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Studies on the $La_{2-x}Sr_xNiO_4$ $(0 \leqslant x \leqslant 1)$ System

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A new series of solid solutions of composition $La_{2-x}Sr_xNiO_4$ $(0 \leqslant x \leqslant 1)$ in which the oxidation state of nickel varies from +2 at $x = 0$ to +3 at $x = 1$ has been prepared. All the members of the system crystallize in the tetragonal K_2NiF_4 structure. The tetragonality ratio c/a shows a maximum at $x = 0.5$ which is interpreted as arising from a weak cooperative Jahn–Teller distortion due to octahedral site low-spin Ni^{3+} ions. The variation of electrical properties in the system is attributed to changes in electronic configuration of Ni^{3+}.

Introduction

Ternary oxides with the general formula A_2BO_4 crystallize in the tetragonal K_2NiF_4 structure (*1*) if the A cation is fairly large (1.0 < r_A < 1.9 Å) and the smaller B cation (0.5 < r_B < 1.2 Å) is stable in octahedral coordination (*2*). The structure is closely related to the perovskite structure in that the B ion octahedra share their corners but only in two dimensions, (001) planes. Along the third direction [001], the B ions are separated from one another by two oxygens and two A ions. Hence any exchange interaction between B ions through oxide ion must be limited to the perovskite-like layers in (001) planes. The structure and physical properties of many lanthanide-3*d* transition metal oxides of Ln_2BO_4 composition with K_2NiF_4 structure have been studied (*2–5*). In the present work, the structure and electrical properties of the system $La_{2-x}Sr_xNiO_4$ are investigated in the composition range $0 \leqslant x \leqslant 1$ in which the oxidation state of nickel is expected to vary from +2 to +3. The end members La_2NiO_4 and $LaSrNiO_4$ have already been reported (*6*, *7*). Electrical transport in La_2NiO_4 has been studied (*3*, *4*) but that of $LaSrNiO_4$ was not known. Very recently Demazeau *et al.* (*8*) have studied $LnSrNiO_4$ oxides.

Experimental

Solid solutions of the $La_{2-x}SR_xNiO_4$ system for various values of x from 0 to 1 were prepared from the component oxides La_2O_3 (dried at 900°C), NiO and $SrCO_3$. The mixtures were thoroughly ground in an agate ball mill for an hour and heated at 1200°C for 3 days with intermittent grinding. After this treatment, the samples were pelletized and sintered for one day under the same conditions. Compositions with $x \leqslant 0.3$ were made in air while those with $x > 0.3$ were prepared in an O_2 atmosphere. A sample of La_2NiO_4 was also prepared in oxygen-free nitrogen. Analyses of oxidation state of nickel were

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TABLE I

ANALYTICAL AND CRYSTALLOGRAPHIC DATA OF THE $La_{2-x}Sr_xNiO_4$ SYSTEM

Composition x	Average oxidation state of Ni	Lattice parameters [Å] a	Lattice parameters [Å] c	c/a
0	2.15	3.865	12.630	3.268
0[a]	2.05	3.865	12.632	3.268
0.1	2.20	3.854	12.646	3.280
0.2	2.31	3.846	12.683	3.298
0.3	2.38	3.836	12.699	3.310
0.5	2.55	3.817	12.766	3.345
0.6	2.63	3.817	12.717	3.332
0.7	2.71	3.821	12.689	3.321
0.8	2.80	3.820	12.645	3.310
0.9	2.91	3.821	12.590	3.295
1.0	3.00	3.821	12.550	3.284

[a] Sample prepared in N_2.

made by the Bunsen method (Table I). The experimental procedures for the determination of lattice constants, electrical conductivity, and Seebeck coefficient were the same as given in an earlier paper (*9*).

