JOURNAL OF MATERIALS SCIENCE 19 (1984) 2493–2500

Electrical properties of ceramics in the system Li_2O–ZnO

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The electrical properties of poly-phase ceramics in the system Li_2O–ZnO were studied. The specimens obtained were confirmed to be composed of Li_2ZnO_2, ZnO and some Li_4ZnO_3, by X-ray diffraction. Li_2ZnO_2 was assumed to possess a hexagonal structure with cell parameters $a = 0.812$ nm and $c = 0.673$ nm. Electrical conductivity increased with increasing temperature up to 420° C, and decreased abruptly above 420° C. The temperature dependence of the ionic transference number showed that ionic conduction was dominating above 300° C, while mixed conduction occurred below 300° C. The dependence of electrical resistivity on relative humidity was also measured at room temperature. Electrical resistivity exponentially decreased five orders of magnitude with increasing relative humidity from 5 to 95%. The decrease in electrical resistivity with increasing relative humidity might be caused by LiOH formed on the surface of the specimens.

1. Introduction

It has been reported that the electrical conductivity of semiconductors is largely influenced by gas adsorption on their surfaces [1]. The change in electrical conductivity caused by adsorption has been utilized recently for gas detectors.

Zinc oxide is one of the typical n-type semiconductors, and the microstructure of a sintered body has been remarkably influenced during densification and sintering by adding Li_2O [2]. Thus the microstructure might play an important role in the preparation of ZnO-based semiconducting ceramics. Zinc oxide varistors and ZnO gas sensors are typical examples.

Reistrick *et al.* [3] reported the temperature dependence of electrical conductivity for Li_6ZnO_4 (cubic, $a = 0.925$ nm) ceramics. Li_6ZnO_4 showed high ionic conductivity above 350° C and was proposed as a candidate for the electrolyte for high-temperature batteries [3]. Hoppe and Kastner [4] found two oxides, Li_4ZnO_3 (hexagonal, $a = 1.313$ nm, $c = 0.798$ nm) and Li_2ZnO_2, but not Li_6ZnO_4. Kalar and Trontelj [5] studied the electrical conductivity of hot-pressed ceramics with various Li_2O/ZnO compositions. However, the electrical properties of the Li_2O–ZnO system have not been completely clarified.

The present work was carried out to synthesize the ceramics in the system Li_2O–ZnO, to identify their compositions and to examine their electrical properties, especially aiming at an application of the porous sinters to humidity-sensing materials.

2. Experimental methods

2.1. Preparation of specimens

The Li_2O/ZnO molar ratios of the starting powder mixtures employed were 1/2, 1/1, 2/1 and 3/1. In the present paper, the sintered ceramic whose starting powder composition is 1/2 in Li_2O/ZnO molar ratio is expressed as LZ2, 1/1 as LZ, 2/1 as L2Z and 3/1 as L3Z.

Lithium carbonate and zinc oxide used as the

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starting materials were 99.99% pure. They were mixed in acetone and dried under an infrared lamp. The mixing and drying procedures were conducted several times. The materials were pressed into pellets and calcined at 850° C for 7 h in vacuum in a platinum boat, and then crushed to powders and dried.

2.2. Analsysis of specimens

The phases present were identified by standard X-ray diffraction techniques using Cu*Kα* radiation with a nickel filter. Differential thermal analysis was carried out on powder samples in a platinum container in air or argon gas, or in vacuum. The lithium content was determined by flame spectrographic analysis and the zinc content by chelatometric titration.

2.3. Measurement of electrical conductivity

The calcined powders were then pressed into cylindrical pellets, and sintered on a platinum plate at 750° C for 3 h in vacuum. Electrical conductivity measurements (temperature-dependence, ionic transference number and humidity sensitivity), X-ray diffraction analysis, apparent porosity measurement and scanning electron microscopic observation were carried out using these pellets with polished surfaces.

