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Phase Relations in the La–Ni–O System: Influence of Temperature and Stoichiometry on the Structure of La_2NiO_4

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This paper reports a study of the stability of the various phases in the La–Ni–O system and of the influence of temperature and stoichiometry on the crystal structure of La_2NiO_4. Several compositions have been synthesized, among which the second term of the homologous series $La_{n+1}Ni_nO_{3n+1}$ is stable in air up to 1200°C, this temperature probably being dependent on the oxygen partial pressure. Above 1200°C for $La/Ni < 2$ the observed phases are La_2NiO_4 and NiO, a result which is important for the preparation of compounds in this system. The observed crystal structure of La_2NiO_4 is affected by the stoichiometry of the compound. Under reducing conditions the structure is orthorhombic rather than tetragonal with $a = 5.4614$ Å, $b = 5.5322$ Å, $c = 12.527$ Å for the most reduced sample. The possibility is raised that this is the real structure of La_2NiO_4. The thermal expansion coefficient has been calculated from the evolution of the unit cell with temperature. Good agreement is obtained between microscopic X-ray data and macroscopic measurements giving a mean thermal expansion coefficient of approximately $\bar{\alpha} = 15 \times 10^{-6}$ °C^{-1} between 20 and 1100°C. The tetragonal c/a ratio has been used to analyze the deformation of the unit cell with temperature. The ratio attains a maximum for $T \sim 600$ K and this is interpreted as being associated with the transition from a semiconductor to a metallic state.

1. Introduction

In the past 2 decades there has been considerable interest in a class of highly conducting ternary oxides (*1*) in which the conductivity arises from the combination of a transition metal with another more stable element such as lanthanum. Among these, doped lanthanum chromite (*2, 3*) has been studied for application in ceramic heating elements for high-temperature furnaces used in oxidizing atmospheres (1800°C in air). More conductive materials than lanthanum chromite have also been developed, some of which are listed in Table I. Among these the lanthanum nickelates are an interesting compromise between high conductivity ($LaNiO_3$ has a conductivity comparable to graphite) and good thermal stability (La_2NiO_4).

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TABLE I

Compound	Electrical conductivity	Comments
	$(\Omega\ \mathrm{cm})^{-1}$	
$La_{1-x}Sr_xCoO_3$ $x = 0.4$	3.5×10^3	Unknown stability, prepared at 1200–1300°C (*4*)
$La_{2-x}Sr_xCuO_{4-x/2+\delta/2}$ $x = 0.33$	1×10^3	Unknown stability, prepared at 1200–1300°C (*5*)
Graphite	1×10^3	Unstable in air above 700°C (*6*)
$LaNiO_3$	$2–4 \times 10^2$ $2–7 \times 10^1$	Decomposes above 850°C in air (*7–9*)
$Ba_3La_3CuO_{14+y}$ $y = 0.43$	8×10^1	Unknown stability, prepared at 1200–1300°C (*10*)
La_2NiO_4	4×10^1 7×10^0	Stable up to 1400–1500°C (*7, 9*)
La_2CuO_4	1×10^1	Prepared at 1200–1300°C (*5*)
$LaSrNiO_4$	2×10^0 4×10^{-2}	Unknown stability, prepared at 1200°C (*11, 12*)
$LaCoO_3$	1.5×10^0 1×10^{-1}	Transforms in lower oxides: $La_4Co_3O_{10}$–La_2CoO_4 (*4, 13*)
$La_{1-x}Ca_xCrO_3$ $x = 0.1$	9×10^{-1}	Stable to very high temperature. Used as heating elements of furnaces (*3*)
$La_{1-x}Sr_xCrO_3$ $x = 0.1$	4×10^{-1}	Stable to very high temperature (*14*)
$LaBaNiO_4$	1×10^{-3}	Unknown stability, prepared at 1200°C (*15*)
$LaCrO_3$	8×10^{-3} 4×10^{-5}	Stable up to its melting point, but loses Cr_2O_3 (*14, 16*)

