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Electrical conduction and effective mass of a hole in single-crystal NiO

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The electrical conductivity and Seebeck coefficient of single-crystal NiO were measured at 1100 to 1400° C. The activation energies for conductivity and thermoelectric power were 84.1 and 76.5 kJ mol^{-1}, respectively, which was interpreted as showing band-like conduction occurring at high temperatures. Doubly ionized cation vacancies were believed to be the dominant point defects, and the impurity effect gave rise to a $P_{O_2}^{1/5}$ dependence of conductivity. The effective mass of a hole, m^*, was calculated based on a band-conduction scheme using the literature value of the deviation from stoichiometry, δ, and the hole mobility μ. The value of m^* was in the range 0.8 to 1.0 m_0, and slightly decreased with increasing temperature.

1. Introduction

Nickel oxide, a 3d transition metal oxide, is known to be a p-type semiconductor at high temperature due to its metal-deficient non-stoichiometry. The electrical conduction mechanism, defect structure, ionic diffusion and optical properties have been investigated extensively.

Both d.c. and a.c. conductivity, thermoelectric power and Hall effect have been measured on undoped and lithium-doped NiO to clarify the conduction mechanism. Two models have been proposed for conduction: one is thermally activated hopping of small polarons [1–4], the other is large polaron conduction in a narrow 3d band [5–11]. Non-activated hole conduction in an oxygen 2p band has also been proposed from theoretical consideration [12]. Many studies have been made to determine the dominant defects by conductivity measurement, thermogravimetry and coulometric titration. The proposed dominant defects are singly ionized vacancies [7, 13–16], doubly ionized vacancies [1, 9, 17–21] and mixed ionized vacancies [22–27].

Only a few investigators determined the effective mass of a hole [9–11, 28] and the values obtained vary widely from 0.35 m_0 to 32 m_0. No study has reported the effective mass of a hole, m^*, at high temperature for NiO.

In the present study the electronic conductivity and Seebeck coefficient were measured to determine the dominant defect structure, conduction mechanism and m^* at high temperatures.

2. Experimental details

2.1. Specimen preparation

Single-crystal NiO was employed to avoid the unfavourable effects of grain boundaries and pores. The specimens were cut from a single-crystal rod grown by the Verneuil method, supplied by Nakazumi Earth Crystal Co. (Osaka). The specimen was cut with a diamond saw into rectangular bars 0.5 mm by 3 mm by 15 mm. A sufficiently thin specimen was easier to equilibrate with the surrounding atmosphere. For thermoelectric power measurements a slightly thicker one was used to give drilled holes for mounting thermocouples. For electrical measurements both specimens were polished with abrasive paper and cleaned ultrasonically with acetone and distilled water to remove surface contamination.

2.2. Electrical measurements

Electrical conductivity was measured using a d.c. four-probe technique at 1100 to 1400° C under various oxygen partial pressures (P_{O_2}). The measurement system used in the present work was similar to that reported previously [29]. Mixtures of argon and oxygen for high P_{O_2} and CO_2 and CO for low P_{O_2} were passed through the measuring chamber and P_{O_2} was measured with a zirconia cell placed close to the specimen. Electrical measurements were performed after sufficient time at each temperature. Equilibrium was checked by recording the variation of voltage drop with time during constant-current supply.

Thermoelectric power was measured at $P_{O_2} = 10^5$ Pa at various temperatures. The heads of two Pt–Pt 13Rh thermocouples were mounted in two holes drilled in the specimen. The thermocouples were used to measure both temperature difference and thermoelectric power generated by the temperature gradient in the furnace. The temperature difference between the two points was controlled within 2 to 10 K by varying the rate of air flowing through an alumina protection tube near one end of the specimen, while the average temperature of the specimen was fixed. The Seebeck coefficient was calculated from the slope of a straight line drawn for the relationship between thermoelectric power and temperature difference.

