

## Luminescence in ZnS: La and ZnS: (Mn, La) phosphors

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**Abstract.** The photo (PL) and electro (EL) luminescence in ZnS: MnLa and ZnS: La have been studied. The enhancement and quenching of emission bands have been observed on the simultaneous application of sinusoidal field and photons. The wave shape, voltage, frequency and temperature dependence of EL brightness have been reported. A study of the phosphorescence and thermoluminescence of these phosphors is also carried out and it is observed that the trap-depth changes slowly with temperature and activator concentration. An attempt has been made to calculate the trap depth by studying temperature dependence of EL brightness. The results are reported and discussed.

**Keywords.** Photoluminescence; electroluminescence; photoelectroluminescence; thermoluminescence; phosphorescence; ZnS phosphor.

### 1. Introduction

Manganese is widely used as an activator in the luminescent ZnS phosphors (Luycks and Stokkink 1955; Levshin and Tunitskaya 1965 and Ostaszewicz 1965). This phosphor emits predominantly in the yellow orange region (5800 Å) of the spectrum and the energy transfer is understood to a fair degree of accuracy and reliability. A number of ZnS phosphors doped with rare-earth impurity have been reported and their PL and EL emission are studied (Anderson *et al* 1965; Kobayashi *et al* 1974 and Tripathi *et al* 1980). But no work on the lanthanum doped ZnS appears to have been done as yet. The authors have recently reported the photo and electroluminescence of ZnS (Cu, La), ZnS. (Ag, La) (Tripathi *et al* 1981) phosphors. It was therefore considered worthwhile to study the luminescence behaviour of ZnS phosphors activated by lanthanum and manganese together and the way the luminescence emission changes with concentration of these ions. The present paper deals with different properties of luminescence such as photo (PL), electro (EL), photoelectro (PEL), phosphorescence and thermoluminescence (TL) of ZnS:La and ZnS:Mn, La phosphors.

### 2. Experimental techniques

An appropriate mixture of ZnS,  $\text{La}_2(\text{SO}_4)_3$  and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  was added with 5ml of pure distilled water. A constant amount of sulphur (0.5% by weight) was added in each of the samples. The slurries were well stirred in a silica crucible and dried in an oven at 300°C. All the samples were fired at 1000°C for 40 minutes in an electrically

heated tubular furnace. The firing was done in carefully controlled inert atmosphere of continuously flowing argon gas. The phosphor powder paste in castor oil was sandwiched between two plates of EL cell. The phosphor was excited to luminescence either by alternating field or by UV radiation (3650 Å) obtained from high pressure mercury lamp. An audio frequency generator connected to a wide band amplifier served as a voltage source to operate the cell. The light emitted from the phosphor was measured by an RCA IP21 photomultiplier tube operated on a regulated power supply. The time-averaged photocurrent was measured by a multiflex galvanometer.

A constant deviation spectrograph was used as an instrument for recording the emission spectrum with an accuracy of 10 Å. To determine the luminescence emission of these phosphors the light emitted from the cell was allowed to fall on the slit of the spectrograph and the whole spectrum was scanned by rotating the wavelength drum.

For the temperature dependence of EL brightness an apparatus was fabricated and set up in which the cell was continuously heated and the EL brightness recorded at different temperatures. The temperature was measured with a chromel-alumel thermocouple. A double beam oscilloscope was used to measure the brightness wave forms.

PEL emission was measured at wavelength positions 5200, 5700 and 5800 Å at which the peak emission from the phosphor occurred. The phosphors were excited by the field and photons for different periods and the intensity of the emitted light was recorded in each case.

The samples were excited for 5 min by 3650 Å radiation and the phosphorescence decay intensity was then recorded at different periods and temperatures. When the decay intensity became negligible the sample was heated at a linear rate to study TL. The thermal glow curves were obtained at two constant warming rates 0.833 and 0.548°K/sec for each of the samples.

### 3. Results and discussion

#### 3.1 Spectral analysis of PL and EL emission

In ZnS:Mn the emission around 5800 Å was found by photon and field excitations (figure 1). The peak emission at 5800 Å remains practically unmodified by varying the frequency although the increase in frequency adds to the light output in accordance with the usual laws of EL emission. The Mn<sup>2+</sup> ion forms localized level and its ground level <sup>6</sup>S<sub>1/2</sub> is situated in the valence band. The upper levels <sup>4</sup>F, <sup>4</sup>D, <sup>4</sup>P and <sup>4</sup>G (Klick and Schulnam 1952 and Curie 1963a) all lie in the forbidden energy gap. These states are split in the crystal field and are lowered in energy with respect to ground state. The electrons accelerated by the applied field make inelastic collision with Mn<sup>2+</sup> ions causing their excitation without ionization and subsequent emission of yellow light resulting from <sup>4</sup>G → <sup>6</sup>S transitions within the Mn<sup>2+</sup> *d* - *d* shell.

