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Nonstoichiometry and Electrical Resistivity in Two Mixed Metal Oxides, La_2NiO_{4-x} and $LaSrNiO_{4-x}$

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Two mixed oxides, La_2NiO_{4-x} and $LaSrNiO_{4-x}$, had the K_2NiF_4 structure in the oxygen-pressure range from 58000 down to 130 Pa at 1173 K. The oxygen-vacancy concentration, x, in both La_2NiO_{4-x} and in $LaSrNiO_{4-x}$ at 1173 K was determined by thermogravimetric analysis in the oxygen-pressure range from 58000 to 1.3 Pa. The vacancy concentration of $LaSrNiO_{4-x}$ was greater than that of La_2NiO_{4-x} at the same oxygen pressure at 1173 K. The electrical resistivities of La_2NiO_{4-x} and $LaSrNiO_{4-x}$ were measured at 473—1173 K under an oxygen atmosphere at 98—58000 Pa. The density of the state and the drift mobility of oxygen stoichiometric La_2NiO_4 and $LaSrNiO_4$ were estimated from the resistivity data and from the results on the thermogravimetric analysis.

The mixed oxide La_2NiO_4, which was first prepared by Kniga and Zaretskaya,[1] has the very attractive property of a "gradual" semiconductor-metal transition.[2–4] Goodenough et al.[5–7] have previously proposed an invaluable band model which gives the origin of the semiconductor-metal transition of La_2NiO_4. The model, however, does not clearly explain why the transition proceeds "gradually."[8] It seemed that it would be worthwhile from the electrochemical point of view to elucidate the driving force of the "gradual" semiconductor-metal transition of La_2NiO_4.

Recently, Rao et al.[9] have reported on the resistivity and the magnetic susceptibility of a single crystal of La_2NiO_4. They have found a very large positive coefficient of temperature, an irreversible transition, in the resistivity curve of La_2NiO_4 at 550 K. It was presumed that the irreversible transition was attributable to the effect of strain, crystal distortion, charge density waves, or nonstoichiometry. Their finding of the irreversible transition raised the question that the "gradual" semiconductor-metal transition of La_2NiO_4 might be related to the nonstoichiometry, particularly to that of the lattice oxygen.

By the way, the analogous compound, $La_{2-x}Sr_xNiO_4$, has also been reported to exhibit the "gradual" semiconductor-metal transition.[3,10] The temperature dependence of the electrical resistivity and the transport property of $La_{2-x}Sr_xNiO_4$ have previously been measured by the present authors under an inert atmosphere,[8] though the effect of oxygen deficiency on the electrical resistivity was not considered.

In this study, the effect of the oxygen vacancy on the electrical resistivity of $La_{2-x}Sr_xNiO_{4-y}$, especially on the resistivity of La_2NiO_{4-y} (x=0) and on that of $LaSrNiO_{4-y}$(x=1), was investigated at various temperatures and oxygen pressures.

Experimental

Preparation. The two oxides, La_2NiO_{4-x} and $LaSrNiO_{4-x'}$ were prepared by heating stoichiometric mixtures of La_2O_3 (Shin-etsu Chem. Ind. Co., Ltd.; 99.9%), $SrCO_3$ (prepared from reagent-grade $Sr(NO_3)_2$), and NiO (Kojundo Kagaku Co., Ltd.; 99.99%) in air at 1433 K for 25 h.

Electrical Resistivity Measurement. A sintered sample, 5 mm² in cross section and 5 mm long, was heated in 58000 Pa of oxygen at 1173 K for 2 h in a measurement cell before the resistivity measurements. The electrical resistivity of the sample was immediately measured in the same cell with the four-prove method in 98—58000 Pa of oxygen at 473—1173 K after preheating.

Thermogravimetric Analyses. The oxygen-vacancy concentrations, x, in La_2NiO_{4-x} and in $LaSrNiO_{4-x}$ were determined by thermogravimetric analyses. A powdered sample (about 5 g) was preheated in 58000 Pa of oxygen at 1173 K for 5 h; it was then weighed at room temperature to an accuracy of 0.01 mg. The sample was heated again at the prescribed oxygen pressure at 1173 K for 5 h and then weighed at room temperature. The oxygen vacancy concentration of a sample was evaluated from the weight and the weight loss of the sample. The vacancy content, x, was calculated from this equation:

$$x = \frac{\Delta W \times M(\mathrm{La_2NiO_4\ or\ LaSrNiO_4})}{W \times M(\mathrm{O})}, \tag{1}$$

where W was the weight of the sample after preheating, ΔW was the weight loss of the sample during the heating process, $M(La_2NiO_4$ or $LaSrNiO_4)$ was the formula weight of La_2NiO_4 or $LaSrNiO_4$, and M(O) was the atomic weight of oxygen. It was conveniently assumed for the calculation of x that La_2NiO_{4-x} an $LaSrNiO_{4-x}$ have very few oxygen vacancies, x=0, after preheating.