3. Results and discussion

The oxygen partial pressure dependences of electrical conductivity for single-crystal NiO at 1100 to 1400° C

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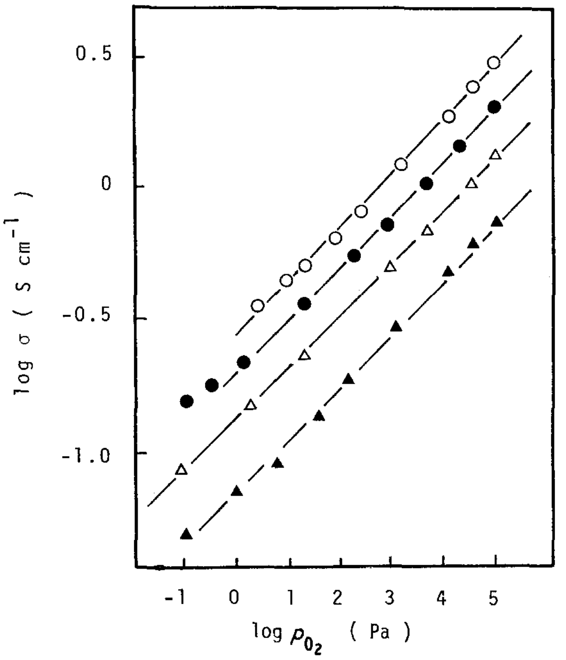

Figure 1 Oxygen partial pressure dependence of electrical conductivity for single-crystal NiO. (▲) 1100° C, (△) 1200° C, (●) 1300° C, (○) 1400° C.

are shown in Fig. 1. The electrical conductivity, σ, is approximately proportional to $P_{O_2}^{1/5}$. Similar oxygen partial pressure dependences have been reported previously. The results were interpreted in two ways; the defects are doubly ionized nickel vacancies which were influenced by impurities [10] or there is a simultaneous presence of singly and doubly ionized nickel vacancies [22–27].

At temperatures high enough for the specimen to equilibriate with the gas phase, nickel vacancies are introduced into NiO according to the following quasi-chemical reactions:

$$\tfrac{1}{2}O_2 = O_O^x + V_{Ni}^x \qquad (1)$$

$$V_{Ni}^x = V'_{Ni} + h^{\cdot} \qquad (2)$$

$$V'_{Ni} = V''_{Ni} + h^{\cdot} \qquad (3)$$

where O_O^x, h, V'_{Ni}, V''_{Ni} represent, respectively, an oxygen atom on its normal lattice site, an electron hole, an unionized cation vacancy, a singly oxidized cation vacancy and a doubly ionized cation vacancy [30]. Taking k_1, k_2 and k_3 as equilibrium constants for Reactions 1, 2 and 3, respectively, a mass action law, assuming an ideal behaviour of defects, would give rise to the following relations:

$$[V_{Ni}^x] = k_1 P_{O_2}^{1/2} \qquad (4)$$

$$[V'_{Ni}]p = k_2[V_{Ni}^x] \qquad (5)$$

$$[V''_{Ni}]p = k_3[V'_{Ni}] \qquad (6)$$

where square brackets denote the concentration and p is the hole concentration. The hole concentration p is approximated by the electroneutrality condition as

$$p = [V'_{Ni}] + 2\,[V''_{Ni}] \qquad (7)$$

If the concentration of singly ionized cation vacancies, V'_{Ni}, is large compared with that of doubly ionized cation vacancies, V''_{Ni}, the neutrality condition of Equation 7 can be approximated as

$$p = [V'_{Ni}] \qquad (8)$$

Combining Equations 4, 5 and 8, the following relation can be obtained:

$$[V'_{Ni}] = p = (k_1k_2)^{1/2} P_{O_2}^{1/4} \qquad (9)$$

Similarly, the following equation can be obtained if the doubly ionized cation vacancies, V''_{Ni}, are predominating:

$$[V''_{Ni}] = \frac{p}{2} = \left(\frac{k_1k_2k_3}{4}\right)^{1/3} P_{O_2}^{1/6} \qquad (10)$$

The above equations are valid for pure NiO with no impurity effect. The influence of impurity is important since non-stoichiometry, δ, is very small in $Ni_{1-\delta}O$.