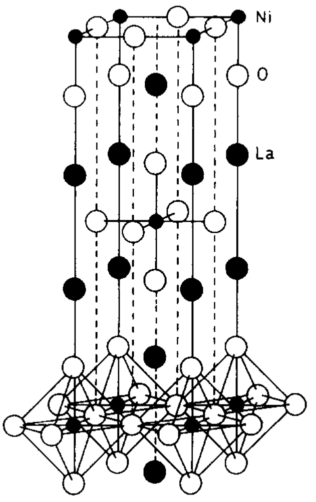

FIG. 1. Structure of La_2NiO_4 (K_2NiF_4).

Fundamental problems are also of interest in this class of compounds. Lanthanum nickelate, La_2NiO_4, belongs to the K_2NiF_4 family (*17*). In this structure, perovskite-type Ni–O octahedra share corners along (001) planes, while in the [001] direction the Ni ions are separated by two oxygen and two La ions, (Fig. 1). Magnetic exchange interactions (*18, 19*) and possibly electrical transport are thought to occur through the Ni–O–Ni bonds in the plane of the perovskite layer giving rise to interesting anisotropic effects (*20*). The conductivity of La_2NiO_4 is "metallic" above 600 K (*7, 9*) but becomes thermally activated below this transition temperature to give a form of semiconductor to metal transition. The metallic conductivity has been explained by the formation of an itinerant $\sigma_{x^2-y^2}$ band due to strong Ni–O–Ni interactions along the basal plane (*21*), whereas d_{z^2} orbitals contain localized electrons as a result of relatively weak interactions between the perovskite layers. The appearance of semiconducting properties has been interpreted to result from the splitting of the $\sigma_{x^2-y^2}$ band by antiferromagnetic ordering. However, no evidence of long-range ordering has been found (*19*) and only short-range ordering has been reported to explain a small deviation from the Curie–Weiss law. However, this deviation does not occur in the same temperature range as the transition from the semiconducting to the metallic state.

One of the weak points of earlier studies has been the neglect of the possible effects of nonstoichiometry. This is paradoxical because from a practical point of view the stability against low oxygen activity is of great importance. Recent studies on the La–Ni–O system have given evidence for a homologous series of compounds whose formula is $La_{n+1}Ni_nO_{3n+1}$ (*22*) and the structure of which give rise to intergrowths for $n > 2$. La_2NiO_4 has been considered a pure phase (see Rao *et al.* (*20*)) and there have been no reports of intergrowths in single crystals of this material. Intergrowths in ceramic sample (*22*) appear to depend on the method of preparation. It is therefore crucial to elucidate the effects of nonstoichiometry (either positive or negative) on the structure and electrical properties.

In a preliminary study we have investigated the thermal stability of several compositions in the system La–Ni–O, and have then considered more carefully the evolution of the structure of La_2NiO_4 as the temperature is increased. An anomaly in the parameter (c/a) has been discovered in the same temperature range as the semiconductor to metal transition, and the effect on the structure of reducing the stoichiometry has been investigated.

II. Experimental

Several batches of powder were prepared to investigate, first, the phase relations in the La–Ni–O system and, second, the thermal expansion of La_2NiO_4. The pure composition of La_2NiO_4 was prepared by repeated firing and grinding cycles at 1200°C in air of stoichiometric mixtures of the starting oxides (La_2O_3 and NiO of 3 *N* purity). Prior to use, the La_2O_3 and NiO were heated at 1200°C for 24 hr and cooled in a water-vapor-free atmosphere. Sintered material was obtained by isostatic compaction at 400 MPa followed by firing at 1300°C for 48 hr in air. The resulting density was close to 90% theoretical. $LaNiO_3$ was synthesized by mixing La_2O_3 with NiO and Na_2CO_3 (*23*). The sodium compound was used as a flux (*7, 23*) and the product was washed several times after firing in order to remove the sodium.

