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Temperature dependent studies of cathodoluminescence of green band of ZnO crystals

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Most of the work on cathode ray excitations of ZnO phosphors has bexen concentrated on low voltage excitations [1, 2]. Shrader and Kaisel [3] observed luminescence in ZnO due to electrons with energies less than that of emitted quantum. Pennebaker and O'Hanlon [4] studied phosphors excited by low energy cathode rays generated by gas discharge. Cathodoluminescence of ZnO-mixed phosphors under low voltage excitations were investigated by Hiraki *et al.* [5]. In addition to these, spontaneous and stimulated emission under the excitation of high energy electron beam (maximum energy 30 keV and current density $4\,A\,cm^{-2}$) were reported in UV region for the temperature range 82 to 300 K by Iwai and Namba [6]. Recently, cathodoluminescence from deformed ZnO ceramics has been reported by Piqueras and Kubalek [7]. More recently, cathodoluminescence spectra of undoped ZnO, ZnO:Ce and ZnO:Nd phosphors have been reported by Bhushan and Asare [8] showing highest efficiency for ZnO:Nd. The present paper reports cathodoluminescence studies of green band of ZnO crystals under high energy (40 keV) of excitation for the temperature range 4.2 to 300 K. These results enhance the utility of the model proposed by Bhushan *et al.* [9] for the green band of ZnO.

The crystals used in the present investigation have been prepared by the hydrothermal method. The excitation energy and the beam current of the cathode rays were 40 keV and $0.005\,\mu A$, respectively. The details of experimental arrangement are published elsewhere [10, 11].

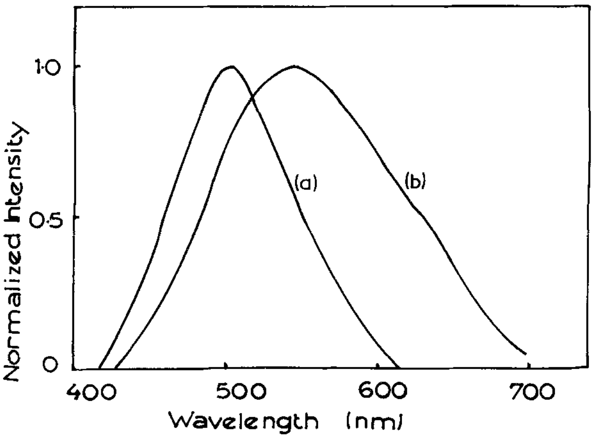

Figure 1 Cathodoluminescence spectra of (a) ZnO crystals (excitation energy 40 keV and beam current $0.005\,\mu A$) and (b) ZnO powder phosphors (excitation energy 10 keV and beam current density $1\,\mu A\,cm^{-2}$).

Fig. 1 shows the cathodoluminescence spectra of undoped ZnO powder phosphors (excitation energy 10 keV, current density $1\,\mu A\,cm^{-2}$) [8] and ZnO crystals (exciting conditions mentioned earlier.) The differences in peak positions may be related to the different preparative and exciting conditions. So far as the origin of this band is concerned, Dingle [12] on the basis of Zeeman and ESR data suggested that a substitutional copper impurity at a regular zinc site could be a possibility for this centre. However, according to Lehmann [13] and Thomson [14] the green band was due to sulphur. Bhushan *et al.* [9] observed this band under photo and electric field excitations for the materials prepared under reduced pressure and thus neglected the possibility of being due to sulphur and attributed this band to stoichiometric zinc. Further, for samples prepared by burning zinc metal in an atmosphere of pure oxygen and thus having the possibility of unoxidized zinc, grinding effect resulted in the reduction of intensity of this band and consequently in the reduction of total intensity [15]. This also favoured the stoichiometric zinc model. Takata *et al.* [16, 17] have condemned Dingle's model and favoured the model of Bhushan *et al.* Matsumoto *et al.* [18] have also supported the stoichiometric zinc model. Since the recombination mechanism in cathodoluminescence is the same [8] as in other kinds of excitations, this model can be retained.

