Formation of C-type rare earth structures in the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ system: a factor in the decrease in oxide-ion conductivity

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It was found that oxide-ion conductivity of Nd-doped CeO_2 ($\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$) increased with an increase in Nd content x up to $x = 0.2$, showing a maximum value at $x = 0.2$, and then decreased with x . In order to clarify the origin of the decrease in the conductivity of the heavily Nd-doped CeO_2 , Rietveld analyses of the X-ray diffraction and neutron diffraction data were carried out, assuming two phases with oxygen deficient fluorite-type and rare-earth C-type structures ($0.45 \leq x \leq 0.7$). The oxide-ion conductivity of the heavily Nd-doped CeO_2 is discussed in relation to the formation of the rare-earth C-type structure, which derives from the oxygen ordering of the defect fluorite-type structure.

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1. Introduction

Oxygen deficient fluorite-type structures and rare-earth C-type structures which is a structure family related to the fluorite-type structure have been attracting great interest as electrolytes for solid oxide fuel cells due to their high oxide-ion conductivities. Aliovalent cation-doped CeO_2 has been widely studied in recent years from various viewpoints, such as electrochemistry, crystallography, and solid-state chemistry. Inaba and Tagawa¹⁾ have summarized the many papers concerning ceria-based solid electrolytes.

Yahiro et al.²⁾ have reported that the ionic transference number of oxygen for $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{1.9}$ above 973 K is almost unity, suggesting that the Nd-doped CeO_2 material is an oxide-ion conductor. Nishino et al.³⁾ have also reported that the electrical conductivity of $\text{Ce}_2\text{Nd}_2\text{O}_7$ ($\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$) increased slightly in proportion to the oxygen partial pressure, indicating the small contribution of a hole conduction. It is generally accepted that when CeO_2 is doped with Nd_2O_3 , oxygen vacancy could be introduced into the oxygen sublattice sites based on the following defect reaction, according to Kröger-Vink notation:

The oxygen vacancy that was introduced by the doping of the aliovalent cation cannot necessarily move freely, but may be bound to the doped cations, producing a defect associate ($\text{Nd}_{\text{Ce}}'-\text{V}_{\text{O}}$) due to their electrostatic interactions.⁴⁾⁻⁵⁾ Therefore, the associates in the oxide-ion conductor will play an important role in relation to the oxide-ion conduction due to the long-range migration of the oxygen vacancy. Several authors have explained

the decrease in oxide-ion conductivity of highly doped CeO_2 or ZrO_2 systems in terms of the dopant-vacancy associates.⁶⁾⁻⁷⁾ It has been reported that the reduced conductivity increased again with the co-doping of secondary elements, for instance, Al_2O_3 in the $\text{ZrO}_2-\text{Sc}_2\text{O}_3$ ⁸⁾ and Li_2O in $\text{CeO}_2-\text{Sm}_2\text{O}_3$ systems.⁹⁾ The authors concluded that the enhancement of conductivity was ascribed to the cleaning effect of the grain boundary phase by the second dopant. On the other hand, Yamamura et al.¹⁰⁾⁻¹¹⁾ reported the appearance of the rare earth C-type phase in the highly doped fluorite-type solid solutions, where the C-type phase derives from the oxygen ordering of the defect fluorite-type structure. Furthermore, they have reported that when the oxide-ion conductivity in the highly Nd-doped CeO_2 decreased, the Debye-type polarizations due to the dopant-vacancy associates also decreased, suggesting that the ordering of the oxygen vacancy suppressed the oxide-ion conductivity.

