Preparation of ZnO phosphors by a new technique

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Abstract. Photo and electroluminescent properties of ZnO phosphors prepared by burning zinc in an atmosphere of pure oxygen have been reported. The peak positions obtained by resolving the experimental curves into Gaussian profiles are explained by assuming that the rare earths form the donor levels while the acceptor levels cause the emission of undoped phosphors. Voltage dependence of electroluminescent brightness shows that the mechanism of excitation consists of acceleration-collision. Brightness waves at different concentrations of rare earths and frequency of excitation are also studied and discussed.

1. Introduction

ZnO phosphors show emission in different regions under different preparative conditions (Lehmann 1968): (i) the near-edge emission at about 3·18-3·20 eV at room temperature when it is n-doped and prepared under reducing atmosphere (Lehmann 1966), (ii) the common green emission band whose origin is still a matter of controversy (Smit and Kröger 1949; Thomson 1950; Lehmann 1968; Joshi and Kumar 1973; Bhushan et al 1979a,b), (iii) a yellow-orange band appearing in the presence of either selenium (Markowski and Orshanskaya 1960; Miller 1954) or excess oxygen (Joshi and Kumar 1973; Bhushan and Asare 1980a) and (iv) a red to infrared band which appears in the presence of NH_3 (Lehmann 1968) and is due to transition between the edge of the conduction band to a hole trapped at 1·60 eV above the edge of the valence band (Lauer 1973). In all earlier investigations ZnO was used as a starting material for preparing such phosphors. We have investigated undoped and rare earth doped ZnO phosphors prepared by a new method. These phosphors are found to be more efficient compared to those prepared by the other method (Bhushan et al 1979a; Bhushan and Asare 1980a). The present paper reports some photo (PL) and electroluminescent (EL) studies of ZnO phosphors prepared by this new method.

2. Experimental procedure

The undoped phosphors were prepared by burning zinc metal (pure up to 10 ppm), procured from Johnson Matthey Chemicals, England, under continuous flow of 99·3% pure oxygen. The burning was done by suddenly rushing the silica boat con-

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taining the zinc metal, into the high temperature zone (1150°C) of a tubular furnace at a temperature of 1150°C and keeping it for 1 hr. Cooling was done in the same atmosphere and a white powder was obtained which showed luminescence under the excitation of UV radiation and electric field. X-ray diffraction studies as well as the PL spectra confirmed that the white material was pure ZnO (Bhushan and Asare 1980a).

Doped phosphors were prepared by thoroughly mixing appropriate amounts of rare earth compounds (99·99% pure cerium oxide and 99·99% pure neodymium nitrate) with ZnO as base material in an agate pestle mortar for 30 min. Grinding for a greater period resulted in a decrease of overall luminescent brightness (Bhushan and Asare 1980b). The mixture was then fired for 3 hr at 1150°C in open air and cooled.

While the PL cell was prepared by depositing the phosphors on a quartz plate with a non-fluorescent volatile organic liquid, the EL cell was prepared by pressing a mixture of the phosphor with araldite between a metal plate and a conducting glass plate of resistance 100 ohm/cm² prepared in the laboratory. The construction of the EL cell is shown in figure 1. Before placing the conducting glass plate a mica sheet was placed on the sample-binder (araldite) mixture to prevent carrier injection. Care was also taken to prevent air bubbles. The general experimental set-up was the same as reported earlier (Bhushan *et al* 1978, 1979a,b). The spectra obtained were after necessary correction for photomultiplier response and monochromator dispersion.

3. Results and discussion

3.1. *Undoped ZnO phosphor*

The PL spectra of undoped ZnO consist of three peaks at 2·47 eV (green), 2·27 eV (yellow), and 2·11 (orange) (Bhushan and Asare 1980a). The peak positions of EL spectra are found to be at 2·47, 2·27 and 2·10 eV which are similar to those of PL spectra thus showing that the centres responsible for PL and EL emission are the
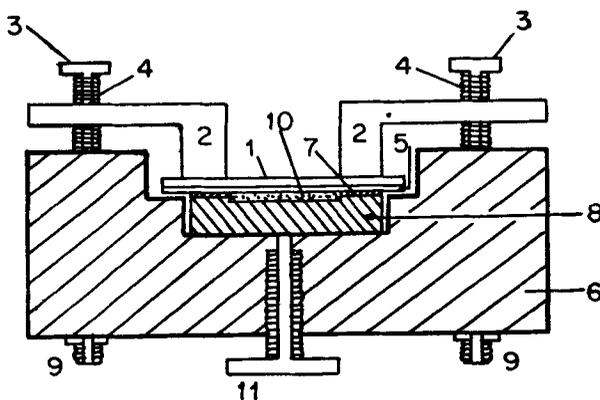

