Thermodynamic analyses of the orthorhombic-to-tetragonal phase transition in Pr$_{2-x}$Nd$_x$NiO$_{4+\delta}$ under controlled oxygen partial pressures

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Supporting Information

Figure S1. Rietveld patterns of Pr$_2$NiO$_{4+\delta}$ by XRD using the computer program Z-code [1, 2]. Crystal structure models are (a) orthorhombic Fmmm and (b) mixed phase of Fmmm and monoclinic F$112/m$. The obtained and calculated patterns and difference plots are shown by red mark, light blue, and dark blue lines, respectively. Bragg peak positions are estimated from the obtained lattice constants. Green and orange tick marks indicate the Bragg peak positions of Fmmm and F$112/m$, respectively.

Figure S2. DSC curves of PrNdNiO$_{4+\delta}$ around the phase transition temperatures under various $P$(O$_2$) during (a) heating and (b) cooling.

Figure S3. DSC curves of Pr$_{0.5}$Nd$_{1.5}$NiO$_{4+\delta}$ around the phase transition temperatures under various $P$(O$_2$) during (a) heating and (b) cooling.

Figure S4. TG curves of PrNdNiO$_{4+\delta}$ around the phase transition temperatures under various $P$(O$_2$) during (a) heating and (b) cooling.

Figure S5. TG curves of Pr$_{0.5}$Nd$_{1.5}$NiO$_{4+\delta}$ around the phase transition temperatures under various $P$(O$_2$) during (a) heating and (b) cooling.

Figure S6. Compositional dependence of oxygen content, $\delta$, of Pr$_{2-x}$Nd$_x$NiO$_{4+\delta}$ at the beginning of the phase transition during heating under $P$(O$_2$) of 1.0 $\times$ 10$^{-2}$ bar. The values in parentheses show the phase transition temperatures.
Figure S7. XRD pattern of Pr$_2$NiO$_{4+\delta}$ after the decomposition reaction under 2%H$_2$/N$_2$. For reference, XRD patterns of Pr$_2$O$_3$ and Ni are also shown in this figure [3, 4].

Figure S8. Compositional dependence of the phase transition temperatures, $T_p$, of Pr$_{2-x}$Nd$_x$NiO$_{4+\delta}$ in air ($P$(O$_2$) = 0.205 bar), estimated using $\Delta S^\circ$ and $\Delta H^\circ$ obtained in this work and measured with DTA [5].

Table S1 (a) Lattice constants and (b) reliability factors for the XRD data of Pr$_2$NiO$_{4+\delta}$ by the Rietveld analysis with two kinds of models; a single phase of the orthorhombic $Fmmm$ (Model 1) and the mixed phase of $Fmmm$ and $F122/m$ (Model 2), as shown in Figures S1 (a) and (b).
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(a) Lattice constants

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<tr>
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<th>a / Å</th>
<th>b / Å</th>
<th>c / Å</th>
<th>β / °</th>
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<td>Model 2</td>
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<td>90</td>
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<tr>
<td></td>
<td>(F122/m)</td>
<td>5.14(49)</td>
<td>5.25(45)</td>
<td>12.45(31)</td>
<td>90.067(9)</td>
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(b) Reliability factors

<table>
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<th>Mode</th>
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<th>$R_B$</th>
<th>$R_F$</th>
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<td>(F122/m)</td>
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<td>0.0362</td>
<td>0.0192</td>
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References