Recently, Mori et al.¹²⁾ have reported that the micro-domain structure that appeared in the doped CeO_2 solid solutions, $\text{Ce}_{0.75}\text{M}_{0.25}\text{O}_{1.875}$ ($\text{M} = \text{Gd}, \text{Yb}, \text{Y}$), can be recognized as a transition structure between the fluorite-type structure and the rare earth C-type structure in an investigation using transmission electron microscopy (TEM). On the other hand, Wang et al.¹³⁾ investigated local structures around both host Ce^{4+} and dopant Y^{3+} in the 10 mol% Y_2O_3 doped ceria solid solution using EXAFS spectroscopy, and they found that the local structures around the dopant Y^{3+} showed a stronger resemblance to the structure around the Y^{3+} cation in the C-type Y_2O_3 structure.

In the present study, we refined the crystal structures of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ assuming two phases of F-type and rare-earth C-type structures by Rietveld analyses of X-ray and neutron powder diffraction data, in order to clarify the relationship between oxide-ion conductivity and the crystal structure of the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ materials.

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2. Experimental

Powder samples of the solid solution system $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7$) were synthesized by a solid-state reaction method, using CeO_2 (99.99%, High Purity Chemicals, Japan) and Nd_2O_3 (99.9%, Huruuchi Chemicals, Japan) as starting materials.

Weighed powders were wet ball-milled for 20 h using a milling pot made of synthetic resin and resin-coated balls, and ethanol as the dispersion reagent. After drying, the powder mixtures were calcined at 1373 K for 5 h in air. The powder samples were molded uniaxially under a pressure of 50 MPa and subjected to rubber press at 200 MPa, after sieving through a 53- μm mesh size. The compacts thus obtained were sintered at 1873 K for 10 h in air. The relative densities of the sintered specimens, which were estimated from the geometrical dimensions and weight, were ~95% of the X-ray density.

The microstructures of the sintered specimens were observed using a scanning electron microscopy (SEM) (Hitachi, Ltd., S-4000), after thermal etching at 1873 K for 1 h in air.

The powdered samples of the sintered specimen were characterized by means of an X-ray diffraction (XRD) radiation (model: RINT-UltimaIII, Rigaku Co.) with monochromated Cu K α . The parallel beam method was used for the X-ray optical system.

In order to carry out the Rietveld analysis, XRD diffraction data was collected in the 2θ scanning range from 10° to 130° with a step interval of 0.02° at room temperature. The data was stimulated up to 20,000 counts for the strongest diffraction peak. No correction on preferred orientation was made because of the fine grained powder samples.

The neutron powder diffraction measurements were conducted in air using the Kinken powder diffractometer, HERMES, of the Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor of the Japan Atomic Energy Agency (JAEA), Tokai.¹⁴⁾ Neutrons with wavelength 0.18204 nm were obtained using the 331 reflection of a Ge monochromator. Diffraction data was collected in the 2θ scanning range from 5° to 155° with a step interval of 0.1° . The collected data was analyzed by the Rietveld method using the RIETAN-2000 application software.¹⁵⁾

The DC electrical conductivity (σ_{dc}) of the sintered specimens was measured by the four-probe method in the temperature range

of 873 to 1273 K in air. The geometrical dimensions of the sintered bar for the DC conductivity measurements were $4 \times 4 \text{ mm}^2$ in cross-sectional area and ~30 mm in length. For the electrical conductivity measurements, platinum electrodes were attached by firing at 1223 K.

3. Results and discussion

The X-ray diffraction (XRD) patterns of the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ system ($0.0 \leq x \leq 0.7$) showed a cubic phase with a fluorite-type (F) structure in the composition range, $0.0 \leq x \leq 0.3$. Some extra peaks appeared in addition to the fluorite-type XRD pattern in the composition range, $0.4 \leq x \leq 0.7$, which were assigned to a rare earth C-type (C) structure. For the sample with $x = 0.4$, only 332 and 134 peaks of the C phase were detected with difficulty by the XRD experiment with a very slow scan speed of 100 s/point. The intensity of diffraction peaks corresponding to the C phase increased with an increasing Nd content in this composition range. In the composition range $x > 0.7$, an Nd_2O_3 phase, which has a rare-earth A-type structure with hexagonal symmetry, appeared, in addition to the C phase.