Results and Discussion

The crystal structure and the oxygen vacancy concentration of La_2NiO_{4-x} and $LaSrNiO_{4-x}$ are summarized in Table 1. The La_2NiO_{4-x} oxide was stable in oxygen down to 140 Pa at 1173 K, but was decomposed to some complex materials in vacuo (7 Pa) at the same temperature, while the $LaSrNiO_{4-x}$ oxide was stable to 1 Pa of oxygen at 1173 K.

The electrical resistivities of La_2NiO_{4-x} and $LaSrNiO_{4-x}$ were measured in the oxygen pressure range from 58000 to 100 Pa (Figs. 1 and 2). The resistivities of La_2NiO_{4-x} and $LaSrNiO_{4-x}$ are not oxygen-pressure-dependent below 581 K, but they decrease with an increase in the oxygen pressure over 673 K. The irreversible transition at 550 K found by Rao et al.[9] was not observed in the resistivity curves of La_2NiO_{4-x} in Fig. 1. The resistivity data in Fig. 1 also show that the electrical resistivity of La_2NiO_{4-x} is not

Table 1. Phases and Oxygen-Defect Concentrations of La_2NiO_{4-x} and $LaSrNiO_{4-x}$ at Various Oxygen Pressures at 1173 K

Formula	P/Pa[a]	$\Delta W/W$[b]	x[c]	Phase
La_2NiO_4	58000	0.00000	0.0000	La_2NiO_4
	31100	−0.00002	−0.0005	La_2NiO_4
	13100	0.00023	0.0057	La_2NiO_4
	5870	0.00032	0.0080	La_2NiO_4
	2670	0.00043	0.0107	La_2NiO_4
	400	0.00083	0.0207	La_2NiO_4
	140	0.00090	0.0226	La_2NiO_4
	7	0.00761	0.1905	Decomposed
$LaSrNiO_4$	58000	0.00000	0.0000	$LaSrNiO_4$
	30700	0.00003	0.0007	$LaSrNiO_4$
	10700	0.00043	0.0093	$LaSrNiO_4$
	4930	0.00076	0.0165	$LaSrNiO_4$
	1330	0.00114	0.0250	$LaSrNiO_4$
	430	0.00149	0.0325	$LaSrNiO_4$
	130	0.00532	0.116	$LaSrNiO_4$
	1	0.01035	0.226	$LaSrNiO_4$

a) Oxygen pressure. b) Decrease in weight of the sample during the heating process in oxygen at 1173 K. c) x in La_2NiO_{4-x} or x in $LaSrNiO_{4-x}$ (see. Eq. 1).

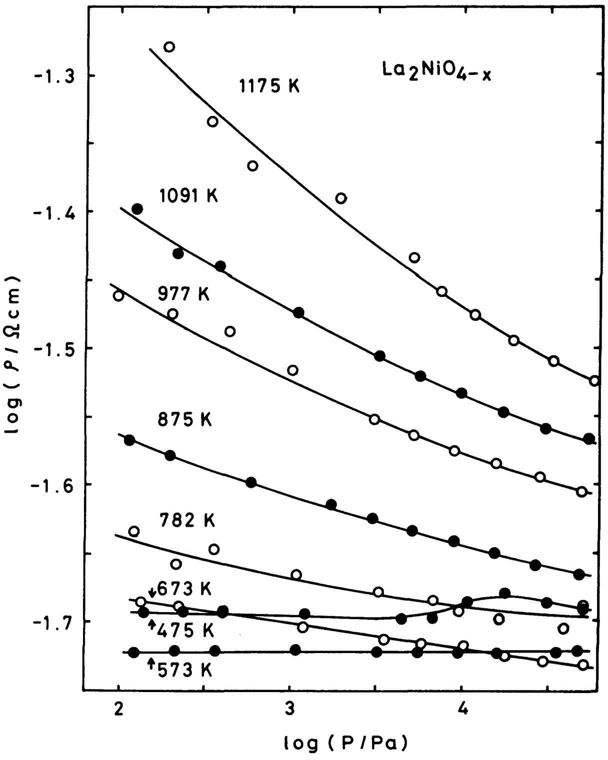

Fig. 1. Oxygen pressure dependence of electrical resistivity for La_2NiO_{4-x}.