The dependence of electrical conductivity on temperature and on relative humidity were measured in air by the a.c. two-probe method using a Hewlett Packard LF Inpedance Analyser (model 4192A). The electrode was prepared by vapour deposition of silver. The ionic transference number was measured by the d.c. polarization method, and the electrode was prepared by sputtering gold. A humid atmosphere was produced by mixing wet air (100% r.h.) and dry air (0% r.h.) at 25° C, and the relative humidity was calculated from their proportion.

3. Results and discussion

3.1. Characterization

3.1.1. Compositions of the specimens

The compositions of the starting powder mixtures and sintered specimens determined by chemical analysis are shown in Table I. The molar ratios of Li_2O to ZnO were found to be 0.51 for LZ2 and 1.0 for LZ. The ratios for L2Z and L3Z were nearly 1.0. The X-ray diffraction patterns for L2Z, L3Z and LZ were observed to be quite similar to each other both in diffraction angles and peak intensities, although the starting compositions were different. These results indicate that the compositions of L2Z and L3Z are similar to that of LZ. The X-ray diffractions patterns of LZ2 and LZ are shown in Fig. 1. Several phases, i.e. Li_4ZnO_3, an unknown phase and ZnO, were observed for both specimens. The powder diffraction pattern of Li_4ZnO_3 was similar to that previously reported [4] for both specimens. The only difference in diffraction patterns between LZ2 and LZ lay in the quantities of ZnO and an unknown phase.

A theoretical diffraction pattern for an unknown phase is shown at the bottom of Fig. 1. This pattern was drawn by subtracting the patterns for ZnO and Li_4ZnO_3 from the pattern for LZ. This unknown phase was not identified with any compound compiled in ASTM powder diffraction cards. Judging from the composition of a sintered specimen, the unknown phase may be Li_2ZnO_2 as reported by Hoppe and Kastner [4].

3.1.2. Crystal structure of the main material

Hoppe and Kastner [4] estimated the crystal structure of Li_2ZnO_2 to be orthorhombic, while the present diffraction pattern could not be explained by any space group belonging to an orthorhombic system. Thus, taking into account all the hexagonal space groups, the possible diffraction angles were

TABLE I The composition of the specimens

Specimen	Composition (mol %)				Molar ratio of sintered specimen (Li_2O/ZnO)
	Raw material		Sintered specimen		
	Li_2O	ZnO	Li_2O	ZnO	
LZ2 (Li_2O/ZnO = 1/2)	33	67	33.8	66.2	0.51 (= 1/2)
LZ (Li_2O/ZnO = 1)	50	50	50.7	49.3	1.0 (= 1)
L2Z (Li_2O/ZnO = 2)	67	33	50.0	50.0	1.0 (= 1)
L3Z (Li_2O/ZnO = 3)	75	25	49.1	50.9	0.98 (= 1)

