

Optical properties of electroluminescent ZnS doped with Cu⁺, Mn²⁺ and Gd³⁺ ions

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Abstract. ZnS:Gd, ZnS: Cu, Gd and ZnS: Mn, Gd phosphors have been prepared by firing the samples in argon atmosphere. Spectral distributions in these phosphors are discussed with appropriate mechanism. ZnS:Cu, Gd and ZnS:Mn, Gd are found to be examples of multiple band phosphors. Enhancement and quenching of the emission band intensities of all these phosphors have been studied in PEL emission. It is observed that Gd³⁺ ions play an important role in transferring their excitation energy to other centres. The voltage and frequency variation of EL brightness are in agreement with collision excitation mechanism in Schottky barrier at the metal semiconductor interface. Studies in phosphorescence and thermoluminescence of these phosphors have also been carried out. It is observed that trap-depth changes slowly with temperature and dopant concentration. The values of trapping parameters have been evaluated. The irregular variation of the life-time of electrons in the traps with temperature shows the existence of retrapping in these phosphors.

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

1. Introduction

Rare earth-doped ZnS phosphors (Anderson *et al* 1965; Razi *et al* 1967; Pankove *et al* 1977; Kobayashi *et al* 1973, 1974; Tripathi *et al* 1980, 1981) have attracted a good deal of attention. Doubly-activated ZnS phosphors have been found to possess good electroluminescence (EL) emission, and energy transfer between the dopant ions is known and has been explained satisfactorily (Hoshina *et al* 1980; Tabel *et al* 1977, 1978). Rare earth ions are in demand as laser dopants in many phosphor lattices as well as for their use in colour television phosphors.

It is well-known that Cu ions in ZnS lattice (Kroger *et al* 1949; Suzuki 1971) produce two broad and featureless emission bands, popularly known as the blue and the green bands situated around 4700 Å (2.64 eV) and 5400 Å (2.30 eV) in cubic modifications respectively. The former is thought to arise due to electron transition from the bottom of conduction band or from a level very near to it in the forbidden gap to the Cu ground level, which acts as the recombination centre. The latter is supposed to arise due to electron transition between the donor levels near the conduction band and the copper acceptor ground level. Mn²⁺ ion (Vlasenko *et al* 1973; Takeda *et al* 1975; Chang *et al* 1978; Walentynowicz *et al* 1978) in the ZnS lattice is also known to produce yellow-orange emission band situated around 5800 Å, which has been attributed to *d-d* internal transition in Mn²⁺ ion.

In the present investigation we have made an attempt to study the photoluminescence (PL), electroluminescence (EL), photoelectroluminescence (PEL), phosphorescence and thermoluminescence in ZnS:Gd, ZnS:(Cu, Gd) and ZnS:(Mn, Gd) phosphors. The purpose of this paper is also to ascertain in what way does the introduction of Gd³⁺ ion together with Cu⁺ and Mn²⁺ into ZnS lattice affect the self-activated (SA) emission.

2. Experimental

Luminescent grade ZnS powder was mixed with appropriate amounts of GdCl₃, Cu(CH₃COO)₂, MnCl₂·4H₂O so as to obtain ZnS:Gd, ZnS:(Cu, Gd) and ZnS:(Mn, Gd) respectively. Five ml of pure distilled water and about 0.5% pure sulphur by weight of ZnS were added to each phosphor in a silica crucible and the resulting slurries were well stirred and dried in an oven at 300°C. All the samples were fired at 1000°C for 40 min in an inert atmosphere of flowing argon gas in a silica tubular furnace. Separate firing was done for ZnS:Gd, ZnS:(Cu, Gd) and ZnS:(Mn, Gd) and a number of these phosphors containing different percentage of activator and coactivator were prepared. No flux was used in any of the phosphors. To study the photoluminescent emission the phosphors were coated in thin layers to a piece of black card-board by means of a non-luminescent binder (quickfix). Samples were excited by 3650 Å radiation from a high pressure mercury discharge lamp.

For EL emission a parallel plate sandwich type cell was arranged. One plate of the cell was a transparent conducting glass plate and the other an uniform flat aluminium plate. A thin (about 10 μ) mica sheet was laid on the aluminium plate over which a suspension of the phosphor in castor oil was spread. The conducting glass plate was placed on the phosphor and gently pressed to avoid air bubble in the phosphor layer. The conducting side of the glass plate was in contact with the phosphor. Total thickness of the cell was around 100 μ.

An audio frequency oscillator coupled to a wide band amplifier capable of giving voltages up to 750 volts (rms) was used to excite the phosphor. The frequency of the AC field could be varied from 50 Hz to 20 kHz.

For detecting the intergrated light output from the EL cell and also the spectral distribution of the emitted light, an RCA IP 21 photomultiplier tube having S-4 response was used. The photomultiplier was operated using a highly stabilised DC power supply giving voltages up to 1250 volts. The output terminal of the multiplier was connected to a sensitive multiflex galvanometer whose current sensitivity was of the order of 10⁻⁹ amp/mm.

A constant deviation type monochromator was used to analyse the spectral distribution of the light from the EL cell and also the photoluminescent emission from the phosphors. The photomultiplier was placed at the focal plane of the spectrograph. The spectrum was scanned by rotating the wavelength drum of the monochromator.

The samples were excited for 5 min by 3650 Å radiation and the decay intensity was then recorded at different times and temperatures. When the decay intensity became negligibly small the sample was heated at a linear rate to study thermoluminescence behaviour.

