

Voltage and frequency dependence of electroluminescence in some ZnS mixed CaS and CaS mixed ZnS phosphors

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Abstract : Voltage (V) and frequency dependence of electroluminescent (EL) brightness (B) has been investigated for ZnS mixed CaS and CaS mixed ZnS phosphors by studying the total EL brightness and those at emission peak positions of these systems when doped with impurities Cu and Sm. Although acceleration-collision mechanism is found to be effective in such systems, differences in slopes of straight lines, obtained between $\log B$ vs $100/\sqrt{V}$ plots, are observed. Slopes depend upon the addition of ZnS/CaS and impurities Cu and Sm. Frequency dependence is also affected due to presence of these impurities. Results of temperature dependence are presented and possible mechanisms are discussed.

Keywords : Electroluminescence, CaS and ZnS phosphors, voltage and frequency dependence

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1. Introduction

Voltage and frequency dependence of EL brightness are such studies which not only provide information about the behaviour of EL brightness with these variables but impart knowledge about the undergoing mechanism. Both alkaline earth sulfide and zinc sulfide phosphors are well known phosphors [1–4]. Properties like crystal structure, ionic radii, ionicity and band gaps *etc.* of these materials are such that possibility of forming mixed lattices may be expected with a result to generate new phosphor systems. Lehmann [5] also anticipated about a possibility of this kind. However, not much efforts were made in this direction by earlier workers. Viney *et al* [6] attempted to mix CaS with CdS. Sen and Bhushan [7] recently reported luminescence in CaS mixed ZnS by doping with impurities like Cu, La and Cl. They found that presence of CaS affected the emission profoundly. They also showed possibilities of replacement of Ca by Zn upto certain proportion, Ca going into interstitials of ZnS and CaS and ZnS with the impurities used giving their

own emissions. Since no gradual shift was found due to mixing of CaS or ZnS to the corresponding other systems, possibility of alloying was ignored. In another publication, structural properties of such systems were reported [8]. The present work discusses the voltage, frequency and temperature dependence of EL brightness of ZnS mixed CaS and CaS mixed ZnS phosphors when doped with impurities like Cu, Sm and Cl.

2. Experimental

The phosphors were prepared by firing a mixture of appropriate amounts of CaS (from National Physical Laboratory, New Delhi), ZnS (grade 1, Johnson Matthey, U.K.), copper acetate (AR, BDH), Samarium nitrate (IRE Ltd., 99.99% pure) and ammonium chloride (AR, BDH) at a temperature of 1050°C under the continuous flow of N₂ and H₂S gases. Pure sulfur (99.99%) was also mixed in the above mixture up to 5%. All the concentrations mentioned are by weight of CaS/ZnS.

The EL cell was prepared by sandwiching the EL materials between a conducting glass plate of resistivity $\approx 100 \Omega/\text{cm}^2$, prepared in the laboratory and an aluminum plate at a gap of 30 μm . An audio-oscillator coupled with a wide band amplifier capable of giving voltages upto 1000 V throughout the audio range was used as AC EL excitation source. EL brightness was recorded in the form of current by using a RCA 6217 photo-multiplier tube alongwith a polyflex galvanometer. Low temperature studies were performed by using a metal cryostat fabricated at this place.

3. Results and discussion

3.1. Voltage dependence of AC EL brightness :

The EL brightness (B) vs voltage (V) studies were performed in two ways, (i) behaviour of total brightness and (ii) behaviour of brightness at emission peaks. B - V plots for total

