Crystal structure, thermal expansion and electrical conduction behavior of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ at high temperature

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In order to evaluate potential of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ as new cathode material for solid oxide fuel cells, single phase preparation, crystal structure at various temperatures, thermal expansion property and electrical conduction behavior at high temperature were investigated. Single phase of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($0.3 \leq x \leq 1.0$) with orthorhombic distorted perovskite structure was successfully prepared by Pechini method. No structural phase transition was observed between room temperature and 1000°C in air. Linear thermal expansion coefficient was evaluated to be around $1.16 \times 10^{-5} \text{ K}^{-1}$, showing fair agreement with that of yttria-stabilized zirconia and gadolinia-doped ceria which were frequently employed as electrolyte material. Electrical conductivity of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ increased with increasing Ni content; however, the conductivity did not exceed that of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. From the comparison of activation energy of variable range hopping conduction and Mössbauer spectroscopy between $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ and $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, it was suggested that hole carrier concentration of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ was lower than that of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ owing to variation of valence of Pr ion.

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1. Introduction

For improvement of energy conversion efficiency of solid oxide fuel cells, cathode material with high electronic and ionic conduction property is required. So far, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ have been employed as cathode material of solid oxide fuel cells. The deficient oxide ion conduction and higher thermal expansion than that of electrolyte material such as yttria-stabilized zirconia are problems for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, respectively. High chemical reactivity of Sr against electrode material is also a serious problem for both materials. For solution of above problems, new cathode material including no Sr is required. One of the candidate materials is $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ with perovskite structure.^{1)–15)} For the specimens with $0.4 \leq x \leq 1.0$, electrical conductivity increases with increasing Ni content, resulting in enough electrical conductivity as cathode material for $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$.^{1),2)} Amount of oxide ion vacancy, δ , as high as 0.10 has been reported in $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$,^{3),4)} suggesting not only high electronic but also high oxide ion conductivity, showing agreement with high oxide ion diffusion property reported by Nishi and coworkers.⁵⁾ However, electrical conduction of the specimens with $0.0 \leq x \leq 0.4$ decreases with increasing Ni content, originating from poor sintering property owing to instability at high temperature.^{6),7)}

One of the probable methods for development of new cathode material is substitution of La site of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. Especially,

$\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ was expected as new cathode material showing peculiar property since valence change between Pr^{3+} and Pr^{4+} was frequently observed. It was also reported that inserting Pr_6O_{11} layer between $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ cathode and electrolyte was effective to improve cathode property.¹⁶⁾ Improvement of property by substitution of Pr for La was expected also from the preceding research reporting that $\text{Pr}_2\text{NiO}_{4+\delta}$ possessed the most superior property as SOFC cathode among $\text{Ln}_2\text{NiO}_{4+\delta}$ ($\text{Ln}=\text{Pr}$, Nd, La) with K_2NiF_4 structure.¹⁷⁾

Although preparation, crystal structure, electrical property and optical property of various LnFeO_3 (Ln : lanthanoid ion) were reported,¹⁸⁾ those of $\text{LnNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ have scarcely been reported. In this study, single phase of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ has been prepared and its crystal structure and electrical property at high temperature have been investigated for evaluation as new cathode material for solid oxide fuel cells. Chemical state of Fe in $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ has been investigated by Mössbauer spectroscopy for discussion on difference of electrical conduction behavior between $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ and $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$.

2. Experimental

$\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ was prepared by Pechini method with starting materials of Pr_6O_{11} (99.9%, Furuuchi Chemical Corp.), Ni ($\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%, Wako Pure Chemical Industries) and Fe ($\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%, Wako Pure Chemical Industries). Prior to weighing, the purity of Pr_6O_{11} was evaluated by EDTA titration. Purity of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was evaluated from the weight of NiO and Fe_2O_3 remained after heat-treatment at 1000°C, respectively, in air. Pr_6O_{11} was dissolved in mixture of dilute HNO_3 and hydrogen peroxide. Ni ($\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Fe

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$(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in H_2O . The solutions were mixed together in the proper ratio of the metal ions. After addition of citric acid and ethylene glycol, the mixed solution was heated at about 450°C until the residual materials was fired, resulting in precursor. The molar ratio of metal ions/citric acid/ethylene glycol was fixed at 1:2:8. The obtained precursor was crushed into powder and calcined at 750°C for 24 h in air, followed by additional heating at 1000°C for 10 h in air and successive heating at 900°C for 12 h in air. The obtained powders were analyzed with X-ray diffraction measurement (Cu $K\alpha$: 50 kV, 250 mA, RINT-2500, Rigaku Co., Ltd.) at room temperature to distinguish whether single phase was obtained or not. Lattice constants and molar volumes were estimated from X-ray diffraction patterns.