Results and Discussion

The crystallographic data of $La_{2-x}Sr_xNiO_4$ solid solutions are given in Table I and Figs. 1 and 2. All the members crystallize in the tetragonal K_2NiF_4 structure as do the end-members (Table II). The unit cell volume shows a smooth, almost linear, decrease with x, although Sr^{2+} ion is bigger (between the radii for CN(VIII) and CN(X) interpolated value for CN(IX) $r_{Sr^{2+}} = 1.27$ Å) than La^{3+} ($r_{La^{3+}}$ = 1.20 Å for CN(IX) (*10*). This is understandable in terms of the change in oxidation state of nickel. Substitution of La^{3+} by Sr^{2+} in La_2NiO_4 is accompanied by oxidation of a corresponding amount of nickel from +2 to +3 to preserve electroneutrality. The series can therefore be formulated as $La^{3+}_{2-x}Sr^{2+}_xNi^{2+}_{1-x}Ni^{3+}_xO_4$. The trivalent nickel created by strontium substitution may exist either in the low-spin ($t_{2g}^6e_g^1$) or high-spin ($t_{2g}^5e_g^2$) state. In many oxide lattices, for example $LaNiO_3$ and $NaNiO_2$ (*11*, *12*), trivalent nickel is known to exist in the low-spin state. Since

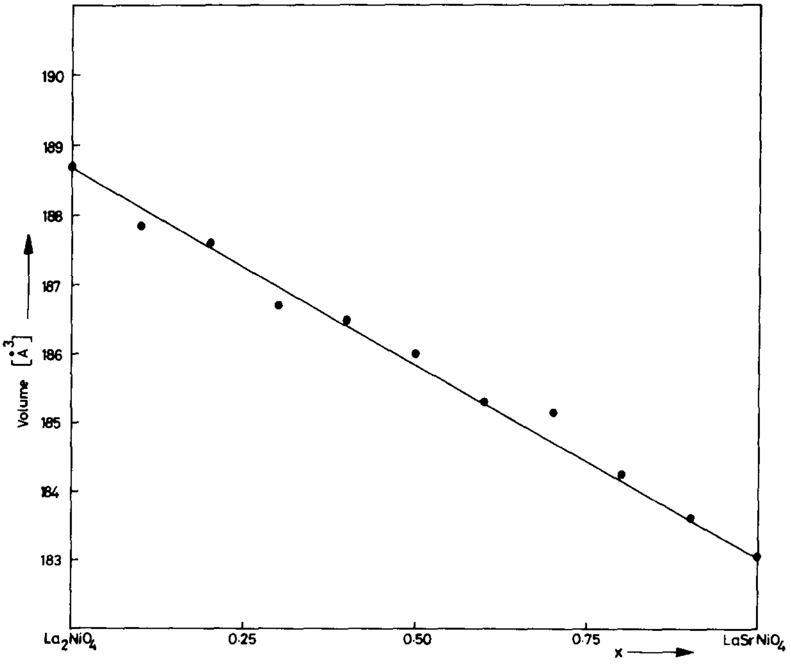

FIG. 1. Variation of unit cell volume in the $La_{2-x}Sr_xNiO_4$ system as a function of x.