3. Results

3.1 PL spectra

In ZnS:Gd maximum emission at 5100 Å is found for Gd concentration of 0.05% by weight. The position of peak shifts towards higher wavelength side when the concentration of Gd³⁺ ions increases (figure 1). A blue band at 4700 Å also appears as a shoulder of green band.

In ZnS:Cu, Gd phosphors, two peaks—the blue peak around 4700 Å and the green peak at 5300 Å—have been observed in the PL spectra (figure 1). The peaks gradually shift towards the shorter wavelength side on increasing the concentration of both activators.

In ZnS:(Mn, Gd) a brilliant yellow-orange emission is found at 5800 Å for higher concentrations of Mn²⁺ ions (2%, 1%, 0.5%, 0.2% by weight) and green emission around 5200 Å for lower concentration of Mn²⁺ ions (0.1%, 0.05%, 0.01%). Another band around 7000 Å of medium intensity is invariably present in the samples at lower concentrations of Mn and Gd (0.1%, 0.05% and 0.01%) as shown in figure 2. At 0.2% Mn and 0.01% Gd concentration there is one broad peak at 5200 Å and another one situated at 5800 Å. As the concentration of Mn ions is gradually increased, the green band loses its brightness and at the same time the orange band at 5800 Å gains intensity so much so that at higher concentration of Mn, only the orange band is present and the green band is practically quenched (figure 2). Also at higher concentrations of Mn, concentration quenching takes place for the same green band.

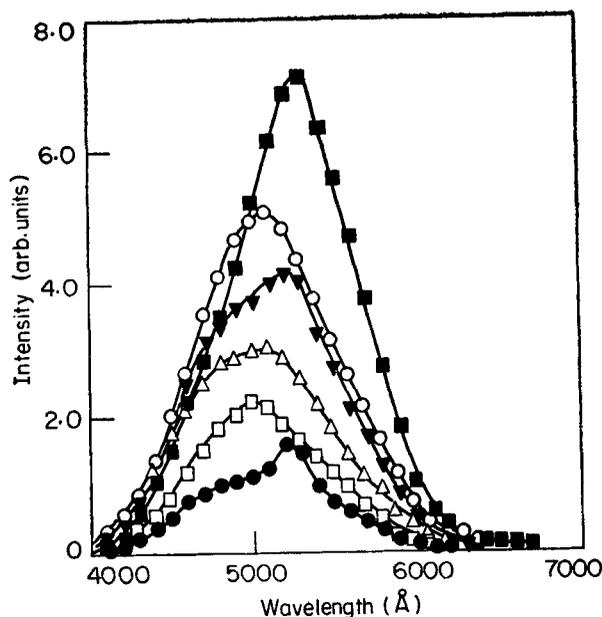


Figure 1. PL spectra in ZnS:Gd for \square , 0.01%; \circ , 0.05%; \triangle , 0.1% Gd³⁺ and in ZnS:Cu, Gd for \blacksquare , 0.01%; \blacktriangledown , 0.05%; \bullet , 0.1% Cu⁺ and Gd³⁺ concentrations.

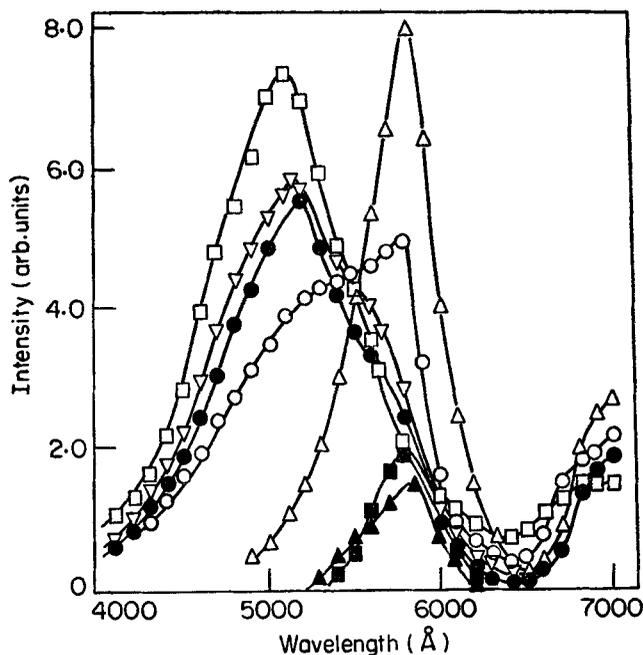


Figure 2. PL spectra in ZnS:Mn, Gd phosphors for ▲, Mn = 2%, Gd = 0.01%; ■, Mn = 1%; Gd = 0.05%; △, Mn = Gd = 0.5%; ○, Mn = 0.2%; Gd = 0.01%; ●, Mn = Gd = 0.1%; ▽, Mn = Gd = 0.05%; and □, Mn = Gd = 0.01% concentrations.

3.2 EL spectra

On AC field excitation ZnS:Gd phosphor emits dominant green band at 5200 Å. This band may be correlated to 5100 Å band found in the PL spectra. This fact suggests that the same centres are responsible for emission of both the bands (figure 3). The EL emission in ZnS:Cu, Gd is located at a prominent band situated at 4700 Å for 0.05 and 0.1% of Cu⁺ and Gd³⁺ ions concentration. The band is sharp towards the shorter wavelength side. The peak position of this band remains stationary and does not change with frequency (figure 4). There is another strong band at 5300 Å for a still lower concentration of copper and gadolinium 0.01% (figure 5). The bands at 4700 and 5800 Å also make their appearance but with moderately strong brightness.