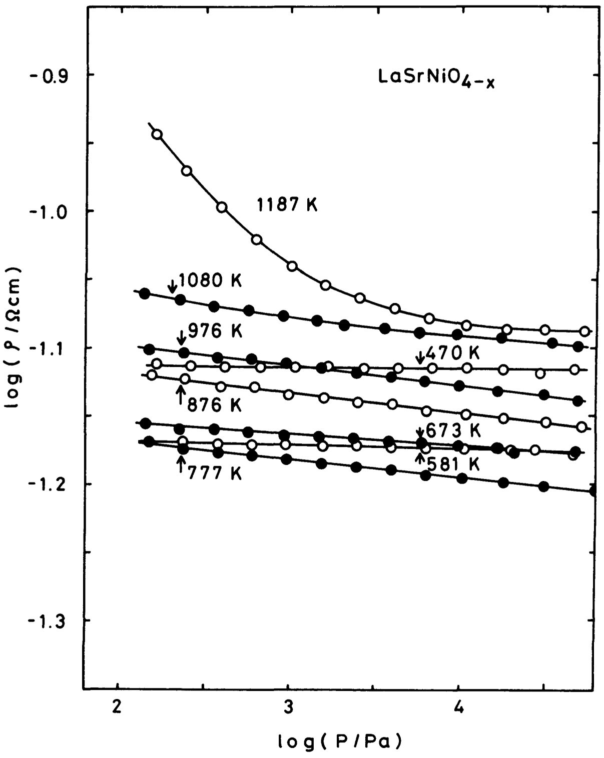

Fig. 2. Oxygen pressure dependence of electrical resistivity for $LaSrNiO_{4-x}$.

oxygen-pressure dependent at 550 K. The irreversible transition by Rao et al. would not be related to the stoichiometry of oxygen of the sample if the resistivity measurements had been performed under an atmosphere containing 100 Pa or more of oxygen.

Figures 1 and 2 show that the slopes in the resistivity curves of La_2NiO_{4-x} and $LaSrNiO_{4-}$ are negative over 673 K. Both La_2NiO_{4-x} and $LaSrNiO_{4-x}$ are p-type conductors in this temperature range. The slope of La_2NiO_{4-x} (Fig. 1) is much larger than that of $LaSrNiO_{4-x}$ (Fig. 2) at the same temperature.

Figure 3 shows the temperature dependence of the electrical resistivities for La_2NiO_{4-x} and $LaSrNiO_{4-x}$ at 316, 3160, and 31600 Pa of oxygen, where the resistivity plots are based on readings of Figs. 1 and 2. A "gradual" semiconductor-metal transition is observed in the resistivity curves of La_2NiO_{4-x} and $LaSrNiO_{4-x}$ at any oxygen pressure. The resistivity curves in Fig. 3 seem to imply that the release of the lattice oxygen is not responsible for the origin of the appearance of the

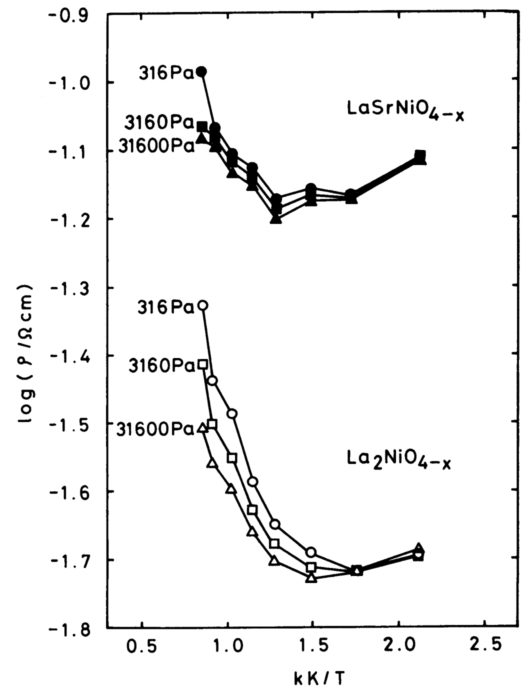

Fig. 3. Temperature dependence of electrical resistivity for La_2NiO_{4-x} and for $LaSrNiO_{4-x}$.

"gradual" semiconductor-metal transition. The transition temperature is, however, apparently affected by the atmospheric oxygen pressure, for the transition point is shifted to a higher temperature with the increase in the oxygen pressure.