Fig. 2 shows the cathodoluminescence spectra of ZnO crystals at different temperatures. The variation of peak intensity with temperature is shown in Fig. 3. The maximum intensity at 53 K may be due to presence of some impurities. Another interesting observation at this temperature has been the appearance of some new peaks. The broad band luminescence is attributed to the fact that electronic transitions in deep lying levels (acceptor) are strongly coupled to various phonon modes [19]. It is further known that as the coupling effects become stronger the ratio of zero phonon line to the phonon coupled lines becomes smaller with the decrease in temperature and thus at lower temperatures low band width is observed. The new peaks at about 53 K may be due to lattice phonon interaction which happens to be maximum at this temperature because of combination of scattering due to lattice phonons and that due to impurities.

The variation of band half width with square root of temperature is shown in Fig. 4. The dependence of band half width of emission spectrum on temperature

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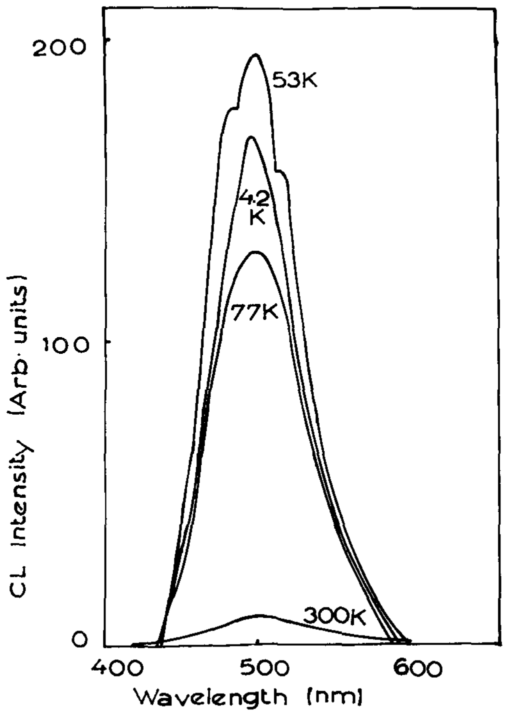

Figure 2 Cathodoluminescence spectra of ZnO crystals at different temperatures.

T is given by [20]

$$W = A\left[\operatorname{Cot} h\left(\frac{h\nu}{2kT}\right)\right]^{1/2} \qquad (1)$$

where ν is the frequency of vibrations associated with the centre, k and h are Boltzmann's and Planck's constant, respectively. At higher temperatures this equation is reduced to

$$W = A\left[\frac{2kT}{h\nu}\right]^{1/2} \qquad (2)$$

If W_0 represents the band half width at lower temperatures (when independent of T) and W_T that at higher temperatures (when proportional to $T^{1/2}$) a simple expression of ν given by

$$\nu = \frac{2kT}{h}\left[\frac{W_0}{W_T}\right]^2 \qquad (3)$$

can be used. Using $T = 144\,\mathrm{K}$, $W_0 = 0.332\,\mathrm{eV}$ and $W_T = 0.38\,\mathrm{eV}$, ν is found to be $4.579 \times 10^{12}\,\mathrm{sec}^{-1}$. W can also be expressed as

$$W = B + A\left[\operatorname{Cot} h\left(\frac{h\nu}{2kT}\right)\right]^{1/2} \qquad (4)$$

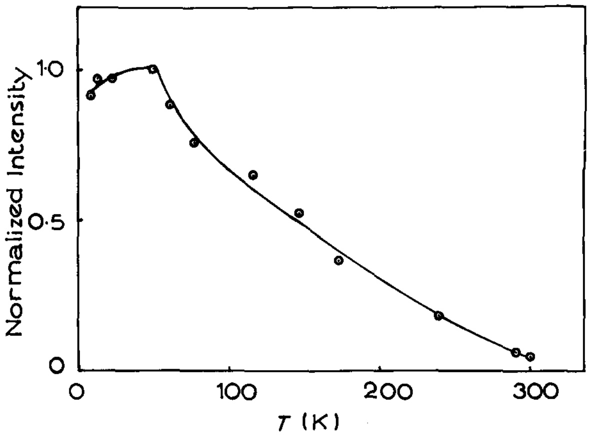

Figure 3 Temperature dependence of peak intensity of cathodoluminescence spectra of ZnO crystals.

