Journal of Alloys and Compounds 408–412 (2006) 1200–1204

Journal of ALLOYS AND COMPOUNDS

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Structural phase transition of $Nd_2NiO_{4+\delta}$ ($0.106 \le \delta \le 0.224$)

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Received 30 July 2004; received in revised form 14 December 2004; accepted 15 December 2004

Abstract

Crystal phases, crystal systems and lattice constants of $Nd_2NiO_{4+\delta}$ at $\delta = 0.106$–0.224 have been studied up to 970 K to examine the orthorhombic–tetragonal phase transition of $Nd_2NiO_{4+\delta}$. In the room temperature phase diagram of $Nd_2NiO_{4+\delta}$, two orthorhombic phases are found at $\delta = 0.13$–0.17 and 0.205–0.224 and two mixed phases are found at $\delta = 0.106$ and 0.17–0.205. The (*b*–*a*) value of the orthorhombic phase at $\delta = 0.205$–0.224 decreases with decreasing the δ value and is expected to become zero at $\delta = 0.13$. A Rietveld analysis of the phase at $\delta = 0.106$ shows that the phase consists of 90% of an orthorhombic phase and 10% of a tetragonal phase. The excess oxygen will be concerned for the orthorhombic–tetragonal phase transition of $Nd_2NiO_{4+\delta}$. However, between the orthorhombic phase at $\delta = 0.205$–0.224 and the phase at $\delta = 0.106$, another orthorhombic phase, which (*b*–*a*) value increases with decreasing the δ value, exists at $\delta = 0.13$–0.17. The concernment of the excess oxygen is not clear. For considering the phase transition, the orthorhombic phase just below the phase transition temperature is the phase at $\delta = 0.205$–0.224 or the phase at $\delta = 0.13$–0.17 is important. The phase transition temperature of $Nd_2NiO_{4+\delta}$ is 880–890 K in air, and at 760–860 K the (*b*–*a*) value increases with increasing the oxygen partial pressure, that is, with increasing the δ value. The orthorhombic phase at 760–860 K is not the phase at $\delta = 0.13$–0.17 but is likely the phase at $\delta = 0.205$–0.224. The phase transition of $Nd_2NiO_{4+\delta}$ should be caused by the decrease of the δ value due to the increase of temperature.

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]. In the previous paper [5], the crystal phase and the δ value changes of $La_{2-x}Nd_xNiO_{4+\delta}$ have been examined up to 1073 K and getting the following conclusion on the phase transition of $La_{2-x}Nd_xNiO_{4+\delta}$. At $\delta < 0.15$, $La_{2-x}Nd_xNiO_{4+\delta}$ is in a quasi-tetragonal symmetry (*Fmmm*), because the (*b*–*a*) value at room temperature (0.36–0.72 pm) is larger than the sum of 3σ of the lattice constants *a* and *b* (0.06–0.08 pm). At $\delta \ge 0.15$, $La_{2-x}Nd_xNiO_{4+\delta}$ is in an orthorhombic symmetry, and the (*b*–*a*) value is 2.8–9.3 pm. A space group of the orthorhombic phase should not be *Fmmm*, because the NiO_6 octahedra cannot tilt in the *Fmmm* structure and the (*b*–*a*) value must be small in the space group. The (*b*–*a*) value of the orthorhombic phase will be caused by the tilt of the NiO_6 octahedra parallel to the *a*-axis induced by the interstitial excess oxygen, because the (*b*–*a*) value increases with increasing the δ value. The space group of the model is *Abma*. Above 650 K, the δ value of $La_{2-x}Nd_xNiO_{4+\delta}$ decreases with increasing temperature, and at the temperature at $\delta = 0.15$, an orthorhombic phase (*Abma*) changes to a quasi-tetragonal phase (*Fmmm*). A phase transition will appear at $\delta = 0.15$ because the *Fmmm* structure cannot store much excess oxygen in the structure.

The phase transition model of the previous paper [5] is showing that a phase transition of $Nd_2NiO_{4+\delta}$ is possibly observed at room temperature by decreasing the δ value from above 0.15 to below 0.15. In this study, X-ray powder diffraction data of $Nd_2NiO_{4+\delta}$ of various δ values have

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doi:10.1016/j.jallcom.2004.12.201

been measured in an air or oxygen flow up to 970 K, and the phase transition model is reexamined.

