will be approximately 6.63 km sec^{-1} for V_p and 3.23 km sec^{-1} for V_s. These data give a Debye temperature of 494 K which is in satisfactory agreement with the above value.

With the exception of perhaps NiO, the elastic Debye temperatures of the NaCl structure oxides form an internally consistent set of data and follow a simple relationship involving the reduced mass.

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The effects of alkali-earth metal ions on the crystalline state of ZnO

The doping effects of alkali-earth metal ions (Mg^{2+}, Ca^{2+}, and Sr^{2+}) on the crystalline state of ZnO were studied using X-ray diffraction methods. The samples were sintered in air at 1200° C for 5 h. X-ray powder diffraction measurements were carried out with Ni-filtered Cu$K\alpha$ radiation.

Fig. 1 shows the results for the lattice parameters and axial ratio. Fig. 1a shows these results for Mg-doped ZnO. The lattice parameter, a, for Mg-doped ZnO increased linearly up to about 5 mol% Mg, which agreed with the solubility limit reported by Segnit and Holland [1]. The lattice parameter, c, on the other hand, decreased until 15 mol% Mg, far exceeding the solubility limit of 5 mol% Mg. Accordingly the axial ratio, c/a, decreased with the increase of MgO. Fig. 1b shows the results for Ca-doped ZnO. Doping with Ca ions resulted in the increase of the both of a and c up to about 1.5 mol% Ca, but the increase of a was much more marked than that of c, and thus the value of c/a decreased sharply in this region. Doping ZnO with Sr ions, Fig. 1c, did not cause any significant changes in a or c. The change of c/a with Mg-content up to 5 mol% is considered to be due to the disolution of Mg ions in the ZnO lattice. It is worthy of notice that the axial ratio, c/a, continues to decrease even after the Mg-content exceeds the solubility limit of 5 mol%. Since c/a for ZnO is said to depend on the surface condition of the crystals [2], this effect is attributed to an interaction between the ZnO lattice and the segregated MgO on the grain boundaries. The solubility of Ca ions in the ZnO lattice is evaluated to be about 1.5 mol% from the lattice parameter data (Fig. 1b). The absence of any apparent change in the lattice parameters as a result of Sr addition indicates that the solubility of Sr ions in

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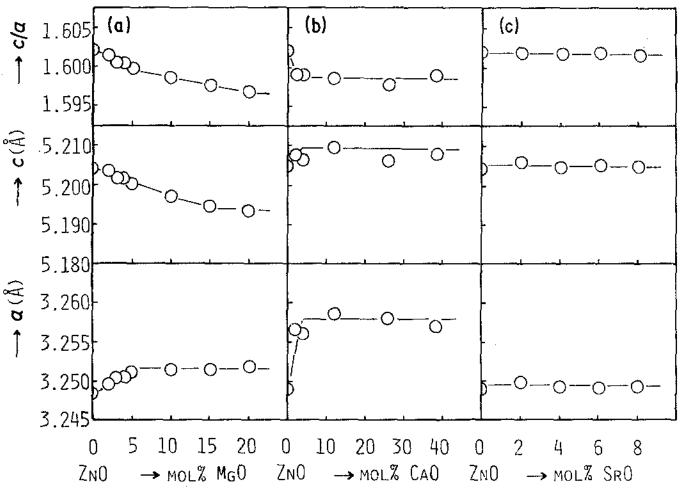

Figure 1 Results of lattice parameter (a and c) measurements and the axial ratio (c/a). (a) Mg-doped ZnO, (b) Ca-doped ZnO and (c) Sr-doped ZnO.

ZnO is extremely low at the temperature of this investigation (1200° C); this low solubility is a result of the large difference in the ionic radii of the Zn and Sr ions ($r_{\mathrm{Zn}^{2+}} = 0.74$ Å; $r_{\mathrm{Sr}^{2+}} = 1.13$ Å). The ratio of the intensities of X-ray diffraction lines (1 0 0) and (1 0 0), I_{110}/I_{100}, suggests that Mg and Ca ions occupy, respectively, tetrahedral and octahedral sites in the ZnO lattice.

Oxygen parameter, u, and effective temperature parameter, B_{eff}, were determined using the procedures described in [3, 4]. The integrated intensity of a diffraction line hkl, $I_{\mathrm{obs}}(hkl)$, is generally given as

$$I_{\mathrm{obs}}(hkl) = kjL_{\mathrm{p}}(\theta)A(\theta)\,|F(hkl)_{\mathrm{t}}|^2\,T(\theta), \tag{1}$$

where k is a scale factor, j is a multiplicity factor, $L_{\mathrm{p}}(\theta)$ is a Lorentz polarization factor, $F(hkl)_{\mathrm{t}}$ is the true structure factor, $T(\theta)$ is a temperature factor, and θ is the diffraction angle of line hkl. For the assumed positions of atoms, the factor is expressed as $I_{\mathrm{calc}}(hkl)$, and $T(\theta)$ is expressed as

$$T(\theta) = \exp\left(-2B\,\frac{\sin^2\theta}{\lambda^2}\right), \tag{2}$$

where λ is the wavelength. Provided that the assumed structure factor is correct, the following expression will result

$$\ln(I_{\mathrm{obs}}/I_{\mathrm{calc}}) = \ln k - 2B\,\frac{\sin^2\theta}{\lambda^2}\ . \tag{3}$$

