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Electrical properties of $(Ni_{1-x}Li_x)O$ ($x = 0.1$ and 0.2) under various relative humidities

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Rocksalt-type $(Ni_{1-x}Li_x)O$ ($x = 0.1$ and 0.2) was synthesized at 1350° C in air and its electrical resistivity (R) was measured under various relative humidities (H). R increases with increasing H in the range $0 \leqslant H \leqslant 79\%$, reaches a maximum value, then decreases in the range $79\% < H \leqslant 100\%$. The increase in R is explained by an electron boundary layer model. On the other hand, the decrease in R is explained by ionic conductivity.

1. Introduction

In recent years, interest has increased in the effect of water adsorption on the electrical properties of solids, and many humidity sensors have been investigated [1]. The electrical resistivity of $(La_{1-x}Sr_x)FeO_3$ ($0 \leqslant x \leqslant 0.5$) was measured under various relative humidities [2]. In $LaFeO_3$, the electrical resistivity decreases with increasing relative humidity. This decrease is due to its ionic conductivity. On the other hand, the electrical resistivity of $(La_{1-x}Sr_x)FeO_3$ ($0.1 \leqslant x \leqslant 0.5$) increases with increasing relative humidity. Since Fe^{3+} and Fe^{4+} ions coexist in the range $0.1 \leqslant x \leqslant 0.5$, the mixed valency is considered to be an important factor in increasing the electrical resistivity. In rocksalt structure $(Ni_{1-x}Li_x)O$, the nickel ions are divalent and trivalent; Ni^{2+} and Ni^{3+} ions occupy octahedral sites [3].

NiO has a rocksalt structure and the lattice is slightly distorted to give a rhombohedral cell with $\alpha = 60°6'$ [4]. The cell constant of $(Ni_{1-x}Li_x)O$ decreases slightly with increasing lithium ion content. NiO is an insulator with $\rho = 5 \times 10^{14}\,\Omega$cm at room temperature. On doping the lithium ion in NiO, $(Ni_{1-x}Li_x)O$ becomes a semiconductor with specific resistance down to $10^{-1}\,\Omega$cm at room temperature [3].

In the present study, we discuss the behaviour of the mixed valency of nickel in the system $(Ni_{1-x}Li_x)O$ from the results of the electrical resistivity measurement under various relative humidities at room temperature. These results will provide some information to help discussion of the effect of water adsorption on the surface of the oxide.

2. Experimental procedure

$(Ni_{1-x}Li_x)O$ ($x = 0.1$ and 0.2) samples were prepared using the standard ceramic technique. Powders of $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ and Li_2CO_3 were weighed in the desired proportions and milled for several hours with acetone. After drying the mixed products at 110° C, they were prefired in air at 800° C for 24 h. The products obtained were reground, and then fired again in air at 1350° C for 12 h. To measure the electrical resistivity, the powder samples were compressed into pellet form (16 mm diameter × 4 mm) under a pressure of about 50 MPa, and then the compressed pellets were sintered in air at 1350° C for 12 h. The phase of the pellets was identified using X-ray powder diffraction with Cu*Kα* radiation.

The density of the pellet-shaped samples was measured by Archimedes' method using distilled water. The samples were then placed in a closed chamber, and the humidity of the chamber was controlled using P_2O_5 and a saturation solution, such as $LiCl \cdot H_2O$, $CaCl_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, NH_4Cl and $NH_4H_2PO_4$. The electrical resistivity of the samples was measured under various relative humidities using the two-electrode method with a.c. (100 Hz) at 288 to 300 K.

3. Results and discussion

X-ray powder diffraction patterns of all samples were completely indexed as the rocksalt structure,

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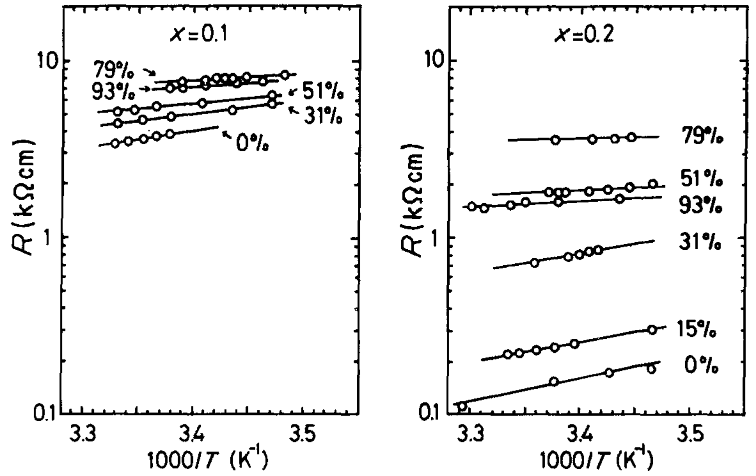

Figure 1 The temperature dependence of the electrical resistivity of $(Ni_{1-x}Li_x)O$ under various relative humidities.

and their cell constant decreased with increasing lithium ion content as a consequence of the difference in ionic radius between Ni^{2+} and Ni^{3+} ions [5]. The density and the relative density of each sample are listed in Table I; they were highly dense.