In ZnS:Mn, Gd the EL emission shows mainly the orange band at 5800 Å for higher percentage of Mn ions (2%, 1%, 0.5% and 0.1%) (figure 6). At lower concentration of Mn (0.05%, 0.01%) also, the orange emission predominates while bands of medium weak intensity appear at 5300 Å and 4800 Å (figure 6). At 0.01% of Mn and Gd concentration, the EL spectra show the presence of a strong band at 5200 Å appearing with suppressed intensity (figure 6).

3.3 Photoelectroluminescence

The PEL of these phosphors shows enhancement and quenching of the emission bands simultaneously in different spectral regions. The orange emission band located at 5800 Å of ZnS:Mn, Gd at higher concentrations of Mn (2%) is enhanced while at

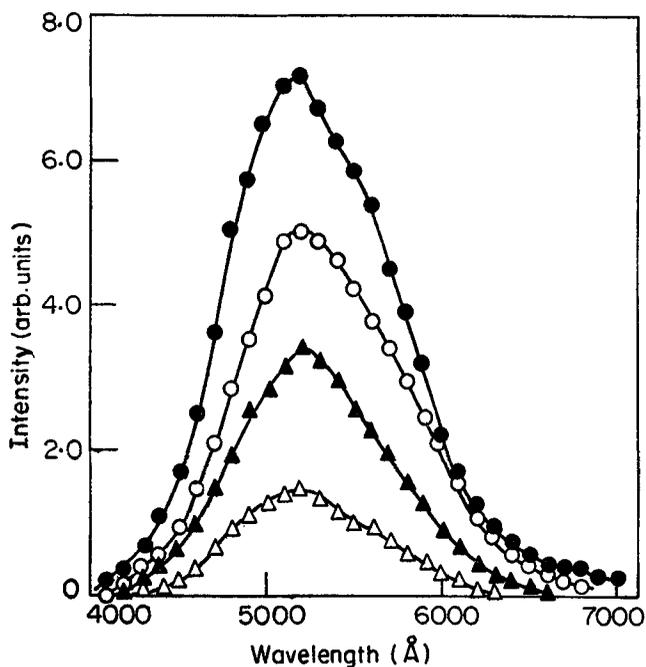


Figure 3. EL spectra in ZnS:Gd phosphors for 0.1% Gd³⁺ at fixed 750 volts (rms) and different field frequencies —▲, 500 Hz; ▲, 1 kHz; ●, 2 kHz and ○, 5 kHz.

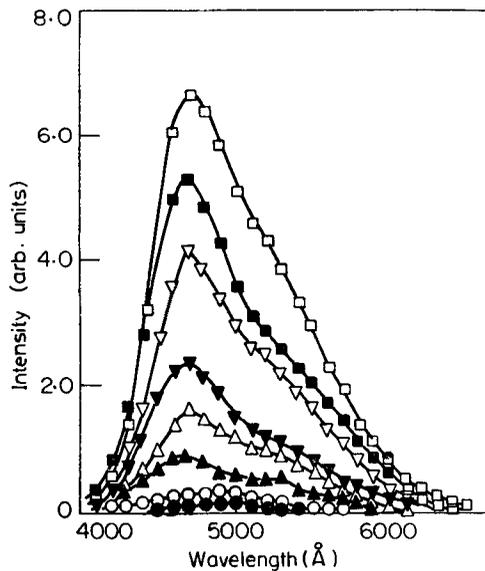


Figure 4. EL spectra in ZnS:(Cu, Gd) phosphors at fixed 750 volts (rms) and different field frequencies. For 0.05% Cu⁺ and Gd³⁺ ions ○, 50 Hz; △, 500 Hz; ▽, 1 kHz and □, 2 kHz. For 0.1% Cu⁺ and Gd³⁺ ions ●, 50 Hz; ▲, 500 Hz; ▼, 1 kHz and ■, 2 kHz.

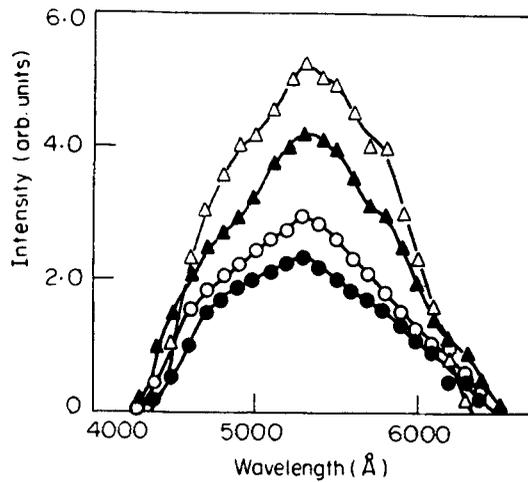


Figure 5. EL spectra in ZnS:Cu, Gd phosphor for 0.01% Cu⁺ and Gd³⁺ ions at 750 volts (rms) and different field frequencies ●, 1 kHz; ▲, 2 kHz; △, 3 kHz and ○, 5 kHz.