Mixtures of La_2NiO_4 and $LaNiO_3$ were also prepared to make materials with a La/Ni ratio ranging from 2 to 1. Special attention was given to the La_2NiO_4-rich side where several compositions were either quenched or slowly cooled in air (La/Ni = 1.99, 1.97, 1.95, 1.925). In subsequent research, the reactivity of the powder was significantly increased by using a pyrolysis technique for liquid mixtures of nitrates in a furnace at 1000°C. The best reactivity was obtained for liquid nitrates sprayed as fine droplets into the hot furnace. This procedure enabled us to synthesize the nominal composition of $La_3Ni_2O_7$ with less than 10% of the unreacted products (La_2NiO_4, NiO).

Thermal expansion measurements were carried out with a laboratory dilatometer and a high-temperature X-ray chamber. For the X-ray measurements, the sintered material was ground into a fine powder and deposited on a platinum ribbon which was used to heat the sample. The temperature was measured with a Pt–PtRh 10% thermocouple (0.2 mm diam.) spot welded onto the centre of the ribbon. Cu*Kα* radiation was used with an angular range 2*θ* between 25 and 60° with a scanning speed of 1° min^{-1}. The position of the ribbon was adjusted in front of the X-ray source by optimization of the peak shape of a known X-ray line and the thermal expansion of the ribbon was mechanically compensated. All the X-ray powders were autocalibrated using the Bragg relations between simple lines ((100) and (200) reflexions, for example). Macroscopic thermal expansion up to 1100°C was measured using a push-rod alumina dilatometer.

III. Results

III.1. Phase Relations in the La–Ni–O System in Air

Samples with La/Ni ratios between 2.0 and 1.925 were slowly cooled or quenched in cold water after annealing at 1300°C for 10 hr. The cell parameters are given in Table II. There is no visible variation of the cell parameters with the ratio La/Ni. A small amount of unreacted NiO is observed, close to the limit of detection.

Below 1200°C in the ratio range 2 > La/Ni > 1.5, mixtures of pure La_2NiO_4 and another phase identified as $La_3Ni_2O_7$ (*22*) have been observed (Fig. 2). The latter compound is the second term of the homologous series $La_{n+1}Ni_nO_{3n+1}$ (*22*). Although difficult to obtain pure, this phase was synthesized with a small amount of unreacted products. Its structure is orthorhombic and despite a slow decomposition above 1200°C remains present until 1290°C (a few molar % is detectable after 14 hr at that temperature). The decomposition reaction is

$$2\ La_3Ni_2O_7 \rightarrow 3\ La_2NiO_4 + NiO + \tfrac{1}{2}\ O_2 \quad (I)$$

and is reversible according to recent experiments.

For the ratio range 1.5 > La/Ni > 1 below 1200°C, mixtures of unresolved phases of the series $La_{n+1}Ni_nO_{3n+1}$ were detected and it is believed that equilibrium had not

TABLE II

La/Ni	Quenched samples (1300°C, in cold water) 2.0	1.99	1.97	1.95	1.925	1.9
a(Å)	3.865	3.872	3.865	3.865	3.865	3.865
c(Å)	12.625	12.630	12.619	12.619	12.619	12.625
c/a	3.266	3.261	3.265	3.265	3.265	3.265
	Slowly cooled samples (1300°C, 200°C hr^{-1})					
La/Ni	2.0	1.99	1.97	1.95	1.925	1.9
a(Å)	3.861	3.862	3.860	3.861	3.859	3.861
c(Å)	12.673	12.659	12.686	12.688	12.684	12.693
c/a	3.282	3.277	3.286	3.286	3.287	3.287

