High-Temperature Defect Structure and Electrical Conduction in Undoped and Li- or Al-Doped NiO

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Electrical conductivity and thermoelectric power were measured on undoped and Li- or Al-doped NiO at 800°-1400°C. The electrical conductivity (σ) of Li-doped NiO was independent of both oxygen partial pressure (P₀₂) and temperature at low P₀₂, which yielded the calculated hole mobility of 0.43 cm²/V·s. From the temperature dependence of σ at P₀₂=10⁵ Pa for Al-doped NiO and the hole mobility of Li-doped NiO, the deviation from stoichiometry δ in Ni₁₋δO was obtained: δ = 7.75 × 10⁻² exp (-16200/RT). The electrical conductivity for both undoped and Al-doped NiO varied with P₀₂¹/₄ at a constant temperature, thus leading to the conclusion that doubly ionized nickel vacancies were dominant at high temperatures. The temperature dependence of Seebeck coefficient was inexplicable by means of a thermally activated hopping mechanism indicative of rather wide band conduction of electron holes.

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1. Introduction

Electrical and magnetic properties of NiO have been extensively investigated along with other transition metal oxides to elucidate the behavior of 3d electrons. High-temperature defect structure, electrical conduction mechanism and ionic diffusion in NiO have also been attractive research problems in relation to its nonstoichiometric nature and electronic structure.
Nickel oxide is considered to be a metal-deficient nonstoichiometric compound, in which cation vacancies are introduced according to the following quasi-chemical reactions when in equilibrium with the surrounding oxygen:

\[
\begin{align*}
\frac{1}{2}O_2 &= V_{Ni}^x + O_2^x \\
V_{Ni}^x &= V_{Ni} + h \\
V_{Ni} &= V_{Ni}^x + h
\end{align*}
\]

The defect notations here are similar to those used by Kroger and Vink. The deviation from stoichiometry \( \delta \) in \( Ni_{1-x}O \) has been reported to be small and of the order of \( \sim 10^{-3} \) at \( 1400^\circ-1600^\circC \). Hence the interaction among defects can be neglected, and no paper reports the effect of defect interactions on the properties of NiO. Then, taking \( K_1, K_2, \) and \( K_3 \) as equilibrium constants for the reactions (1), (2), and (3), respectively, a mass action law would give rise to following relations:

\[
\begin{align*}
[ V_{Ni}^x ] &= K_1 P_{O_2}^{1/2} \\
[ V_{Ni}^x ] p &= K_2 [ V_{Ni} ] \\
[ V_{Ni}^x ] &= K_3 [ V_{Ni} ]
\end{align*}
\]

where \([ \ ]\) denotes the concentration and \( p \) is the electron hole concentration. The deviation from stoichiometry \( \delta \) is expressed as

\[
\delta = [ V_{Ni} ] + [ V_{Ni}^x ] + [ V_{Ni}^x ]
\]

The electroneutrality condition is approximated as

\[
p = [ V_{Ni} ] + 2 [ V_{Ni}^x ]
\]

when the concentrations of other defects like electrons, oxygen vacancies, nickel interstitials, impurity ions etc. are small compared with those of electron holes and nickel vacancies.

If the concentration of singly ionized nickel vacancies, \( V_{Ni}^x \) is large compared with that of doubly ionized nickel vacancies, the neutrality condition of Eq. (8) can be further approximated as

\[
p = [ V_{Ni} ]
\]

Combining Eqs. (4), (5), (7) and (9), the following relation can be obtained:

\[
\delta = [ V_{Ni} ] = p = (K_1 K_2)^{1/2} P_{O_2}^{1/4}
\]

Similarly, the following relation can be obtained if the doubly ionized nickel vacancies, \( V_{Ni}^x \) are predominating:

\[
\delta = [ V_{Ni} ] = p/2 = (K_1 K_2 K_3/4)^{1/2} P_{O_2}^{1/4}
\]

To determine the defect structure (mainly the charge of nickel vacancies for NiO), the properties related directly to the concentrations of electron holes and/or nickel vacancies may well be measured, judging from Eqs. (10) and (11). For this purpose electrical conductivity, chemical diffusion coefficient, and deviation from stoichiometry have been measured as functions of temperature and oxygen partial pressure. However, conflicting results have been reported in the literatures \(^{21-22}\), possibly due to effects of impurities on the defect equilibria.

