

Some optical properties of rare earth (Dy, Nd and Sm) activated ZnO phosphors

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Abstract. Some rare earth (Dy, Nd and Sm) doped ZnO electroluminors have been prepared in vacuum (1 torr) and their photo (PL) and electroluminescence (EL) spectra investigated at room temperature at different concentrations of rare earth (RE) ions. Compared to the spectra of undoped ZnO, these spectra consist of the same bands shifted either towards low or high energy side and the intensity of high energy band is decreased while that of low energy band is enhanced. In any case no additional band or line was observed. The experimental results have been explained on the basis of donor-acceptor pair model of recombination process where donor levels are due to RE ions and the acceptors are the luminescent centres of undoped ZnO electroluminors. The mechanism of excitation is of acceleration-collision type.

Keywords. Photoluminescence; electroluminescence; rare earth activated ZnO.

1. Introduction

Phosphors which are activated by rare earth elements are acquiring more and more importance in technology. In the last few years self activated ZnO system have been extensively studied and different luminescent centres have been recognised (Lehmann 1968; Lauer 1973; Joshi and Kumar 1973; Bhushan *et al* 1977). These different centres depend on different methods of preparation of the phosphors. Addition of some donor levels in these phosphors may reveal some salient features of the mechanism of luminescence. Rare earth (RE) ions may solve this purpose with their valence electron $6s^2 5d^1$. In our previous publication (Bhushan *et al* 1976, 1977, 1978), we have reported some results of rare earth doped ZnO system. In continuation of the above studies this paper reports the electro (EL) and photoluminescence (PL) spectra of some rare earth (Dy, Nd and Sm) doped ZnO system.

2. Experimental procedure

2.1. Preparation of the material

ZnO (from M/s. Kotech Light Laboratories 99.998%) and 99.9% pure dysprosium oxide and nitrates of neodymium and samarium (from M/s. Indian Rare Earths Limited) were taken in proper proportions and were thoroughly mixed. The mixture was fired at 1050°C in a tubular furnace under reduced pressure of about 1

torr for 1 hr and was cooled slowly to room temperature at the same pressure. The fired content was finely ground in an agate pestle and mortar and the homogeneity of the samples checked under a black wood glass U.V. lamp.

2.2. Cell preparation

EL cell was prepared by first fixing a mixture of electroluminor with araldite resin in a 100μ thick groove on a stainless steel plate. It was then gently pressed by a thin mica sheet of 30μ thickness. A conducting glass plate with conducting surface in contact with mica sheet was then placed. The cell could not be prepared by direct sandwiching the phosphor between two electrode plates because it was highly photoconducting with high dark current at room temperature. The PL cell was prepared by depositing the material on a glass plate with the help of suitable organic liquid.

2.3. Measuring instruments

An audio oscillator (50 Hz–20 kHz) coupled with a wide band amplifier (0–1000 V) was used for EL excitations and the PL excitation was done by $365\text{ m}\mu$ line of high pressure mercury vapour lamp filtered by Carl Zeiss interference filter. Light output