The ultraviolet excitation by 3650 Å radiation of ZnS:La shows peak emission around 5100 Å (for 0.01% La by weight). This gradually shifts towards higher wavelength side with increase in lanthanum concentration (figure 2) showing that the trivalent lanthanum is mostly in the interstitial positions in ZnS lattice (Leverenze 1948). The EL emission in ZnS:La having 0.01% La<sup>3+</sup> shows maximum emission

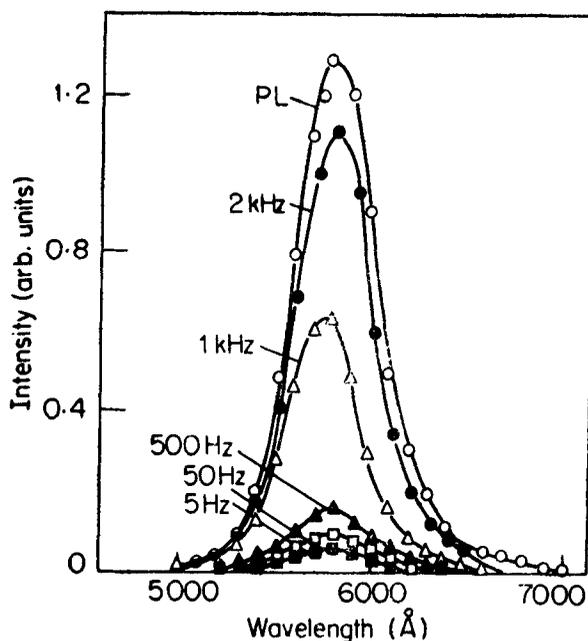


Figure 1. Spectral distribution of ZnS:Mn phosphor photoluminescence (PL) and electroluminescence at 50, 500, 1K, 2K and 5 kHz at 750 volts (rms).

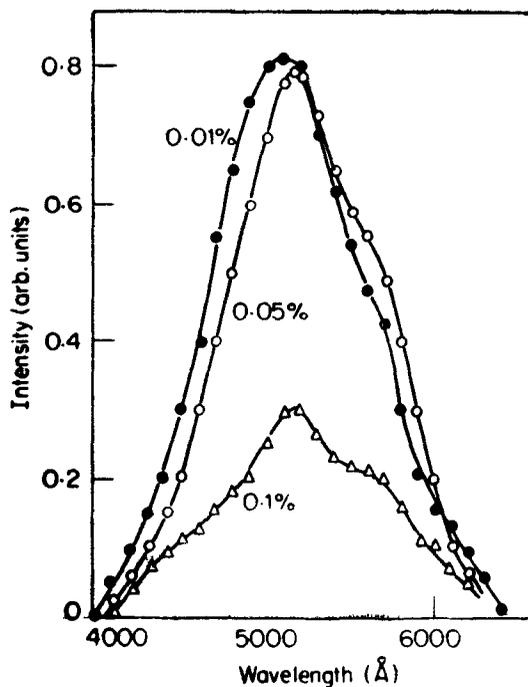


Figure 2. Photoluminescence spectra of ZnS:La phosphors for 0.01, 0.05 and 0.1% concentrations of  $\text{La}^{+3}$  ions.

around 5200 Å with a shoulder band around 5700 Å while for 0.05% La<sup>3+</sup> concentration the maximum appears around 5700 Å with a shoulder band around 5200 Å and for 0.1% lanthanum, the 5200 Å band is further quenched and a sharp emission peak dominates around 5700 Å (figure 3). It was observed that for 0.01% La in ZnS:La, the green emission due to DA pairs between La<sup>3+</sup> and Zn<sup>2+</sup> is shifted towards shorter wavelength side with increase in the frequency of the applied field (not shown in figure 3). The 5700 Å band like the 5800 Å band in ZnS:Mn does not change with frequency. The stability of this emission peak with frequency and the sharp emission at higher concentration of La imply that the yellow band around 5700 Å is associated with radiative transition  $E_g \rightarrow T_{2g}$  between the localized electronic states of lanthanum ions.

The lanthanum atom occupies the Zn<sup>2+</sup> ion site in the ZnS lattice and gives off its two outermost valence electrons ( $6S^2$ ) to the neighbouring sulphur atoms to form a stable bond. In the process it becomes La<sup>2+</sup>. There is still one  $5d'$  electron on its outer shell which it can donate to the lattice. This outer  $d$  electron is subjected to the intense octahedral electric field of the neighbouring ions. The degeneracy of the  $d$  orbital is thus removed and the splitting of the energy level (original  $D$  state) into triply degenerate  $T_{2g}$  and doubly degenerate  $E_g$  states takes place. The transition  $E_g \rightarrow T_{2g}$  is allowed.