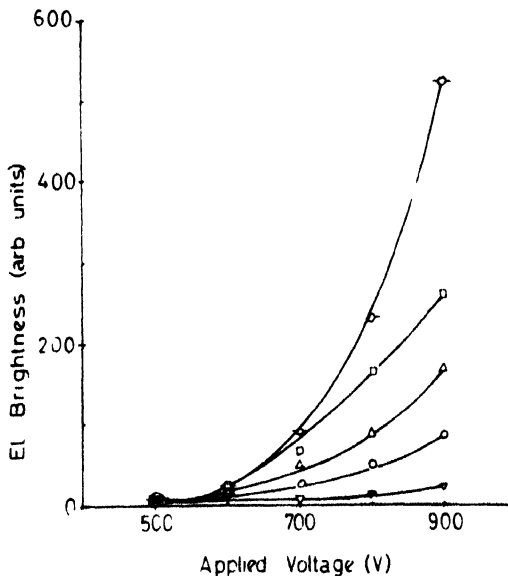


Figure 1. Voltage dependence of total AC EL brightness for ZnS mixed CaS : Cu, Sn, Cl phosphors at different frequencies \circ 300 Hz, Δ 500 Hz, \square 1 KHz, \diamond 5 KHz and ∇ 10 KHz.

brightness of ZnS mixed CaS : Cu, Sm, Cl phosphor at different frequencies of applied field are shown in Figure 1. It is observed that the behaviour is non-linear. At lower voltages, the variation in brightness is low, but as the voltage increases, the brightness picks up faster. A similar variation although with changed magnitude was observed for CaS : Cu, Cl and ZnS mixed CaS : Cu, Cl and CaS : Sm, Cl phosphors. The nature of $B-V$ plots observed at emission peaks of these systems were found to be similar but again with changed magnitude.

In an attempt to find mechanism of EL excitation, plots between $\log B$ vs $100/\sqrt{V}$ were considered for different cases. Such plots for the total brightness in ZnS mixed CaS :

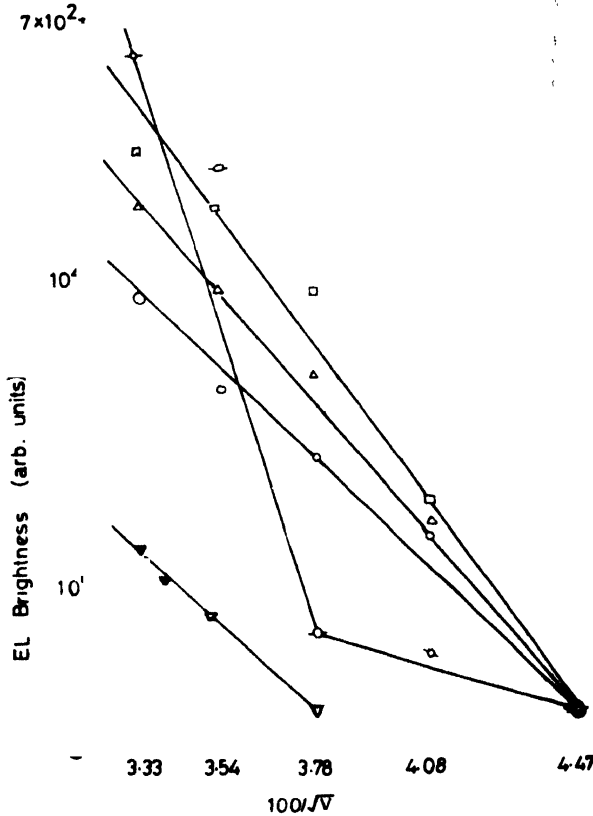


Figure 2. Plots of $\log B$ vs $100/\sqrt{V}$ for ZnS mixed CaS : Cu, Sm, Cl phosphors at different frequencies.

○ 300 Hz, Δ 500 Hz, □ 1 KHz, ○-○ 5 KHz and ▽ 10 KHz.

Cu, Sm, Cl are shown in Figure 2. It is observed that with increasing frequency from 300 Hz to 1 KHz, the slopes increase *i.e.* more and more centres are excited which give higher variation rate. At 5 KHz, two straight lines represent the behaviour : one with higher and the other with lower slopes as compared to the slope at lower frequencies. At 10 KHz, the slope decreases further. The straight line behaviour is represented by the formula

$$B = B_0 \exp(-b/\sqrt{V}), \tag{1}$$

behaviour at peak positions, it is again found that the slopes of straight lines corresponding to lower wavelength peak are higher as compared to those of the red peak.

