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Structural phase transition of $La_{2-x}Nd_xNiO_{4+\delta}$ $(0.0 \le x \le 2.0)$

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Abstract

Crystal phases, crystal systems, lattice constants, and thermal properties of $La_{2-x}Nd_xNiO_{4+\delta}$ $(0.0 \le x \le 2.0,\ 0.11 \le \delta \le 0.22)$ have been studied up to 1073 K to examine the orthorhombic–tetragonal phase transitions of $La_2NiO_{4+\delta}$ and $Nd_2NiO_{4+\delta}$. The crystal phase at room temperature of $La_{2-x}Nd_xNiO_{4+\delta}$ is settled by the x-value and the thermal history of the sample. A tetragonal phase is found at $x \le 0.75$ for a quenched sample and at $x \le 0.50$ for an annealed one, and an orthorhombic phase is, respectively, found at $x > 0.75$ and at $x > 0.50$. The $(b–a)$ and the δ values at room temperature of $La_{2-x}Nd_xNiO_{4+\delta}$ are also settled by the x-value and the thermal history of the sample. Both $(b–a)$ and δ values of an annealed sample are larger than the values of the corresponding quenched one. Although the δ-value at room temperature varies according to the x-value and the thermal history of the sample, the δ-value at phase transition temperature is ~0.15. A sample is in the orthorhombic symmetry at $\delta > 0.15$ and in the tetragonal one at $\delta \le 0.15$. The orthorhombic–tetragonal phase transition of $La_{2-x}Nd_xNiO_{4+\delta}$ is caused by the decrease of the δ-value due to the increase of temperature. No phase transition is expected for $La_2NiO_{4+\delta}$, because the δ-value of $La_2NiO_{4+\delta}$ at room temperature is less than 0.15. Because a length of a-axes of the orthorhombic phase decreases with increasing the δ-value, the orthorhombic phase is expected to be formed by a tilt of the NiO_6 octahedra parallel to the a-axis induced by the interstitial oxygen.

Keywords: Disordered systems; Chemical synthesis; X-ray diffraction; Ionic conduction; Thermal analysis

1. Introduction

Only three compounds are now available as $Ln_2NiO_{4+\delta}$ ($Ln = La$, Pr, or Nd). At room temperature, $La_2NiO_{4+\delta}$ is in the orthorhombic symmetry [1] or in the quasi-tetragonal symmetry [2,3], while $Pr_2NiO_{4+\delta}$ and $Nd_2NiO_{4+\delta}$ are in the orthorhombic symmetry [3]. A phenomenon commonly found in these compounds is the existence of the excess oxygen, that is, δ in $Ln_2NiO_{4+\delta}$ [4]. The crystal system of $Ln_2NiO_{4+\delta}$ will be settled by the δ-value and the ionic radius of the lanthanide ion. In $Ln_2NiO_{4+\delta}$, La and Nd exist as Ln^{3+}, but Pr exists as Pr^{3+} or Pr^{4+}. The properties of $Pr_2NiO_{4+\delta}$ [5] are differing from the properties of $La_2NiO_{4+\delta}$ and $Nd_2NiO_{4+\delta}$, because Pr^{4+} is in the crystal. For discussing the effects of the δ-value and the Ln^{3+} radius on the crystal system, the existence of Pr^{4+} in the crystal will complicate the discussion.

In this study, solid solutions of $La_{2-x}Nd_xNiO_{4+\delta}$ $(0.0 \le x \le 2.0)$ were prepared, and the crystal phases of the solid solutions were examined. The effects of the δ-value and the Ln^{3+} radius on the crystal system of $Ln_2NiO_{4+\delta}$ are discussed with the successive data of the solid solutions. The orthorhombic–tetragonal phase transition of $La_2NiO_{4+\delta}$ is considered in the paper.

2. Experimental

Polycrystalline samples of $La_{2-x}Nd_xNiO_{4+\delta}$ ($x = 0.00$, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00) were prepared by the solid-state reaction of La_2O_3 (99.5%, Wako Chem. Indus.), Nd_2O_3 (99.9%, Wako Chem. Indus), and NiO (99.97%, High Purity Chemicals). A stoichiometric mixture

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of the chemicals was ground and pressed into pellets, and the pellets were heated in air at 1073–1473 K with intermittent grinding and pelletizing until a single phase was obtained. The obtained sample was powdered again for a continuing heat treatment.