The temperature dependence of the electrical resistivitiy (R) under various humidities (H) was measured in the temperature range 288 to 300 K, and is shown in Fig. 1. $(Ni_{1-x}Li_x)O$ was a p-type semiconductor with the conductivity given as $\sigma = \sigma_0(-\Delta E/KT)$. Fig. 2 shows the relationship betwen the electrical resistivity of $(Ni_{1-x}Li_x)O$ and various relative humidities at 298 K. The electrical resistivity increased with increasing relative humidity in the range $0 \leqslant H \leqslant 79\%$, reached a maximum value at $H = 79\%$, then decreased in the range $79\% < H \leqslant 100\%$. The thermal band gap (ΔE) calculated from Fig. 1 is shown in Fig. 3. ΔE under $H = 0$ is ~ 0.2 eV; this value agreed with that reported by Van Houten [3]. ΔE of $x = 0.1$ and 0.2 decreased with increasing H. This result suggests that the acceptor level of $(Ni_{1-x}Li_x)O$ is lowered by adsorbed water.

The electrical resistivity is generally expressed as follows:

$$R = R_s + R_{con} \qquad (1)$$

where R is the observed electrical resistivity, R_s is the true electrical resistivity of the sample and R_{con} is the electrical contact resistivity between the sample and the electrode. By assuming that R_{con} is not influenced by the relative humidity, R under $H = 0$ and $H = a$ is expressed as follows:

TABLE I The value of the density and the relative density in the system $(Ni_{1-x}Li_x)O$

x	Density	Relative density (%)
0.1	6.15	96.6
0.2	5.90	99.1

$$R_0 = R_s^0 + R_{con} \qquad (2)$$

$$R_a = R_s^a + R_{con} \qquad (3)$$

where R_s^0 and R_s^a is the true electrical resistivity under $H = 0$ and $H = a$, respectively. $\Delta R/R_0$ and ΔR between R_0 and R_a are expressed as follows [6]:

$$\begin{aligned} \Delta R/R_0 &= (R_a - R_0)/R_0 \\ &= (R_s^a - R_s^0)/(R_s^0 + R_{con}) \qquad (4) \end{aligned}$$

$$\Delta R = R_a - R_0 = R_s^a - R_s^0 \qquad (5)$$

In the present measurements, using the two-electrode method, the observed value is very much larger than that reported [3]. This result suggests that R_{con} is very large in comparison with R_s^0, and Equation 5 is reasonable to evaluate the electrical resistivity of $(Ni_{1-x}Li_x)O$ under various relative humidities. Fig. 4 shows the relationship between

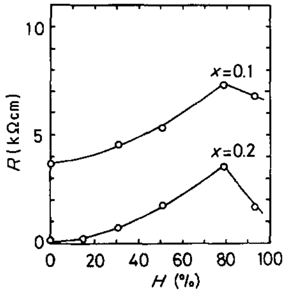

Figure 2 The relationship between the relative humidity and the electrical resistivity of $(Ni_{1-x}Li_x)O$ at 298 K.

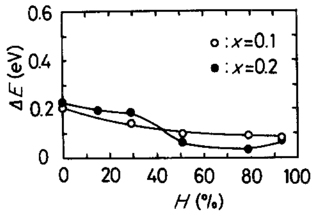

Figure 3 The relationship between the band gap and relative humidity in the system $(Ni_{1-x}Li_x)O$.

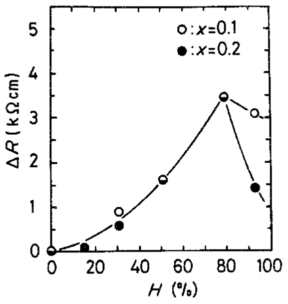

Figure 4 The relationship between ΔR and relative humidity in the system $(Ni_{1-x}Li_x)O$ at 298 K.

ΔR of $(Ni_{1-x}Li_x)O$ and the relative humidity. ΔR abruptly increased with increasing H and reached a maximum value of ~3.5 kΩcm at $H = 79\%$. In spite of the increase in the lithium ion content, ΔR has a constant value similar to ΔE in Fig. 3. These results suggest that ΔE has an important role in the increase in the electrical resistivity.

According to the electron boundary layer model [7], in a p-type semiconductor, the adsorbed molecules have an ionization potential I and the transfer of electrons from chemisorbed molecules to the solid creates space charges. The donation continues until the resulting charge transfer has raised the Fermi level of the solid to coincide with that in the adsorbate, by an amount $E_0 = \Phi - I$, where Φ is the work function. The space charges in the electron boundary layer cause the increase in the electrical resistivity. In the system $(Ni_{1-x}Li_x)O$, since samples are p-type semiconductors, the increase in the electrical resistivity is explained by the electron boundary layer model. From the results of Fig. 3, it is apparent that the increase in the Fermi level owing to the charge transfer decreases with increasing adsorbed water.

It is assumed that ionic conductivity of adsorbed water on the surface of $(Ni_{1-x}Li_x)O$ also takes place. The electrical resistivity due to the ionic conductivity is very high in the low relative humidity region, and exponentially decreases with increasing relative humidity [1]. In the range $0 \leqslant H \leqslant 79\%$, the electrical conductivity of $(Ni_{1-x}Li_x)O$ is produced according to the electron boundary layer model. On the other hand, in the range $79\% < H \leqslant 100\%$, the electrical conductivity due to the ionic conductivity is larger than that due to the electron boundary layer model. From these results, it is apparent that the electrical resistivity has a maximum value at $\sim H = 79\%$ as shown in Fig. 2.

4. Conclusion

It is concluded that the electrical resistivity in the system $(Ni_{1-x}Li_x)O$ increases with increasing relative humidity in the range $0 \leqslant H \leqslant 79\%$. This increase is explained by the electron boundary layer model, and ΔR of $(Ni_{1-x}Li_x)O$ is independent of the lithium ion content. In the range $79\% < H \leqslant 100\%$, the electrical resistivity decreases. This decrease is due to the ionic conductivity of adsorbed water on the oxide.

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