Figure 1. Electroluminescent cell. 1. Conducting glass plate, 2. Metallic ring (projected), 3. Screw, 4. Spring, 5. Aluminium foil, 6. Ebonite base. 7. Mica Sheet (30 μthick) 8. Steel plate with circular groove in the centre, 9. Bolt, 10. Luminor in araldite (100 μthick), 11. Electrode.

same. However the shapes of PL and EL spectra are different perhaps due to the different mechanisms of excitations used for the two processes.

3.2. *ZnO:Ce and ZnO:Nd phosphors*

The PL spectra of ZnO:Ce under the excitations of 3650 Å Hg radiation at different concentrations of Ce are shown in figure 2 and when resolved into its Gaussian profiles consist of four peaks. Compared to the spectrum of undoped phosphor the following points are noted: (i) one additional weak band at 2·63 eV (ii) all the bands are shifted towards lower energy side, the shift increasing with increase in Ce concentration. (iii) intensity of the higher energy band (2·47 eV) is suppressed while that of the lower energy and (2·27 eV) is enhanced. Further, while the three bands on higher energy side are maximum at 0·1 % of Ce the band with lowest energy peak is maximum at 0·05 %. The decrease in intensity may be because of differential concentration quenching for these two types of bands.

The EL spectra at different concentrations of Ce are shown in figure 3 and it is seen that these also consist of four peaks and in this case comparing with the spectrum of undoped phosphor the following points are noted: (i) an additional band occurs at 2·63 eV; (ii) with increase in concentration of Ce the green band gradually shifts towards the higher energy side, the yellow and orange bands shift towards lower
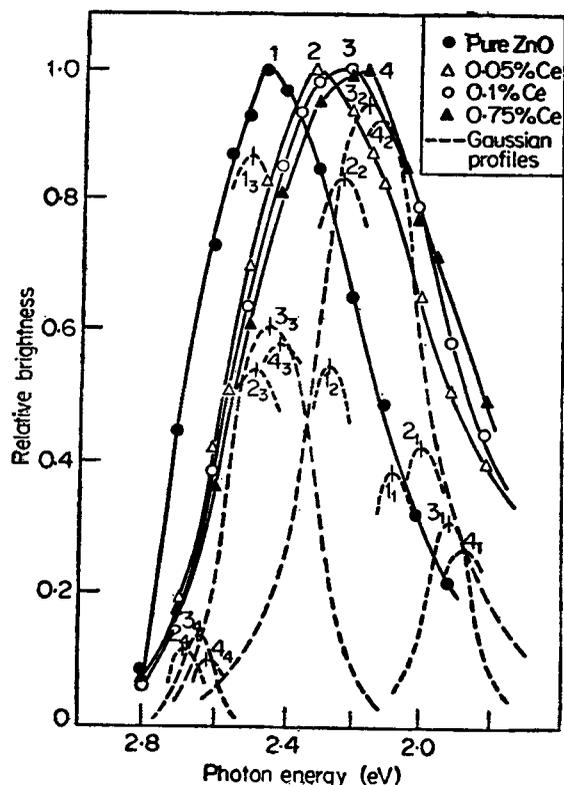