2. Experimental

A polycrystalline sample of $Nd_2NiO_{4+\delta}$ was prepared by the solid state reaction of Nd_2O_3 and NiO [5]. One of the following heat treatments was done for the sample powder: (1) the powder was heated in oxygen at 773 K and slowly cooled to room temperature at 0.3 K/min. (2) The powder was heated in air at 1073 K and slowly cooled to room temperature at 0.143 K/min. (3) The powder was heated in air at 1073 K and rapidly cooled to room temperature. (4) The powder rapidly cooled in air from 1073 K was heated in a helium flow at predetermined temperature of 643–973 K for 2 h.

The δ values of the heat-treated samples were evaluated by hydrogen reduction [5]. X-ray powder diffraction data of the heat-treated samples were collected at room temperature by a diffractometer Rigaku RINT1200 with a Cu Kα radiation source. X-ray diffraction data at 760–970 K were also collected with the same diffractometer in an air or oxygen flow. The Rietveld analyses were done for the collected data with a program RIETAN-2000 [6]. A *Fmmm* space group [1] was used for the lattice constant evaluation, and *Fmmm*, *I*4/*mmm* and *Abma* space groups were used for the structure and the composition analyses.

3. Results and discussion

Lattice constants at room temperature of the heat-treated samples are shown in Fig. 1(A). At $\delta = 0.205–0.224$, the *c* and the (*b*–*a*) values increase with increasing the δ value, but at $\delta = 0.13–0.17$, the *c* value increases but the (*b*–*a*) value decreases with increasing the δ value. At $\delta = 0.17–0.205$, the *c* and the (*b*–*a*) values do not change with the δ value. Since the excess oxygen is existing as an interstitial oxygen between two Nd–O layers perpendicular to the *c*-axis [1], the *c* value must increase with increasing the δ value in a single phase region. With increasing the δ value, the *c* value increases at $\delta = 0.13–0.17$ and 0.205–0.224 but do not change at $\delta = 0.17–0.205$. Phases at $\delta = 0.13–0.17$ and 0.205–0.224 will be single phases but a phase at $\delta = 0.17–0.205$ is a mixed phase of $Nd_2NiO_{4.205}$ and $Nd_2NiO_{4.17}$. An analogous phase separation is reported for $La_2NiO_{4+\delta}$ [1]. The orthorhombic phases of $La_2NiO_{4+\delta}$ at $\delta = 0.17–0.205$ and of $La_{2-x}Nd_xNiO_{4+\delta}$ [5] are the same phases, but the phase at $\delta = 0.13–0.17$ is a new phase.

In Fig. 1(A), the δ value changes from above 0.15 to below 0.15, but no orthorhombic–tetragonal phase transition is found in the phase diagram. However, in Fig. 1(B), an orthorhombic distortion of the phase at $\delta = 0.205–0.224$ is expected to be disappearing at $\delta = 0.13$. In the phase diagram of Fig. 1(A), $Nd_2NiO_{4.106}$ is the only sample that δ value is below 0.13. In addition, the lattice constants of $Nd_2NiO_{4.106}$ and $Nd_2NiO_{4.133}$ are almost identical. The $Nd_2NiO_{4.106}$ phase is possibly a mixed phase of a tetragonal phase and the orthorhombic phase.

The Rietveld analyses done for $Nd_2NiO_{4.106}$ give the following data: When the phase is an orthorhombic phase (*Fmmm*), $R_{wp} = 22.19$ and $S = 1.42$. When the phase is composed of a tetragonal phase (*I*4/*mmm*) and an orthorhombic phase (*Fmmm*), $R_{wp} = 19.18$ and $S = 1.23$. Statistic data show that the phase is composed of the tetragonal phase and the orthorhombic phase. The phase consists of 10% of the tetragonal phase ($\sqrt{2}a = 545.79(6)$ pm, $c = 1222.4(1)$ pm)