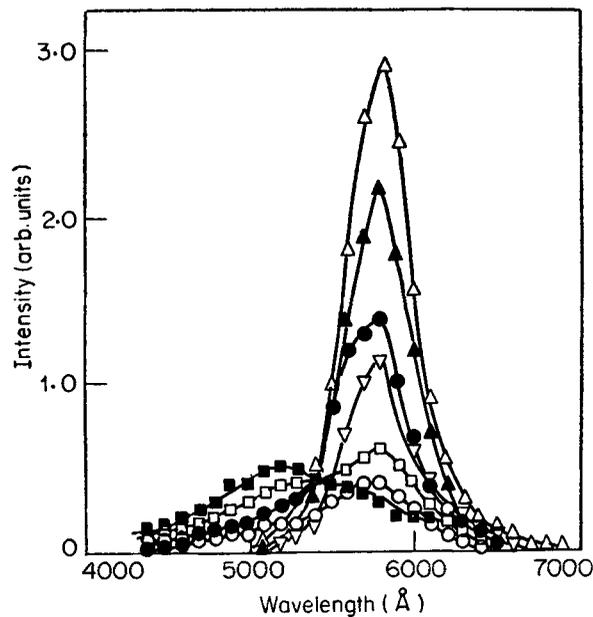


Figure 6. EL spectra in ZnS:Mn, Gd phosphors for different concentrations of activators as given below.

Symbols	■	○	●	□	▲	△	▽
Frequencies (kHz) at 750 volts (rms)	5	2	1	2	2	2	2
Conc. of Mn ²⁺ (%)	0.01	0.05	0.1	0.2	0.5	1	2
Conc. of Gd ³⁺ (%)	0.01	0.05	0.1	0.1	0.5	0.05	0.01

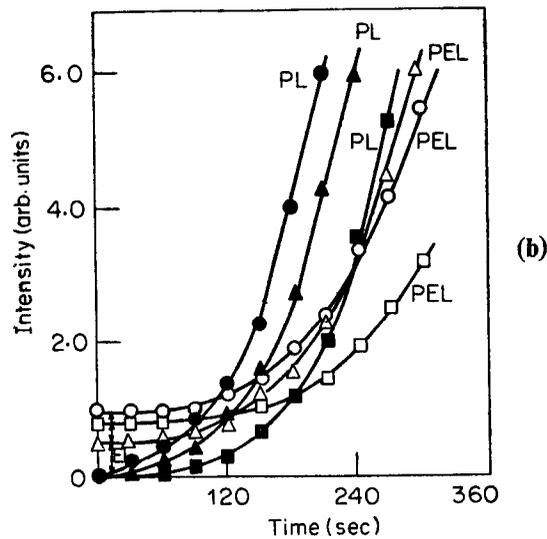
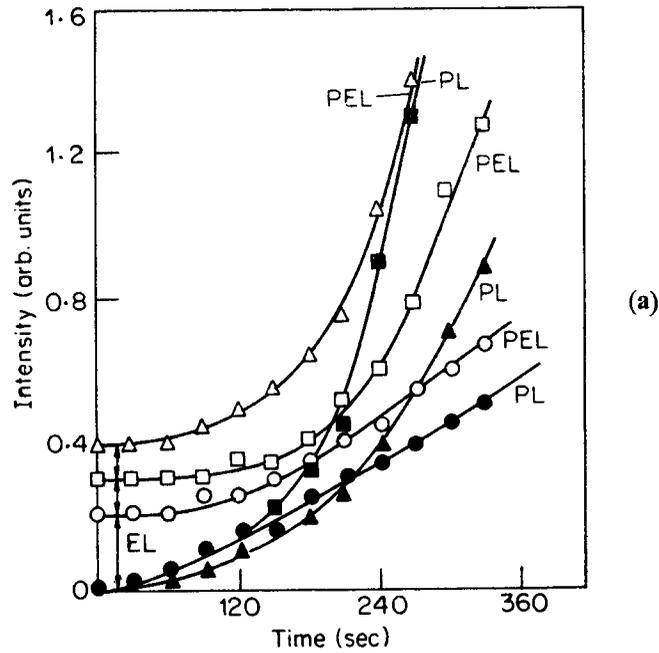


Figure 7. Variation of PL, EL and PEL emission intensities with exciting time (for EL $f = 2$ kHz, $V = 750$ volts (rms) and PL by 3650 \AA radiations).

(a) In ZnS:Mn, Gd, phosphors

- (●, ○) Mn = 2%, Gd = 0.01% at 5800 \AA
- (▲, △) Mn = Gd = 0.01% at 5200 \AA
- (■, □) Mn = Gd = 0.01% at 5800 \AA

(b) In ZnS:Gd and ZnS:Cu Gd, phosphors

- (●, ○) Gd = 0.1% at 5200 \AA
- (▲, △) Cu = Gd = 0.1% at 5200 \AA
- (■, □) Cu = Gd = 0.1% at 4700 \AA