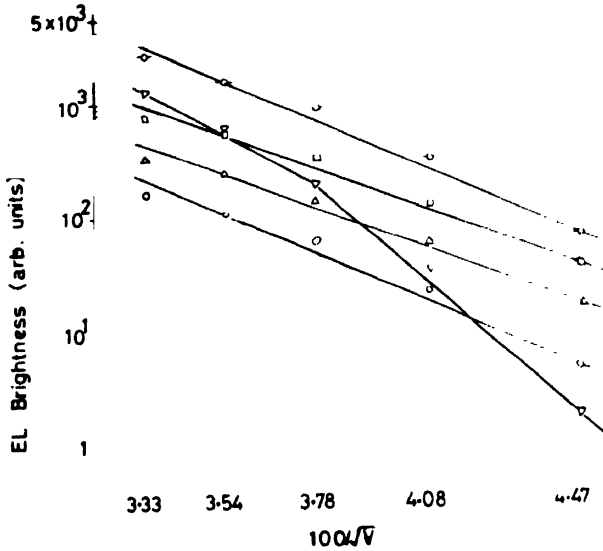


Figure 5. Plots of $\log B$ vs $100/\sqrt{V}$ for CaS mixed ZnS : Cu, Sm, Cl phosphors at different frequencies.

○ 300 Hz, Δ 500 Hz, □ 1 KHz, —○— 5 KHz and ▽ 10 KHz.

On comparing the behaviour of ZnS mixed CaS phosphors and CaS mixed ZnS phosphors, it is found that although the brightness is higher in the later systems, the variation is faster with the applied voltage in the former cases. The straight lines in later class are almost parallel *i.e.* due to change in frequency the slopes are not much affected.

Values of constants B_0 and b appearing in eq. (1) were also determined for different samples and the corresponding values are summarized in Tables 1 and 2. It is observed that

Table 1. Values of constants B_0 and b for different phosphors (from total EL brightness plots).

Phosphors	Frequencies					
	300 Hz	500 Hz	1 KHz	5 KHz	10 KHz	
CaS : Cu, Cl	B_0	5.0×10^7	0.8×10^9	2.5×10^{10}	1.3×10^{12}	1.1×10^3 1.2×10^6
	b	66.96	201.26	202.74	241.31	55.49 361.90
ZnS mixed CaS : Cu, Cl	B_0	5.8×10^3	3.0×10^7	1.4×10^5	1.1×10^4 9×10^6	51 5×10^6
	b	57.99	79.79	83.95	133.18 65.64	4.062 144.95
ZnS mixed CaS : Cu, Sm, Cl	B_0	1.3×10^6	1.8×10^7	3.0×10^8	2.0×10^2 5.0×10^5	5.15×10^3
	b	117.36	150.52	177.64	38.86 551.31	116.29

these constants generally show first an increasing nature followed by decreasing trend with increase in frequency. In some cases, continuously decreasing behaviour of B_0 and b (Table 3) are also observed. It should be noted that the total EL brightness is obtained from

Table 2. Values of constants B_0 and b for different phosphors (from plots of EL brightness of emission peaks)

Phosphors	Frequency					
	300 Hz	500 Hz	1 KHz	5 KHz	10 KHz	
CaS : Cu, Cl (420 nm)	B_0	1.8×10^3	6.0×10^3	5.2×10^4	9.0	9.0
	b	66.79	91.99	104.93	5.8×10^8	3.0×10^2
ZnS mixed CaS : Cu, Cl (480 nm)	B_0	7.0×10^2	3.2×10^3	1.5×10^4	1.4×10^7	9.4×10^{11}
	b	63.82	75.26	93.92	294.02	58.56
ZnS mixed CaS : Cu, Sm, Cl (~480 nm)	B_0	1.1×10^3	3.0×10^3	3.3×10^4	2.0×10^7	2.4×10^6
	b	71.80	88.05	121.84	227.89	207.07
ZnS mixed CaS : Cu, Sm, Cl (~730 nm)	B_0	22	37	110	5.2×10^3	5.4×10^4
	b	23.19	31.24	45.38	101.77	162.58

Table 3. The values of constants B_0 and b for different CaS phosphors (from total EL brightness plot at 50 Hz).