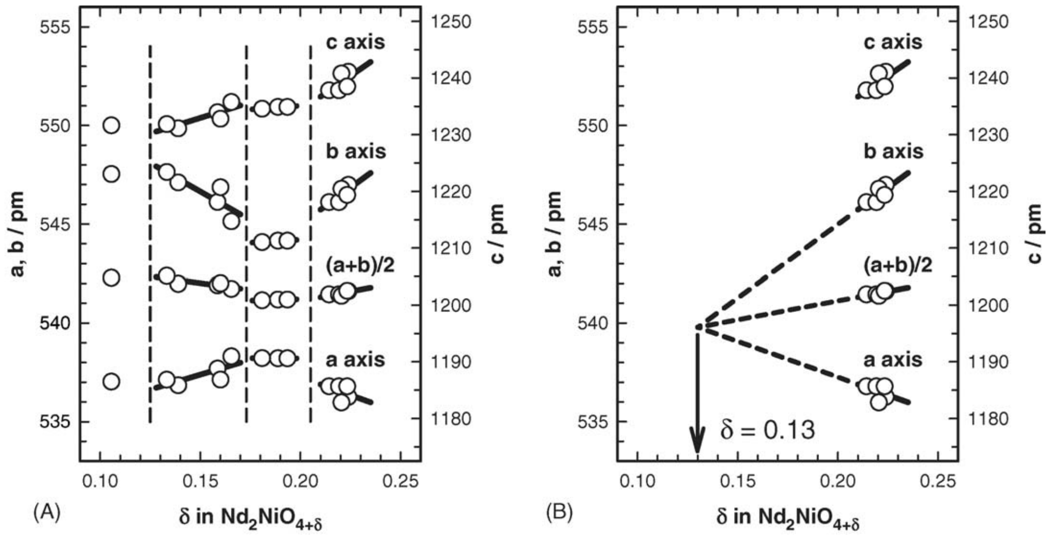

Fig. 1. Lattice constants of $Nd_2NiO_{4+\delta}$ at room temperature (A) and the expected δ value at $(b–a) = 0$ pm at room temperature for the $Nd_2NiO_{4+\delta}$ phase at $0.205 \leq \delta \leq 0.224$ (B).

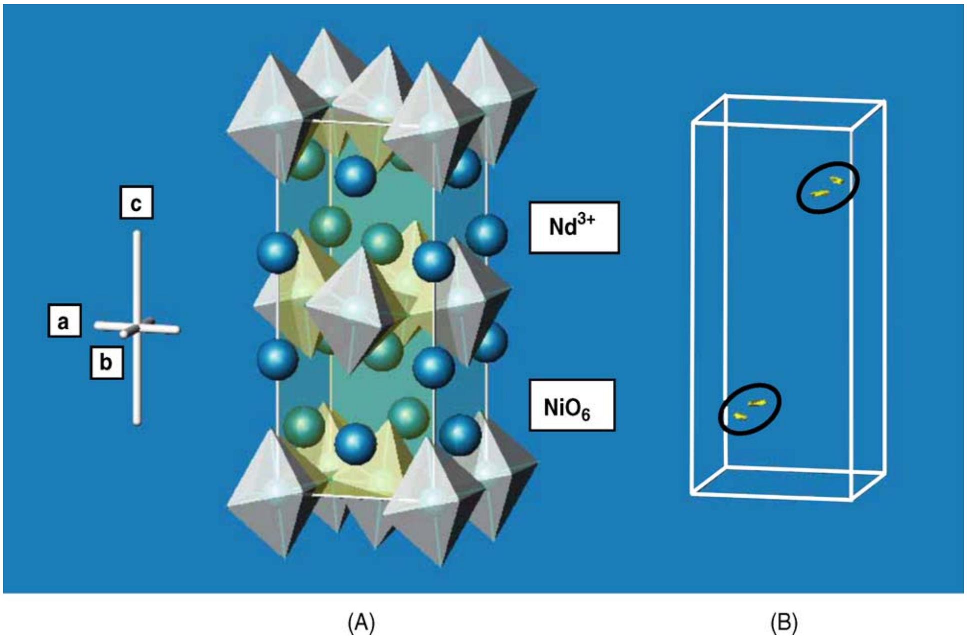

Fig. 2. Orthorhombic *Abma* structure of $Nd_2NiO_{4.223}$ at room temperature (A) and open spaces (cavities) in the *Abma* structure (B).

and 90% of the orthorhombic phase ($a = 537.24(1)$ pm, $b = 548.01(1)$ pm, $c = 1232.29(3)$ pm). The crystal system of $Nd_2NiO_{4+\delta}$ at $\delta < 0.106$ is now under investigation, and our unpublished data show that a single tetragonal phase is given at $\delta = 0.09$.