The trivalent impurity Fe^{3+} was picked up considerably during the experiment as shown in Table I. If the Fe^{3+} ion is substitutionally incorporated into a cation site, the electroneutrality condition requires the following relation:

$$[V'_{Ni}] + 2[V''_{Ni}] = p + [Fe^{\cdot}_{Ni}] \qquad (11)$$

If singly ionized cation vacancies, V'_{Ni}, are dominant at lower oxygen partial pressures, the trivalent impurity concentration $[Fe^{\cdot}_{Ni}]$ is considered to be much larger than the hole concentration p, so that the approximation for $[Fe_{Ni}] \gg p$ would be reasonable.

The neutrality condition is then further approximated as

$$[V'_{Ni}] = [Fe^{\cdot}_{Ni}] = \text{constant} \qquad (12)$$

Combining Equations 4, 5 and 11 then gives

$$p = \frac{k_1k_2P_{O_2}^{1/2}}{[Fe^{\cdot}_{Ni}]} \qquad (13)$$

If singly ionized cation vacancies, V'_{Ni}, are dominant at high oxygen partial pressures, the hole concentration p is considered to be much larger than the trivalent impurity concentration $[Fe^{\cdot}_{Ni}]$, so that the approximation for $p \gg [Fe^{\cdot}_{Ni}]$ would be reasonable. The neutrality condition is further approximated according to Equation 8, and the hole concentration p is proportional to $P_{O_2}^{1/4}$ according to Equation 9. If V''_{Ni} is dominant at lower oxygen partial pressures, Equation 10 becomes

$$2[V''_{Ni}] = [Fe^{\cdot}_{Ni}] = \text{constant} \qquad (14)$$

and combining Equations 5, 6, 7 and 13 gives

$$p = \left(\frac{2k_1k_2k_3}{[Fe^{\cdot}_{Ni}]}\right)^{1/2} P_{O_2}^{1/4} \qquad (15)$$

TABLE I Spectrographic analysis of NiO before and after the experiments (in parts per million by weight)

Element	Before measurement	After measurement
Fe	72	240
Mn	5.8	16
Mg	66	80
Na	< 100	180
K	< 100	106

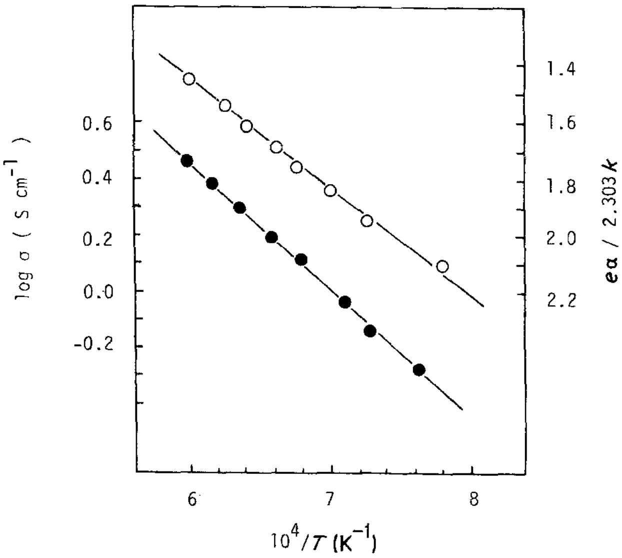

Figure 2 Temperature dependences of (●) electrical conductivity and (○) Seebeck coefficient. $\Delta Q_c = 84.1\,\mathrm{kJ\,mol^{-1}}$, $\Delta Q_S = 76.5\,\mathrm{kcal\,mol^{-1}}$.

At high oxygen partial pressures where V_{Ni}'' is dominant, p is considered to be much larger than $[Fe_{Ni}^{\cdot}]$ so that the approximation for $p \gg [Fe_{Ni}^{\cdot}]$ would be reasonable. The neutrality condition is further approximated by Equation 10 and p is proportional to $P_{O_2}^{1/6}$. On the other hand, it is necessary to take into account the oxygen partial pressure dependence of the non-stoichiometry δ. The impurity effect changed with non-stoichiometry; at low oxygen pressures where δ is small, the impurity effect is significant whereas at high oxygen pressures, where δ is large, the impurity effect is insignificant. The 1/5 power oxygen pressure dependence observed in the present work could be interpreted as showing that the dominant defect is V_{Ni}'', with the characteristic of a transition between 1/4 and 1/6 dependences. The vacancy concentration in NiO also shows a $P_{O_2}^{1/5}$ oxygen pressure dependence as reported by Tripp and Tallan [27], who concluded that the dominant defects were impurity-affected V_{Ni}''.