The oxygen-pressure dependence of the oxygen-vacancy concentration of La_2NiO_{4-x} and $LaSrNiO_{4-x}$ is given in Fig. 4. The x values, the oxygen-vacancy concentration, of La_2NiO_{4-x} and $LaSrNiO_{4-x}$ are almost equal to 0.00 at $\log(P/\mathrm{Pa})=4.5$ and 4.8. The x value of La_2NiO_{4-x} is greater than that of $LaSrNiO_{4-x}$ at the same oxygen pressure at 1173 K. The lattice oxygen of $LaSrNiO_{4-x}$ is much easily released from the bulk than that of La_2NiO_{4-x}.

Figure 5 shows the electrical conductivity vs. the oxygen vacancy concentration plots of La_2NiO_{4-x} and $LaSrNiO_{4-x}$ at 1173 K. The density of the charge carriers of $LaSrNiO_4$ should be larger than that of La_2NiO_4 at 1173 K, as the slope of the conductivity curve of La_2NiO_{4-x} is larger than that of $LaSrNiO_{4-x}$.

For obtaining the density of the charge carriers of oxygenical-stoichiometric La_2NiO_4 and $LaSrNiO_4$, the data were treated as follows. In general, the electrical conductivity, σ, of a compound can be written as:

$$\sigma = ne\mu, \tag{2}$$

where n is the density of the charge carriers and where μ is the drift mobility. If (the density of the charge carriers) n is divided into two densities, that is, the electronic density at the stoichiometric oxygen composition, n_0, and the density produced from the oxygen vacancy, n_v, the electrical conductivity of the compound will be altered thus:

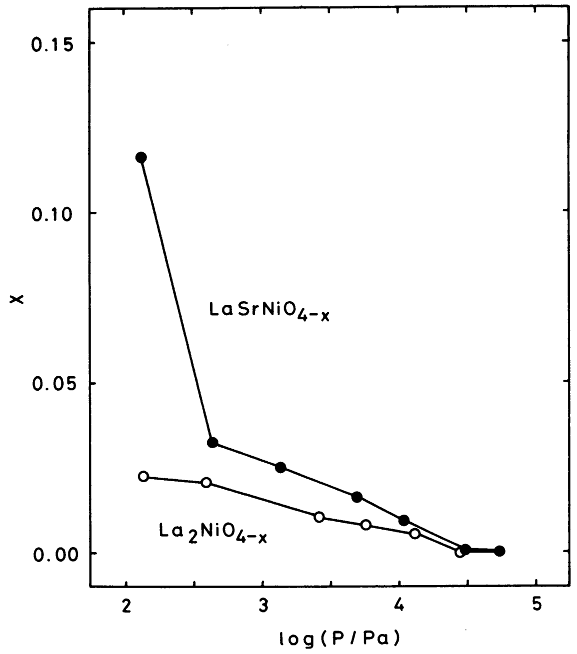

Fig. 4. Oxygen pressure dependence of oxygen content x for La_2NiO_{4-x} and for $LaSrNiO_{4-x}$.

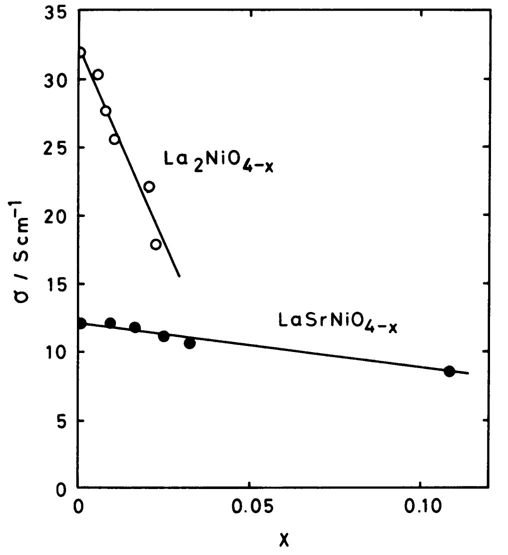

Fig. 5. Oxygen content dependence of electrical conductivity for La_2NiO_{4-x} and for $LaSrNiO_{4-x}$.

$$\begin{aligned}\sigma &= (n_0 + n_V)e\mu \\ &= (n_0 e\mu) + (e\mu)n_V. \end{aligned}\tag{3}$$