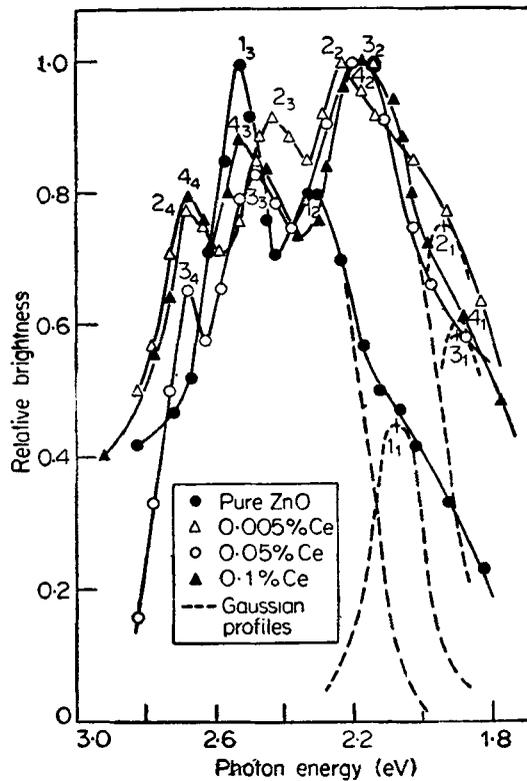**Figure 2.** Photoluminescent spectra of ZnO:Ce at different concentrations of Ce.

Figure 3. Electroluminescent spectra of ZnO:Ce at different concentrations of Ce.

energy side; (iii) while the intensity of yellow band remains the same, those of the other bands do not vary in a regular way with concentration of Ce.

In ZnO:Nd however PL and EL spectra at different concentrations of Nd (figures 4 and 5) consist of only three peaks but shifted on the lower energy side compared to those of undoped phosphor. In EL spectra the shift in green band is appreciable while the yellow band remains nearly fixed. As regards intensities the following points could be noted: (i) In PL spectra the green band (2·23 eV) is enhanced with increase in concentration of Nd. (ii) The intensity of lower energy band (2·04 eV) in EL spectra however increases with concentration.

The effect of increase in frequency of excitations on the EL spectra was also studied and it was found that all peaks shift towards higher energy side with increasing excitation frequency for both the systems.

Bhushan *et al* (1978, 1979) showed the suitability of the donor-acceptor (DA) model for rare earth doped ZnO phosphors. According to this model the actual emission takes place because of transitions between donor and acceptor levels. The donor levels are created due to the rare earth ions and the acceptor levels cause emission of undoped host. The level of donor is shallow while that of the acceptor is fairly deep. Electronic transitions involving such deep lying levels are generally strongly coupled with various phonon modes and hence give rise to emission of a bell-shaped spectrum. The weak additional band appearing at 2·63 eV in ZnO:Ce may be attri-
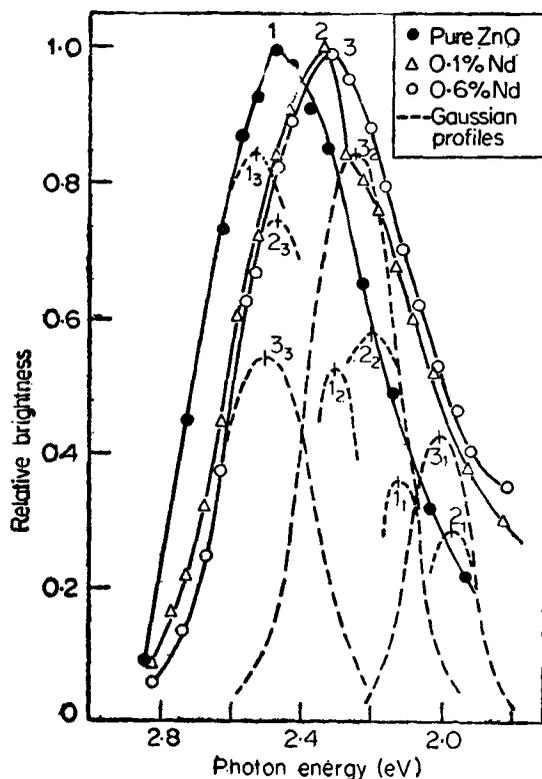
Figure 4. Photoluminescent spectra of ZnO:Nd at different concentrations of Nd.

buted to transitions between some donor level due to Ce and the centres responsible for the usually observed edge emission in ZnO. The intensities of the bands of ZnO:Ce and ZnO:Nd are different and shifted on the lower energy side indicating substitution of rare earths in the lattice. The shift of the bands towards lower or higher energies may be due to the involvement of different DA pairs in radiative recombination. The DA pairs of nearest site may be responsible for the higher energy shift while pairs at larger distances for the lower energy shifts.