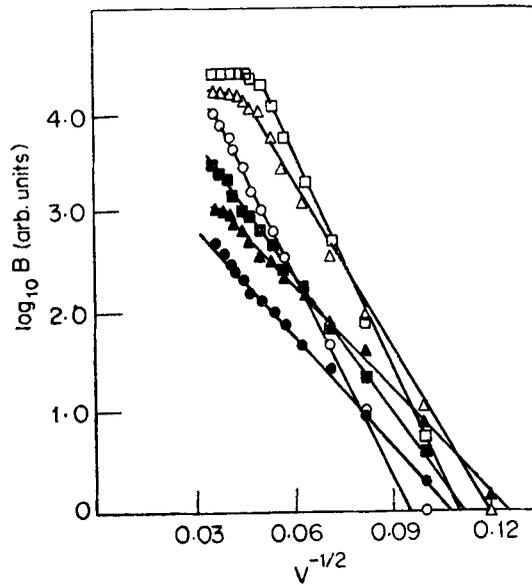


Figure 8. Voltage dependence of EL brightness for 0.05% concentration of activators in (\blacktriangle , \triangle) ZnS:Gd, (\blacksquare , \square) ZnS:Cu, Gd and (\bullet , \circ) ZnS:Mn, Cd phosphors at field frequencies 50 Hz (\blacktriangle , \blacksquare , \bullet) and 2 kHz (\triangle , \square , \circ) respectively.

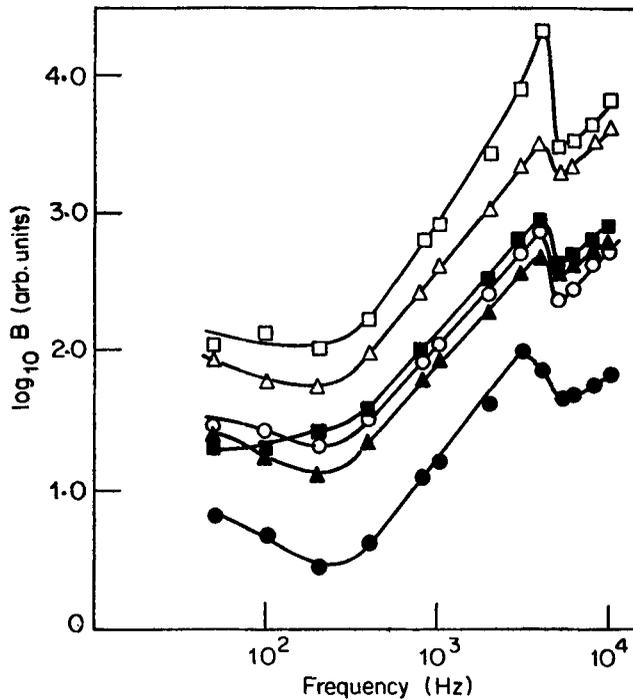


Figure 9. Frequency dependence of EL brightness at (\blacktriangle , \blacksquare , \bullet) 200 volts and (\triangle , \square , \circ) 300 volts (rms) for 0.05% concentrations in (\blacktriangle , \triangle) ZnS:Gd, (\blacksquare , \square) ZnS:Cu, Gd and (\bullet , \circ) ZnS:Mn, Gd phosphors.

lower concentrations (0.01%) this band is quenched and the band at 5200 Å is enhanced (figure 7a). In the case of ZnS:Gd and ZnS:Cu, Gd all the characteristic emission bands are quenched (figure 7b).

3.4 Voltage and frequency dependence of EL brightness

The log of brightness has been plotted against $V^{-1/2}$ (V is the rms value of the applied voltage) for each phosphor. The plot is found to be a straight line (figure 8) obeying the relation (Tayler *et al* 1964; Zalm *et al* 1954) $B = B_0 \exp(-b/V^{1/2})$ where B_0 and b are constants.

Frequency dependence of EL brightness increases linearly with frequency between 200 Hz to 3 kHz (figure 9). A drop in EL brightness was observed within the frequency range 3 kHz to 5 kHz, and thereafter, the brightness shows an increasing trend.

3.5 Phosphorescence decay

Decay curves for ZnS:Gd, ZnS:Cu, Gd and ZnS:Mn, Gd phosphors at temperatures 306, 311 and 312°K respectively (figure 10) are hyperbolic in nature. These curves were analysed by peeling off the hyperbolic curve into three exponentials. The values of trap-depth (E) corresponding to these exponentials were calculated by the relation (Randall *et al* 1945) $P = S \exp(-E/kT)$ where P is the probability of radiative recombination of carriers, k is Boltzmann constant, S is the attempt to escape frequency and T is the absolute temperature. The calculated values are given in table 1. It is seen that the value of trap-depth increases slowly with temperature.

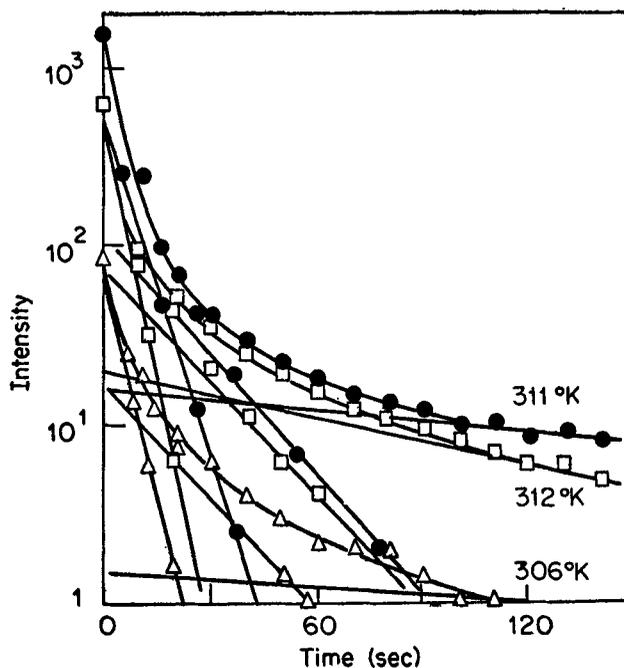


Figure 10. Decay curves and their peeling into three exponentials in Δ , ZnS:Gd for 0.05% at 306°K; \square , ZnS:Mn, Gd for Mn = 1%, Gd = 0.05% at 312°K and \bullet ZnS:Cu, Gd for Cu = Gd = 0.05% at 311°K.