The temperature dependence of electrical conductivity σ and Seebeck coefficient α are shown in Fig. 2. The activation energy for σ, ΔQ_c, is $84.1\,\mathrm{kJ\,mol^{-1}}$ which is in agreement with previously reported values [9, 31]. The high-temperature dependence of α was measured only by Bransky and Tallan [31] at 1000 to 1600° C [30]. The reported value of ΔQ_S, is $92.0\,\mathrm{kJ\,mol^{-1}}$, which is comparable with the present value of $76.5\,\mathrm{kJ\,mol^{-1}}$. The electrical conductivity σ for a p-type semiconductor is expressed by

$$\sigma = pe\mu \tag{16}$$

where p is the hole concentration, e the electronic charge and μ the drift mobility of charge carriers. The Seebeck coefficient α for a non-degenerate p-type semiconductor is expressed as

$$\alpha = \left(\frac{k}{e}\right)\left[\ln\left(\frac{p_0}{p}\right) + A\right] \tag{17}$$

where p_0 is the effective density of states at the transport level, k the Boltzmann constant and A the kinetic transport term. Differentiating Equations 16 and 17 with respect to $1/kT$, the following expression can be derived:

$$\frac{\mathrm{d}(\log\sigma)}{\mathrm{d}(1/kT)} - \frac{\mathrm{d}(-e\alpha/2.303\,k)}{\mathrm{d}(1/kT)} = \Delta Q_c - \Delta Q_S$$
$$= \frac{\mathrm{d}(\log\mu)}{\mathrm{d}(1/kT)} + \frac{\mathrm{d}(\log p_0)}{\mathrm{d}(1/kT)} + \frac{\mathrm{d}(A/2.303)}{\mathrm{d}(1/kT)} \tag{18}$$

Equation 18 indicates that the energy difference calculated from the temperature dependences of σ and α at a fixed oxygen potential gives us insight into the conduction mechanism of the material, and it has been applied to various systems such as NiO and CoO [32]. For a broad-band semiconductor $\mathrm{d}(\log p_0)/\mathrm{d}(1/kT) = -\frac{3}{2}kT$, which gives us the activation energy 9.6 to $13.5\,\mathrm{kJ\,mol^{-1}}$ for the temperature range 900 to 1400° C. For a narrow-band semiconductor $\mathrm{d}(\log p_0)/\mathrm{d}(1/kT)$ is not more than a small fraction of the hopping energy. The term $\mathrm{d}(A/2.303)/\mathrm{d}(1/kT)$ may be negligible in both cases [32]. The difference in the temperature dependence of the measured conductivity and Seebeck coefficient for NiO is $6.35\,\mathrm{kJ\,mol^{-1}}$, as shown in Fig. 2. This value is attributable to $\mathrm{d}(\log p_0)/\mathrm{d}(1/kT)$ and the term $\mathrm{d}(\log\mu)/\mathrm{d}(1/kT)$ has only a small positive or negative value.

The above analysis does not lead us to suppose that thermally activated polaron hopping takes place in NiO. It may be more reasonable to assume that band-like conduction is dominant at high temperatures. On the assumption of a broad-band conduction, the effective mass of a hole, m^*, can be determined as follows.