For confirmation of existence of the structural phase transition in $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ as is in $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, X-ray diffraction measurements were performed at high temperatures in air. Temperatures employed for the measurement were between 100 and 1000°C at interval of 100°C . The lattice constant and the molar volume of each temperature were calculated from the Bragg angles of the peaks indexed as 204, 223 224 and 025 of orthorhombic symmetry. In some cases, the separations of overlapping XRD peaks were performed using Pearson VII function with JADE 5.0 (Materials Data, Inc.).

The powder specimen was pressed into cylindrical shape with 5 mm diameter and about 10 mm height and sintered at 1000°C for more than 12 h in air. Linear thermal expansion of the sintered samples was measured with dilatometer (TMA8310, Rigaku Co., Ltd.) whose sample stage, push rod, and reference were made of silica. The samples were heated with $5^\circ\text{C}/\text{min}$ to 900°C and successively cooled to 250°C also with $5^\circ\text{C}/\text{min}$. The heating and cooling measurements were repeated to confirm reproducibility. Total TEC, $\varepsilon_{\text{total}}$, were estimated from the slope between the temperature, T , and linear thermal expansion using the following equation,

$$\varepsilon_{\text{total}} = 1/l_0(dl/dT) \quad (1)$$

where l and l_0 are the length of the bulk specimen at measurement temperature and before the measurement, respectively. In this

study, dl/dT at each temperature was approximated using the differential of the length of the sample at temperature intervals of 5°C for smoothing.

The electrical conductivity of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ at temperatures between 300 and 800°C in air was measured using the sintered specimens with DC four probe method with Pt electrodes and wires. SEM observation of fractured cross section of the samples was also carried out and the relationship between composition and grain size was investigated.

Mössbauer spectroscopy using 14.4 keV γ -ray from $^{57}\text{Co}/\text{Rh}$ foil was measured at room temperature for the pulverized powder. In order to analyze magnetic property and chemical state of Fe, curve fitting using Lorentz function was carried out for the obtained spectra with originally manufactured program. Intensity, isomer shift, line width, quadrupole splitting and internal magnetic field were employed as parameters. Line widths and peak areas within each quadrupole doublet were assumed to be equal. Isomer shifts were expressed with respect to the centroid of the spectrum of metallic iron foil.

3. Results and discussion

3.1 Preparation of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ single phase with Pechini method

X-ray diffraction patterns of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ powder with $0.2 \leq x \leq 1.0$ prepared by the Pechini method are shown in Fig. 1(a). All the peaks of $\text{PrFeO}_{3-\delta}$ ($x = 1.0$) were successfully indexed as orthorhombic distorted perovskite with $a \approx \sqrt{2}a_p$, $b \approx \sqrt{2}a_p$ and $c \approx 2a_p$, where a_p is lattice constant of pseudo-cubic perovskite structure, showing agreement with the preceding report.¹⁸⁾ Apparently, the number of the peaks decreased with increasing Ni content as shown in Fig. 1(b); however, peak with the specimens with $x = 0.5$ – 0.3 in Fig. 1(b) can be explained as overlapping of several peaks due to similar $a/\sqrt{2}$, $b/\sqrt{2}$ and $c/2$ rather than single peak because of wide full width at half maximum. Disappearance of minor peaks and appearance of new peaks were never observed with increasing Ni content for the diffraction patterns of the specimens with $1.0 \geq x \geq 0.3$. Especially, the peaks indexed as 111, 021, 113, 122 and 212, which

Fig. 1. (a) X-ray diffraction patterns of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.2$ – 1.0) at room temperature obtained using Cu $K\alpha$ radiation. (b) Close up of (a) for $x = 0.3$ – 1.0 around $2\theta = 66.5$ – 69.5° . All the diffraction patterns for $x = 0.3$ – 1.0 can be indexed as orthorhombic distorted perovskite structure. The peaks of unidentified impurity and NiO were represented as ● and ○, respectively.

should disappear for rhombohedral symmetry,²⁾ were observed for all the specimens. This indicates orthorhombic crystal structure and no structural phase transition in $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, which shows different behavior from that of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ with structural phase transition from orthorhombic to rhombohedral distorted perovskite at $x = 0.50$.^{2),8),9)} For the specimen with $x = 0.2$, unidentified impurity and trace amount of NiO were observed, suggesting that solution limit exists between $x = 0.2$ and 0.3 .