Mechanism of p-type semiconduction in NiO has also been a controversial problem. Both d.c. and a.c. conductivity, thermoelectric power, and Hall effect have been measured on undoped and Li-doped NiO to clarify the conduction mechanism. There are two proposed models for conduction mechanism; thermally activated hopping of small polarons \(^{21,41,71,13}\) and large polaron conduction in a narrow 3d band \(^{41-46}\). Non-activated hole conduction in a wide 2p band has also been proposed from theoretical considerations \(^{37}\).

This paper reports a further examination of the charge of nickel vacancies and electrical conduction mechanism at high temperatures based on conductivity and thermoelectric power measurements on undoped and Li- or Al-doped NiO.

2. Experimental procedure

2.1 Materials

The commercially available NiO powder of 99.99% purity was employed as a starting material. The powder was wrapped tightly with a thin rubber and pressed hydrostatically in a steel dye containing silicone oil under the pressure of \( \sim 130 \text{ MPa} \). The powder compact was sintered at \( 1500^\circ-1600^\circC \) for 5 h in air. For Li or Al doping, the NiO powder was poured into a Li or Al nitrate aqueous solution and dried, followed by the similar procedure for undoped NiO to obtain dense sinters. The obtained sintered compacts were cut with a diamond saw into rectangular bars \( \sim 4 \times 4 \times 15 \text{ mm} \), polished by an abrasive paper and cleaned with acetone to be subjected to electrical measurements.

2.2 Electrical measurements

Four dips were recessed on a rectangular specimen with a diamond saw and platinum wire electrode of 0.3 mm in dia. was wound along each dip. To prevent the contamination of a specimen from electrodes, high-purity platinum wires were used and usual platinum pasting was
An electrode configuration is shown in Fig. 1 (a). Electrical conductivity was measured using a d.c. four-probe technique at 800–1400°C in varying oxygen partial pressure ($P_{O_2}$). Mixtures of Ar and O₂ or CO₂ and CO diluted by N₂ were used to control $P_{O_2}$ which was known from the emf of the zirconia cell placed close to the specimen as reported previously. Equilibrium was checked by recording the variation of a voltage drop with time during constant current supply after temperature and $P_{O_2}$ became constant within experimental errors. It took 10 to 30 minutes for the present specimens to equilibrate depending on temperature and $P_{O_2}$.

Thermoelectric power measurements were performed mainly at $P_{O_2} = 10^5$ Pa varying temperature. Heads of the two Pt-Pt 13Rh thermocouples were embedded in two drilled holes of a specimen and they were fixed by platinum wires, respectively, as shown in Fig. 1 (b). Platinum paste was not used in this case, either. The specimen was set in the middle of the furnace and the temperature gradient in the specimen was generated by the cool air flowing in an alumina protection tube placed near the one end of the specimen. Two platinum leads of the thermocouples were used to measure thermoelectric power. The temperature difference between the two points was controlled to be 2-10 K by varying the flow rate of air, while the average temperature of the specimen was fixed. Plots of thermoelectric power vs. temperature difference gave rise to a straight line in all cases, and Seebeck coefficient was calculated from its slope.

3. Results and Discussion

3.1 Electrical conductivity

Due to a small deviation from stoichiometry in NiO, the electrical properties obtained tended to be misinterpreted unless high-purity samples are used for measurements. In the present study, the impurity effect was studied by using Li and Al dopants, both of which have stable valences in an oxide. Doping level of Li mixed in the starting powder was $2 \times 10^{-3}$ cation fraction ($0.1 \text{ mol} \% \text{ Li}_2\text{O}$) and was considered to be within the solubility limit. The level of Al doping was chosen to be $4 \times 10^{-3}$ cation fraction ($0.2 \text{ mol} \% \text{ Al}_2\text{O}_3$). Extrapolation of the reported solubility limit of Al in NiO at high temperatures by Minford and Stubican to the lower temperature range showed that the present doping level corresponded to the solubility limit at $\sim 1200^\circ$C. Below $1200^\circ$C the precipitation of spinel phase ($\text{NiAl}_2\text{O}_4$) was expected.