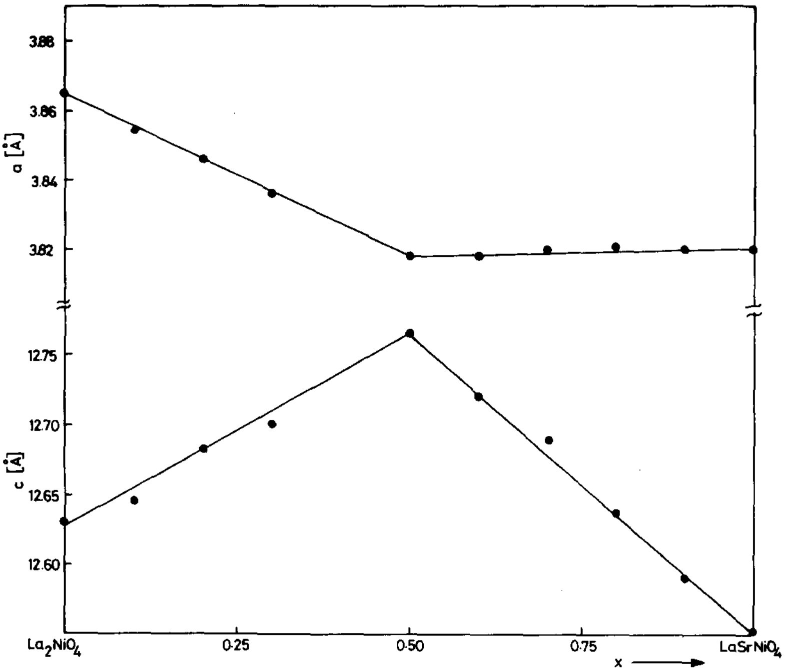

FIG. 2. Variation of the lattice parameters in the $La_{2-x}Sr_xNiO_4$ system as a function of x.

TABLE II

X-RAY POWDER DIFFRACTION PATTERN OF $La_{1.5}Sr_{0.5}NiO_4$

d_{obs} [Å] (I)	$d_{calc}{}^a$ [Å]	$h\,k\,l$
6.39 (vw)	6.383	0 0 2
3.65 (m)	3.657	1 0 1
3.188 (m)	3.190	0 0 4
2.837 (vs)	2.841	1 0 3
2.698 (vs)	2.699	1 1 0
2.125 (m)	2.127	0 0 6
2.058 (m)	2.060	1 1 4
1.908 (s)	1.908	2 0 0
1.691 (w)	1.692	2 1 1
1.669 (w)	1.670	1 1 6
1.643 (w)	1.645	1 0 7
1.637 (w)	1.638	2 0 4
1.583 (m)	1.584	2 1 3
1.419 (w)	1.420	2 0 6
1.372 (w)	1.373	1 1 8
1.349 (w)	1.349	2 2 0
1.244 (vw)	1.243	2 2 4
1.222 (w)	1.219	3 0 3
1.206 (m)	1.207	3 1 0

[a] $a = 3.817 \pm 0.002$ Å; $c = 12.766 \pm 0.013$ Å.

the Ni–O–Ni distance (~3.85 Å) in the present system is smaller than that in NiO (4.177 Å), it is reasonable to expect that the trivalent nickel in $La_{2-x}Sr_xNiO_4$ exists in the low-spin state. Magnetic susceptibility measurements on $LaSrNiO_4$ (*8*) has also revealed that Ni^{3+} in this compound is present in the low-spin state. The ionic radius of Ni^{3+} in low-spin state (0.56 Å) is much smaller than that of Ni^{2+} (0.70 Å) (*10*) and therefore the increase in A-ion size by Sr^{2+} substitution is more than compensated by the decrease of the nickel ion size due to oxidation and an overall decrease in unit cell volume occurs with increasing x.

The variation of the tetragonal lattice parameters a and c in the system does not follow Vegard's rule (Fig. 2); instead, while the a axis decreases up to $x = 0.5$ and remains constant thereafter, the c axis shows an increase up to $x = 0.5$ and a decrease in the region $0.5 < x < 1.0$. The tetragonality ratio c/a shows a maximum at the composition $x = 0.5$ (3.345)