Table 1. Values of trap-depth (E) corresponding to three exponentials of slow, normal and fast decay rates at different temperatures (T)

Phosphors	Temperature °K	Trap-depth (E) in eV		
		I exp	II exp	III exp
ZnS:Gd 0.05%	270	0.41	0.45	0.47
	306	0.48	0.52	0.59
	322	0.51	0.54	0.61
	353	0.55	0.60	0.67
	384	0.60	0.64	0.74
ZnS:(Cu, Gd) Cu = Gd 0.05%	270	0.41	0.46	0.49
	311	0.50	0.52	0.59
	324	0.51	0.54	0.59
	355	0.57	0.60	0.66
	388	0.60	0.65	0.71
ZnS:(Mn, Gd) Mn = 1.0% Gd = 0.05%	270	0.42	0.46	0.54
	312	0.49	0.53	0.57
	323	0.50	0.54	0.59
	354	0.56	0.60	0.65
	385	0.61	0.65	0.71

3.6 Thermoluminescence

The thermal glow curves for ZnS:Gd, ZnS:(Cu, Gd) and ZnS:(Mn, Gd) are shown in figure 11. These curves were obtained experimentally at a single uniform heating rate 0.64°K/sec. The values of trap-depth corresponding to each peak maxima which appear in glow curves were calculated by employing the relation

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

where T^* is peak temperature, β the heating rate T_0 and k are constants. Their values have been obtained graphically by Curie (1963).

4. Discussions

The PL emission bands of phosphors studied above are in general similar to those obtained by the AC field excitation. The relative intensities of the bands in the two cases are different. ZnS:Cu, Gd and ZnS:Mn, Gd are examples of multiple band phosphors. The former emits two bands, blue and green and the other emits 4 bands blue, green, yellow-orange and red as is evident from the respective EL spectra. The intensities of these bands are strongly dependent on the concentration of dopant ions (figures 2 and 6). The luminescent light emission in these phosphors can be explained fairly well on the basis of Prener-Williams (1956) associated donor-acceptor models of energy transfer among different centres.

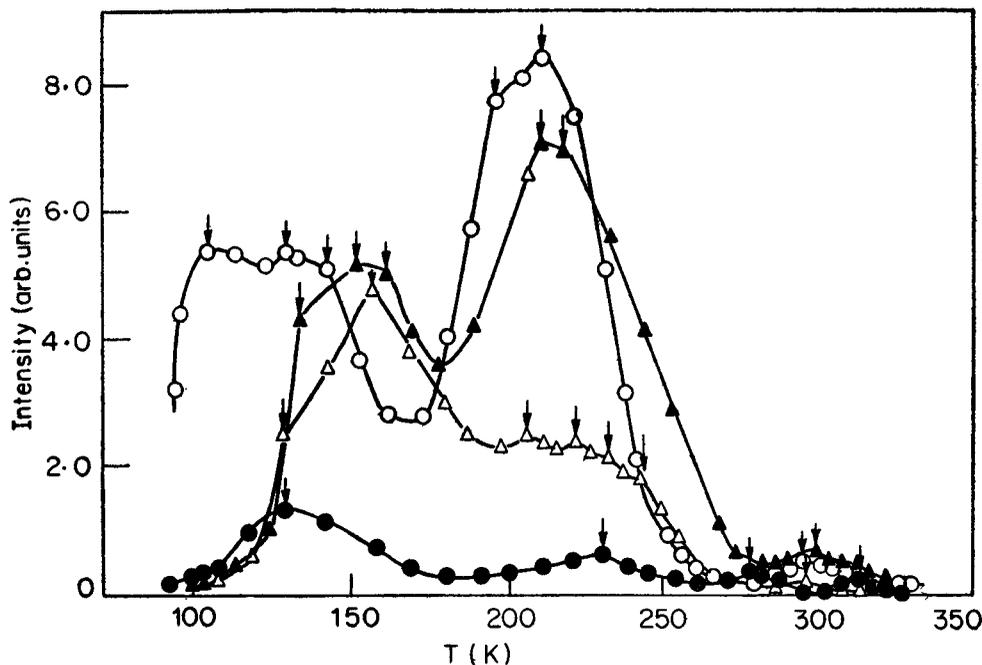


Figure 11. Thermal glow curves at uniform heating rate $0.64^{\circ}\text{K}/\text{sec}$.

- ▲, ZnS:Gd for Gd = 0.05%
- , ZnS:Cu, Gd for Cu = Gd = 0.05%
- , ZnS:Mn, Gd for Mn = 1.0% Gd = 0.05%
- △, ZnS:Mn, Gd for Mn = Gd = 0.05%.