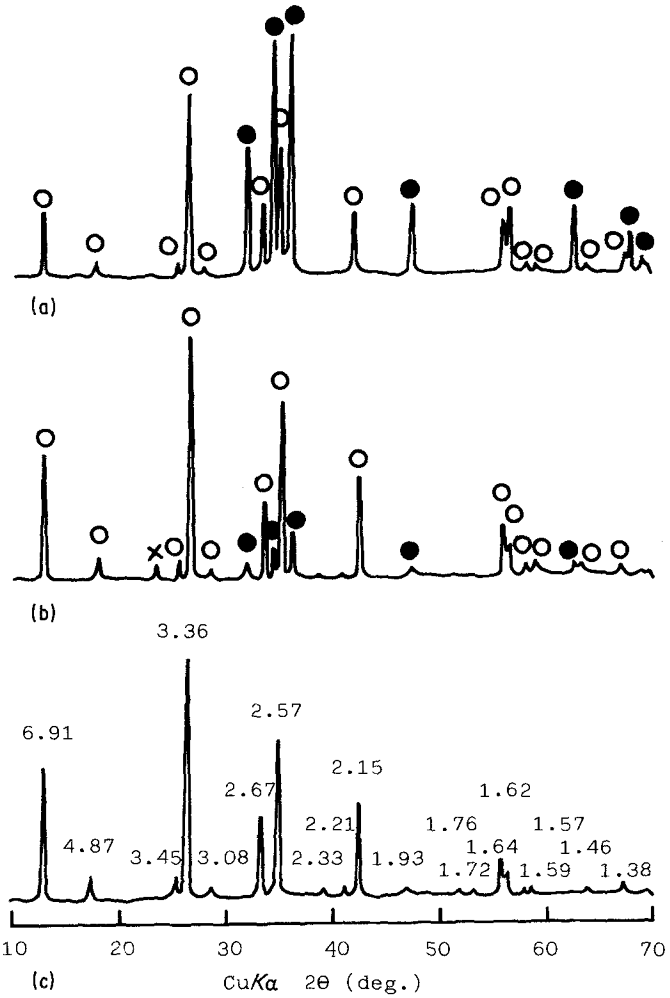

Figure 1 The X-ray diffraction patterns for LZ2, LZ and an unknown phase. (a) LZ2 ($1/2Li_2O \cdot ZnO$); (b)|LZ ($Li_2O \cdot ZnO$); (c) unknown phase (Li_2ZnO_2). ○, unknown; ●, ZnO; ×, Li_4ZnO_3.

calculated by an electronic computer using the program given by Yamaguchi and Miyabe [6]. The observed angles were best fitted to the calculated ones (see Table II) if the 168 space group was assumed, although the atomic coordinates could not be determined. The possible lattice parameters of a hexagonal unit cell were $a = 0.812$ nm and $c = 0.673$ nm.

3.1.3. Thermal analysis of the specimens

Thermal analyses were carried out in air for LZ2 and LZ. The results are shown in Fig. 2. These curves are similar to each other, and endothermic peaks at 150, 420, 590 and 680° C were found. The peak at 150° C was due to the physical desorption of H_2O molecules from the surface of the specimen. To examine the other peak, the X-ray diffraction analysis was carried out for LZ heated at 500, 650 and 750° C in air. But differences in diffraction patterns among these specimens were not observed.

TABLE II X-ray powder diffraction data for the compound Li_2ZnO_2 using CuKα radiation (hexagonal: $a = 0.812$ nm, $c = 0.673$ nm)

$d_{(obs)}$ (nm)	$d_{(calc)}$ (nm)	$I_{(obs)}$	hkl
0.691	0.7029	55	0 1 0
0.487	0.4862	8	0 1 1
0.345	0.3475	6	1 1 1
0.336	0.3366	100	0 0 2
0.308	0.3115	2	0 2 1
0.267	0.2657	45	1 2 0
0.257	0.2591	60	1 1 2
0.233	0.2343	3	0 3 0
0.221	0.2213	4	0 3 1
0.215	0.2138	34	0 1 3
0.193	0.1923	3	0 3 2
0.176	0.1757	1	0 4 0
0.172	0.1714	2	1 2 3, 2 1 3
0.164	0.1637	20	0 1 4
0.162	0.1621	15	0 3 3
0.159	0.1612	2	2 3 0, 3 2 0
0.157	0.1568	5	2 3 1, 3 2 1
0.146	0.1472	9	1 3 3, 3 1 3
0.138	0.1383	12	0 4 3

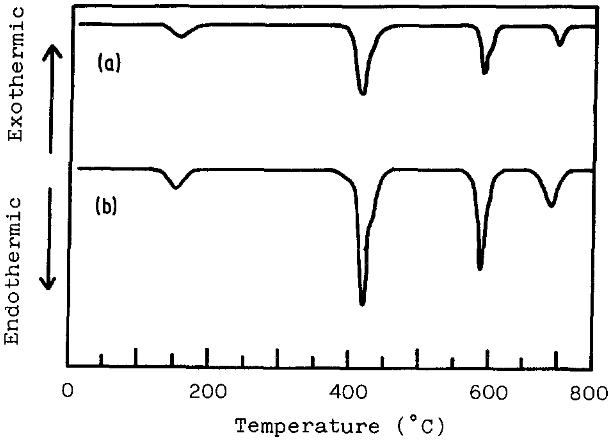

Figure 2 The differential thermal analysis heating curves for LZ2 and LZ. (a) LZ2 ($1/2Li_2O \cdot ZnO$), (b) LZ ($Li_2O \cdot ZnO$).

