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Oxygen Nonstoichiometry and Its Effect on the Structure of $LaNiO_3$

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$LaNiO_3$ is known to have a slightly distorted perovskite structure, making it hexagonal with cell parameters a = 5.455 Å and c = 6.561 Å. In this paper it is shown that stoichiometric $LaNiO_3$ is an ideal cubic perovskite with cell parameter a = 3.851 Å. The cubic $LaNiO_3$ loses a little oxygen when heated at higher temperatures and transforms gradually to the hexagonal phase. Such an oxygen deficiency and structural change also take place whenever a flux of Na_2CO_3 is used for the preparation of $LaNiO_3$. This is due to incorporation of a little sodium impurity into the lattice during the preparation. Another interesting feature of the transformation is that it undergoes a transient tetragonal phase. $LaNiO_3$ containing sodium impurity and the cubic $LaNiO_3$ differ in the manner in which they are reduced by hydrogen; the former is converted to $La_2Ni_2O_5$ and then to $LaNiO_2$, whereas the latter gives $La_2Ni_2O_5$ and then a mixture of La_2O_3 and Ni. © 1994 Academic Press, Inc.

INTRODUCTION

Nonstoichiometry in metal oxides adopting the perovskite structure has been a subject of detailed study during the past several years (1, 2). These studies have pointed out how in these nonstoichiometric oxides point defects are eliminated by their ordering producing new structural features (3). This type of ordering of point defects is more common in anion deficient perovskite structures (4). $LaNiO_3$ has a slightly distorted perovskite structure, making it hexagonal. Vacancy ordering in anion-deficient $LaNiO_3$ has been studied by several workers (3, 4). These studies provided evidence for formation of a series of phases with the general formula $La_nNi_nO_{3n-1}$ (5). In this paper it is shown that the hexagonal distortion is itself due to oxygen deficiency, and that stoichiometric $LaNiO_3$ is an ideal cubic perovskite. It is also shown that the hexagonal phase is stabilized by impurities such as sodium.

EXPERIMENTAL

With a view to obtain samples of $LaNiO_3$ with different oxygen stoichiometries, two different procedures were used for the preparation: (a) samples were prepared by the standard reported procedure (6) of reacting stoichiometric mixtures of precalcined La_2O_3 and NiO in a flux of Na_2CO_3 at 800°C for 72 hr and washing the product several times with distilled water until the washings are free from sodium ions; (b) several samples were also prepared by mixing appropriate ratios of La_2O_3 and $Ni(NO_3)_2$, calcining this mixture at 600°C for 4 days in flowing oxygen, and thoroughly milling and pelletizing. These pellets were heated in the temperature range 750–900°C for different periods of time in oxygen atmosphere and cooled gradually in oxygen. The stoichiometric quantity of $Ni(NO_3)_2$ was obtained by evaporating the required volume of a standard solution of $Ni(NO_3)_2$ in distilled water. All chemicals used in these preparations had a purity greater than 99.5%.

The structural characteristics of the samples were obtained by X-ray powder diffraction using CuK_α radiation. The oxygen stoichiometry was estimated by iodometric titrations (7, 8). This was also determined from weight loss measurement on reduction with hydrogen using a Cahn–TGA system. The overall error in estimating the oxygen stoichiometry was ±0.01 in the number of oxygen atoms. The samples were also analyzed for sodium impurity using the standard photometric method. This had an error less than 5%. Thermogravimetry of samples in hydrogen was performed to a temperature of 900°C using the TGA system.

RESULTS

Samples prepared by the first method gave the reported X-ray patterns, showing that these samples had the hexagonal structure with lattice parameters a = 5.455 Å and c = 6.561 Å (rhombohedral pseudocell with a = 7.676 Å and α = 90°43′). However, these samples showed on analysis an impurity of sodium to the extent of 0.48% by weight. Since the ionic radii of La^{3+} and Na^+ are very similar (radius of La^{3+} = 1.36 Å and that of Na^+ = 1.39 Å for a coordination number of 12), it is reasonable to expect that sodium is present in the sample as a substitutional impurity in place of lanthanum. This would suggest that about 5% of lanthanum is replaced by sodium in this

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TABLE 1

X-Ray Diffraction Pattern of $LaNiO_3$, System-Cubic, Lattice Parameter, a = 3.851(3) Å

d	I/I^a	*h*	*k*	*l*
3.848	16	1	0	0
2.722	100	1	1	0
2.222	15	1	1	1
1.9217	46	2	0	0
1.7187	6	2	1	0
1.5728	32	2	1	1
1.3610	9	2	2	0
1.2800	4	3	0	0
1.2178	9	3	1	0
1.1600	3	3	1	1
1.1118	4	2	2	2
1.0690	2	3	2	0
1.0301	9	3	2	1
0.9602	4	4	0	0
0.9337	4	4	1	0
0.9085	6	4	1	1
0.8614	3	4	2	0
0.8235	3	3	3	2

[a] Only peak heights have been used for these data.