In ZnS:(Mn, La) phosphors the PL emission was found around 5800 Å for higher concentrations of Mn<sup>2+</sup> ions (2%, 1%, 0.5% by weight and green emission around

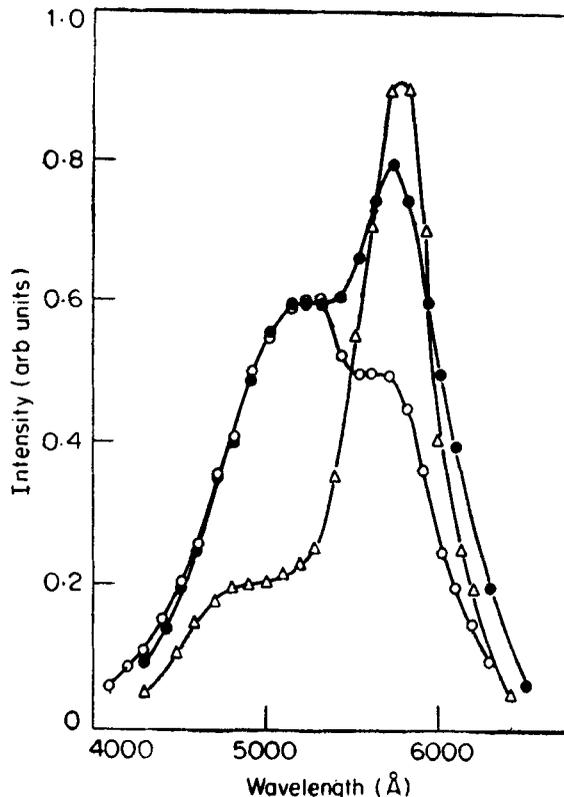


Figure 3. Electroluminescence spectra of ZnS:La phosphors at field frequency 2 kHz at 750 volts (rms). (O) 0.01%, (●) 0.05% and (▲) 0.1% concentration of La.

5200 Å for lower concentration of  $Mn^{2+}$  ions (0.01%). For 0.05% and 0.1% concentrations of manganese and lanthanum, peak emission occurs at 5200 Å with a shoulder band around 5800 Å. The green band at 5200 Å loses its brightness on increasing the concentration of  $Mn^{2+}$ , and at higher concentrations of  $Mn^{2+}$  ion (above 0.5%) only the orange band at 5800 Å is present and the green band is suppressed (figure 4).

The EL spectral emissions of ZnS: (Mn, La) are shown in figure 5 for higher (2%) and lower (0.01%) concentrations of  $Mn^{2+}$  ion. The peak emission occurs around 5800 Å for higher and 5200 Å for lower concentration of  $Mn^{2+}$  ion. It is further observed that a shift in the peak position of emission bands towards shorter wavelength side for higher concentrations of  $Mn^{2+}$  and towards longer wavelength side for lower concentrations of  $Mn^{2+}$  takes place with increase of field frequency. This shifting of emission band with frequency and concentration of the impurity ion shows some sort of energy transfer between manganese and lanthanum centres. The mechanisms of this transfer is still not fully understood.

The green emission may be explained on the basis of associated donor acceptor model (Prener and Williams 1956) of luminescence. It appears due to radiative  $D-A$  electron transition between  $La^{3+}$  (donor) and  $V_{zn}^{++}$  (acceptor) in the host lattice. The yellow orange emission in these phosphors is attributed to radiative transitions among the localized  $d$  levels of  $Mn^{2+}$  and  $La^{2+}$  ions.

### 3.2 Voltage and frequency dependence of EL brightness

It was observed experimentally that the brightness varies with voltage and frequency of the exciting field (figures 6 and 7). The dependence of EL brightness (B) on volta-

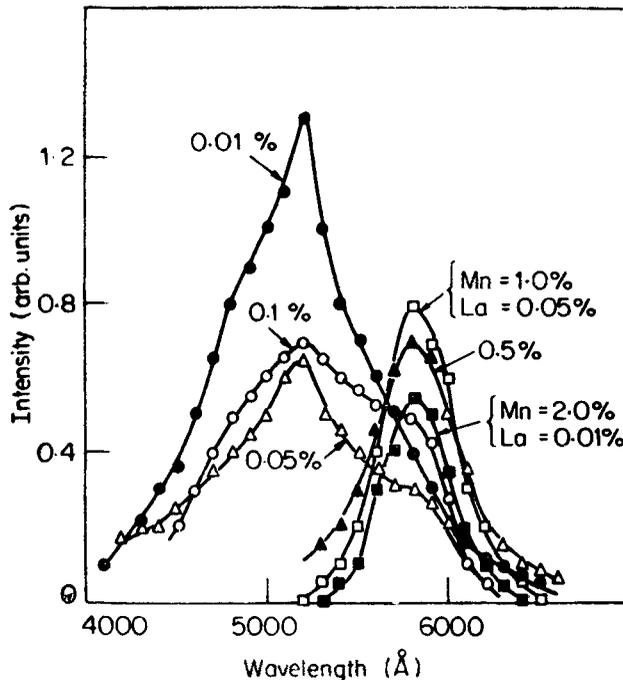


Figure 4. Photoluminescence spectral distribution of ZnS: (Mn, La) phosphors for different concentrations of Mn and La.