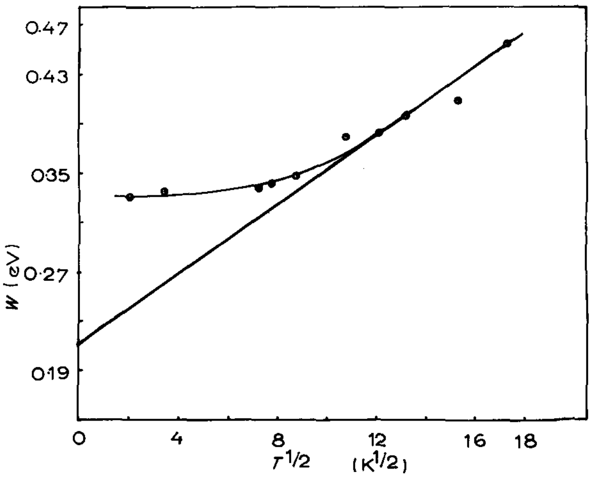

Figure 4 Temperature dependence of band half width of cathodoluminescence spectra of ZnO crystals.

Thus a plot between W and $T^{1/2}$ will yield the values of constants B and A. It is found that an equation described by

$$W\,(\mathrm{eV}) = 0.21 + 0.014\,T^{1/2} \qquad (5)$$

describes satisfactorily the straight line drawn in Fig. 4. Slight deviation may be due to stokes losses not being high and departure from Gaussian nature [21]. From these considerations it is inferred that the configuration coordinate model can be applied in this case. Thus, as expressed earlier the green band of ZnO may be considered due to stoichiometric zinc the levels of which are localized levels located in the energy gap.

An attempt has been made to represent the temperature dependence of cathodoluminescence intensity by

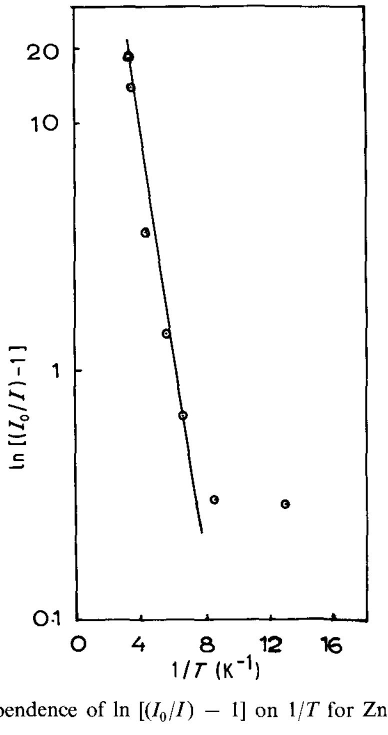

Figure 5 Dependence of ln $[(I_0/I) - 1]$ on $1/T$ for ZnO crystals.

an exponential form

$$I = \frac{I_0}{1 + c\exp(-E/kT)} \tag{6}$$

where c is a constant and E the activation energy of the thermal quenching process. Using $I_0 = I\,(4.2k)$ it is found that a plot between ln $[(I_0/I) - 1]$ against $1/T$ shows a straight line up to liquid nitrogen temperature (Fig. 5) giving $E = 0.59$ eV. This nature is against the observations made by Lauer [22] on the photoluminescence green band. Such large activation energies may be due to direct thermal excitation of trapped holes into the valence band [22]. Below liquid nitrogen temperature a straight line nature was found because of the nature of I against T (Fig. 3) which shows a maximum at around 53 K.

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