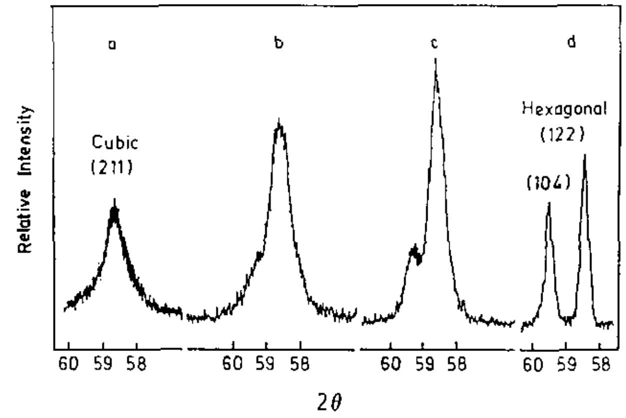

FIG. 1. X-ray diffraction lines recorded during the transformation of cubic to hexagonal $LaNiO_3$: Radiation, Cu*K*α; 2θ range, 57–61°; *a*, 4 hr of heating; *b*, 8 hr of heating; *c*, 12 hr of heating; *d*, 16 hr of heating at 800°C.

sample. Therefore, taking into consideration the charge neutrality of the sample, its overall composition may be written as $La_{0.95}Na_{0.05}NiO_{2.95}$. Analysis of the oxygen concentration also showed a slight deficiency of oxygen supporting such a composition for the samples.

The X-ray diffraction patterns of samples prepared by the second method at temperatures between 750–790°C showed that they were mixtures of unreacted component oxides and a new phase. Samples prepared by this method by heating at 800°C for 4 hr gave a pattern purely of the new phase. Examination of this pattern suggested this phase to be cubic with lattice parameter a = 3.851 Å. X-ray diffraction data of this phase are given in Table 1. The indices of the reflections as well as their relative intensities suggest an ideal cubic perovskite structure for this phase. The reflections in the X-ray diffraction patterns were considerably broad, suggesting that the particle size of the samples was very small. Due to this broadening, the lines at high angles could not be resolved, and this limited the measurements to a *d* spacing of about 0.82 Å. Analysis of the cubic phase showed that it had the stoichiometric oxygen concentration. Samples prepared by heating at 800°C for longer periods showed a gradual conversion of the cubic phase to the hexagonal phase. This conversion could be followed by the appearance, and the subsequent increase in intensity, of the diffraction lines due to the hexagonal phase. This conversion was studied both by thermogravimetric (TGA) and X-ray powder diffraction methods. The TGA performed on the cubic phase as a function of time, keeping the temperature constant at 800°C, showed that there was a small loss of oxygen of about 0.05% by weight during the conversion. The values of the *d* spacings of the hexagonal phase during the transformation indicated a gradual evolution of this structure. Figure 1 shows the positions of (104) and (122) reflections of the hexagonal phase, which correspond to (211) and $(21\bar{1})$ reflections of the rhombohedral lattice after 4, 8, 12, and 16 hr of heating at 800°C. It may be noted that the (211) reflection of the cubic phase and the $(21\bar{1})$ reflection of the rhombohedral phase have approximately the same *d* spacing, 1.573 and 1.578 Å, respectively. Therefore, during this conversion these two reflections coincided. We have taken the *d* spacing of this superposed reflection as that of the $(21\bar{1})$ of the rhombohedral phase for calculating the rhombohedral angle. These calculations showed rhombohedral angles of 90°16′, 90°21′, 90°26′, and 90°33′, respectively, after the four different periods of heating. Thus, the conversion involves (1) a continuous but small loss of oxygen and (2) a gradual increase in the rhombohedral angle from 90° in the cubic phase to about 90°43′ when it is completely transformed to the hexagonal phase.

An interesting feature observed during this conversion was that, at the initial stage of this conversion from the cubic to the hexagonal phase, a transient phase appeared. This phase showed its presence only through one additional line at lower angles. Figure 2 shows this region. This line had a *d* spacing of 5.45 Å, which is exactly $\sqrt{2}$ times the lattice parameter of the cubic phase. Therefore this reflection could be interpreted as a tetragonal superlattice with cell parameters a = 5.45 Å and c = 3.851 Å.