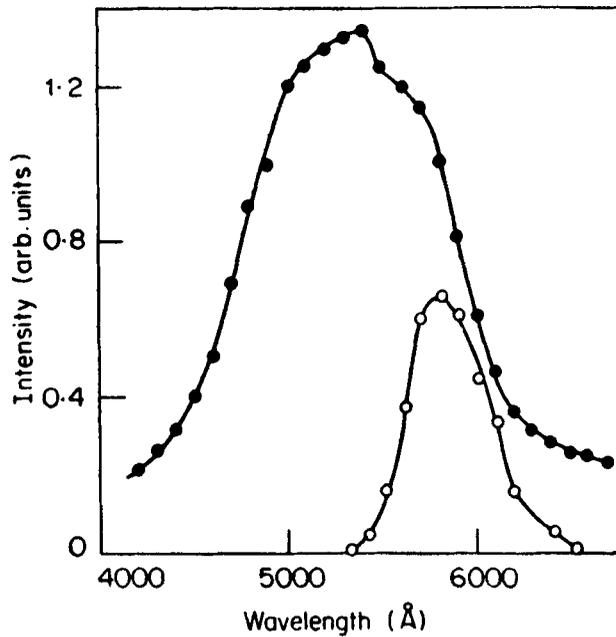


Figure 5. Electroluminescence spectral distribution of ZnS:(Mn, La) phosphors at field frequency 2kHz at 750 volts (rms). (○) Mn (2%), La (0.01%), (●) Mn (0.01%), La (0.01%).

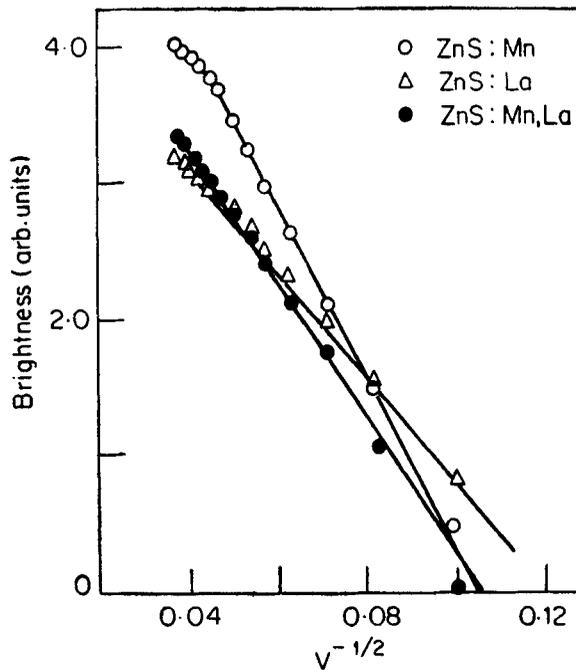


Figure 6. Voltage dependence of EL brightness in ZnS:Mn (1%), ZnS:La (0.01%) and ZnS:(Mn, La) (0.01% Mn = La) at 400 volts (rms.)

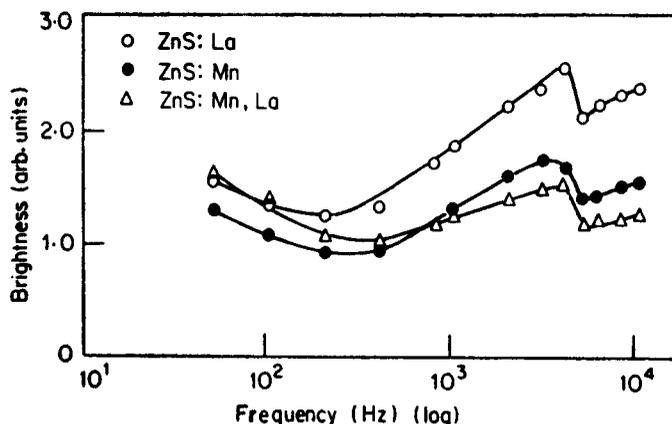


Figure 7. Frequency dependence of EL brightness in ZnS:Mn (1%), ZnS:La (0.01%) and ZnS:(Mn, La), (0.01% Mn = La) at 400 volts (rms).

age (V) can be described by the relation (Taylor and Alfrey 1964; Zalm *et al* 1954) (shown in figure 6)

$$B = B_0 \exp(-b/V^{1/2})$$

where  $B_0$  and  $b$  are constants. This shows that the excitation of EL emission is due to acceleration collision at the Schottky barrier layers in metal semiconductor contact.

The frequency dependence of EL brightness at constant voltages is shown in figure 7. The brightness increases linearly with frequency in range 200 Hz to 4 kHz. At lower frequencies between 50 and 200 Hz, the brightness decreases slowly with frequency. The brightness abruptly decreases in the frequency range 4 to 5 kHz and above 5 kHz the brightness shows increasing trend with frequency.