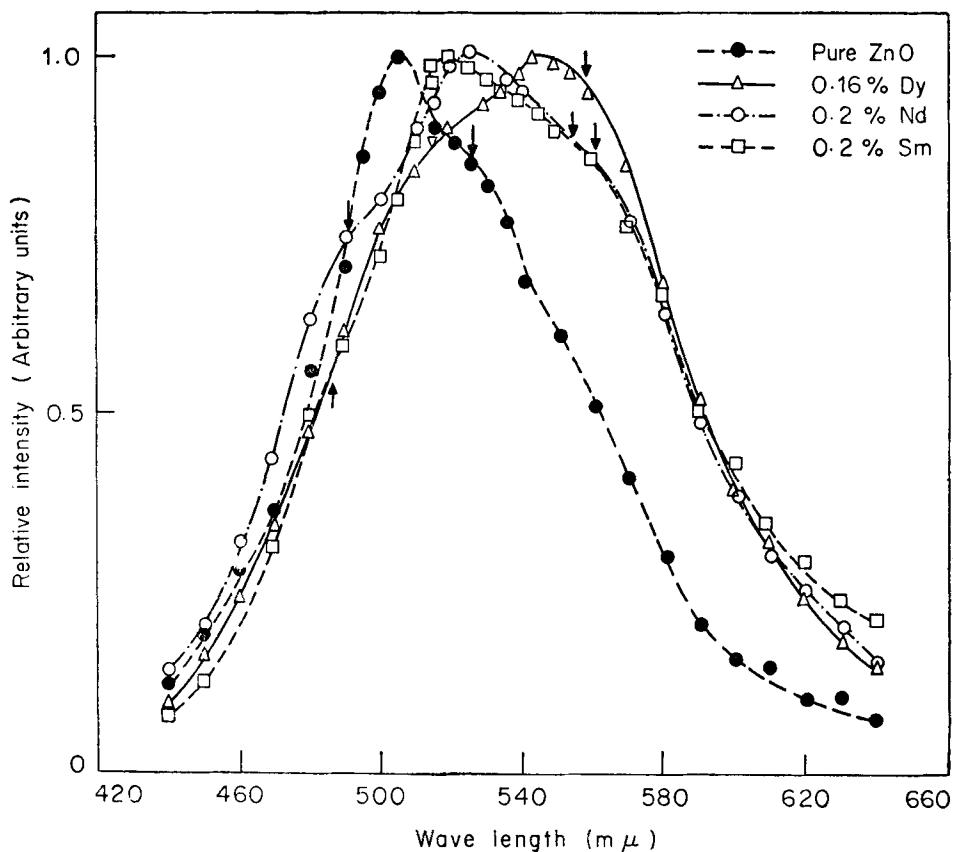


Figure 1. PL spectra of ZnO:Dy, ZnO:Nd and ZnO:Sm electroluminors.

was detected by an RCA IP21 photomultiplier tube which was operated by a regulated power supply (HV 218 ECIL) at 1000 V and the integrated light output in the form of current was recorded by polyflex galvanometer (10^{-9} A/mm). For spectral studies a prism monochromator (400–700 $m\mu$) was used.

3. Results and discussions

The PL spectra of the phosphors ZnO:Dy, ZnO:Nd and ZnO:Sm are shown in figure 1. In general these spectra consist of three bands (1) blue (2) green (3) green-yellow, each corresponding to that of undoped ZnO electroluminor. Comparing with that of undoped ZnO prepared in the same firing condition (Bhushan *et al* 1977) the common feature of PL spectra of these systems are (1) broadening of spectra, (2) shift of bands towards low energy side (3) disappearance of some of the bands with increase in concentration of RE ions. In ZnO:Sm electroluminor with the increase in the concentration of Sm ions no appreciable effect on the position of bands is seen. However, for ZnO:Dy the bands shift towards higher energy side and in ZnO:Nd towards lower energy side with increase in concentration of RE ions.

Figure 2 illustrates the EL spectra of ZnO:Dy, ZnO:Nd and ZnO:Sm electroluminors. All the systems show the three bands of undoped ZnO electroluminors