In order to determine u, $I_{\mathrm{calc}}(hkl)$ was calculated with various assumed values of u, and the linear relation between $\ln(I_{\mathrm{obs}}/I_{\mathrm{calc}})$ and $\sin^2\theta/\lambda^2$ was examined. The most probable value of u was determined by minimizing the deviation from the linear relation (Equation 3). The value of B was obtained from the slope of this plot. For defective or disordered crystals, B indicates, not only the extent of the thermal vibration, but also apparent distributional displacements of the ions, and is called the effective temperature parameter, B_{eff}. Fig. 2 shows the values of u and B_{eff}. The value of u for pure ZnO was 0.380 ± 0.001. The values of u given by other authors are 0.374 [5], 0.3825 [6] and 0.3826 [7]. The first value was obtained from ZnO powder; the other values were obtained from ZnO single crystals. For Mg-doped ZnO, the value

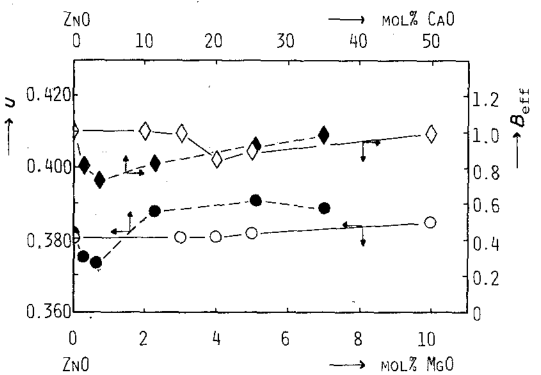

Figure 2 Changes of u and of effective temperature parameter, B_{eff}, of Mg- and Ca-doped ZnO, where ○ refers to u of Mg-doped ZnO; ● refers to u of Ca-doped ZnO; ◇ refers to B_{eff} of Mg-doped ZnO and ◆ refers to B_{eff} of Ca-doped ZnO.

of u increases with increasing amount of Mg. This indicates that the incorporation of Mg ions in the ZnO lattice causes an attraction between the cations and the basal plane. The decrease in u for Ca-doped ZnO up to 3 mol% is considered to result primarily from an expansion of the lattice due to the incorporation of Ca ions; the increase in u with further increase in Ca amount is attributed to some effects of the segregated CaO on the grain boundaries of ZnO. B_{eff} (the value for pure ZnO is taken as 1.0) for Mg-doped ZnO decreased at first, and then increased up to 10 mol% Mg. For Ca-doped ZnO, B_{eff} showed changes similar to those for Mg-doped ZnO. The initial decrease in B_{eff} is considered to result from the strain generated in the lattice by the incorporation of foreign ions producing local stress which leads to a suppression of atomic vibration. The increase in B_{eff} observed with addition of foreign ions may be caused by segregation of MgO or CaO on the grain boundaries, which has an influence on the surface states of the ZnO particles. We also observed that excess MgO, CaO and SrO form amorphous layers on the surface of the ZnO lattice; the details will be reported in a future publication.

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Phase relationships and their effect on cathodoluminscence in the yttrium oxide–tungsten oxide system

Rare-earth tungstates as host lattices for rare-earth luminescent ions have been widely studied. The original work was performed by Borchardt [1, 2] and subsequently work was done by Van Uitert [3] Nassau [4] and Blasse [5]. Not all of this work specifically involved the tungstates of yttrium with trivalent europium as the emitting ion. For example Van Uitert [3] studied trivalent europium only in tungstate lattices which had the scheelite structure and Blasse [5] studied mixed tungstate–molydate lattices. With reference to the present work the experiments of Borchardt [1, 2] are most relevant.

Borchardt gave an outline phase diagram of the yttrium oxide–tungsten oxide system which indicated that four compounds exist. Of these, only one melted congruently, another melted incongruently and the remainder did not melt. Borchardt also gave the minimum temperature of formation and limited crystallographic data. He also studied the emission of two undoped tungstates, when irradiated by light of wavelength 253.7 nm at both room temperature and liquid nitrogen temperature. He found that both emitted light at about 450 nm. One emitted strongly at low temperature only and the other emitted strongly at both low and room temperatures. The work recorded below is a further study of the luminescent properties of the compounds in the yttrium–tungstate phase diagram with special reference to how the luminescence is affected by stoichiometry as given by the diagram.

The starting materials used were commercially available high purity yttrium oxide and tungsten oxide. The former was subjected to cathode-ray tube tests for impurities and the spectra showed no significant amounts of any other rare-earth ions.

The phosphors were all prepared in the following manner. The appropriate quantities of the

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