The oxygen partial pressure dependences of electrical conductivity at $800^\circ$–$1400^\circ$C are shown in Figs. 2, 3, and 4. Conductivity of both undoped and Al-doped NiO was found to change with $P_{O_2}^{1/4}$ at high oxygen partial pressures. The oxygen partial pressure dependence of $\sigma$ becomes moderate with decreasing $P_{O_2}$. Conductivity was measured down to the equilibrium decomposition pressure of NiO at each temperature and the appearance of electrons near the Ni-NiO phase boundary may have contributed to the total conductivity in the low $P_{O_2}$ region. Fisher and Tannhauser

![Fig. 2. Oxygen partial pressure dependence of electrical conductivity for undoped NiO.](image)
reported the contribution of electron conduction to Seebeck coefficient of CoO near the Co-CoO phase boundary. However, the behavior of conductivity of NiO at low $P_{O2}$ was not analysed in detail in the present study.

Light absorption analyses after the measurements showed that significant amount of Al was found in both samples ($1.4 \times 10^{-3}$ cation fraction in an undoped NiO and $5.8 \times 10^{-3}$ cation fraction in an Al-doped NiO). Hence aluminum is responsible for the similar $P_{O2}$ dependences of conductivity in undoped and Al-doped NiO. The specimens may have picked up Al from alumina tubes during electrical measurements.

The electrical neutrality condition for both undoped and Al-doped NiO is expressed as follows:

$$[V_{Ni}^+]+2[V_{Ni}^0]=p+[Al_{Ni}] \quad (12)$$

As mentioned before, the deviation from stoichiometry $\delta$ in Ni$_{1-\delta}$O is less than $\sim 10^{-3}$, and the approximation as $[Al_{Ni}] \gg p$ is assumed in the present case. If singly ionized nickel vacancies are dominant, Eq. (12) can be further approximated as,

$$[V_{Ni}^+]=[Al_{Ni}]=\text{const.} \quad (13)$$

Combining Eqs. (4), (5), and (13) gives the following relation:

$$p=K_1K_2P_{O2}^{1/2}/[Al_{Ni}] \quad (14)$$

If doubly ionized nickel vacancies are dominant, Eq. (12) becomes

$$2[V_{Ni}^0]=[Al_{Ni}]=\text{const.} \quad (15)$$

and combining Eqs. (4), (5), (6), and (15) gives the following relation:

$$p=(2K_1K_2K_3/[Al_{Ni}])^{1/2}P_{O2}^{1/4} \quad (16)$$

Electrical conductivity $\sigma$ for the hole conduction is expressed in general as:

$$\sigma=pe\mu \quad (17)$$

where $e$ is the electronic charge and $\mu$ is the hole mobility. The oxygen partial pressure dependences of $p$ and $\sigma$ at a fixed temperature is consequently similar if the hole mobility is independent of $P_{O2}$. The results shown in Figs. 2 and 3 show that the hole concentration is
proportional to \( P_{o_2}^{1/4} \) and that doubly ionized nickel vacancies, \( \text{V}_{\text{Ni}}^{2+} \), are the dominant defects in NiO at high temperatures.