As shown in Fig. 1(b), diffraction peaks shifted to higher 2θ with increasing Ni content, indicating successful Ni solution for Fe site. Since clear separation of 040, 224, 041, 400, 025 and 140 peaks was not observed for the specimens with $0.3 \leq x \leq 0.8$, the peak separation was performed to calculate lattice constants and molar volumes. **Figure 2** shows compositional dependence of lattice constants and molar volume of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ calculated from the Bragg angle of 204, 223, 224 and 025 peaks. Being different from $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$,^{2),8)} almost linear relationship obeying Vegard's law was observed, indicating homogeneous distribution of Ni and Fe in B-site of orthorhombic distorted

Fig. 2. Variation of lattice constants and molar volume of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.3$ – 1.0) on Fe content.

perovskite phase without structural phase transition. At $x = 0.8$, slight bending, which could be attributed to magnetic phase transition discussed later, was observed.

3.2 Analysis of crystal structure and phase transition behavior of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ by high temperature X-ray diffraction measurements

Figure 3(a) shows X-ray diffraction patterns of PrFeO_3 at various temperatures in air. Drastic variation of diffraction patterns such as peak disappearance and appearance of new peaks by variation of temperature was not observed, indicating no structural phase transition between room temperature and 1000°C . **Figure 3(b)** shows X-ray diffraction peaks in 2θ range between 66.5 and 69.0° obtained with high resolution for evaluation of lattice constants and molar volume. The diffraction peaks shifted to low 2θ without variation of peak shape with increasing temperature, which could be ascribed to thermal expansion.

X-ray diffraction patterns in air at various temperatures between 30 and 1000°C of $\text{PrNi}_{0.1}\text{Fe}_{0.9}\text{O}_{3-\delta}$, $\text{PrNi}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$, $\text{PrNi}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ and $\text{PrNi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ are shown in **Figs. 4–7**. All the peaks shown in **Figs. 4(a)–7(a)** could be indexed as orthorhombic symmetry, indicating no structural phase transition from orthorhombic to rhombohedral, which was observed in $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$.⁸⁾ Diffraction peaks in 2θ range of 66.5 – 70.5° were shown in **Figs. 4(b)–7(b)**. The peak shift to low 2θ by increase of temperature without variation of peak shape was observed, indicating thermal expansion without structural phase transition. For the diffraction peaks in 2θ range of 66.5 – 70.5° for the specimens with x below 0.7 , the separation of overlapping peaks was carried out to evaluate lattice constants and molar volume. **Figure 8** shows temperature dependence of the molar volume of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_3$. Almost linear relationship and no anomaly were observed regardless of composition, showing agreement with no structural phase transition between 30 and 1000°C .

It can be speculated that the structural phase transition from orthorhombic to rhombohedral perovskite hardly occurs for perovskite with low crystal symmetry since transition involves heightening of crystal symmetry. Due to smaller ionic radius of

Fig. 3. (a) X-ray diffraction patterns of PrFeO_3 at 30 – 1000°C in $2\theta = 20$ – 70° . (b) Close up of (a) around $2\theta = 66.5$ – 69.0° . All the diffraction patterns can be indexed as orthorhombic symmetry.

Fig. 7. (a) X-ray diffraction patterns of $\text{PrNi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ at 30–1000°C in $2\theta = 20\text{--}70^\circ$. (b) Close up of (a) around $2\theta = 67.5\text{--}70.5^\circ$. All the diffraction patterns can be indexed as orthorhombic symmetry.

Fig. 8. Variation of molar volume of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ on temperature between 30–1000°C in air measured with high temperature X-ray diffraction.