Either of two heat treatments was done for the sample powder. (1) The powder was heated in air at 1073 K and rapidly cooled to room temperature. (2) The powder was heated in air at 1073 K and slowly cooled to room temperature at 0.143 K/min. In this paper, the rapidly cooled sample is called a quenched sample and the slowly cooled sample is an annealed sample.

The δ values of the heat-treated samples were evaluated by hydrogen reduction. A sample powder (∼2 g) was contained in a weighed Pt boat (5–9 g), and the Pt boat was repeatedly heated in air at 393 K until a constant weight is given. The Pt boat was also repeatedly heated in a dry hydrogen flow (650 Pa) at 1073 K for 2 h until a constant weight is given. The δ-value of the sample was evaluated from the weights of the sample before and after hydrogen reduction. Since La, Nd, and Ni of the sample heated in hydrogen above 800 K exist as La^{3+}, Nd^{3+}, and Ni^0 [1], the following nominal reaction is used for the δ-value evaluation:

$$La_{2-x}Nd_xNiO_{4+\delta} \xrightarrow{H_2} \left(\frac{1-x}{2}\right) La_2O_3 + \left(\frac{x}{2}\right) Nd_2O_3 + Ni. \quad (1)$$

X-ray powder diffraction data of the heat-treated samples were collected at room temperature for Rietveld analyses by a diffractometer Rigaku RINT1200 with a Cu Kα radiation source. The lattice constants of the samples were evaluated by fitting the data with a crystallographic program RIETAN-2000 [6]. A structure model of $La_2NiO_{4+\delta}$ proposed by Jorgensen et al. [1] was used for the lattice constant evaluation, that is, La and Nd, Ni, O(1), and O(2) were, respectively, located at (0,0,z; $z \approx 0.36$), (0,0,0), (1/4,1/4,0), and at (0,0,z; $z \approx 0.175$) in the *Fmmm* structure. The validity of the space group employed for the lattice constant evaluation is reconsidered in Section 3.

X-ray powder diffraction data at high temperature up to 960 K were also collected with the same diffractometer for finding the structural phase transition temperatures of the samples. Non-heat-treated samples were used for the measurements, because the δ-value changes above 570 K and the phase transition temperature is above 570 K. The X-ray measurements were done in an air or oxygen flow, because the δ-value and the phase transition temperature of the samples change with oxygen partial pressure of the atmosphere.

TG–DTA data of the heat-treated samples were measured in an air or oxygen flow up to 1073 K at a heating or cooling rate of 5 K/min. A thermobalance Rigaku Thermo Plus TG8120 was used for the measurements. The δ-value at the phase transition temperature was evaluated from the δ-value at room temperature and the TG–DTA data.

3. Results and discussion

TG–DTA data of the quenched or annealed samples of $Nd_2NiO_{4+\delta}$ are shown in Fig. 1 (A), and TGA data of the quenched samples of $La_{2-x}Nd_xNiO_{4+\delta}$ are shown in Fig. 1 (B). In the heating curves of the TGA data of the quenched samples (a, d–h), weight gains due to the absorption of oxygen from the atmosphere are found at 570–650 K. However, no weight gain is seen in the heating curves of the annealed ones as an example is shown for $Nd_2NiO_{4+\delta}$ (b).

The weight gains for the quenched samples and the no-weight gain for the annealed samples at 570–650 K and the shapes of the TGA curves below 700 K bring the following conclusions. (1) The absorption of oxygen to and the des-