The thermal analysis for LZ was then carried out in vacuum and flowing argon atmosphere. The results are shown in Fig. 3. The curves were found to be similar to that obtained in air. The weight loss corresponding to the endothermic peak at 590° C was not found in thermogravimetric curves. It was also found that the pellet heated at 750° C in vacuum did not melt, although evidence of partial melting was observed on the scanning electron micrographs as shown in Fig. 4. These results indicate that the endothermic peak at 590° C must have been caused by melting of the minor compound, Li_4ZnO_3.

On the other hand, it has been reported that LiOH is formed on the surface by water adsorption, when a lithium compound is exposed to air for a long time [7]. Lithium hydrate has two endothermic peaks at 415 and 450° C, the former is due to a solid state phase transition and the latter to melting [8], and dehydration into Li_2O and H_2O at 675 ± 10° C [9]. As shown in Fig. 3, weight loss was observed above 680° C. Consequently, the endothermic peaks at 420 and 680° C are related to the formation of LiOH on the surface. The endothermic peak at 420° C is considered to have been caused by phase transformation and/or melting of LiOH, and the peak at 680° C corresponded to dehydration of LiOH.

3.2. Electrical measurements

3.2.1. Dependence of electrical conductivity on temperature

Electrical measurements were carried out on the pellets sintered at 750° C in vacuum. Before electrical measurements, the apparent porosities were measured in toluene using Archimedes' method

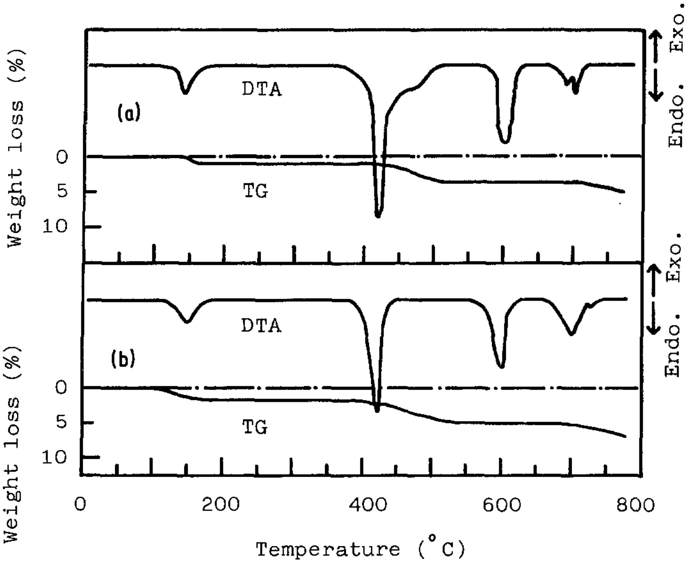

Figure 3 DTA and TGA heating curves for LZ ($Li_2O \cdot ZnO$). (a) In vacuum, (b) flowing argon gas.