Phosphors	Temperature							
	RT		0°C		-20°C		-40°C	
	B_0	b	B_0	b	B_0	b	B_0	b
CaS : Cu, Cl	4.0	≈ 0	1.0×10^1	2.06	5.0×10^1	4.14	3.8×10^2	7.98
	4.8×10^7	153.38	3.6×10^4	78.50	1.8×10^5	90.43	3.6×10^5	96.51
ZnS mixed CaS : Cu, Cl	4.0	≈ 0	7	≈ 0	1.1×10^2	1.27	2.8×10^2	9.30
	2.8×10^6	31.24	1.6×10^5	101.87	3.1×10^5	108.18	4.0×10^5	113.07
ZnS mixed CaS : Cu, Sm, Cl	1.6×10^4	78.82	1.2×10^3	41.05	1.6×10^3	42.66	2.2×10^3	38.73

the combined effects of two constants controlled by eq. (1). Normally high brightness should be expected for higher values of B_0 and lower values of b .

3.2. Frequency dependence of AC EL brightness :

Figure 6 shows the frequency dependence of total EL brightness for ZnS mixed CaS : Cu, Sm, Cl phosphors. The behaviour of EL brightness observed at two peak positions (blue and red) are represented in Figure 7. The general nature of curves consists of first

increasing with increasing frequencies then passing through a maximum at some moderate frequency and finally decreasing at further higher frequencies. The general behaviour in

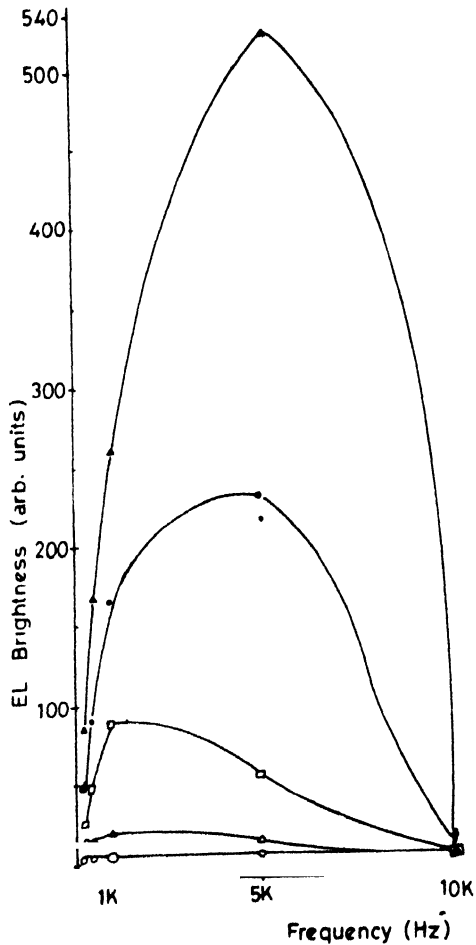


Figure 6. Frequency dependence of total AC EL brightness for ZnS mixed CaS : Cu, Sm, Cl phosphors at different voltages

500 V, Δ 600 V, \square 700 V, \bullet 800 V and \blacktriangle 900 V.

case of light emissions at peak positions is similar to that of total light emission but with improved brightness in the later case.

The increase in EL brightness with frequency can be understood on the basis that vacating and refilling of EL centres take place more rapidly with increase in frequency. When the time period of applied AC cycles becomes comparable with the lifetime of excited electrons, the electron does not have enough time to emerge out from the trap. Thus, the time averaged brightness will not increase linearly with frequency. The non-linearity of frequency dependence at particularly lower frequencies is also attributed to the polarization effect combined with the nature of depletion of ionized activator [10]. The decreasing

nature of brightness at higher frequencies may be attributed to heating of the sample and voltage losses in the transparent electrode etc. [8,11]. From the diagram, it also appears that