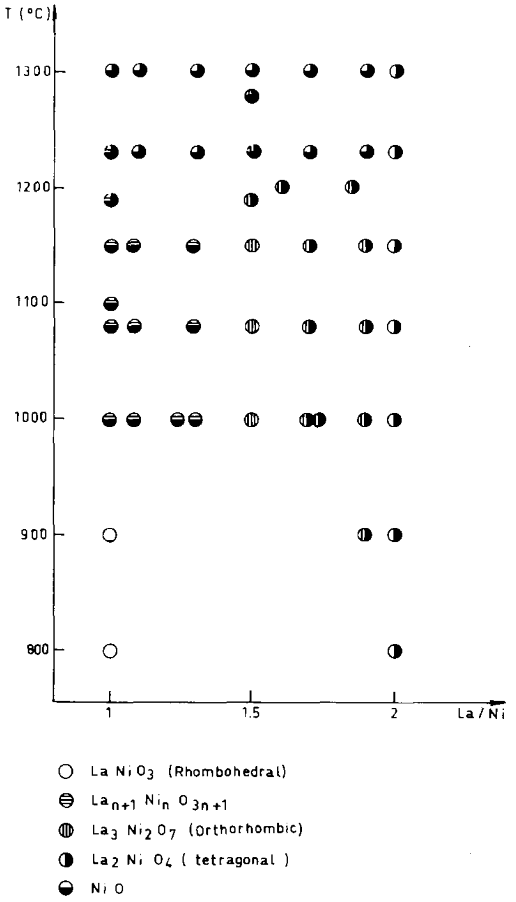

FIG. 2. Observed phases in the La–Ni–O system prepared in air.

been reached for these compositions: La/Ni = 1.3, 1.25, 1.09.

The pure rhombohedral $LaNiO_3$ phase cannot be obtained in air above 860°C since it then decomposes (*22*) according to:

$$LaNiO_3 \rightarrow 1/(n+1)La_{n+1}Ni_nO_{3n+1} + 1/(n+1)NiO + 1/(n+1)O_2 \quad \text{(II)}.$$

As reported in Fig. 2, a mixture of La_2NiO_4 and NiO was observed above 1200°C for all compositions ranging from $LaNiO_3$ to La_2NiO_4.

III.2. Thermal Expansion and High-Temperature Crystallography

X-Ray spectra at high temperatures show that La_2NiO_4 (tetragonal, space group *I4/mmm*-$z = 2$) is stable in air up to more than 1500°C. However, above 1000°C new X-ray reflections appeared ($d_{obs} = 2.825$ and 1.9968 Å) but then disappeared above 1400°C. These extra lines could be attributed to the formation of a compound between platinum oxides and La_2NiO_4 that decomposes at high temperature.

The reproducibility in the determination of the cell parameters was checked in five independent trials and their variation with *T* is shown in Fig. 3. This figure indicates a linear increase of parameter *a* and hence of cell volume with *T*. However, parameter *c* displays a break at approximately 350°C (620 K). This feature is more apparent on a plot of the ratio *c*/*a* versus *T* as shown in Fig. 4. A clear maximum in *c*/*a* occurs between 350 and 600°C.

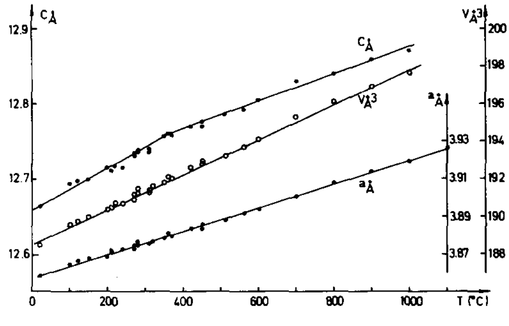

FIG. 3. Cell parameters versus temperature for La_2NiO_4 in air, assuming a tetragonal unit cell.

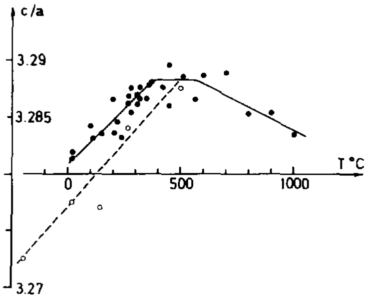

FIG. 4. The *c*/*a* versus temperature *T* in air: (●) present data; (○) J. B. Goodenough *et al.* (*31*) (broken line).