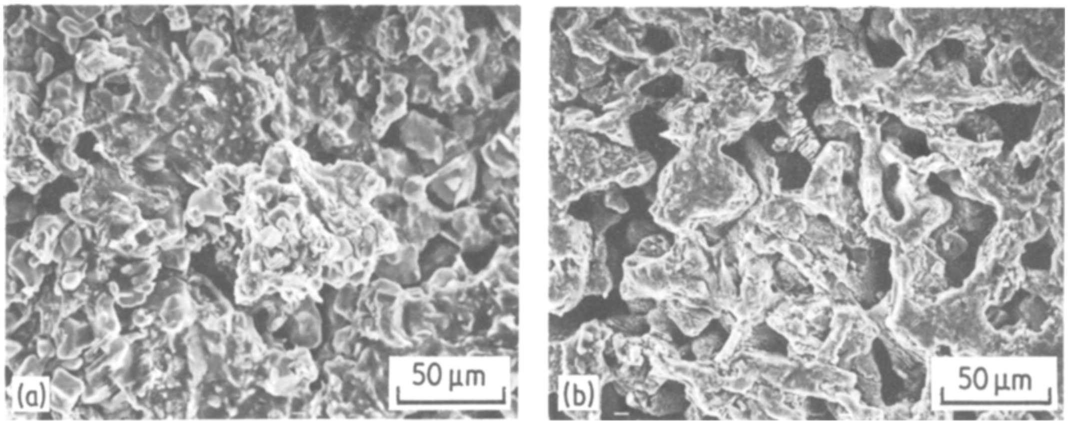

Figure 4 The scanning electron micrographs of the fracture surface for LZ2 and LZ. (a) LZ2 ($1/2Li_2O \cdot ZnO$), (b) LZ ($Li_2O \cdot ZnO$).

and the scanning electron micrographs of the fracture surfaces were observed.

The apparent porosities shown in Table III are about 27% for LZ2 and 34% for LZ, so the pellets for electrical measurements were very porous, as shown in Fig. 4, the fracture surfaces of LZ2 and LZ are similar to each other, and they seem to be very porous and show some evidence of melting as mentioned above.

The electrical conductivity was measured in air for LZ2 and LZ in the temperature range 100 to 650° C. The results are given in Fig. 5. The electrical conductivity of both LZ2 and LZ is found to increase with increasing temperature from 100 to 400° C. Kolar and Trontelj [5] reported the apparent activation energy for conduction to be 1.02 eV for the hot-pressed specimen with the composition $Li_2O/ZnO = 1.0$. However, the present relationship between σ and $1/T$ was not linear, possibly due to the facts that the present sintered specimens subjected to conductivity measurements were composed of several different phases, and that both electronic and ionic conduction contributed to total conductivity, as will be shown later. Above 400° C, the conductivity for LZ containues to increase even more dramatically, and levels off with a peak value of 4×10^{-2} $ohm^{-1} cm^{-1}$ at about 420° C. This increase cannot be well explained, but might be caused by the influence of the partial presence of liquid LiOH as reported by Biefeld and Johnson [10]. The conductivity decreases slowly with increasing temperature above 420° C. The decrease might be affected by solid state phase transition and/or melting of LiOH, as observed by differential thermal analysis (Fig. 2).

TABLE III Pellet density for LZ2 and LZ

Specimen	Bulk density ($g cm^{-3}$)	Apparent porosity (%)
LZ2 ($Li_2O/ZnO = 1/2$)	4.04	27.2
LZ ($Li_2O/ZnO = 1$)	3.30	33.6

The dependence of ionic transference number (T_i) on temperature was measured in air by the d.c. polarization method. The results for LZ are given in Fig. 6. The ionic transference number is over 0.9 above about 300° C, and decreases with decreasing temperature below 300° C. This result indicates that the ionic conduction is dominating above 300° C, while the mixed conduction might occur below 300° C.

3.2.2. *Dependence of electrical resistivity on relative humidity*

The surface and volume resistivity of two specimens were measured in various relative humidities at room temperature (25° C). The results are shown in Fig. 7. The surface resistivities for both specimens decrease by about two orders of magnitude in an exponential manner with increasing relative humidity from 60 to 90%. On the other hand, the volume resistivity decreases about 5 orders of magnitude in an exponential manner with increasing relative humidity from 5 to 95% for LZ and from 20 to 95% for LZ2. The relationship between resistivity (ρ) and relative humidity (h) is shown by the following equation:

$$\rho = \rho_0 \exp(k'h) \tag{1}$$

where k' is the slope of the plot of $\ln \rho$ against h.

