CHEMISTRY LETTERS, pp. 1735-1738, 1982.

LATTICE PARAMETERS AND ELECTRICAL CONDUCTIVITY IN Li_2O DOPED ZnO

Masaru MIYAYAMA*, Yasuhisa TAKUMA, and Hiroaki YANAGIDA
Department of Industrial Chemistry, Faculty of Engineering,
University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Lattice parameters, electrical conductivity and optical absorption for Li_2O doped ZnO were examined as a function of Li_2O content. As the Li_2O content increased, both c-axis dimension and conductivity decreased initially reaching the minima at the Li_2O content of 0.05 ~ 0.1 mol% and later increased. These results can be interpreted such that the incorporation of Li took place at substitutional sites for low Li_2O content and at both interstitial and substitutional sites for more than 0.05mol% Li_2O.

Zinc oxide is well known to be an n-type semiconductor with excess Zn atoms at interstitial sites acting as electron donors.[1)-3)] Interstitial Zn atoms and electrons are generated according to the following quasi-equilibrium reactions ;

$$ZnO = Zn_i^* + 1/2\ O_2 \quad (1)$$

$$Zn_i^* = Zn_i^{\cdot} + e' \quad (2)$$

$$Zn_i^{\cdot} = Zn_i^{\cdot\cdot} + e' \quad (3)$$

where Kroeger-Vink notation is used ; $Zn_i^{\cdot}$ and $Zn_i^{\cdot\cdot}$ represent interstitial Zn^+ and Zn^{2+}, respectively.[4)] Doping of small amount of lithium decreases electrical conductivity of ZnO.[1)5)6)] The reported observations are interpreted in terms of the model that Li^+ ions are substituted for Zn^{2+} ions consuming conduction electrons. However, it is also reported that interstitially dissolved lithium increases the conductivity of ZnO acting as donors.[5)] The critical amount of Li^+ ions at substitutional or interstitial sites is still not clear.

When ZnO is heated in Zn vapor or at high temperature it is known to acquire an increased conductivity and an optical absorption near the edge of the fundamental absorption band of ZnO and hence to show yellow color. This absorption has been attributed to interstitial Zn atoms or ions[7)8)] and to oxygen ion vacancies[9)10)].

In the present study, measurements of lattice paremeters, electrical conductivity and optical absorption were performed on Li_2O doped ZnO to clarify the mechanism for incorporation of lithium into ZnO.

An aqueous slurry containing ZnO powder (99.99% pure) and reagent grade $LiNO_3$ was dried, ground in an agate morter, calcined at 500°C for 4 h in an alumina crucible and ground again. The resulting powders were pressed into pellets or rods under the pressure of 160 Kg/cm^2 and sintered at 1100°C for 5 h in air for samples containing ~ 0.1 mol% Li_2O and at 900°C for those with higher Li_2O content.

Lattice parameters were determined from X-ray diffraction patterns using 203, 211 and 213 reflection of wurtzite phase. Electrical conductivity was measured in

air by an ac two-probe method at a frequency of 10 KHz with In ohmic electrodes and by a dc four-probe method. No polarization phenomena in the dc measurement could be observed. In order to eliminate an effect of oxygen adsorption, the measurements were performed on cooling from 700°C at the rate of 100°C/h.[11] Optical absorption measurements were performed at room temperature with a spectrophotometer (340-type, Hitachi,Ltd.).

Lattice parameters versus Li_2O content are plotted in Fig.1. As the Li_2O content increased, the c-axis dimension decreased initially, reaching a minimum at the concentration of Li_2O around 0.05 mol%, and later increased, while the a-axis was remained almost unchanged.

Temperature dependences of electrical conductivity for Li_2O doped ZnO are shown in Fig.2. Below 400°C the activation energy for electrical conduction increased with increasing Li_2O content, but above 400°C it was almost unchanged except for 1 and 10 mol% Li_2O doped ZnO. Figure 3 shows dependences of the conductivity on the Li_2O content obtained at several temperatures. Similar to the dependence of the c-axis dimension on the Li_2O content, the conductivity decreased initially, reaching a minimum at 1 mol% Li_2O, and later increased.

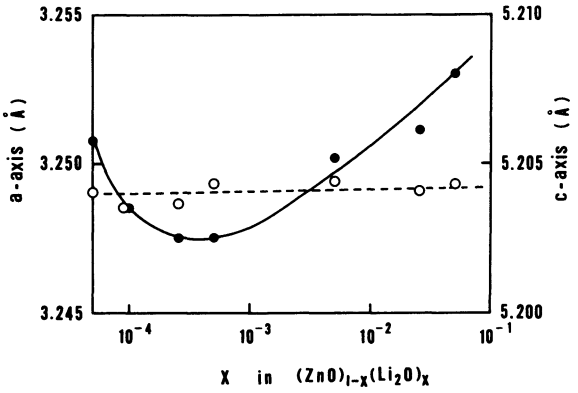

Fig.1 Lattice parameters (○: a-axis, ●: c-axis) vs Li_2O content for Li_2O doped ZnO.