When the dominant defects are V_{Ni}'', the hole concentration p and the deviation from stoichiometry δ have the following relation:

$$p = 2[V_{Ni}''] = 2\delta \tag{19}$$

Combining Equations 17 and 19, the following relation can be obtained:

$$\frac{e\alpha}{2.303\,k} = \log\left(\frac{p_0 e^A}{2}\right) - \log\delta \tag{20}$$

where the value for the energy transport term A can be taken as 1.5, according to Bosman and Crevecoeur [5]. The deviation from stoichiometry, δ, has been reported by various investigators, but here we employed the value of Tripp and Tallan [27], taken from their thermogravimetric measurement showing a 1/5 power oxygen pressure dependence of δ. The deviation from stoichiometry, δ, is expressed at 800 to 1100° C by

$$\delta = 0.168\exp\left(\frac{-19600}{RT}\right) \tag{21}$$

Equation 20 can be used to determine p_0. Based on the expectation that band conduction takes place, the effective density of states is expressed as

$$p_0 = 4.829 \times 10^{15}(\gamma T)^{3/2}\,\mathrm{cm}^{-3} \tag{22}$$

where γ is the ratio of the effective mass of a hole to the mass of a free electron ($\gamma = m^*/m_0$). From Equations 19, 20, 21 and 22, the γ values can be calculated as shown in Fig. 3.

On the other hand, the γ values can be determined from the mobility values μ. The hole mobility for NiO

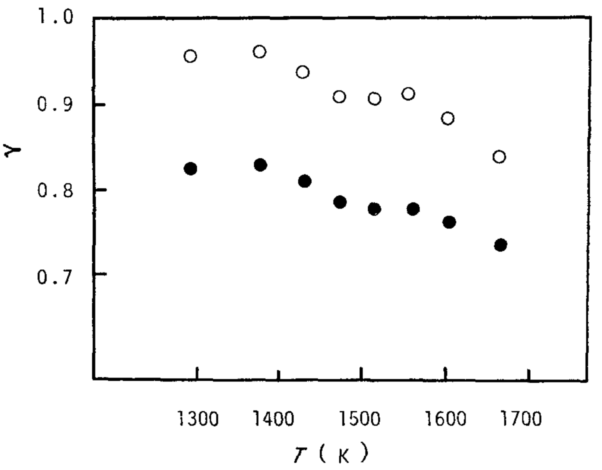

Figure 3 Temperature dependence of γ values for single-crystal NiO. (●) $\mu = 0.43\,\mathrm{cm^2\,V^{-1}\,sec^{-1}}$ [10]; (○) $\delta = 0.168 \exp(-19600/RT)$ [27].

has been reported by many investigators. The present authors have previously determined the temperature-independent μ values for NiO as $0.43\,\mathrm{cm^2\,V^{-1}\,sec^{-1}}$ at 900 to 1400° C [10]. The hole concentration p can be deduced from σ and μ using Equation 16. Combining Equations 16, 17 and 22, the γ values can be determined for various temperatures. The γ values thus determined are also shown in Fig. 3. The values determined from δ and μ data show similar temperature dependences, i.e. decreasing with increasing temperature. The effective mass of a hole for NiO has been reported by several investigators and the results are shown in Table II.

4. Conclusions

The electrical conductivity and Seebeck coefficient of single-crystal NiO were measured at 1100 to 1400° C. The activation energies for conductivity and thermoelectric power were 84.1 and $76.5\,\mathrm{kJ\,mol^{-1}}$, respectively, which was interpreted as showing band-like conduction occurring at high temperatures. Doubly ionized cation vacancies were believed to be the dominant point defects and the impurity effect gave rise to a $P_{\mathrm{O}_2}^{1/5}$ dependence of conductivity. The effective mass of a hole, m^*, was calculated based on a band conduction scheme using the literature value of the deviation from stoichiometry, δ, and the hole mobility μ. The value of m^* was in the range 0.8 to $1.0\,m_0$ and slightly decreased with increasing temperature.

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TABLE II Previously reported values of the effective mass of a hole

Specimen	Investigators	Temperature (K)	m^*
Li–NiO	Austin *et al.* [8]	523 to 673	$32\,m_0$
NiO	Osburn and Vest [9]	1027 to 1673	$1\,m_0$
Al–NiO	Koumoto *et al.* [10]	1473 to 1673	$2.4\,m_0$
Li–NiO	Ksenzov *et al.* [11]	673 to 923	0.35 to $2.2\,m_0$
NiO	Wilson [28]		$2\,m_0$
NiO	This work	1373 to 1673	0.8 to $1.0\,m_0$

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