In all these phosphors Gd^{3+} ions form donor levels near the conduction band. The position of these levels is not very definite but it is believed to be about 0.4 eV below the conduction band. Cu^{+} ions form acceptor levels in the ZnS lattice. The Mn^{2+} ions form localized level and its ground level ${}^6\text{S}_{5/2}$ is situated in the valence band. The upper levels ${}^4\text{F}$, ${}^4\text{D}$, ${}^4\text{P}$ and ${}^4\text{G}$ (Klick *et al* 1952; Curie 1963) all lie in the forbidden energy gap. These states are split in the crystal field and are lowered in energy with respect to the ground state.

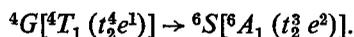
The single band green emission (510 nm) in ZnS:Gd may be due to electronic transition between the ground level of Gd^{3+} ions and the acceptor like Zn^{2+} ion vacancies, which act as hole traps. The gradual shift in the peak position indicates that Gd^{3+} ions are mainly incorporated at interstitial sites (Leverenze 1948). The green band in ZnS:Cu, Gd may be ascribed to electronic transition from Gd^{3+} ground level to substitutional acceptor Cu^{+} level which acts as a recombination centre. Blue band may likewise be due to radiative electronic transition from the bottom of the conduction band to the Cu^{+} centre. The transition of electrons from the conduction band to the Zn^{2+} ion vacancies is also possible giving rise to the self-activated blue emission. Due to mixing of two bands it is not possible to state with certainty which transition is actively predominant. To this the EL spectra (figure 4) comes to our rescue. The spectrum has a peak at 4700 \AA . At higher concentrations of Cu and Gd^{3+} the number of Zn^{2+} vacancies will be smaller and therefore the number of radiative transitions due to impact ionization and subsequent emission at copper will predominate over the blue transitions due to Zn^{2+} vacancies. The self-activated emission

will, therefore, be feeble and the dominant transition will be blue copper. Assuming that Cu^+ ground level 0.9 eV is above the valence band (Curie *et al* 1960) and adding to it the energy of the green band (530 nm) 2.34 eV we may locate the Gd^{3+} level at 3.24 eV *i.e.* 0.4 eV below the conduction band. The position of the Gd^{3+} level explains also the green emission in $\text{ZnS}:\text{Gd}$. At lower concentrations of Cu^+ and Gd^{3+} probably the excitation probability for copper centres to emit blue band is more than the radiative recombination of electron from the Gd^{3+} centre to the copper level (green emission). This explains the strong blue and moderate green emission in EL (figure 4). There is also a possibility of a red band which could not be fully recorded with certainty in view of the poor intensity (figure 5).

In $\text{ZnS}:\text{Mn}$, Gd the situation is quite different and interesting. The appearance and intensity of the bands change with concentration (figures 2 and 6). At lower concentrations of Mn^{2+} in $\text{ZnS}:\text{Mn}$, Gd the green emission due to radiative transition from Gd^{3+} centre to Zn^{2+} vacancies predominates. At higher concentrations of manganese the Mn^{2+} ground state ${}^6\text{S}$ is directly excited by the photons (3650 Å). The electrons are raised to ${}^4\text{F}$ upper level, which relax non-radiatively to ${}^4\text{G}$ level. The electrons in this level are de-excited to ground level ${}^6\text{S}$ and spontaneously emit yellow-orange light of wavelength 5800 Å. Reduction in the intensity of the green band arising due to Gd^{3+} ions and subsequent increase in the intensity of Mn^{2+} yellow band points to some sort of energy transfer from Gd^{3+} to Mn centres. Photoelectron and hole transfer to the centres is more probable than the resonant energy transfer between Gd^{3+} and Mn^{2+} as the Gd^{3+} levels lie in UV region and the levels of Mn^{2+} mismatch.

In the EL spectra the 5800 Å band is predominant in all the samples having a higher concentration of Mn^{2+} ions. In this case the electrons which are accelerated by the applied field make elastic collision with Mn^{2+} ions causing excitation without ionization and subsequent emission of yellow light (${}^4\text{G} \rightarrow {}^6\text{S}$ transition within the Mn *d-d* shell). The impact ionization is less probable as it has been shown that in ZnS phosphor containing Mn^{2+} , no increase in photoconductivity is observed along with light emission (Piper 1953). The positions of the EL bands do not change either with voltage or frequency.

The enhancement of the 5800 Å band in PEL emission may be understood as follows: under simultaneous excitation of electric field and 3650 Å radiation, more and more electrons are fed to the conduction band by the external radiation creating a higher density of conduction electrons. These electrons are accelerated in the applied electric field and when they gain sufficient energy from the field, their impact excites the Mn^{2+} centres to higher levels ${}^4\text{D}$, ${}^4\text{P}$, ${}^4\text{F}$, which relax to the ground level giving yellow light. ${}^4\text{G}$, ${}^6\text{S}$ are free ion electronic terms. They are modified and split under the crystal field of octahedral symmetry in the ZnS lattice. In fact the electronic transition which takes place is



We could not get fine structure in the yellow band due to low resolving power of the spectrograph. Moreover as pointed out earlier the 3650 Å photons also directly excite the Mn^{2+} ions. The field and photonic excitation thus reinforce each other and the light emission is enhanced.

Quenching of blue and green bands in other phosphors could be understood

qualitatively, if it is supposed that some kind of trapping of excited carriers takes place at some deeper traps.