Apparent densities of the sintered specimen were 96 ~ 98% of the theoretical for ~ 0.1 mol% Li_2O, 91 ~ 92% for 1 mol% Li_2O and 78 ~ 79% for 10 mol% Li_2O doped specimens, respectively. Scanning electron micrographs showed an acceleration of grain growth with increasing Li_2O content and an increase of pore size for more than 0.1 mol% Li_2O doped specimens. Therefore, the change in conductivity shown in Fig.3 is supposed to be due to that in carrier concentration or conduction mechanism, not to that in microstructure.

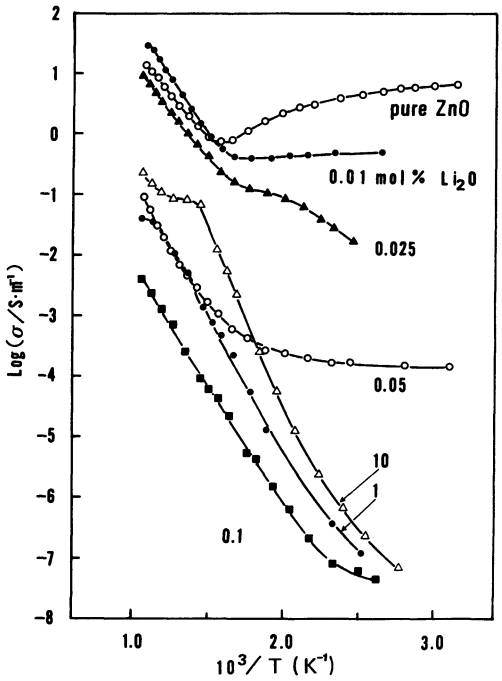

Fig.2 Temperature dependences of electrical conductivity for pure and Li_2O doped ZnO.

Generally, the incorporation of Li_2O into ZnO is explained by the following reactions ;

$$Li_2O + 2e' + 1/2\ O_2 \rightarrow 2Li_{Zn}' + 2O_o^* \quad (4) \text{ or}$$

$$Li_2O + 2e' \rightarrow 2Li_{Zn}' + 2Zn_i^* + 1/2\ O_2 \quad (5)$$

where Li_{Zn}' and O_o^* represent Li^+ and O^{2-}

at normal Zn^{2+} and O^{2-} sites, respectively. The equation (5) is valid for a small amount of Li_2O because the solubility limit of Zn_i* in ZnO is reported to be about 1.8×10^{-2} atm% at 1100°C.[12] The reactions (4) and (5) would bring about a decrease in the conductivity due to a consumption of electrons. Reported ionic radii of 4 co-ordinated Li^+ and Zn^{2+} are 0.64 and 0.71 Å by Ahrens[13] and 0,59 and 0.60 Å by Shannon and Prewitt[14], respectively, assuming the ionic radius of 6 co-ordinated O^{2-} to be 1.40 Å. However, in the wurtzite structure of ZnO, Zn - O bonds have highly covalent nature and essential covalent radius of Zn is reported to be 1.31 Å by Pauling.[15] Therefore, it is assumed that the substituted Li^+ ions lead to a increase in ionic nature of the bonds and hence decrease the interatomic distances in the structure. Accordingly, the reactions (4) and (5) could explain the present results for ~ 0.05 mol% Li_2O doped ZnO. However the next reaction cannot be neglected;

$$Li_2O \rightarrow 2Li_{Zn}' + O_O^* + V_O^{\cdot\cdot} \qquad (6).$$

If generated oxygen vacancies associate with electrons resulting in a decrease in the concentration of conduction electrons, the reaction (6) would also bring about a decrease in the conductivity and the c-axis dimension.

On the other hand, a possible explanation for increased c-axis dimension and conductivity for more than 0.1 mol% Li_2O is the following reaction ;

$$Li_2O \rightarrow 2Li_i^{\cdot} + 2e' + 1/2\ O_2 \qquad (7).$$

Lander has also reported an increased conductivity of ZnO crystal exposed to Li vapor at moderate temperature (300° ~ 600°C) and ascribed it to interstitial Li donors.[5]

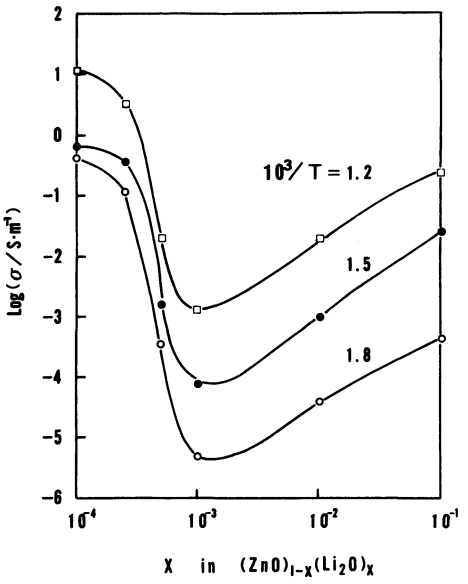

Fig.3 Dependences of electrical conductivity on Li_2O content for Li_2O doped ZnO.