(Table I). The result may be explained as follows. Assuming that the trivalent nickel formed with increasing x is in the low-spin state, its electronic configuration $t_{2g}^6e_g^1$ is susceptible to Jahn–Teller distortion. The fact that the c axis increases while the a axis decreases up to $x = 0.5$ seems to indicate that the distortion of the low-spin state Ni^{3+}–O octahedra is to produce four short and two long bonds and that the single e_g electron is ordered in the d_{z^2} orbital. For the tetragonal K_2NiF_4 structure, the c/a ratio is always found to be around 3.30 except when there is a Jahn–Teller ion present (*2*). For example, K_2CuF_4 shows a c/a ratio of 3.07, while for La_2CuO_4 the ratio is found to be 3.46 (*13*). For $La_2Ni_{0.5}Li_{0.5}O_4$, a compound containing Ni^{3+} in low-spin state, a similar abnormal c/a (3.43) has been reported (*7*). In the present system, the distortions however appear to be very weak as indicated by only a slight increase of the c/a ratio from its normal value of 3.3. It is interesting to note that in the $La_{2-x}Sr_xNiO_4$ system, maximum distortion is found at a composition with 50% Ni^{3+} and 50% Ni^{2+}. With increasing Ni^{3+} concentration, the c/a ratio decreases reaching a normal value of 3.3 at 100% Ni^{3+} in $LaSrNiO_4$. This seems to indicate that with increasing concentration of trivalent nickel, its electronic configuration switches over to $t_{2g}^6d_{x^2-y^2}^1$ from $t_{2g}^6d_{z^2}$, the reason being that the former configuration would permit greater covalent interaction between $d_{x^2-y^2}$ orbitals of nickel with the p_σ orbitals of the oxide ion in the perovskite layers. This is also supported by the finding that the electrical resistivity decreases for $x >$ 0.5, finally reaching a low value at $x = 1.0$ (Fig. 3). Demazeau *et al.* (*8*) also found that the electrical resistivity of $SrLnNiO_4$ (*Ln* = La, Sm, Gd, and Eu) is small having a low activation energy ($\Delta E \simeq 0.01$ eV). These authors interpret their results by assuming that the e_g electron of Ni^{3+} in $LaSrNiO_4$ is present in $d_{x^2-y^2}$ orbital which broadens out into a narrow σ^*-band because of strong Ni^{3+}–O covalent interaction along the perovskite layers, (001) planes.

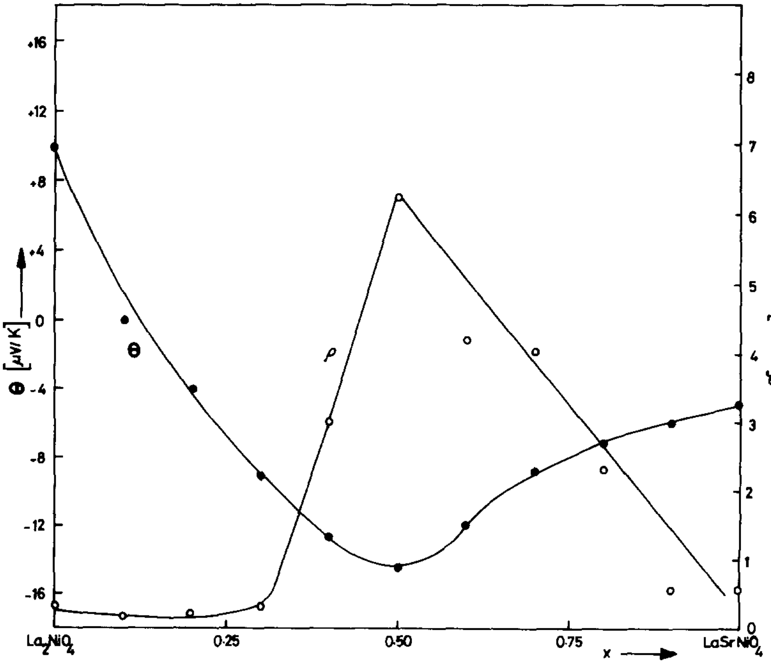

FIG. 3. Room temperature resistivity ρ and Seebeck coefficient Θ in the $La_{2-x}Sr_xNiO_4$ system as a function of x.