The variation of *a* and *c* versus *T* in air allows the average linear thermal expansion coefficients to be obtained: $\alpha_a(20\text{–}1100°C) = 16.1 \times 10^{-6}\ °C^{-1}$, $\alpha_c(20\text{–}350°C) = 22.7 \times 10^{-6}\ °C^{-1}$, and $\alpha_c(350\text{–}1100°C) = 12.3 \times 10^{-6}\ °C^{-1}$. From these results the mean thermal expansion coefficient $\bar{\alpha} = \frac{1}{3}(2\alpha_a + \alpha_c)$ can be calculated

$$\bar{\alpha}(20\text{–}350°C) = 18.3 \times 10^{-6}\ °C^{-1}$$

and

$$\bar{\alpha}(350\text{–}1100°C) = 14.8 \times 10^{-6}\ °C^{-1}.$$

These values compare very well with macroscopic measurements made on sintered polycrystalline bars. Macroscopic thermal expansion coefficients measured on several samples between 20 and 1100°C ranged from 14 to 15.5 × 10^{-6} °C^{-1}.

III.3. Structure of Reduced Samples

Several samples were quenched in low oxygen partial pressure at 1000°C. The crystallographic structure was identified using X-ray measurements on samples which had been ground into a powder. The cell shape changes with the oxygen pressure of quenching: *a* remaining relatively constant and *c* weakly decreasing.

The ratio *c*/*a* for the tetragonal unit cell decreases from nearly 3.3 for the well-oxidized samples to 3.22 for those which had been strongly reduced (10^{-7} Pa at 1000°C). In fact a slight distortion to an orthorhombic structure is visible though the exact partial pressure at which it occurs is not known. However, compounds quenched under pure argon (P_{O_2} = 1 Pa) have such a structure. For the most strongly reduced samples (10^{-7} Pa), the orthorhombic structure cell has the parameters: a = 5.4614 Å, b = 5.5322 Å, c = 12.527 Å from which c/a_T = 3.22 was calculated assuming $a_T \simeq (a + b)/2\sqrt{2}$.

High-temperature X-ray structure studies were made on these reduced samples by the technique described previously. However, in order to avoid reoxidation during heating a mixture of 95% He + 5% H_2 gas was passed through the chamber and it is believed that below 650°C the samples were not further reduced. The variation of the ratio c/a was determined and is plotted in Fig. 5. The change of c/a versus the temperature is faster for reduced samples and the maximum is shifted to a higher temperature.

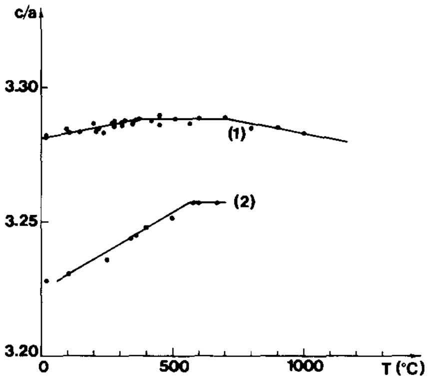

FIG. 5. The c/a versus temperature T for: (1) a sample of La_2NiO_4 prepared in air (data taken from Fig. 4); (2) a sample quenched from 1000°C under 10^{-7} Pa partial pressure of oxygen assuming a tetragonal cell.

IV. Discussion

IV.1. Phase Relations in the La–Ni–O System

Figure 2 shows the different phases that are observed in air for this complex system. These results are consistent with the recent work of Cherepanov *et al.* (*24*) except for the presence of $La_3Ni_2O_7$ which has been found here with La_2NiO_4 instead of $La_4Ni_3O_{10}$ as reported. A study of the best conditions for the synthesis of $La_3Ni_2O_7$ shows that La_2NiO_4 is always formed before any significant amount of $La_3Ni_2O_7$ is visible in X-ray analysis. It is therefore concluded that the formation of $La_3Ni_2O_7$ is controlled by the reverse path of reaction I that provide a mechanism which typically leads to intergrowth layers in K_2NiF_4 structures (*22, 25*). The composition $La_3Ni_2O_7$ is the second term of the homologous series $La_{n+1}Ni_nO_{3n+1}$ and reaction I is reversible. At 1300°C in air it is completely displaced to the right-hand side.