The space group of the phase at $\delta = 0.205$–0.224 will be *Abma* [5]. The Rietveld analyses done for $Nd_2NiO_{4.223}$ with *Fmmm* and *Abma* space groups give the following data: When the space group of the phase is *Fmmm*, $R_{wp} = 19.42$ and $S = 1.35$. When the space group of the phase is *Abma*, $R_{wp} = 19.04$ and $S = 1.32$. Although the difference of two statistic data is small, the data show that the space group of the $Nd_2NiO_{4.223}$ phase is *Abma*.

In Fig. 2(A), an *Abma* structure of $Nd_2NiO_{4.223}$ is drawn with the data: $a = 536.96(2)$ pm; $b = 546.65(2)$ pm; $c = 1238.91(4)$ pm; Nd1: (0, 0, 0.3577(1)); Ni1: (0, 0, 0); O1: (1/4, 1/4, 0.975(1)); O2: (0.046(3), 0, 0.177(1)). In the *Abma* structure, the NiO_6 octahedra tilts parallel to the *a*-axis, and the lengths of *a*- and *b*-axes are determined by the projection of the NiO_6 octahedra onto the *ab*-plane. The tilt of the

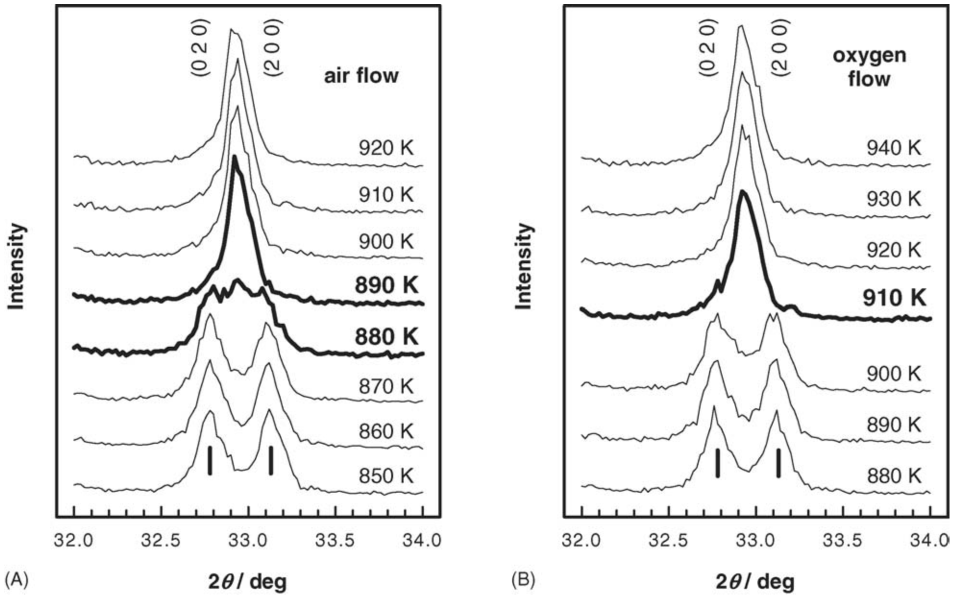

Fig. 3. X-ray powder diffraction patterns of $Nd_2NiO_{4+\delta}$ measured in an air flow (A) or an oxygen flow (B).