Electrical

La_2NiO_4 is reported to be an *n*-type semiconductor at room temperature undergoing a transition to metallic conductor around 500°K (*4*). We have found that La_2NiO_4 prepared in air contains about 15% of trivalent nickel. When the preparation is made in oxygen-free nitrogen, almost stoichiometric La_2NiO_4 with 3–5% trivalent nickel is obtained. The electrical properties of both the samples are slightly different: a sample prepared in air shows a lower resistivity ($\rho_{300°K} = 0.3$ ohm cm) and a lower Seebeck coefficient ($\Theta_{300°K} = +10$ $\mu V/°K$) than those of the sample prepared in N_2 ($\rho_{300°K} = 2$ ohm cm; $\Theta_{300°K} = +70$ $\mu V/°K$). The transition to metallic conduction occurs however, in both the samples around 600°K.

The variation of room temperature resistivity and Seebeck coefficient in the $La_{2-x}Sr_xNiO_4$ system is given in Fig. 3. Both the resistivity and the Seebeck coefficient remain fairly low throughout the series. Even then a progressive trend in the variation can be discerned. Both ρ and Θ show extreme values at $x = 0.5$, the same point where there is a break in the lattice parameters. The increase of resistivity with x up to $x = 0.5$ may arise from the oxidation of Ni^{2+} to a low-spin state Ni^{3+}. Goodenough (*5*) argues from structure and electronic considerations that in La_2NiO_4 the d_{z^2} orbitals are localized because of weak interaction between Ni ions along the *c* axis, while the $d_{x^2-y^2}$ orbitals within perovskite layers become itinerant through strong Ni–O–Ni interaction. The fairly low resistivity at room temperature and the transition to metallic behavior of La_2NiO_4 have been attributed to the delocalized $d_{x^2-y^2}$ orbitals. In the $La_{2-x}Sr_xNiO_4$ system, the crystallographic data indicate that the low-spin Ni^{3+} experiences a weak Jahn–Teller distortion up to $x = 0.5$ with the possible electron configuration, $t_{2g}^6 d_{z^2}^1$. Introduction of such Ni^{3+} ions having no $d_{x^2-y^2}$ electrons would bring about a decrease in the Ni ($d_{x^2-y^2}$)–O (p_σ)–Ni ($d_{x^2-y^2}$) interaction which would result in increased localization of charge carriers with increasing x. The maximum in the resistivity and Seebeck coefficient at $x = 0.5$ is thus understandable in terms of the Jahn–Teller distortion of Ni^{3+} ions. In the region $x > 0.5$, the resistivity decreases while the Seebeck coefficient becomes less negative, which may arise from a change of the electronic configuration of Ni^{3+} to $t_{2g}^6 d_{x^2-y^2}^1$ and a consequent increase of covalent interaction between nickel and oxygen ions, as already explained.

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References

1. D. BALZ AND K. PLIETH, *Z. Elektrochem.* **59**, 545 (1955).
2. J. M. LONGO AND P. M. RACCAH, *J. Solid State Chem.* **6**, 526 (1973).
3. M. FOEX, *Bull. Soc. Chim. France* **1961**, 109.
4. P. GANGULY AND C. N. R. RAO, *Mater. Res. Bull.* **8**, 405 (1973).
5. J. B. GOODENOUGH, *Mater. Res. Bull.* **8**, 423 (1973).
6. A. RABENAU AND P. ECKERLIN, *Acta Crystallogr.* **11**, 304 (1958).
7. G. BLASSE, *J. Inorg. Nucl. Chem.* **27**, 2683 (1965).
8. G. DEMAZEAU, M. POUCHARD, AND P. HAGENMULLER, *J. Solid. State Chem.* **18**, 159 (1976).
9. J. GOPALAKRISHNAN, G. COLSMANN, AND B. REUTER, *Z. Anorg. Allg. Chem.* **424**, 155 (1976).
10. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr. Part B* **25**, 925 (1969).
11. J. B. GOODENOUGH AND P. M. RACCAH, *J. Appl. Phys.* **36**, 1031 (1965).
12. R. WARD, *Prog. Inorg. Chem.* **1**, 475 (1959).
13. D. BABEL, *Struct. Bonding* **3**, 34 (1967).