Pr^{3+} than La^{3+} , tolerance factor of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ should be smaller than that of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, which was confirmed for PrFeO_3 and LaFeO_3 .¹⁸⁾

3.3 Thermal expansion behavior of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$

Figure 9(a) shows thermal expansion behavior of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ at temperatures between room temperature and 900°C. Linear and reversible thermal expansion without anomaly was observed in every specimen, showing agreement with no structural phase transition. By using Eq. (1), thermal expansion coefficient was calculated and its temperature dependence was depicted in Fig. 9(b). For the specimens with $0.3 \leq x \leq 0.7$, nearly constant thermal expansion coefficient and no anomaly were observed, showing agreement with no structural transition between room temperature and 900°C observed by high temperature X-ray diffraction measurements. For the specimens with $x = 0.8\text{--}1.0$, slight anomaly was observed at the temperatures represented by arrows. Since no structural phase transition was observed in the specimens by high temperature X-ray diffraction, the anomaly

was ascribed to another kind of phase transition. One possible candidate was magnetic phase transition from antiferromagnetic to paramagnetic phase, which was also observed for $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$,^{8)–10)} which will be discussed later.

From the slope of Fig. 8, volume thermal expansion coefficient was calculated. Assuming isotropic crystal structure, linear thermal expansion coefficient can be calculated to be 1/3 of volume thermal expansion. Figure 10 shows thus calculated linear thermal expansion coefficient together with those evaluated by dilatometry around 700°C. Both linear thermal expansion coefficients showed good agreement. In addition, little difference was observed between thermal expansion coefficient of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ and that of electrolyte material such as yttria stabilized zirconia and gadolinia-doped Ceria.

3.4 Electrical conductivity of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$

Figure 11(a) shows temperature dependence of electrical conductivity of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ in air. Electrical conductivity of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ increased with increasing Ni contents. The maximum electrical conductivity was obtained for $\text{PrNi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$. Apparently, temperature dependence of electrical conductivity varied from semiconducting to semimetallic; however, almost linear relationship was observed between $\ln \sigma T$ and $1/T$ as Fig. 11(b) shows, indicating that variable range hopping model could be applicable for $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ as $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$.⁴⁾

Figure 12 shows comparison of (a) electrical conductivity at 800°C and (b) activation energy for conduction, E_a , assuming variable range hopping model, between $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ⁴⁾ and $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. Electrical conductivity of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ monotonically increased with increase of Ni content. Drastic decrease of conductivity by increasing Ni content more than 0.6 detected in $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ was not observed. This is because sintering density was almost constant to be about 60% regardless of Ni content in $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ as Fig. 13 shows. As shown in SEM images of the cross section depicted in Fig. 14, density of void was almost constant against Ni content although a little decrease of particle size with increasing Ni content was observed. The maximum conductivity was about $90 \text{ S}\cdot\text{cm}^{-1}$ for $\text{PrNi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$; however, the conductivity of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ did not exceed that of $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$.

Fig. 9. (a) Thermal expansion and (b) thermal expansion coefficient of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($0.3 \leq x \leq 1.0$) measured with dilatometry. Heating rate is 5 °C/min.

Fig. 10. Linear thermal expansion coefficient of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($0.3 \leq x \leq 1.0$) evaluated with high temperature X-ray diffraction (●) and dilatometry (○).

As a reason for lower electrical conductivity of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ than that of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, difference of sintering density cannot be acceptable since similar sintering density and morphology were obtained for $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ and $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ as shown in Figs. 13 and 14. Lower carrier mobility derived from crystal structure or lower carrier concentration is probable. As shown in Fig. 12(b), although higher E_a was observed for $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ than $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ for Fe-rich specimens, there was little difference in E_a between $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ and $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ for Ni-rich specimens. Since E_a corresponds to carrier mobility, it can be concluded that there was little difference in carrier mobility between $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ and $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ for Ni-rich specimens. If difference of carrier density should be the main reason

of the difference of electrical conductivity, chemical state of Fe should be different between $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ and $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. Since it was reported that Mössbauer spectroscopy is powerful tool for analysis of chemical state of Fe in $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$,⁸⁾⁻¹⁰⁾ Mössbauer spectroscopy of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ was carried out and results were compared.