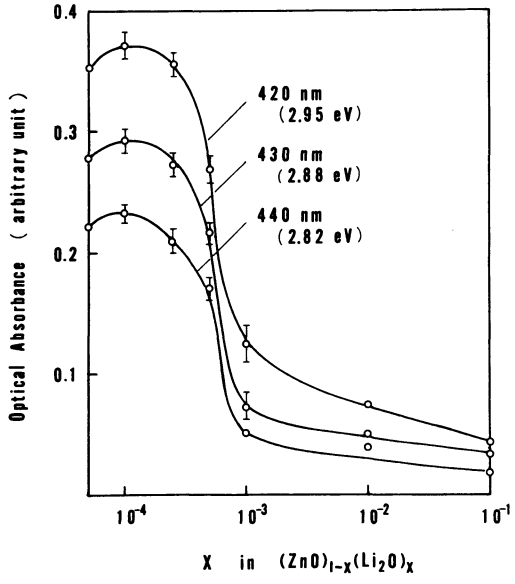

Fig.4 Dependences of optical absorption on Li_2O content for Li_2O doped ZnO.

Figure 4 shows optical absorption near the edge of the fundamental absorption band of ZnO. The absorption decreased for more than 0.05 mol% Li_2O and almost disappeared at 10 mol% Li_2O.

The origin of an increased absorption in the region of 2.6 to 3.1 eV has been proposed by several workers to be interstitial Zn atoms or ions[7)8)] and to be oxygen vacancies[9)10)]. Mohanty and Azaroff[7)] measured electron density distributions for uncolored and colored ZnO single crystals and concluded that there were large amount of Zn atoms at the octahedral interstices of the wurtzite structure of the colored crystal. Vehse et al.[8)] has proposed that, assuming the model of Mohanty and Azaroff, substituted Li^+ ions would act as hole traps which are available to stabilize the interstitial Zn atoms and hence increase the coloration. On the other hand, Kasai[9)] and Smith and Vehse[10)] proposed on the basis of ESR measurements that electron trapped oxygen vacancies are responsible for the coloration. Kasai also suggested that the concentration of electron trapped oxygen vacancies would be decreased with an increase in the concentration of Li acceptors due to strong association.

From the present study it is impossible to decide which model is correct when Li^+ ions are substituted for Zn^{2+} ions in the lattice. However, when Li^+ ions are incorporated at interstitial sites a decrease in coloration would be clearly expected because of the reduced probability of forming interstitial Zn atoms or oxygen vacancies. The abrupt decrease in optical absorption for more than 0.05 mol% Li_2O doped specimens shown in Fig.4 would support the existance of interstitial Li^+ ions.

References

1) K. Hauffe and A. L. Vierk, Z. Phys. Chem., 196, 160 (1950).
2) S. E. Harrison, Phys.Rev., 93, 52 (1954).
3) D. G. Thomas, J. Phys. Chem. Solids, 3, 229 (1957).
4) F. A. Kroeger and H. J. Vink; pp 307-435 in Solid State Physics, Vol.3, Edited by F. Seitz and D. Turnbull, Academic Press, Inc., New York, 1956.
5) J. J. Lander, J. Phys. Chem. Solids, 15, 324 (1960).
6) Y. Takuma, M. Miyayama and H. Yanagida, Chem. Lett., 1982, 345.
7) G. P. Mohanty and L. V. Azaroff, J. Chem. Phys., 35, 1268 (1961).
8) W. E. Vehse, W. A. Sibley, F. J. Keller and Y. Chen, Phys. Rev., 167, 828 (1968).
9) P. H. Kasai, Phys. Rev., 130, 989 (1963).
10) J. M. Smith and W. E. Vehse, Phys. Lett., 31A, 147 (1970).
11) M. Takata, D. Tsubone and H. Yanagida, J. Am. Ceram. Soc., 59, 4 (1976).
12) K. I. Hagemark and P. E. Toren, J. Electrochem. Soc., 122, 992 (1975).
13) L. H. Ahrens, Geochim. Cosmochim. Acta, 2, 155 (1952).
14) R. D. Shannon and C. T. Prewitt, Acta Cryst., B25, 925 (1969).
15) L. Pauling, The Nature of the Chemical Bond, 3rd. Ed., p.244, Cornell Univ. Press, Ithaca, 1960.

(Received August 9, 1982)