The relation $B = B_0 \exp(-b/\sqrt{V})$ shows the excitation mechanism of EL emission in acceleration-collision at Schottky barrier layer at metal-semiconductor contact. The thickness of the barrier layer varies as $V^{1/2}$. The drop in the EL brightness in the frequency range 3 to 5 kHz may be attributed to the trapping of some of the electrons in the empty donor levels and/or traps in such frequency range of the applied field. The trapped electrons are subsequently released by the field at still higher frequencies and increase in brightness results beyond 5 kHz. The sublinear increase in brightness with frequency is in good agreement with the work on the other ZnS phosphors (Ivey 1963; Piper *et al* 1955).

The slow increase of trap-depth with temperature can be explained by the fact that some thermally stimulated electrons may recombine and others may be retrapped at lower trapping levels. The retrapping process may introduce a redistribution of electrons; that is why the trap-depth increases slowly with temperature. This may also be due to a change in the positions of trapping levels due to increase in band gap with temperature (Schonhofer 1958; Seiwert 1949).

The group of traps in these phosphors are indicated in figure 11 and table 2. A group of traps about 129°K in Gd doped ZnS is enhanced in the presence of Mn, while the group of traps about 218°K are quenched at higher concentration of Mn in ZnS:Mn, Gd. For 0.05% concentration of Mn and Gd, many new traps arise. ZnS:Cu, Gd also produces some extra group of traps. These trapping states may be attributed to different intrinsic lattice defects of impurities in different valency states, such as Gd^{3+} state results in Gd^{2+} state by capturing an electron, which consequently behaves like a trap.

Table 2. Values of trap-depth (E) obtained by thermal glow curves at uniform heating rate 0.64 °K/Sec.

Phosphors	Peak temperature (°K)	E (eV)
ZnS:Gd 0.05%	132	0.25
	152	0.30
	161	0.31
	208	0.41
	218	0.43
	299	0.60
ZnS:(Cu, Gd) Cu = Gd = 0.05%	103	0.19
	129	0.25
	143	0.28
	195	0.39
	211	0.42
	296	0.60
ZnS:(Mn, Gd) Mn = 1.0% Gd = 0.05%	129	0.25
	231	0.46
	278	0.56
	313	0.63
ZnS:(Mn, Gd) Mn = Gd = 0.05%	129	0.25
	157	0.31
	208	0.41
	222	0.44
	233	0.46
	243	0.49
	301	0.61

5. Conclusions

Incorporation of Gd^{3+} ion in ZnS lattice together with Cu^+ or Mn^{2+} produces new emission bands and makes them as multiband phosphor. Gd^{3+} ion also creates new groups of traps due to its different valency states and strongly affects the quenching and enhancement properties of the phosphors.

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References

- Anderson W W Razi S and Walsh J 1965 *J. Chem. Phys.* **43** 1153
Chang I F and Ya P Y 1978 *Appl. Phys. Lett.* **32** 7
Curie G and Curie D 1960 *J. Phys. Radium* **21** 127
Curie D 1963 *Luminescence in crystals* (London: Methuen) p. 122, 162
Hoshina T and Kawai H 1980 *Jpn. J. Appl. Phys.* **19** 267, 279
Ivey H F 1963 *Electroluminescence and related effects* (New York: Academic Press), p. 56.
Klick C C and Schulnan R T 1952 *J. Opt. Soc. Am.* **42** 910
Kobayaski H, Tanaka S and Sasakura H 1973 *Jpn. J. Appl. Phys.* **12** 1637
Kobayaski H, Tanaka S, Sasakura H and Hamokawa H 1973 *Jpn. J. Appl. Phys.* **12** 1854
Kobayaski H, Tanaka S, Sasakura H and Hamokawa H 1974 *Jpn. J. Appl. Phys.* **13** 1110
Kroger F A, Hellingman J E and Smit N W 1949 *Physica* **15** 990.
Leverenze H W 1948 *Cornell Symposium* p. 146
Pankove J I, Lampest M A, Hanak J J and Berkeyheiser J E 1977 *J. Lumin.* **15** 349
Piper W W 1953 *Phys. Rev.* **92** 23
Piper W W and Williams F E 1955 *Br. J. Appl. Phys. Suppl.* **4** S-39
Prener J S and Williams F E 1956 *J. Phys. Radium* **17** 667
Randall J T and Wilkins M H F 1945 *Proc. R. Soc. (London)* **A184** 366, 390
Razi S and Anderson W W 1967 *Trans. Metall. Soc. AIME* **239** 350
Schonhofer A 1958 *Z. Phys.* **150** 67
Seiwert R 1949 *Ann. Phys. (Leipzig)* **6** 241
Suzuki A and Shionoya S 1971 *J. Phys. Soc. Jpn.* **31** 1455, 1462
Tabel M and Shionoya S 1977 *J. Lumin.* **15** 201
Tabel M and Shinoya S 1978 *J. Lumin.* **16** 161
Takeda M and Kakishora Y 1975 *OYO Butsuri* **44** Suppl. 103
Tayler J B and Alfrey G F 1964 *Br. J. Appl. Phys. Suppl.* **4** 39
Tripathi L N, Chaubey B R and Mishra C P 1980 *Phys. Status Solidi* **A60** 185
Tripathi L N, Chaubey B R and Mishra C P 1981 *Pramana* **16** 155
Vlasenko N A, Pekar S I and Pekar V S 1973 *Sov. Phys. JETP (USA)* **37** 190
Walentynowicz E and Chimozaek E 1978 *J. Lumin.* **47** 109
Zalm P, Diemer D and Klaseus H A 1954 *Philips Res. Rep.* **9** 81