The decrease in EL brightness in the frequency range (4 to 5 kHz) may be due to trapping of some of the electrons in the empty donor levels and/or traps in the such frequency range of the applied field. The trapped electrons are subsequently released by the field at still higher frequencies. Thus the brightness increases beyond 5 kHz. The slow decrease in brightness within the frequency range 50 to 200 Hz may be understood by assuming that the EL light initially acts as a exciting source which fills the traps. The number of conduction electrons therefore is reduced from the original value. These traps are emptied by the sinusoidal field and thus the number of carriers increases for the acceleration and subsequent collision with the lattice. The linear increase in the brightness with frequency is in good agreement with the studies on other ZnS phosphors (Ivey 1963; Piper and Williams 1955).

### 3.3 Brightness wave form

Figure 8 shows the wave shape of light emission from ZnS:Mn, ZnS:La and ZnS:(Mn, La) phosphors. Two peaks are observed in each cycle of the applied voltage. The light emission in main peak is higher than that in the secondary peak. The wave shape in ZnS:(Mn, La) shows the variation of secondary emission peak maxima with frequency. The secondary peak maximum decreases with increasing

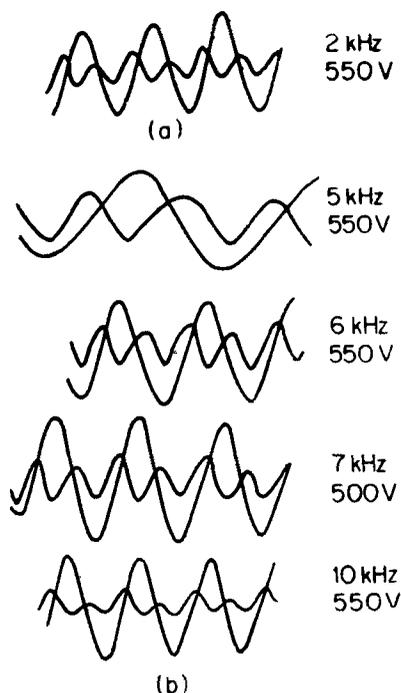


Figure 8. Brightness wave form: (a) ZnS:La (0.01%); (b) ZnS:Mn, La (0.01 % Mn and La).

frequency. This shows that the secondary peak maximum is related to the recombination of trapped electrons (Zalm *et al* 1954; Curie 1963).

The change of phase angle with the frequency and voltage of the applied field is in close agreement with the previous work on ZnS phosphors (Destriau 1955).

### 3.4 Temperature dependence of EL

The temperature dependence of EL brightness was studied in ZnS:Mn, ZnS:La and ZnS:(Mn, La) phosphors. Figure 9 presents the EL brightness of ZnS:Mn and ZnS:La phosphors at fixed voltage and frequency. The brightness decreases with increasing temperature in ZnS:Mn while as in ZnS:La it first diminishes slowly and after 460°K rises and attains a peak around 500°K. Beyond 500°K the brightness decreases again showing the presence of a group of traps in ZnS:La at the temperature range where the brightness peak occurs (figure 9).

The EL brightness in ZnS:(Mn, La) phosphor as a function of temperature at different frequencies and constant voltage within the temperature range studied are shown in figure 10. As the frequency is increased, the peaks of the brightness temperature curves shift towards higher temperature side. This result is in close agreement with that reported by Halstead and Koller (1954). The shifting of peaks has been explained by the trapping action of electrons (Thornton 1956). As the temperature of the phosphor is increased it is observed that generally two peak maxima develop in ZnS:(Mn, La) in the brightness versus temperature curves (figure 10). In ZnS:La (0.01%) and ZnS:Mn (1%) only one peak is found to develop above room temperature. As seen in figure 9, one can infer that the other peak may also develop

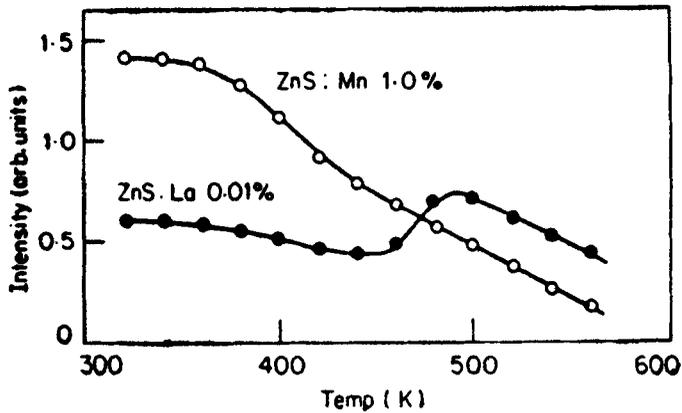


Figure 9. Temperature dependence of EL brightness in ZnS:Mn (1%) and ZnS:La (0.01%) phosphors.