The samples prepared by the two methods differed in the manner in which they are reduced by hydrogen. The thermograms taken for the two samples are shown in Fig. 3. It is clearly seen that pure $LaNiO_3$ first gets reduced

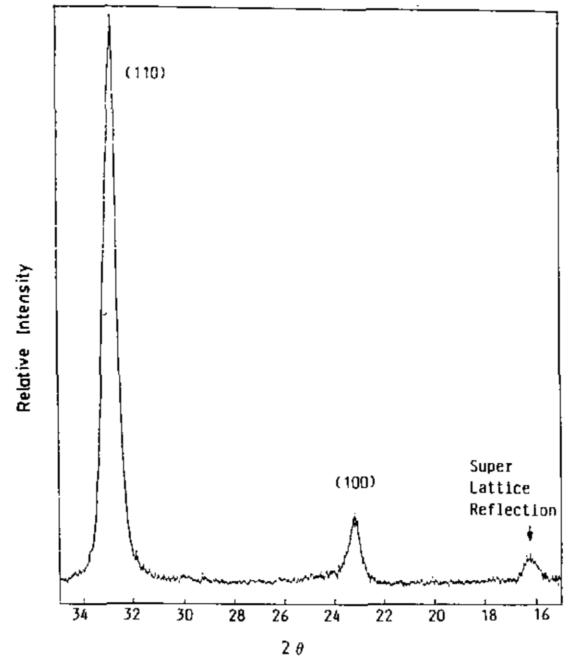

FIG. 2. Low angle region of the X-ray diffraction pattern recorded during the initial stage of the transformation. Apart from the (100) and (110) reflections of the cubic phase an additional super-lattice reflection can be seen.

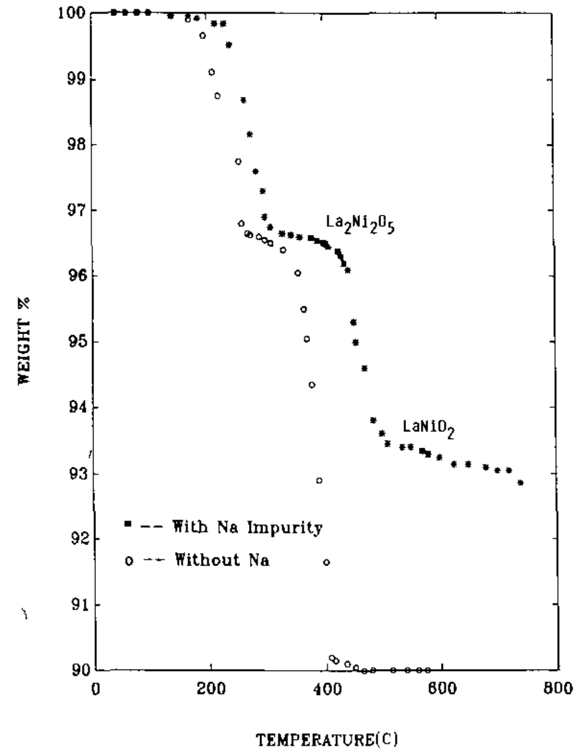

FIG. 3. Thermograms of $LaNiO_3$ with and without sodium impurity.

to $La_2Ni_2O_5$ at 200°C and finally to a mixture of La_2O_3 and Ni at 370°C. The $LaNiO_3$ containing sodium impurity is reduced to $La_2Ni_2O_5$ at 265°C and then to a phase having an overall composition of $LaNiO_2$ at 442°C. Complete reduction to La_2O_3 and Ni takes place only at much higher temperatures. From the figure it is also clear that the sample with sodium impurity is reduced comparatively at higher temperatures.

DISCUSSION

It is necessary to understand why stoichiometric $LaNiO_3$ has the ideal cubic structure. Generally one uses the value of the tolerance factor for explaining the ideality or deviations from ideality of the perovskite structure. In the case of $LaNiO_3$, if the ionic radii (9) used for calculating the tolerance factor are those taking into consideration their proper coordination number, one obtains a value of 1.003 for this factor. Therefore the cubic structure for $LaNiO_3$ is not surprising. However, it is interesting to note that in $LaNiO_{3-x}$ a value of x as small as 0.05 is sufficient to transform the cubic structure to the tetragonal and then to rhombohedral structure. The deficiency of oxygen in the rhombohedral phase indicates that part of the nickel in $LaNiO_{3-x}$ is reduced to Ni^{2+} and that the oxygen vacancies are ordered. The gradual change of the rhombohedral angle with loss of oxygen probably suggests that the coordination polyhedron of Ni^{2+} is only a distorted octahedron. A detailed analysis of its structure is needed to confirm this.

The formation of $LaNiO_2$ on reduction of $LaNiO_3$ with hydrogen has been reported by various workers (6, 10). During this study a compound with overall composition $LaNiO_2$ was observed only when samples containing sodium impurity were used for the reduction. However, attempts to prepare a pure phase of this composition were not successful. These samples had small quantities of free nickel, suggesting that this phase was also deficient in nickel. These point out that the formation of pure $LaNiO_2$ containing Ni in +1 state is doubtful.

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