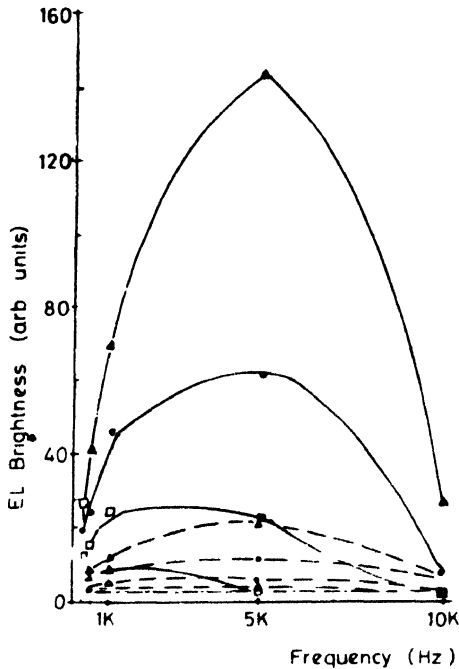


Figure 7. Frequency dependence of AC EL brightness at peak positions for ZnS mixed CaS : Cu, Sm, Cl phosphors at different voltages

-----○ Blue peak - - - - -△ Red peak
● 500 V, - - - - -△ 600 V, - · - · - □ 700 V, ● 800 V and ▲ 900 V

the vacating and refilling is affected with the strength of the field and thus the peak positions appear at different frequencies at higher voltages as compared to those at lower voltages. This behaviour is mainly found in blue band.

3.3. Temperature dependence of AC EL brightness :

The EL brightness vs temperature curves at different applied voltages ($f = 50$ Hz) for ZnS mixed CaS : Cu, Sm, Cl phosphors are shown in Figure 8. A similar nature was found for CaS : Cu, Cl; CaS : Sm, Cl and ZnS mixed CaS : Cu, Cl. In all the cases, it is found that with increasing temperature the EL brightness decreases. Decrease in emission due to increase in temperature may be related to a number of following factors [12] :

- (i) Change in the equilibrium occupancy of shallow centre : At absolute-zero, all the acceptor centres are occupied but with increasing temperature a certain fraction gets occupied at thermal equilibrium by electron from the valence band resulting in decrease in emission intensity.

- (ii) Variation of radiative transition probability : The average radiative transition probability for electrons in the conduction band into shallow acceptor centres is sensibly a constant while this is not the case for transition of holes from the valence band into shallow donors and

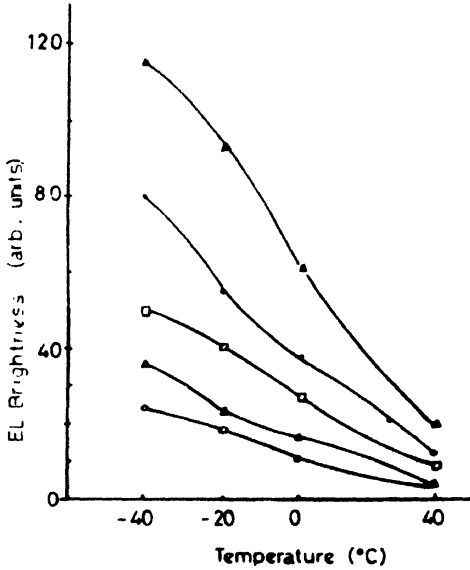


Figure 8. Temperature dependence of AC EL (50 Hz) brightness for ZnS mixed CaS : Cu, Sm, Cl phosphors at different voltages

○ 400 V, △ 500 V, □ 600 V, ● 700 V and ▲ 800 V

- (iii) Non-radiative effects : any excited state in a solid can collapse to the ground state and dissipate its energy non-radiatively in the form of phonons.

In CaS : Cu, Cl and ZnS mixed CaS : Cu, Cl the emission peaks are observed in blue region, therefore, for such systems process (iii) appears to be more logical as deeper acceptor centres are involved in such systems. The non-radiative processes occurring at higher temperatures in such systems can be described in terms of the configuration coordinate model. In Sm doped phosphors, which show red emission, processes (i) and (ii) may also be effective alongwith process (iii).

Results of EL brightness vs voltage at different temperatures for ZnS mixed CaS : Cu, Sm, Cl phosphors are shown in Figure 9. For comparison room temperature plot is also shown. The general behaviour in all the cases is the same alongwith the fact that higher emission alongwith faster variation rate appears at lower temperature. This occurs due to ceasing of non-radiative process at lower temperatures. Figure 10 shows the $\log B$ vs $100/\sqrt{V}$ plot for the systems mentioned in Figure 8. It is found that the straight-line behaviour appears alongwith two modes of excitations in some cases. Thus, the mechanism

of excitations remains as the acceleration-collision one. Reasons for two modes of excitations have already been mentioned earlier.