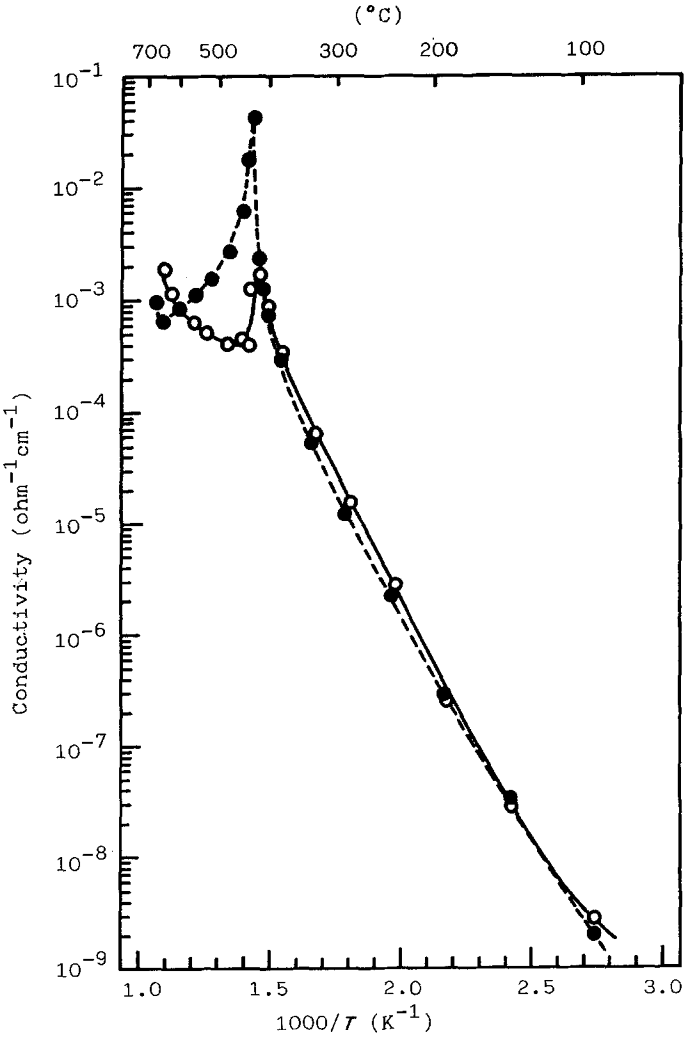

Figure 5 The dependence of electrical conductivity on temperature for LZ2 and LZ at 1 kHz. -o-, LZ2 (1/2Li_2O·ZnO); --●--, LZ (Li_2OJ ZnO).

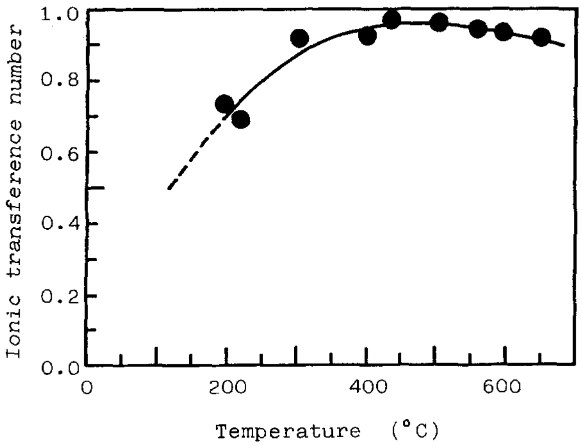

Figure 6 The dependence of ionic transference number (T_i) on temperature for LZ (Li_2O·ZnO).