3.3. *Voltage and frequency dependence of EL brightness*

The voltage (V) dependence of EL brightness (B) for both ZnO:Ce and ZnO:Nd satisfy the relation $B = B_0 \exp(-b/V^{1/2})$. This behaviour for one representative sample of ZnO:Ce is shown in figure 6. In this relation B_0 and b are constants. This relation indicates that barriers of the Mott-Schottky are formed in which the thickness varies as the square root of the voltage. The mechanism of EL is therefore an acceleration-collision one (Piper and Williams 1955).

Further, results of the frequency dependence of EL brightness at different voltages showed a linear variation at lower frequencies and a tendency to saturation towards higher frequencies. This behaviour implies that emptying and refilling of EL centres take place more rapidly with increase in frequency but when the time period of applied alternating field becomes comparable with the life-time of the excited states, the
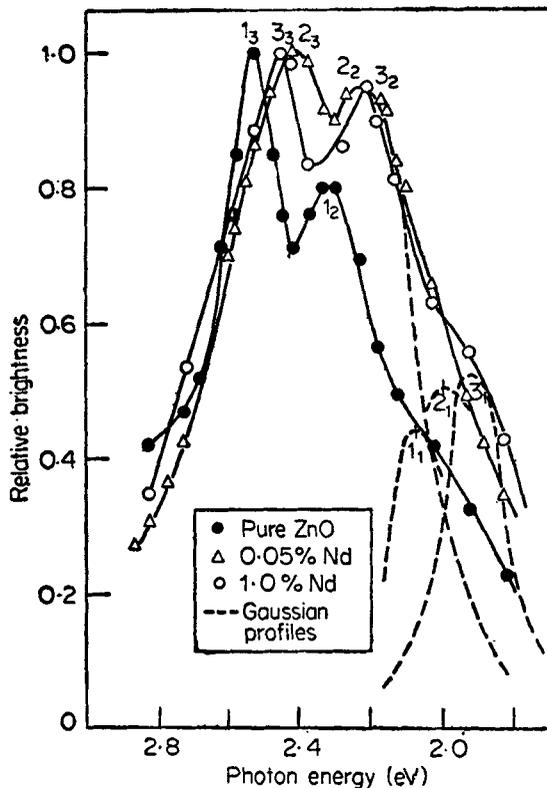
Figure 5. Electroluminescent spectra of ZnO:Nd at different concentrations of Nd.
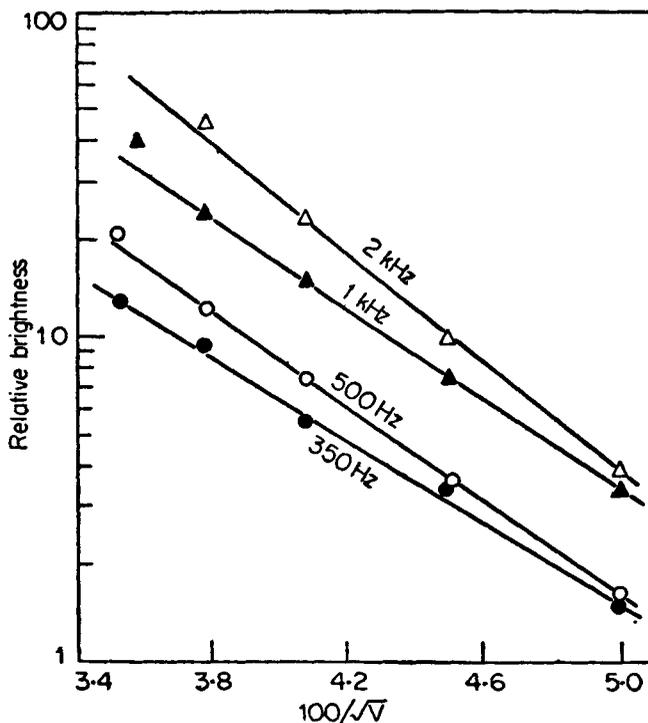

Figure 6. Voltage dependence of electroluminescent brightness of ZnO:Ce at different frequencies of the applied field.

electron does not have sufficient time to emerge out from the trap and the brightness does not vary linearly with the frequency.