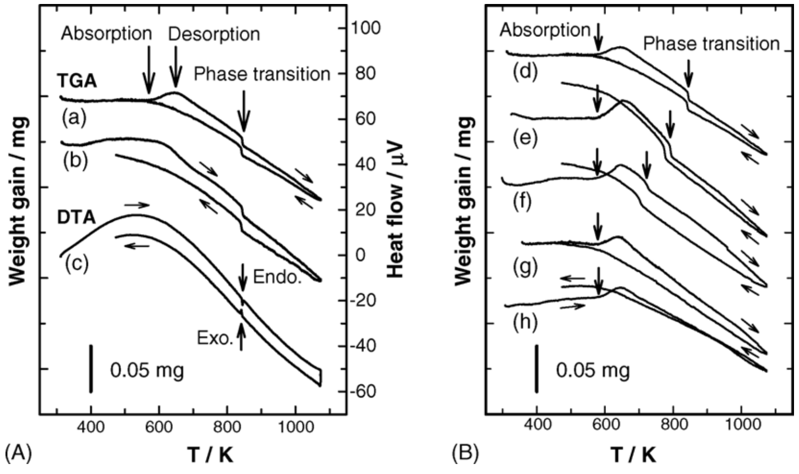

Fig. 1. TG–DTA curves of the quenched or annealed samples of $Nd_2NiO_{4+\delta}$ (A) and the quenched samples of $La_{2-x}Nd_xNiO_{4+\delta}$ (B). Measurements were done in airflow at the heating or cooling rate of 5 K/min. The quenched samples (a, c–h) were samples rapidly cooled in air from 1073 K to room temperature and the annealed sample (b) was a sample slowly cooled from 1073 K to room temperature at 0.143 K/min. (a, c, d) $x = 2.00$ (29.425 mg); (b) $x = 2.00$ (33.809 mg); (e) $x = 1.75$ (53.333 mg); (f) $x = 1.50$ (36.332 mg); (g) $x = 1.00$ (50.966 mg); (h) $x = 0.25$ (44.975 mg).

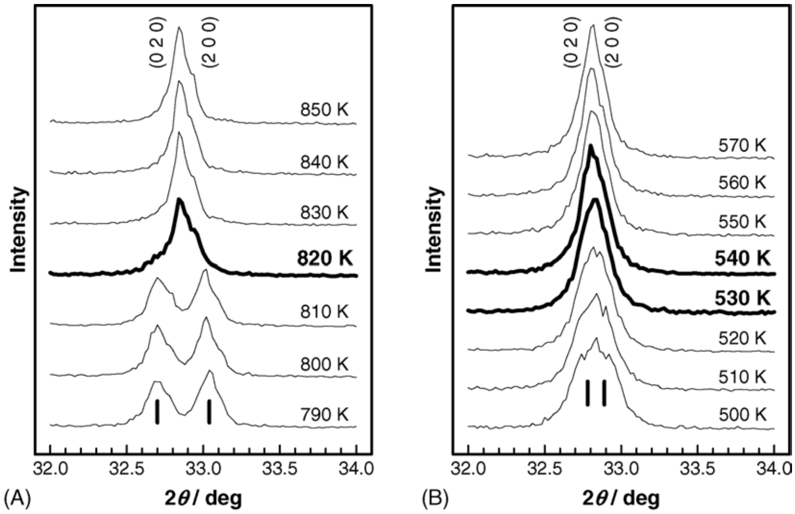

Fig. 2. X-ray powder diffraction patterns of $La_{2-x}Nd_xNiO_{4+\delta}$ at $x = 1.75$ (A) and at $x = 1.0$ (B) measured in an airflow at high temperature.

orption of oxygen from the quenched or annealed samples begin at 570 K. (2) The δ values at room temperature of the quenched samples are the equilibrium δ values of the samples in air at ∼700 K. (3) The δ values at room temperature of the annealed samples are the equilibrium δ values of the samples in air at or below 570 K. (4) The δ values of the quenched samples are smaller than the δ values of the corresponding annealed ones at room temperature.

In the TG–DTA data of the samples at $x \geq 1.5$ (a–f) above 700 K, abrupt weight losses with endothermic peaks and abrupt weight gains with exothermic peaks are found. These weight changes and the peaks above 700 K are concerned to the phase transitions of the samples.

The structural phase transition temperatures of the samples are determined not from the TG–DTA data but from the high temperature X-ray diffraction data. Examples of the X-ray diffraction data are shown in Fig. 2. Since the difference between the peak positions of the (2 0 0) and (0 2 0) peaks decreases with decreasing the x-value, the phase transition temperatures are successfully determined only for the samples at $x \geq 1.25$. Evaluated phase transition temperatures in air are given in Fig. 3. The phase transition temperatures of the samples at $x \geq 1.25$ are higher than 570 K, which is the beginning temperature of the δ-value fluctuations of the quenched or annealed samples.