For Li-doped NiO, electrical conductivity becomes independent of both temperature and oxygen partial pressure as decreasing \( P_{o_2} \), while it is dependent on \( P_{o_2} \) at rather high \( P_{o_2} \) as shown in Fig. 4. Atomic absorption analyses showed that the composition changed during high-temperature measurements possibly by evaporation of Li\(_2\)O, and that the residual amount of Li in NiO was \( 1.4 \times 10^{-3} \) cation fraction. As a main impurity, Al of \( 8.3 \times 10^{-4} \) cation fraction was also found in the Li-doped specimen. Assuming that the hole concentration is fixed by dopant in the low \( P_{o_2} \) region, the hole mobility can be calculated with Eq. (17) and experimental values: \( \sigma = 1.78 \text{ S} \cdot \text{cm}^{-1} \), relative density of the specimen = 81.7 \%, lattice constant = 0.4177 nm, and \( p = [\text{Li}_{\text{Ni}}^{3+}] - [\text{Al}_{\text{Ni}}] = 5.7 \times 10^{-4} \) cation fraction. The calculated hole mobility of 0.43 cm\(^2\)/V\( \cdot \)s in the present temperature range (Fig. 5) agrees fairly well with the reported values, 0.16-0.53 cm\(^2\)/V\( \cdot \)s. Osburn and Vest\(^3\) obtained a temperature-independent hole mobility of 0.53 cm\(^2\)/V\( \cdot \)s from their measurements of electrical conductivity and the deviation from stoichiometry on a high-purity NiO single crystal. Our value is slightly smaller than theirs, but its temperature dependence is similar. The temperature-independent hole mobility shows that no activation energy is needed for hole conduction. This result cannot be explained by a small polaron hopping mechanism proposed for NiO by Bransky and Tallan\(^7\). Conduction mechanism will be further discussed in Section 3.2.

The electrical neutrality condition among defects at high \( P_{o_2} \) is expressed as follows, in which doubly ionized nickel vacancies are assumed to be dominant,

\[
2[\text{V}_{\text{Ni}}^{2+}] + [\text{Li}_{\text{Ni}}^{3+}] = p + [\text{Al}_{\text{Ni}}] \quad (18)
\]

From Eqs. (4), (5), (6) and (18), the following equation for hole concentration can be deduced:

\[
p = p - 5.7 \times 10^{-4} = 2 K_1 K_2 K_3 P_{o_2}^{1/4} \quad (19)
\]

Equation (19) can be solved if the product of equilibrium constants is known. Since the following expression is known from Eqs. (16) and (17), the product of equilibrium constants can be calculated,

\[
\sigma = e\mu(2 K_1 K_3 K_4 [\text{Al}_{\text{Ni}}]^{1/2} P_{o_2}^{1/4}) \quad (20)
\]

The temperature dependence of conductivity for Al-doped NiO above 1200°C at \( P_{o_2} = 10^5 \) Pa is expressed as:

\[
\sigma = 2.29 \times 10^3 \left( -24500 / RT \right) \left[ \text{S} \cdot \text{cm}^{-1} \right] \quad (21)
\]

Following values are found in experiment: relative density = 75.6 \%, lattice constant = 0.4177 nm, \([\text{Al}_{\text{Ni}}] = 5.8 \times 10^{-3} \) cation fraction, and \( \mu = 0.43 \text{ cm}^2/\text{V} \cdot \text{s} \). The calculated product is expressed as:

\[
K_1 K_2 K_3 = 1.86 \times 10^{-3} (-48600 / RT) \quad (22)
\]

Assuming doubly ionized nickel vacancies predominate, the deviation from stoichiometry \( \delta \) can also be calculated with Eqs. (4) to (7), and (22) as:

\[
\delta = [\text{V}_{\text{Ni}}] = (K_1 K_2 K_3 / 4) P_{o_2}^{1/6}
\]

\[
= 7.75 \times 10^{-5} \exp \left( -16200 / RT \right) \cdot P_{o_2}^{1/6} \quad (23)
\]

Fig. 5. Hole mobility vs. temperature as compared with the reported values. Numbers in parentheses are reference numbers.
observed results as shown in Fig. 6.