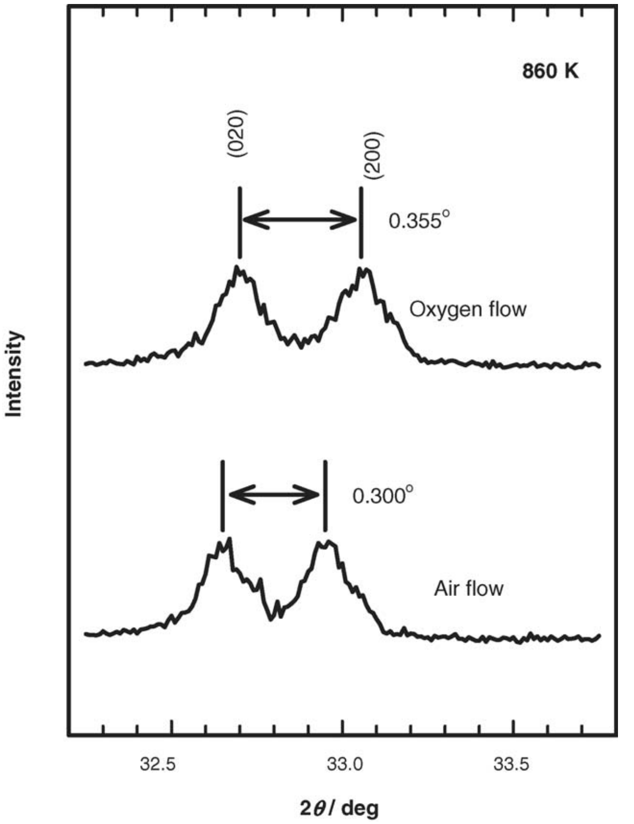

Fig. 4. X-ray powder diffraction patterns of $Nd_2NiO_{4+\delta}$ measured in an air or oxygen flow at 860 K.

NiO_6 octahedra shortens the length of *a*-axis but does not change the length of *b*-axis. The tilt of the NiO_6 octahedra is induced by the excess oxygen existing as an interstitial oxygen between two Nd–O layers. Positions of the excess oxygen cannot be determined by the Rietveld analysis of the X-ray data, but the oxygen should exist at open spaces in the cell, called cavities. In Fig. 2(B), cavities in the *Abma* structure are given with a computer program ATOMS Version 5.1. Cavities are locating at an 8e-site of (1/4, 1/4, 0.194), while only 4 cavities are found in Fig. 2(B) for the resolution of the program.

The excess oxygen is concerned for the orthorhombic–tetragonal phase transition of $Nd_2NiO_{4+\delta}$. However, at room temperature, between the orthorhombic phase at $\delta = 0.205$–0.224 and the phase at $\delta = 0.106$, another orthorhombic phase at $\delta = 0.13$–0.17 exists, and then the concernment of the excess oxygen is not clear. For considering the phase transition, the orthorhombic phase just below the phase transition temperature is the phase at $\delta = 0.205$–0.224 or the phase at $\delta = 0.13$–0.17 is important. As the temperature just below the phase transition temperature, 860 K is selected, since in Fig. 3 the phase transition is observed at 880–890 K in an air flow and at 910 K in an oxygen flow.

In Fig. 4, (2 0 0) and (0 2 0) peaks of $Nd_2NiO_{4+\delta}$ at 860 K in an air or oxygen flow are shown. The difference between the peak positions of the (2 0 0) and the (0 2 0) peaks, which is an index of the orthorhombic distortion, in an oxygen flow is larger than the difference in an air flow. Since the δ value of the sample in an oxygen flow

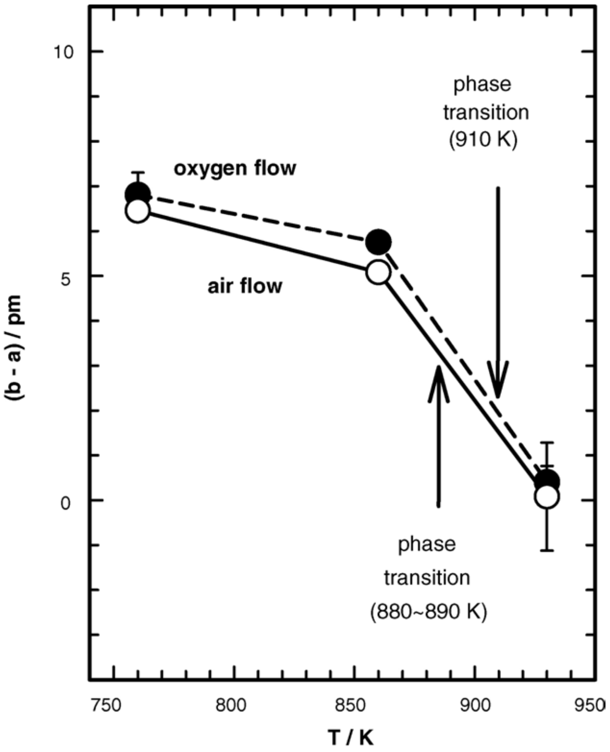

Fig. 5. Orthorhombic distortions of the (*b*–*a*) values of $Nd_2NiO_{4+\delta}$ in an air or oxygen flow at 760–930 K. Error bars are the sum of 3σ of the lattice constants *a* and *b*.