Lattice constants at room temperature of the quenched or annealed samples are shown in Fig. 4. The values of the lattice constants are apparently influenced by the thermal histories. At $x \geq 0.75$, the (b–a) value, which is an index of the orthorhombic distortion, of the annealed samples is larger than the value of the corresponding quenched one. The annealed samples are in the orthorhombic symmetry at $x \geq 0.75$ and the quenched samples are in the orthorhombic symmetry at $x \geq 1.00$.

The δ values at room or phase transition temperature of the quenched or annealed samples are shown in Fig. 5. At room temperature, the δ-value of the quenched or annealed samples increases with increasing the x-value. The δ-value of an annealed sample is 0.022–0.028 larger than the value of the corresponding quenched one at room temperature. However, at the respective phase transition temperatures, the δ-value is ∼0.15.

The crystal phases of $La_{2-x}Nd_xNiO_{4+\delta}$ are as follows. At $\delta < 0.15$, the samples are in the tetragonal ($I4/mmm$) or in the quasi-tetragonal symmetry ($Fmmm$). Since the (b–a) value at room temperature (0.36 ∼ 0.72 pm) is larger than the sum

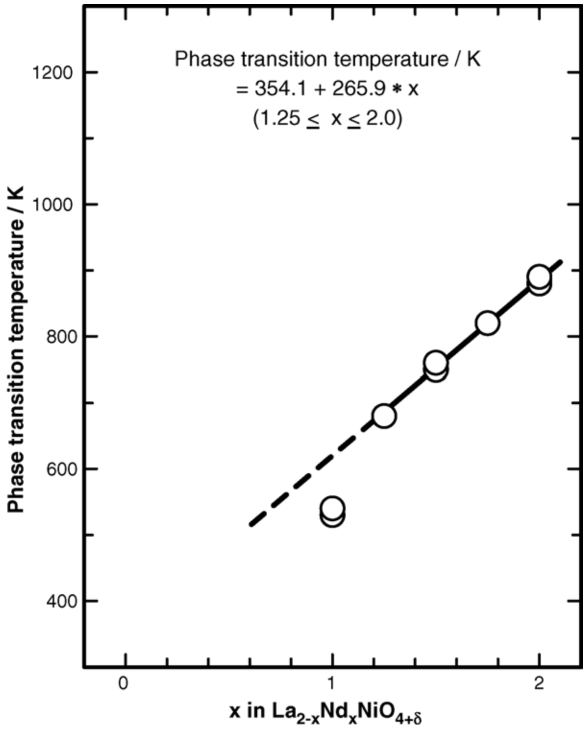

Fig. 3. Orthorhombic–tetragonal phase transition temperatures of $La_{2-x}Nd_xNiO_{4+\delta}$ measured in an airflow by high temperature X-ray diffraction technique.

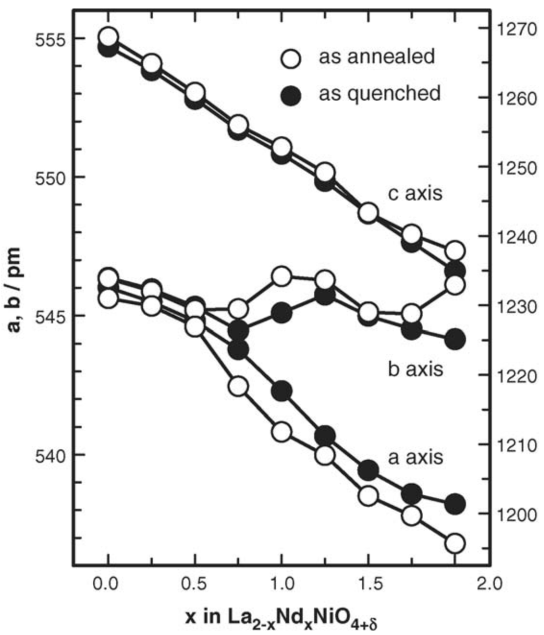

Fig. 4. Lattice constants of the quenched or annealed samples of $La_{2-x}Nd_xNiO_{4+\delta}$ at room temperature.