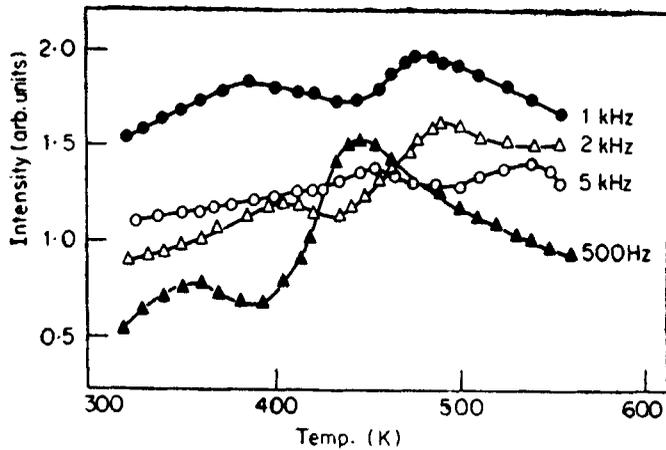


Figure 10. Temperature dependence of EL brightness in ZnS:Mn, La (0.01%) phosphors at field frequencies 500, 1K, 2K and 3 kHz at 300 volts (rms).

below the room temperature. The appearance of peaks may be attributed to the fact that at a certain temperature the life-time of electron in traps is less than one half period of a cycle of the applied voltage so that the traps do not act as storage centres. The brightness decreases beyond this temperature due to thermal quenching. In this way one peak maximum arises. Similiary the other group of deeper traps in phosphor provides the second peak maxima. The temperature at which the peak maxima occurs at a particular frequency can be related by (Chukova 1972).

$$f = S \exp(-E/kT)$$

where  $f$  = the frequency of applied field,  $S$  = attempt to escape frequency of electrons,  $E$  = trap-depth,  $k$  = Boltzmann constant and  $T$  = temperature of the peak maxima in °K.

Figure 11 depicts the  $\log f$  vs  $1/kT$  plot in a straight line. The slope of the line gives the value of the trap-depth and the intercept on the ordinate axis gives the value of

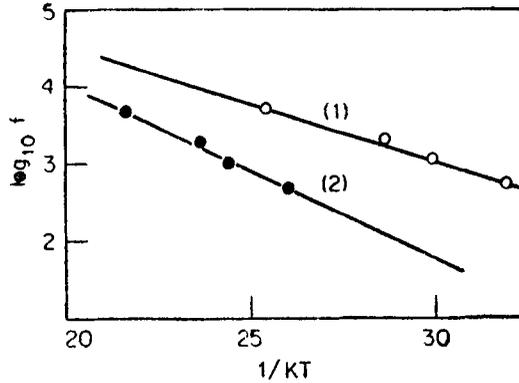


Figure 11.  $\log_{10} f$  versus  $1/kT$  plot for ZnS:(Mn, La) phosphors corresponding to first (1) and second (2) group of traps.

$\log_{10} S$ . The  $E$  and  $S$  values corresponding to two groups of traps thus obtained are found to be 0.30, 0.46 eV and  $2.99 \times 10^{10}$ ,  $2.11 \times 10^9$ /sec respectively.

### 3.5 Photoelectroluminescence

The comparison of PL, EL and PEL emission intensities provides information about the enhancement and quenching of a particular emission band. The quenching and enhancement ratio is determined as follows:

$$I_{PEL} > I_{PL} + I_{EL} \quad \text{enhancement}$$

$$I_{PEL} < I_{PL} + I_{EL} \quad \text{quenching}$$

The enhancement of orange emission band (5800 Å) in ZnS:Mn was found to agree with that of Vlasenko (1965) and Cusano (1957). In ZnS:La phosphors the quenching of both the bands (5200 and 5700 Å) is found to occur for 0.01% and 0.05% concentrations of La<sup>3+</sup> ion, while for 0.1% La<sup>3+</sup> ion concentration the green band is quenched and the yellow band (5700 Å) is enhanced. In ZnS:(Mn, La) phosphors the orange emission band at 5800 Å is enhanced for manganese concentrations (2%, 1%, 0.5% and 0.1%) while quenching occurs for both bands (5200 and 5800 Å) for 0.05% and 0.01% manganese concentrations.

The band gap in ZnS is 3.64 eV. The UV photons of energy 3.40 eV are sufficient to excite or ionize the filled traps. The liberated electrons are fed to the conduction band where they are accelerated by the applied electric field and subsequently ionize the luminescence center after collision resulting in luminescence and hence the enhancement. Similarly quenching can be explained by further trapping of the electrons in the deep trap centres which are not easily detrapped by the applied field.