3.4. *Brightness waves*

Brightness waves (BW) of EL due to sinusoidal excitations (fixed voltage 1 kV and frequency 350 Hz) for ZnO:Ce and ZnO:Nd are shown in figure 7. For the two systems the BW at fixed voltage and different frequencies are shown in figure 8. During each cycle of excitation the BW shows two primary peaks (P_1 and P_2) and one secondary peak (S). In both the cases with increasing concentration of rare earth the secondary peaks become weaker.

The secondary peaks are associated with the excess oxygen in the lattice. Due to substitution of trivalent rare earths in place of bivalent zinc the excess oxygen is
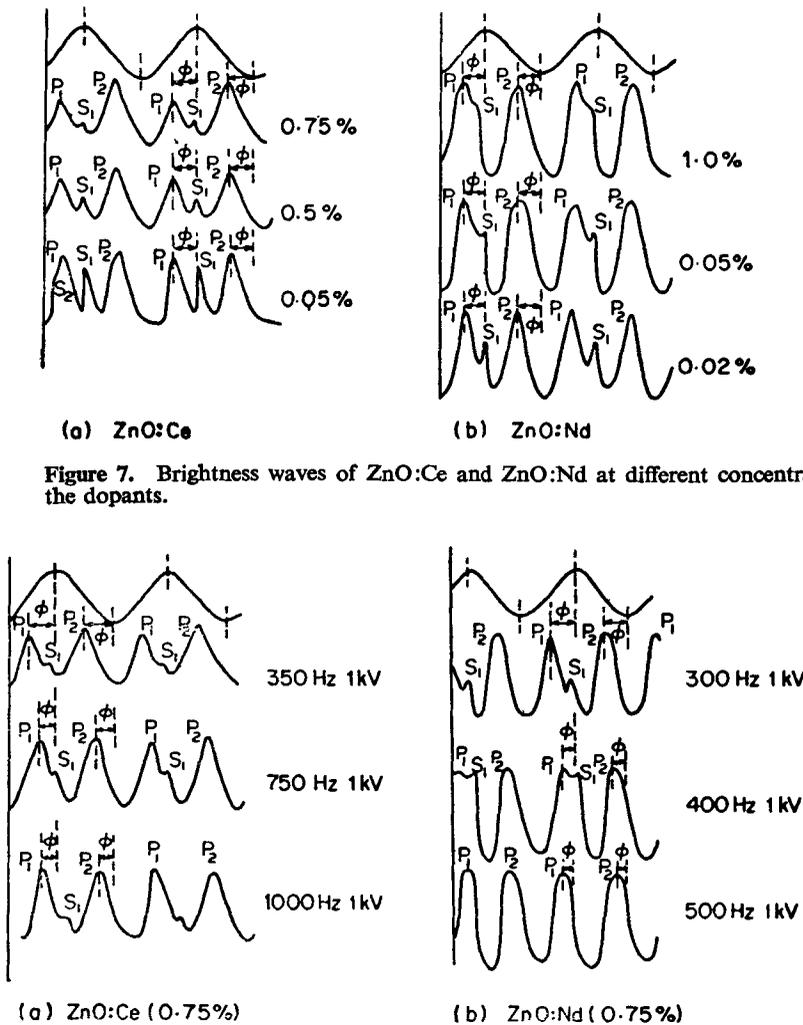
Figure 7. Brightness waves of ZnO:Ce and ZnO:Nd at different concentrations of the dopants.

Figure 8. Brightness waves of ZnO:Ce and ZnO:Nd at different frequencies of the applied field.

compensated more and more and therefore secondary peaks become weaker. Figure 8 shows that the phase difference ϕ decreases with increasing frequency of the applied field which agrees with the relation tan $\phi = 4\pi\sigma/\epsilon\omega$ (Destriau and Ivey 1955) where ϵ is permittivity, σ the conductivity and $\omega = 2\pi f$ (f the frequency).

Acknowledgement

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