The absence of visible variations of the cell parameter with the ratio La/Ni in the range 1.925–1.99 seems to exclude the possibility of a solid solution of NiO in La_2NiO_4 at least for air-annealed compounds. This confirms previous work (*26*).

The range between La/Ni = 1 and 1.5 is less understood because the various elements of the homologous series $La_{n+1}Ni_nO_{3n+1}$ are difficult or almost impossible to distinguish by X rays. Homologous phases with $n > 2$ were observed however by electron microscopy (*22*) and they have similarities with the La–Cu–O system (*27*). These phases probably decompose at high temperature in air as does $LaNiO_3$. $LaNiO_3$ has a less stable structure and starts to reduce itself to the lower oxide $La_{n+1}Ni_nO_{3n+1}$ according to reaction II above 850°C in air. It should be noted that these phases obtained in equilibrium conditions are significantly different from the phases reported by Crespin *et al.* (*28*) after the reduction of $LaNiO_3$ in H_2, viz., $La_2Ni_2O_5$ and $LaNiO_2$.

IV.2. Crystal Structure Evolution with Temperature

Two observations are of significance: (i) the occurrence of a new structure for reduced stoichiometry; (ii) the anomalous maximum observed in the variation of *c/a* with temperature.

Under reducing conditions the unit cell changes from a tetragonal to an orthorhombic structure whose parameters were given in Part III. There is in fact a small increase of the unit cell volume during reduction while the ratio *c/a* decreases (*c* decreases and *a* increases slightly). A plot of *c/a* versus the oxygen pressure of quenching at 1000°C (Fig. 6), reveals that *c/a* varies smoothly. Clearly this demonstrates that the stoichiometry has an important influence on the crystal structure. On the other hand if a crystallographic transition takes place between the tetragonal and the orthorhombic phases it should occur at a relatively well-defined oxygen partial pressure (e.g., stoichiometry) and produce an effect on *c/a*. The absence of any visible anomaly in the *c/a* curves raises the question of the existence of such a transition. In view of other compounds such as Nd_2NiO_4 (*29*) or La_2CuO_4 (*30*) that differ from the parent structure K_2NiF_4 (tetragonal) by a slight distortion to an orthorhombic structure, even when prepared in air, it must be asked whether La_2NiO_4 really has a tetragonal structure in air and what is the origin of the observed transformation under reducing conditions.

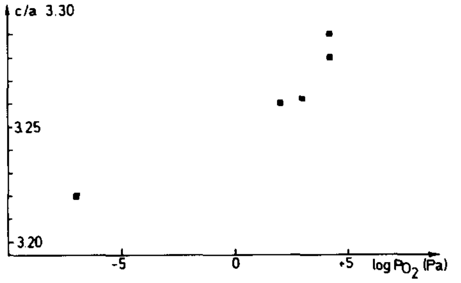

FIG. 6. The *c/a* versus oxygen partial pressure for samples quenched from 1000°C. General assumption of a tetragonal unit cell, for orthorhombic structures *a* is approximated by $a_T = (a + b)/2\sqrt{2}$.

It is now known that even in the tetragonal structure (Fig. 1) of La_2NiO_4 (*17, 31*), the local octahedron of oxygen ions surrounding the Ni cations is distorted with a distortion parameter of 1.02 → 1.18. The larger value was calculated (*29*) assuming a tetragonal unit cell, and would differ if the structure is orthorhombic as proposed in the present discussion. The octahedron of oxygen ions has four short bonds in the basal plane and two longer bonds along the *c* axis. Such a configuration has a local distortion parameter which differs from the K_2NiF_4 parent structure for which the value is <1, and this difference has been explaned by geometric and bond strength considerations (*31*). According to Goodenough and Ramasesha (*31*), the larger ratio is due to itinerant $\sigma_{x^2-y^2}$ electrons with the remaining electrons localized in d_{z^2} orbitals parallel to the *c*-axis. The Ni–O separation in the latter direction is assumed to be directly related to the electron delocalization; the higher the delocalization, the larger the Ni–O separation. This assumption is in good qualitative agreement with the observed variations of the *c/a* ratio on the tetragonal unit cell with stoichiometry, as well as with electrical data obtained on quenched samples (*32*). The room-temperature conductivity increases with *c/a* indicating progressive electron delocalisation.