### 3.6 Phosphorescence

The phosphorescence decay of all these phosphor was studied at different temperatures. Figure 12 shows the decay curves of ZnS:(Mn, La) phosphor at different temperatures. The log of phosphorescence intensity versus log of time curves obey the relation

$$I_t = I_0 t^{-b}$$

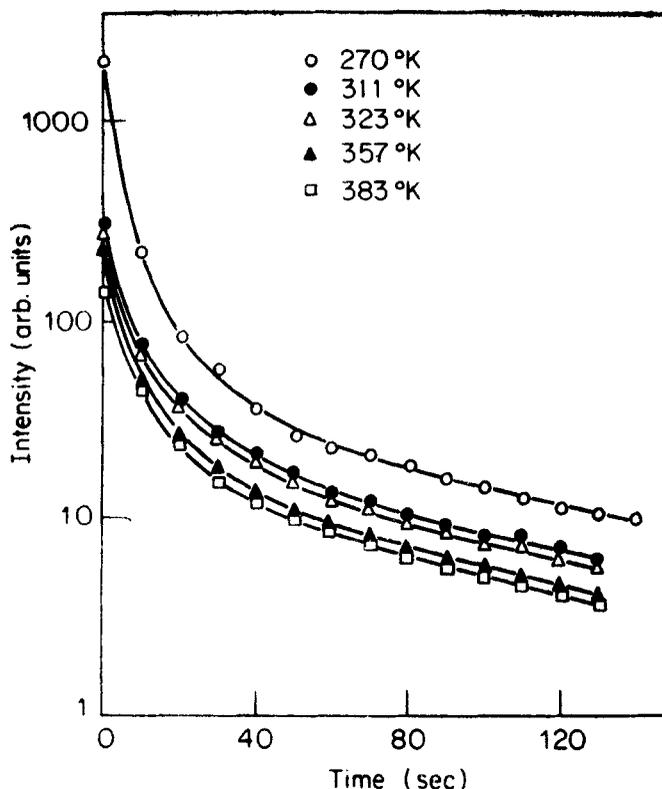


Figure 12. Phosphorescence decay curves of ZnS:(Mn, La) phosphors at different temperatures for 0.05% Mn and La.

where  $I_t$  = decay intensity at time  $t$ ,  $I_0$  = constant intensity at time  $t=0$  and  $b$  = decay constant. The slope of the line gives the value of decay constant  $b$ . The decay curves are described as the superposition of different exponential curves obeying the mono-molecular decay kinetics. The 'peeling off' of the decay curves was done into three exponentials corresponding to slow, fast and normal decay rates. The trap-depth values and the life-time of electrons in the trap ( $\tau$ ) for these three exponential decays were determined.

It is found that trap depth increases slowly with the temperature of the samples. The life-time of electron in traps varies irregularly with temperature suggesting the possibility of retrapping in these phosphors. This explains the increase in the trap-depth with temperature. The change in the band gap with the temperature is also one of the reasons.

### 3.7 Thermoluminescence

**3.7a Trapping parameters.** The trap-depth values and the attempt to escape frequency are evaluated by peak shifting method (Booth 1954) shown in figure 13 and given in table 1. It is seen that the trap-depth changes with activator and coactivator concentrations and the attempt to escape frequency of trapped electrons varies according to these depths. It is also observed that the trap-depth is constant at higher concentrations (2%, 1% and 0.5%) and varies slowly at the lower concentrations (0.01%

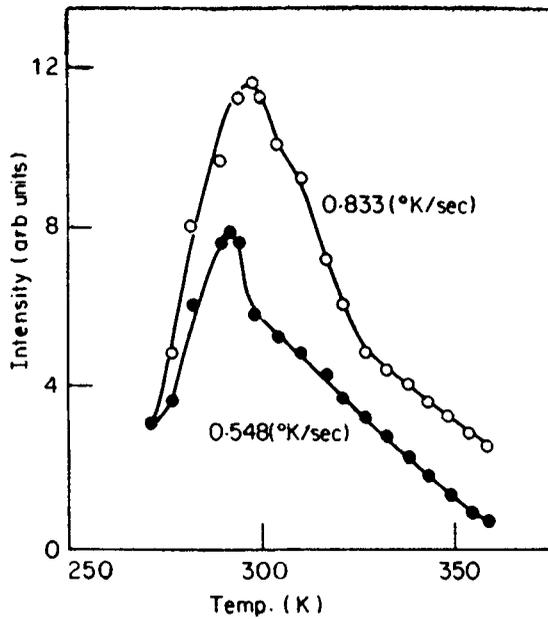


Figure 13. Thermal glow curves of ZnS:(Mn, La) phosphors for 0.05% Mn and La concentrations at two heating rates.