In the case of La_2NiO_{4-x} and $LaSrNiO_{4-x}$, the electronic density, n_v, is written as:

$$\begin{aligned} n_V &= \frac{Ax}{V(La_2NiO_{4-x} \text{ and } LaSrNiO_{4-x})} \\ &= \frac{AZx}{a_0{}^2 c_0}, \end{aligned}\tag{4}$$

where A is a constant of 1 or 2, x is the x in La_2NiO_{4-x} or $LaSrNiO_{4-x}$, $V(La_2NiO_{4-x}$ or $LaSrNiO_{4-x})$ is the lattice volume[10,11], Z is the crystallographic Z value (which is 2 in the case of La_2NiO_4 and $LaSrNiO_4$), and a_0 and c_0 are the lattice constant at room temperature (a_0=0.38617 nm, c_0=1.2683 nm for La_2NiO_{4-x}11) and a_0=0.3821 nm, c_0=1.2550 nm for $LaSrNiO_{4-x}$10)).

In the case of the electron conduction, the A constant is unity when a neutral oxygen vacancy, which is formed by the transfer of an oxygen on a normal site to the gaseous state, donates only one electron to the conduction band:

$$V_O^X \rightleftharpoons V_O^{\cdot} + e'. \qquad (5)$$

The A constant is 2 when the vacancy gives two electrons to the band12):

$$V_O^X \rightleftharpoons V_O^{\cdot\cdot} + 2e', \qquad (6)$$

but A is −1 (Eq. 5) or −2 (Eq. 6) in the case of hole conduction.

The electrical conductivity of La_2NiO_{4-x} or $LaSrNiO_{4-x}$, therefore, can be expressed as:

$$\sigma = (n_0 e\mu) + \frac{AZxe\mu}{a_0^2 c_0}. \qquad (7)$$

The electrical conductivity vs. x plot in Fig. 5 show that the conductivities of La_2NiO_{4-x} and $LaSrNiO_{4-x}$ decrease linearly with the increase in x, as is to be expected from Eq. 7. This result supports the validity of the assumption at the induction of Eq. 7 that is, Eqs. 3 and 4. The negative slopes in the conductivity curves imply that the holes are charge carriers of La_2NiO_{4-x} and of $LaSrNiO_{4-x}$ ($A<0$).

The drift mobility, μ, and the density of the holes, n_0, of oxygen stoichiometric La_2NiO_4 or $LaSrNiO_4$ are given from the slope and the intercept of the conductivity line in Fig. 5 by applying Eq. 7. The results are tabulated in Table 2. Unfortunately, the calculated values of n_0 and μ have some equivocality, as it is difficult to determine from the conductivity data where A is −1 or where it is −2. Thus, n_0 and μ were calculated in two ways, namely, in the cases of A=−1 and −2.

The drift mobility of La_2NiO_4 is significantly larger than that of $LaSrNiO_4$. However, the density of the charge carriers of $LaSrNiO_4$ is much greater than that of La_2NiO_4. Table 2 shows that the 0.056—0.112 electron for La_2NiO_4 and the 0.38—0.76 electron for $LaSrNiO_4$ are in a formula.

Goodenough's model for $La_2NiO_4$5−7) suggests that the electronic density of a state is not so high at the top of the conduction band of La_2NiO_4 in the metallic state. The observed value of the density, n_0, was 5.9—11.9×10^{20} cm^{-3}, as is shown in Table 2.

The $LaSrNiO_4$ oxide has the same crystal structure as La_2NiO_4. If the band structure of $LaSrNiO_4$ is the same as that of Goodenough's model for La_2NiO_4 and if $LaSrNiO_4$ has fewer conduction electrons than $LaSrNiO_4$ by one electron a formula, one hole must exist in $LaSrNiO_4$. Table 2 indicates that the number of holes in $LaSrNiO_4$ is somewhat smaller than the expected value of one. This result may imply that a few holes are not free in the conduction band of $LaSrNiO_4$.

Table 2. Drift Mobilities and Densities of State for La_2NiO_4 and $LaSrNiO_4$ at 1173 K

Formula	A a)	μ(drift) b)	n_0 c)	Electrons
		cm^2 V^{-1} s^{-1}	10^{20} cm^{-3}	Formula
La_2NiO_4	−1	0.34	5.9	0.056
	−2	0.17	11.9	0.112
$LaSrNiO_4$	−1	0.018	41.3	0.38
	−2	0.0091	82.6	0.76

a) "A" is a constant in Eq. 7

$$O \rightleftarrows V_O^X + 1/2O_2$$
$$A=\pm1:\ V_O^X \rightleftarrows V_O^{\cdot} + e'$$
$$A=\pm2:\ V_O^X \rightleftarrows V_O^{\cdot\cdot} + 2e'$$

b) Drift mobility. c) Density of state.

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