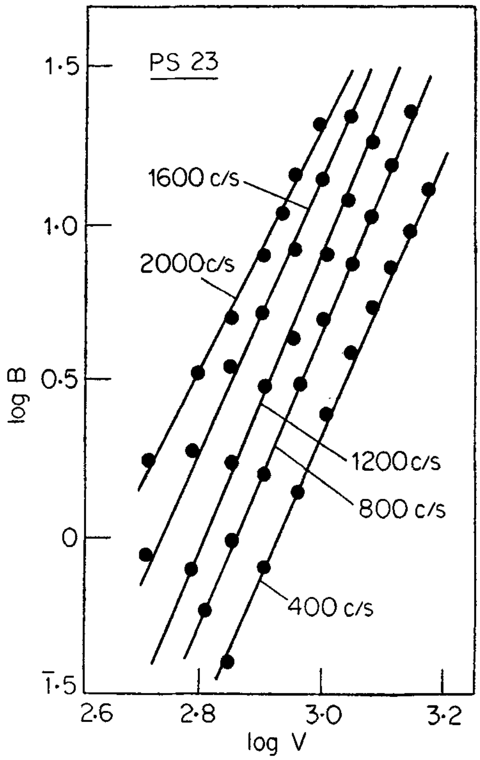

Figure 3. Plots of log B against log V for phosphor PS 23 (Sm=0.62 wt. %)

3.2 *Frequency dependence of brightness*

Keeping the voltage constant, the brightness increases with frequency. This agrees with the results reported earlier (Piper and Williams 1955; and Zalm 1956). The variation of brightness with frequency can be understood as follows: In AC electroluminescence, in one cycle the maximum peak value of the voltage is applied twice to the phosphor system. At maximum peak value of the voltage, the electron is excited from its ionized impurity state and combines with the luminescence centre giving out a flash of light. In every cycle of excitation, two quanta of light are emitted. As the frequency of electric field increases, the number of quanta and hence the brightness increases with frequency.

Various relations (Curie 1952; Thornton 1956; Taylor and Alfrey 1955) have been used to study the behaviour of brightness with the frequency. However, in the present investigation, the following relation given by Ballentine and Ray (1963) is found to obey the results

$$B = a_0 F^n \exp(-b_0/V^{0.5}) \tag{5}$$

where a_0 and b_0 are constants which are independent of voltage and frequency. The plots of log B versus log F are linear for all the phosphors studied. The plots of log B versus log F for the typical phosphor PS 23 (figure 4) shows that the intercept on the log B axis is higher for large voltage which also agrees with equation (5).

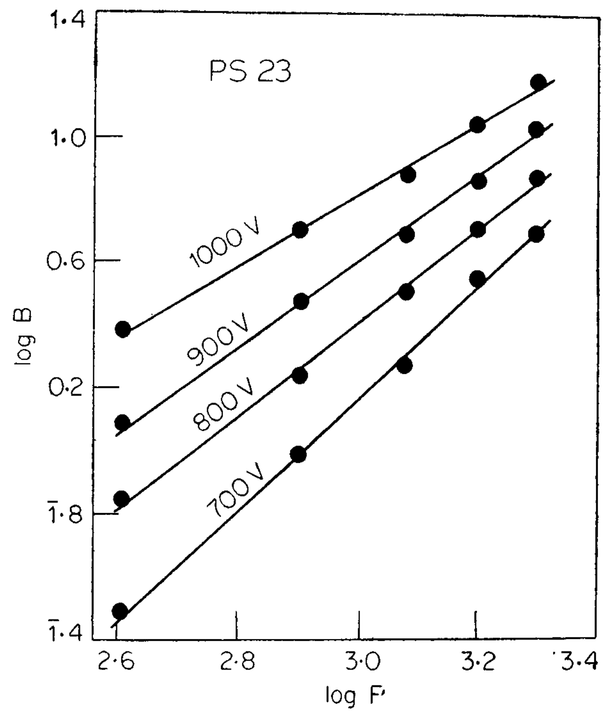

Figure 4. Plots of log B against log f for phosphor PS 23.

3.3 *Threshold voltage and its dependence on frequency*

The values of threshold voltage (V_{th}) for the phosphors studied were found to decrease with increase in frequency of applied voltage. This is possible as, in AC electroluminescence, in one cycle, the maximum peak value of the voltage is applied twice the phosphor system. When the frequency of applied voltage is increased, the impurity ion might receive energy at a rapid rate. As a result, it gets excited at comparatively smaller field. This explains the decrease of V_{th} with increase in frequency of applied field for all the phosphors studied.

3.4 *Possible mechanism of electroluminescence in $CaSO_4$ phosphors*

Unlike other types of luminescence, the most important stage involved in the EL process is the excitation of charge carriers. As the phosphor material is P-type (Pawar 1978), the carrier injection mechanism for exciting the charge carriers in the phosphor system appears to be improbable. However, the data obtained from the voltage dependence study indicate that the radiative system is likely to be excited by the field ionization of impurity ion electron. The charge carriers so created, are then further accelerated by the action of field localized in a narrow region (Piper and Williams 1955) and energy is transported to radiating sites. The accelerated charge carriers are captured by the radiating centres taking them to the excited state. De-excitation leads to the emission of light.

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References

Ballentine D W G and Ray B 1963 *Br. J. Phys.* **14** 157
Curie D 1952 *J. Phys. Radium* **13** 317
Franz W 1952 *Ann. Phys.* **11** 17
Goldberg P (1966) (ed.) in *Luminescence of inorganic solids* (London: Academic Press) p. 307
Harman G G and Raybold R L 1956 *Phys. Rev.* **104** 1498
Nambi K S V, Bapat V N and Ganguli A K 1974 *J. Phys.* **C7** 4403
Piper W W and Williams F E 1955 *Phys. Rev.* **98** 1809
Pankove J I 1977 *Electroluminescence* (Berlin: Springer-Verleg & New York: Heidelberg)
Pawar S H 1978 *Indian J. Pure Appl. Phys.* **16** 1034
Sabnis S G and Pawar S H 1977 *Indian J. Pure Appl. Phys.* **15** 817
Shashi Bhushan 1979 *J. Phys. Edn.* **6** 1
Taylor J B and Alfrey G F 1955 *Br. J. Appl. Phys. Suppl.* **4** 44
Thornton W A 1956 *Phys. Rev.* **102** 38
Zalm P 1956 *Phillips. Res. Rep.* **11** 353