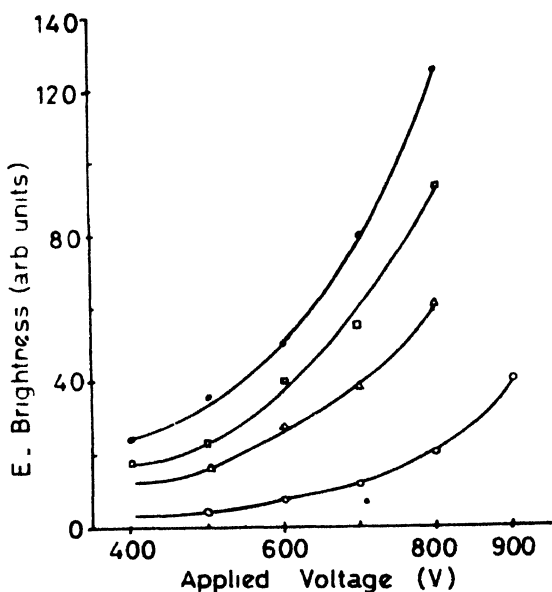


Figure 9. Voltage dependence of total AC EL (50 Hz) brightness for ZnS mixed CaS : Cu, Sm, Cl phosphors at different temperature
 ○ RT, △ 0°C, □ 20°C, and ● -40°C

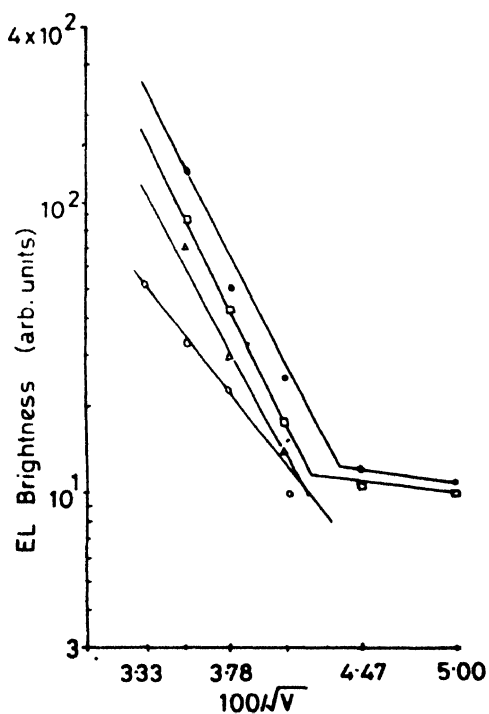


Figure 10. Plots of $\log B$ vs $100/\sqrt{V}$ for ZnS mixed CaS : Cu, Sm, Cl phosphors at different temperatures
 ○ RT, △ 0°C, □ -20°C, and ● -40°C

The values of constants derived from these straight lines are summarized in Table 3. The values of the constants are different from those of RT values which should be expected

as the brightness is different (higher) at lower temperatures. B_0 is found to be higher at lower temperatures as compared to those of RT values.

4. Conclusions

Observation of total EL brightness and those at peak positions with applied voltage show that acceleration-collision mechanism is effective in ZnS mixed CaS or CaS mixed ZnS phosphors. Due to mixing of ZnS slopes of straight lines obtained from plots of $\log B$ vs $100/\sqrt{V}$ decrease. Similarly, while slopes increase due to addition of Cu, addition of Sm decreases the slopes. Variation of EL brightness is found to be more faster in blue peak as compared to that of red peak. Similarly, variation of EL brightness with applied voltage in ZnS mixed CaS phosphors is more faster as compared to those of CaS mixed ZnS phosphors although the total brightness is higher in later case.

Frequency dependence of EL brightness shows first an increasing trend and after passing through a maximum it decreases. The peak observed in this way is found to shift with the applied voltage for the blue emission. Temperature dependence of EL brightness shows a decreasing nature with the increasing temperature.

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