3.5 Mössbauer spectroscopy of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$

Figure 15(a) shows Mössbauer spectra of single phase $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. Sextet peaks were observed for PrFeO_3 , indicating antiferromagnetic property at room temperature. Sextet peaks were also observed for $\text{PrNi}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, indicating antiferromagnetic phase at room temperature for the specimens with $x = 0.8$ and 1.0. Sextet peaks disappeared and apparent single peak was observed, indicating paramagnetic property, for the specimens with $0.3 \leq x \leq 0.7$. Anomaly observed at $x = 0.8$ in compositional dependence of molar volume of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ in Fig. 2 can be ascribed to the magnetic phase transition. This phase transition from antiferromagnetic to paramagnetic was also observed for $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$,^{8),9)} although the phase boundary was observed at x less than 0.7 for $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. Figure 15(b) shows enlarged apparent single peak of Mössbauer spectra for $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ with $0.3 \leq x \leq 0.7$. The peaks of the specimens were composed of doublet peak due to quadrupole splitting. The isomer shift decreased with increasing Ni content, indicating Fe valence increased from 3+ to 4+. This tendency was also reported for the Mössbauer spectra for paramagnetic $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$.¹⁰⁾

Figure 16 summarizes (a) quadrupole splitting and (b) isomer shift obtained by curve fitting of the Mössbauer spectra shown in Fig. 15(b). Quadrupole splitting and isomer shift of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ¹⁰⁾ were shown for comparison. Quadrupole splitting corresponds to symmetry of electronic field around Fe ion. For $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, drastic variation of quadrupole splitting was

Fig. 11. Temperature dependence of electrical conductivity of PrNi_{1-x}Fe_xO_{3-δ} in air. (a) Arrhenius plot, (b) plot assuming variable range hopping.

Fig. 12. (a) Electrical conductivity at 800°C and (b) activation energy for hopping conduction of PrNi_{1-x}Fe_xO_{3-δ} in air. Those for LaNi_{1-x}Fe_xO_{3-δ}^{1),2),4)} are shown for comparison.

Fig. 13. Sintering density of PrNi_{1-x}Fe_xO_{3-δ} and LaNi_{1-x}Fe_xO_{3-δ}.²⁾

observed at $x = 0.5$, which could be attributed to structural phase transition between orthorhombic and rhombohedral. Almost constant quadrupole splitting against Ni content was observed in PrNi_{1-x}Fe_xO_{3-δ}, corresponding to no structural phase transition with Ni content observed with X-ray diffraction measurements.

Isomer shift of both PrNi_{1-x}Fe_xO_{3-δ} and LaNi_{1-x}Fe_xO_{3-δ} decreased with increasing Ni content, indicating Fe valence approaches 4+ by introduction of carrier hole with increasing Ni content. It was observed that isomer shifts of PrNi_{1-x}Fe_xO_{3-δ} was higher than those of LaNi_{1-x}Fe_xO_{3-δ}, indicating lower Fe valence, i.e., lower hole carrier density in PrNi_{1-x}Fe_xO_{3-δ}, showing agreement with electrical conduction measurements.

It is probable that part of hole carrier generated by Ni substitution is localized around Pr site according to following chemical equation,

Fig. 14. SEM images of cross section of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.3$ – 1.0). Fig. 15. (a) Mössbauer spectra of single phase $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.3$ – 1.0). (b) Close up of (a) around -0.2 – 1.0 mm/s. Apparent single but doublet peak was observed for $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.3$ – 0.7). Fig. 16. (a) Quadrupole splitting and (b) isomer shift of the Mössbauer spectra of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. Those for $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}^{10)}$ were depicted for comparison.

since Pr^{4+} is stable in air. If some part of Pr are tetravalent, density of delocalized hole carrier decreases and higher crystal symmetry is not observed even by substitution of Ni and increasing temperature since tolerance factor decreases. Obtained behavior of electrical conductivity and crystal structure of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ showed fair agreement with this hypothesis.

4. Conclusions

Single phase of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($0.3 \leq x \leq 1.0$) with orthorhombic distorted perovskite structure was successfully prepared by Pechini method. No structural phase transition was observed between room temperature and 1000°C in air. Linear thermal expansion coefficient evaluated by high temperature X-ray diffraction and dilatometry was measured to be around $1.16 \times 10^{-5} \text{ K}^{-1}$, showing fair agreement with that of yttria-stabilized zirconia and gadolinia-doped ceria which were frequently employed as electrolyte material. Electrical conductivity increased with increasing Ni content; however, the maximum electrical conductivity was below $10^2 \text{ S} \cdot \text{cm}^{-1}$ and did not exceed that of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. From the comparison of activation energy of variable range hopping conduction and Mössbauer spectroscopy between $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ and $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, it was suggested that hole carrier concentration of $\text{PrNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ was lower than that of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ owing to localization of hole carrier around Pr, resulting in variation of valence of Pr ion.

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