3.2 Seebeck coefficient

In Figs. 7 and 8 are shown the temperature dependences of Seebeck coefficient obtained at $P_0=10^5$ Pa. It is seen for Li-doped NiO that Seebeck coefficient increases with increasing temperature. For Al-doped NiO a simple relation cannot be found due to a scatter of plots which may have been caused by the precipitation of a spinel phase below 1200°C. However, Seebeck coefficient of Al-doped NiO decreases monotonically with increasing temperature above 1200°C.

In general, Seebeck coefficient $\alpha$ for one kind of charge carrier (electron hole in the present case) is expressed by the following equation:

$$\alpha = (k/e) \ln (N_v/p) + A \quad (24)$$

where $N_v$ is the effective density of states at the transport level, $A$ a kinetic energy transport term, and $k$ the Boltzmann constant. For the case where the thermally activated hopping of small polarons is a dominant conduction mechanism, $N_v$ is equivalent to the density of available sites on which carriers can be localized and is independent of temperature. By assuming a localized electron hole on one Ni$^{2+}$ ion site the density of states for NiO is calculated from lattice constant (0.4177 nm) and was $\sim 5.5 \times 10^{22}$ cm$^{-3}$. Since the hole concentration $p$ can be calculated as a function of
temperature for Li-doped NiO from Eqs. (19) and (22) and for Al-doped NiO from Eqs. (16) and (22), Seebeck coefficient \( \alpha \) can also be calculated with a reasonable assumed value of \( A \) which is very small or negligible for small polaron hopping. Solid lines in Figs. 7 and 8 show the calculated variations of Seebeck coefficient assuming \( A \) to be zero. The calculated coefficients are much larger than those observed for both Li- and Al-doped NiO. This is due to the assumption of too large density of states. As reported in our previous study on Co\(_{1-x}\)Mg\(_x\)O\(_2\)), if an electron hole is shared by more than one cation site, \( \alpha \) would become comparable to the observed values at higher temperatures. The density of states calculated from Seebeck coefficient is less than 1.4 \( \times 10^{22} \) cm\(^{-3} \) for Li-doped NiO and 8.7 \( \times 10^{21} \) cm\(^{-3} \) for Al-doped NiO. In these cases, an electron hole is regarded as shared by more than 4 Ni\(^{2+} \) ions in Li-doped NiO and 7 Ni\(^{2+} \) ions in Al-doped NiO. However, the calculated temperature dependences remain too high compared with the observed ones, and it is doubtful whether an electron hole shared by 4 to 7 or more cations can still be regarded as a "small" polaron.

For the case where the band conduction takes place, the effective density of states is expressed as:

\[
N_e = \frac{2}{\pi} \frac{m^* h k T}{h^2} \gamma^{3/2} 
= 4.829 \times 10^{15} \gamma^{3/2} \quad \text{[cm}^{-3}\text{]} \quad (25)
\]

where \( m^* \) is the effective mass of an electron hole, \( h \) the Planck constant, and \( \gamma \) a ratio of \( m^* \) to the mass of a free electron. Using 1.6 for \( \gamma \) as reported by Bosman and Crevecoeur\(^{(1)} \) on Li-doped NiO, Seebeck coefficients were calculated for the present specimens and the results are shown as dashed lines in Figs. 7 and 8. For Al-doped NiO the calculated coefficients agree very well with the observed ones above 1200°C when \( \gamma \) is taken to be 2.4, while for Li-doped NiO \( \gamma \) varies from 1.7 to 6 as temperature increases. The values for \( \gamma \) reported by various investigators are not consistent\(^{(31,14,28,22)} \), ranging from one to 6, and cannot be compared quantitatively with the present results.

4. Conclusion

Electrical properties of NiO could be significantly affected by impurities due to its small deviation from a stoichiometric composition. In the present study, the reduction of an impurity effect was attempted by doping Li or Al, and the following conclusions concerning the high-temperature defect structure and conduction mechanism were drawn: (1) dominant defects at 800°-1400°C in pure NiO should be doubly ionized nickel vacancies, V\(_{\text{Ni}}\)\(^{2+} \), and (2) conduction of electron holes takes place in a rather wide band instead of a thermally activated hopping of small polarons.

References