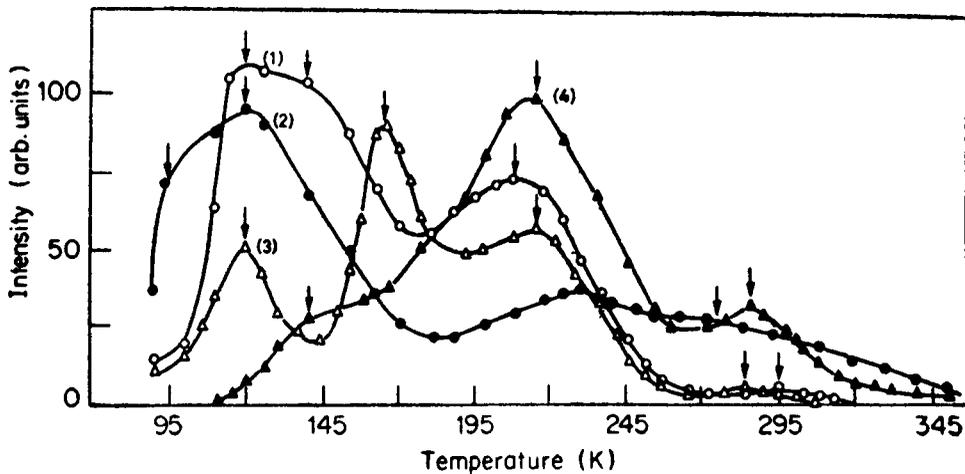


Figure 14. Thermal glow curves for ZnS:La, 0.05% (1); ZnS:Mn 1% (2); ZnS:(Mn, La), 0.05% (3); and pure ZnS (4).

0.05% and 0.1%) of Mn. The life-time of electron in the trap increases with the concentration of Mn and is found to be constant above 0.5% Mn concentration (table 1).

The capture cross-section ( $\sigma$ ) of electron trap is also calculated using Mott and Gurney (1940) relation which is of the order of  $10^{-18}$  cm<sup>2</sup>. The  $\sigma$  values for different samples are given in table 1 and is seen to increase with trap-depth.

The values of trap-depth ( $E$ ) and the attempt to escape frequency ( $S$ ) in ZnS:Mn,La (0.01%) obtained from different methods are in reasonably good agreement.

**Table 1.** Values of  $E$ ,  $S$ ,  $\sigma$  and glow peak temperature ( $T$ ) for different concentration of activator and coactivator.

% of Mn <sup>2+</sup> and La <sup>3+</sup>	$T(^{\circ}\text{K})$ at heating rate		$E$ (eV)	$S$ sec <sup>-1</sup> ( $\times 10^9$ )	$\sigma$ cm <sup>2</sup> ( $\times 10^{-18}$ )
	0.584 °K/sec.	0.833 °K/sec.			
Mn = La 0.01%	294	299	0.58	0.43	3.07
Mn = La 0.05%	292	297	0.57	0.36	2.61
Mn = La 0.1%	299	304	0.60	0.68	4.68
Mn = La 0.5%	289	294	0.56	0.27	2.01
Mn = La La = 0.05%	283	288	0.54	0.17	1.30
Mn = 2% La = 0.01%	289	294	0.56	0.27	2.01

**Table 2.** Values of trap-depths corresponding to different peak temperatures obtained in thermal glow experiment at uniform heating rate 0.64/sec. (approx.)

Phosphors	$T(^{\circ}\text{K})$	$E$ (eV)
ZnS	143	0.28
	208	0.41
	218	0.43
	289	0.58
ZnS:Mn 1%	98	0.18
	123	0.24
	233	0.46
	278	0.56
ZnS:La 0.05%	123	0.24
	143	0.28
	211	0.42
	298	0.60
ZnS:Mn, La 0.05% each	123	0.24
	168	0.33
	218	0.43
	287	0.58

**3.7b Thermal depths of traps and their origin.** The thermal glow curves at low temperatures for ZnS, ZnS:Mn, ZnS:La and ZnS:(Mn, La) were also studied (figure 14). These curves were obtained at uniform heating rate as given in table 2. It is seen that in pure ZnS four groups of traps at 143, 208, 218 and 289 °K are present, whereas in ZnS:Mn there are also four groups of traps at 98, 123, 233 and 278 °K. In ZnS:La and ZnS:(Mn, La) the traps are found at temperatures 123, 143, 211, 298 °K and 123, 168, 218, 287 °K respectively. The trap-depth values have been calculated by employing the relation

$$E \text{ (eV)} = \frac{T^* \text{ (}^{\circ}\text{K)} - T_0 \text{ (}\beta/S\text{)}}{K \text{ (}\beta/S\text{)}}$$

where  $T^*$  = peak temperature,  $\beta$  the heating rate,  $T_0$  and  $K$  are constants. Their values have been obtained graphically by Curie (1963). The  $S$  values used in the calculation is obtained from peak shifting method as discussed in § 3.7 of this paper. Table 4 represents the values of trap-depths corresponding to different group of traps at different temperatures.

Comparison of glow curves in figure 14 shows that in ZnS:(Mn, La) a special group of traps exist at temperature 168°K which is different from the other group of traps found in ZnS, ZnS:Mn and ZnS:La. These trapping states may be attributed to lattice defects or impurities in different valency states. We believe that the capture of electrons at  $La^{3+}$  centre results in formation of  $La^{2+}$  centre which consequently behaves like a trap. The other groups of traps are related to the different intrinsic lattice defects.

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