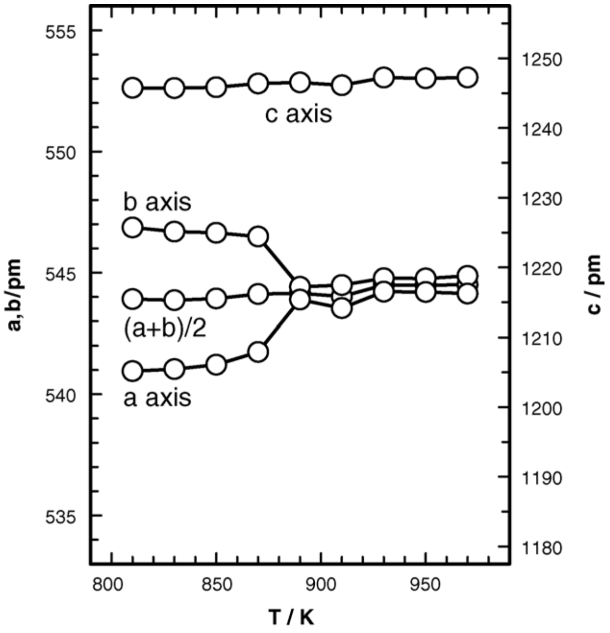

Fig. 6. Lattice constants of $Nd_2NiO_{4+\delta}$ measured in an air flow at 810–970 K.

should be larger than the value in an air flow, the difference between the peak positions is increased with increasing the δ value. The orthorhombic phase just below the phase transition temperature cannot be the room temperature phase at $\delta = 0.13$–0.17.

In Fig. 5, the (*b*–*a*) values, which are indexes of the orthorhombic distortions, of $Nd_2NiO_{4+\delta}$ at 760–930 K in an air or oxygen flow are shown. The (*b*–*a*) values in an oxygen flow are larger than the corresponding values in an air flow at 760–860 K. The orthorhombic phase at 760–860 K is not the room temperature phase at $\delta = 0.13$–0.17. This phase will be the room temperature phase at $\delta = 0.205$–0.224.

Mauvy et al. have reported an electrocatalytic activity of $Nd_2NiO_{4+\delta}$ for a cathode material of solid oxide fuel cells [7]. On using $Nd_2NiO_{4+\delta}$ for an electrochemical material, a coefficient of cubical expansion and changes of the lattice constants and of the cell volume at the phase transition temperature will be important quantities. In Fig. 6, the lattice constants of $Nd_2NiO_{4+\delta}$ in an air flow at 810–970 K are shown. At the phase transition temperature, the values of a and b are changed but the values of $(a + b)/2$ and c are not changed with temperature. No volume change is found at the phase transition temperature for $Nd_2NiO_{4+\delta}$. Relative changes of $\Delta a/a$ and $\Delta b/b$ at the phase transition temperature are, respectively, 0.39% and 0.49%. The coefficient of cubical expansion of $Nd_2NiO_{4+\delta}$ in air evaluated from the X-ray data in Fig. 6 is 2.47 H 10^{-5} K^{-1} at 810–970 K.

4. Conclusions

Although the orthorhombic–tetragonal phase transition is not found at room temperature at $\delta = 0.15$, the $Nd_2NiO_{4.106}$ phase consists of 10% of the tetragonal phase and 90% of the orthorhombic phase. Excess oxygen is concerned for the orthorhombic–tetragonal phase transition of $Nd_2NiO_{4+\delta}$. The orthorhombic phase just below the phase transition temperature will be the room temperature phase of $\delta = 0.205$–0.224, of which space-group is *Abma*. A high temperature orthorhombic–tetragonal phase transition of $Nd_2NiO_{4+\delta}$ will be an *Abma*–*Fmmm* transition caused by the decrease of the δ value due to the increase of temperature.

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