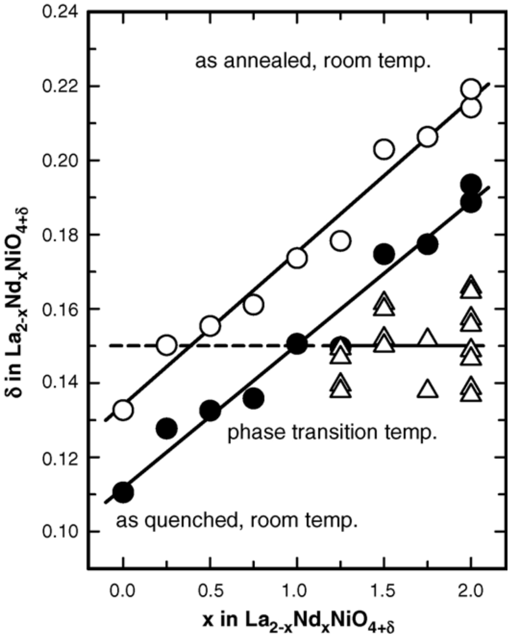

Fig. 5. Excess oxygen concentrations of the quenched or annealed samples of $La_{2-x}Nd_xNiO_{4+\delta}$ at room temperature and at phase transition temperature in an airflow.

of 3σ of the lattice constants a and b (0.06–0.08 pm), the samples at $\delta < 0.15$ are in the quasi-tetragonal symmetry. In the *Fmmm* space group, the (b–a) value of $La_{2-x}Nd_xNiO_{4+\delta}$ is small and does not very change with the δ-value, since the NiO_6 octahedra cannot tilt in the *Fmmm* structure. The small orthorhombic distortion should be caused by the distortion of the NiO_6 octahedra.

At $\delta \geq 0.15$, the samples are in the orthorhombic symmetry. The space group of the samples at $\delta \geq 0.15$ should not be *Fmmm*, because the (b–a) value at room temperature is large (2.8–9.3 pm) and increases with increasing the δ-value (Figs. 4 and 5). This orthorhombic distortion of the (b–a) value will be caused by the tilt of the NiO_6 octahedra parallel to the a-axis induced by the interstitial excess oxygen. In this model, lengths of the a- and b-axes are determined by the projection of the NiO_6 octahedra onto the ab-plane, and the tilt of the NiO_6 octahedra parallel to the a-axis shortens the length of a-axis but does not change the length of b-axis. This model can explain the reason that the (b–a) value at room temperature is large and increases with increasing the δ-value. The space group of the model is *Abma*. Results of the Rietveld analyses for $Nd_2NiO_{4.223}$ with space *Fmmm* and *Abma* groups are given in Ref. [7].

4. Conclusions

The orthorhombic–tetragonal phase transition of $La_{2-x}Nd_xNiO_{4+\delta}$ is explained as follows. A sample is in the orthorhombic symmetry (*Abma*) at $\delta > 0.15$ and in the quasi-tetragonal one (*Fmmm*) at $\delta \leq 0.15$. Below 570 K, the δ-value of a sample does not change with temperature. At 570–650 K, the δ-value increases or decreases with increasing temperature depending on the thermal history of the sample. Above 650 K, the δ-value decreases with increasing temperature. At the temperature at $\delta = 0.15$, the orthorhombic–tetragonal phase transition is observed. No phase transition is expected for $La_2NiO_{4+\delta}$, because the δ-value at room temperature is less than 0.15. The δ-value at room temperature is settled by the x-value and the thermal history of the sample. The reason that the δ-value at room temperature increases with increasing the x-value is as follows: The excess oxygen O(3) locates near at (1/4,1/4,1/4) site between two Ln–O layers of $La_{2-x}Nd_xNiO_{4+\delta}$ [1]. Since the ionic radius of Nd^{3+} is smaller than the ionic radius of La^{3+}, a space that the excess oxygen can locate increases and the δ-value increase with increasing the Nd concentration x.

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