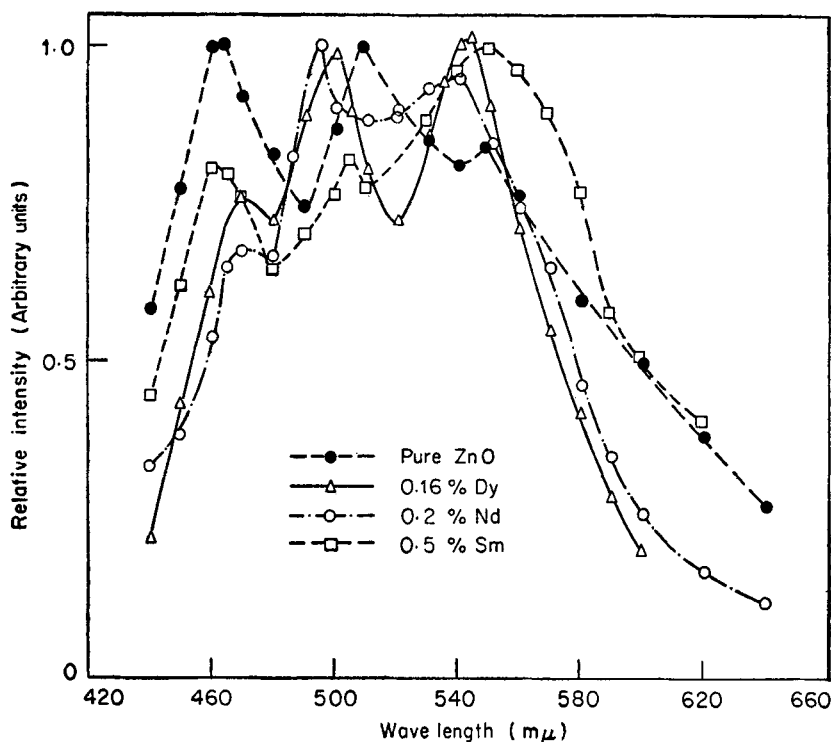


Figure 2. EL spectra of ZnO:Dy, ZnO:Nd and ZnO:Sm electroluminors.

Table 1. Peak positions of photo (PL) and electroluminescence (EL) spectra of ZnO luminors.

Sl. No.	Luminors	PL Spectra (Å)		EL Spectra (Å)	
		At the lowest concentrations of the added ions	At the highest concentrations of the added ions	At the lowest concentrations of the added ions	At the highest concentrations of the added ions
1.	ZnO (in vacuum)	~4800, 5050, ~5250	—	4640, 5080, 5490	—
2.	ZnO : Dy	(at 0.16%) ~5100, 5430, ~5550	(at 2.0%) ~5100, 5270, ~5450	(at 0.16%) 4700, 5000, 5440	(at 2.0%) 4700, 4950, 5380
3.	ZnO : Nd	(at 0.2%) ~4900, 5250, ~5600	(at 1.0%) ~4900, 5300, ~5500	(at 0.2%) 4700, 4950, 5400	(at 1.0%) 4650, 5050, 5400
4.	ZnO : Sm	(at 0.2%) ~4850, 5200, 5550	(at 1.0%) 5200, 5550	(at 1.5%) 4600, 5050, 5550	(at 1.0%) 4640, 5100, 5400

with a common characteristic of suppressed relative intensity of blue band and enhancement of green-yellow band. Shift of the bands compared to the undoped ZnO electroluminor show quite irregular behaviour. For example comparing with that of undoped electroluminor while the blue band of ZnO:Dy (at 0.16%) system shift towards lower energy side the other two bands shift towards higher energy side. With further increase of concentration of Dy ions the blue band remains unaffected but the other two shift towards higher energy side. Table 1 gives the peak positions of the different bands of undoped and RE doped ZnO systems.

We may attempt the donor-acceptor (DA) pair model for the recombination process in our system to explain the experimental results. This model was first proposed by Prener and Williams (1956) and Apple and Williams (1959) to interpret the broad green and red luminescence bands in ZnS and detailed evidence for mechanism was obtained by Thomas *et al* (1964, 1965) to explain the sharp lines in GaP. Shionoya (1970) has implemented the detailed mechanism for the very broad feature-less bands in ZnS. The recombination of an electron trapped at a donor and a hole trapped at an acceptor will result in radiation of frequency ν which will depend on the separation r between donor and acceptor levels as follows

$$h\nu(r) = E_g - (E_a + E_d) + e^2/\epsilon_0 r \quad (1)$$

where E_g is the band gap of the semiconductor, E_a and E_d are the binding energies of acceptor and donor respectively, e the electronic charge and ϵ_0 is the static dielectric constant.