However, these arguments do not explain why *c/a* varies with nonstoichiometry. It is well known that a proportion of the nickel ions (1–10%) in La_2NiO_4 prepared by conventional ceramic procedures is in the higher Ni^{3+} valence state (*20, 31, 33*) similar to the lanthanum copper oxides (*27, 34*). These proportions have been detected by iodometric titration. If a Ni^{3+} (d^7) ion is located in an octahedral site it probably enhances the *c/a* ratio as observed in the $La_{1-x}Sr_xNi_x^{3+}Ni_{1-x}^{2+}O_4$ system (*11*). This therefore suggests that a link could exist between delocalization and the presence of Ni^{3+} in the compound. Such a possibility is under investigation at CNRS Orléans, France.

The *c/a* ratio varies not only with stoichiometry but also with temperature. Goodenough and Ramasesha (*31*) have recently studied the thermal expansion of La_2NiO_4 between −200 and 500°C by the X-ray method described earlier. Their value of *c/a* is lower than ours and does not have a maximum in the range of temperatures studied. However, this is not in contradiction with our observations since the smaller *c/a* ratio probably implies a higher degree of reduction in their samples so that the maximum is expected to occur at a higher temperature. Second, their range of temperature was possibly not sufficient to detect a smooth maximum.

The increase with temperature of the *c/a* ratio may have two origins. On one hand there is no reason to assume an isotropic thermal expansion in a material that is anisotropic in its structure (i.e., the tetragonal structure) and thus the *c/a* ratio is not expected to remain constant with temperature. Several examples of anisotropic thermal expansion are known (*35*). On the other hand, as discussed earlier, a gradual delocalization of the d_{z^2} electrons with temperature would result in an increase in *c/a* linked with an increase in electrical conductivity as observed in the thermally activated state below 600 K (*7, 9*). The new result which is reported here is the occurrence of a maximum in *c/a* at $T \sim 600$ K. It is well established that this temperature is approximately the temperature at which La_2NiO_4 becomes metallic (*7, 9, 21*). This indicates that the energy gap induced by electron correlation at lower temperatures tends to zero and does not become negative as originally suggested by Goodenough and Ramasesha (*31*) in order to explain the absence of a maximum in their results. The decrease of *c/a* at higher temperature could be due to the beginning of reduction which increases the localization of the carriers. This underlines the need for direct measurement of the stoichiometry for a complete understanding of these phenomena.

An alternative explanation that accounts for the maximum in *c/a* is to consider the influence of Ni^{3+} ions which change from a high-spin state at low temperature to a low spin at high temperature. The decrease of size that would result from such a transition could explain a plateau in the ratio *c/a* at high temperature. However, there are two arguments against this explanation: first the Ni^{3+} concentration is small, certainly lower than 10% of the total nickel concentration and, second, the low-spin state is favored at low temperatures in similar materials such as $BaLaNiO_4$ (*15*).

V. Conclusions

Above 1200°C the various phases observed in the La–Ni–O system decompose into La_2NiO_4 and NiO. The second term, $n = 2$ of the homologous series $La_{n+1}Ni_nO_{3n+1}$ is stable up to 1200°C, with this temperature depending upon the oxygen partial pressure. These results are important for defining the preparation conditions of these materials.

The unit cell of the crystallographic structure is modified by temperature and stoichiometry. The deformation of the unit cell measured in air as a function of temperature is related to the electrical properties and particularly to the occurrence of the transition from a semiconducting to metallic state at high temperature.

Acknowledgments

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