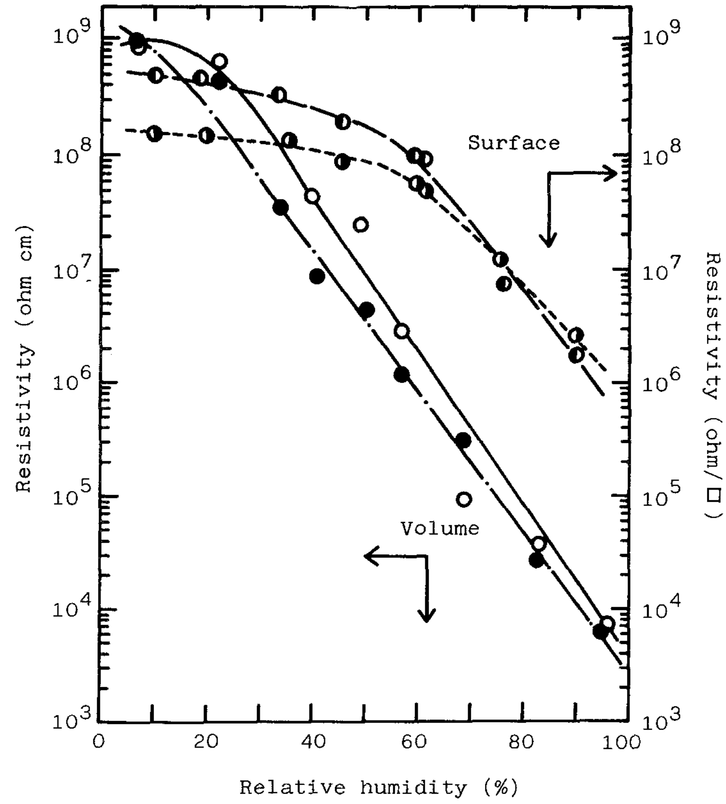

Figure 7 The dependence of electrical resistivity on relative humidity for LZ2 and LZ at 25° C. Surface resistivity: —◐—, LZ2 ($1/2Li_2O \cdot ZnO$); --◑--, LZ ($Li_2O \cdot ZnO$). Volume resistivity: —○—, LZ2 ($1/2Li_2O \cdot ZnO$); -·●·-, LZ ($Li_2O \cdot ZnO$).

In the relative humidity range of 60 to 90% the surface resistivity and volume resistivity are quite different; however, the proportion of change in resistivity is nearly equal as shown in Fig. 7. This indicates that a similar kind of conduction might occur on the surface and in the bulk (mainly in the grain-boundary regions).

In another experiment, a pelletted specimen of LZ was exposed to a high relative humidity at room temperature for 7 days. The X-ray diffraction patterns due to Li_2ZnO_2, Li_4ZnO_3, ZnO and a little $LiOH \cdot H_2O$ were detected for the specimen. These results suggest that the following reactions (Equation 2 and/or 3) have taken place partially by adsorption of H_2O molecules at room temperature on the surface and in the grain-boundary regions:

$$Li_2ZnO_2 + H_2O \rightleftharpoons LiOH + ZnO \qquad (2)$$

$$Li_2ZnO_2 + 3H_2O \rightleftharpoons 2LiOH \cdot H_2O + ZnO \qquad (3)$$

The sensitivity to humidity in electrical resistivity is caused by LiOH formed by partial adsorption of H_2O molecules and reaction between Li_2ZnO_2 and H_2O. The difference in resistivities between surface and bulk might be due to the difference in area participating in electrical conduction.

4. Conclusions

The electrical properties of the ceramics in the system Li_2O–ZnO were studied, and the following conclusions were obtained.

The ceramics with molar ratios Li_2O/ZnO equal to 1/2 and 1/1 were prepared by heating at 850° C in vacuum. The main composition of the specimen with molar ratio $Li_2O/ZnO = 1/1$ was Li_2ZnO_2 which possesses a hexagonal structure with cell parameters $a = 0.812$ nm and $c = 0.673$ nm.

The electrical conductivity was found to increase with increasing temperature below 400° C, and to increase more abruptly from 400 to 420° C. This abrupt increase might be caused by the influence of the partial presence of the liquid LiOH. Ionic conduction is dominating above 300° C, while mixed conduction may occur below 300° C.

The electrical resistivity is found to decrease exponentially with increasing relative humidity from 60 to 90% for surface resistivity and from 5 to 95% for volume resistivity. The similar kind of conduction might occur on the surface and in the bulk, and the change in resistivity might be caused by LiOH formed by partial adsorption of H_2O and reaction between Li_2ZnO_2 and H_2O. These ceramics may be suitable for use as ceramic humidity sensors.

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Received 1 March
and accept 24 October 1983