Equation (1) reveals that the energy of the emitted photon increases with decreasing intra-pair separation. This brings about the apparent shift of the emission band peak towards lower energies during decay (time shift) and also with decreasing excitation energy (intensity shift). One of the features of this model i.e. the intensity shift has been observed for this system (Bhushan *et al* 1977) and therefore it confirms the application of this model.

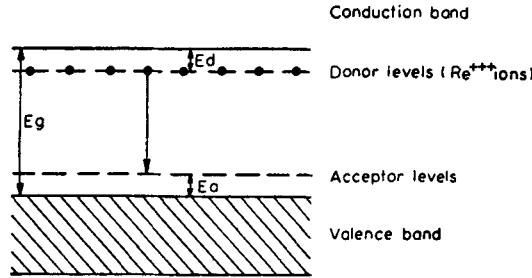


Figure 3. Energy level diagram of donor-acceptor model.

The RE^{++} valence electron $6S^2 5d^1$ form donor level in our system and the acceptor levels are due to different centres responsible for the emission of undoped electroluminors. The energy level diagram is shown in figure 3. The level of donor is shallow while that of the acceptor is fairly deep. Electronic transitions involving such deep lying levels are generally known to be strongly coupled with various phonon modes and hence in spite of the line emission they give the emission of a bell-shaped spectrum. The radiative capture pair cross section $\sigma(r)$ of a pair for an electron and a hole was estimated theoretically (Lax 1959; Thomas *et al* 1964) to depend on intrapair separation ' r ' as follows

$$\sigma(r) = Ar^2 \quad (2)$$

where A is constant. From this expression it is clear that the recombination cross section for a DA pair decreases with decreasing the intra pair separation and hence the emission of high energy bands will quench while the lower energy bands will be favoured. This explains the relatively suppressed intensity of blue band and the enhancement of green-yellow band, particularly in the case of EL spectra where the bands are well resolved and may not be more effective in PL, where the green band predominates.

The shift of the bands towards longer wave-length side in some cases and shorter wavelength in the others may be due to different DA pairs involved in radiative recombination. The DA pairs of the nearest site may be responsible for the shorter wave length shift while pairs at a larger distances for the higher wave length shift. The disappearance of some of the bands at higher concentration may be due to concentration quenching.

Figure 4 represents the dependence of EL brightness on applied field for ZnO:Sm electroluminor to satisfy the relation

$$B = B_0 \exp(-b/V^{1/2}) \quad (3)$$

Similar behaviour is found for other systems also. This shows the existence of Mott-Schottky barrier and hence the mechanism of EL excitation is acceleration-collision type. The difference in the shapes of PL and EL spectra may be because of their different mechanism of excitations.

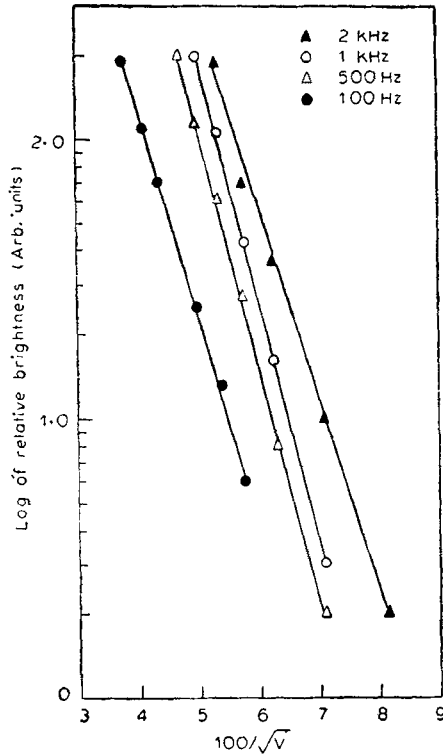


Figure 4. Dependence of electro-luminescent brightness on voltage for ZnO:Sm electroluminescent.

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