Figure 1 shows Arrhenius plots of DC electrical conductivity (σ_{dc}) of the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ ($0.0 \leq x \leq 0.6$) system in the temperature range from 873 to 1273 K in air. Figure 2 shows the compositional dependences of σ_{dc} at various temperatures. The σ_{dc} values increased with increasing x , showing the maximum value at $x = 0.2$, and then decreased until $x = 0.6$. The lowering of σ_{dc} in the range of $x > 0.2$ has been discussed in relation to dopant (Nd)-vacancy associates, which occurred by the electrostatic interaction between dopant (Nd_{Ce}') and oxygen vacancy ($\text{V}_{\text{O}}^{\bullet}$).⁶⁻⁷⁾ As shown in Fig. 1, the activation energy for oxide-ion conduction, which was estimated to be 176 kJ mol⁻¹ for $x = 0.0$, decreased with increasing x , reaching a minimum value of 69.2 kJ mol⁻¹ at $x = 0.2$, where the maximum conductivity was observed, and then increased linearly with increasing x . The activation energies for oxide-ion conduction agreed with the values after Faber et al.¹⁶⁾ They suggested that the activation energy for the oxide-ion conductivity is the sum of two contributing factors, that is, the migration enthalpy and the association enthalpy of the doped ion-oxygen vacancy. Therefore, the high activation energy in the heavily doped samples may originate from the large contribution due to the high concentration of the associate.

In order to clarify the relationship between the oxygen defect structure and oxide-ion conductivity, we refined the crystal struc-

Fig. 1. Arrhenius plots of electrical conductivity for the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ system, where numbers represent the activation energies for electrical conduction.

Fig. 2. Compositional dependences of dc-conductivity in the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ system at various temperatures, 873 K (◆), 973 K (○), 1073 K (●).

Fig. 3. Rietveld analysis of XRD data for $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$ on the basis of the two models.

ture of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ by means of the Rietveld analysis of X-ray and neutron powder diffraction data. Rietveld analyses of the XRD data for the samples with a composition range of $0.0 \leq x \leq 0.4$ were carried out assuming the F structure (space group $Fm\bar{3}m$, No. 225), where the sample with $x = 0.4$ was treated as the F phase because no C phase peak was observed in the XRD data for the Rietveld analyses. On the other hand, for the samples in the range of $0.45 \leq x \leq 0.7$, which comprise the C and F phases, the Rietveld analyses were carried out assuming the following two structure-models: the C structure (space group $Ia\bar{3}$, No. 206) containing an excess oxygen which is placed on 16c site (Model I), and the mixed phases of oxygen deficient F (space group $Fm\bar{3}m$, No. 225) and stoichiometric C structures (Model II).

Figure 3 shows the final profile fits and the difference patterns of $x = 0.5$, which were analyzed on the basis of the two models, I and II. The structural parameters estimated on the basis of the two models are summarized in Table 1. The R_{wp} value of Rietveld analyses on the basis of Model II for $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$ ($x = 0.5$) was estimated to be 10.86% ($S = 1.57$), while the R_{wp} value of Model I was 13.64% ($S = 1.97$). This fact shows that Model II has relatively higher reliability than the Model I. The Rietveld analyses on the basis of Model II show that the phase of $x = 0.5$ is composed of 66.2 % F phase and 33.9 % C phase.

The Rietveld analysis of the neutron diffraction data was carried out for a typical sample of $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$ ($x = 0.5$) on the basis of Model II. Figure 4 shows the final profile fits and differences between the observed and calculated values in the neutron diffraction pattern of $x = 0.5$. The structural parameters estimated are summarized in Table 2, where the weighed reliability factor R_{wp} was 6.81 % ($S = 1.89$), which indicates high reliability. The fraction of F phase was estimated to be 68.5%, which was close in value to that of XRD. Furthermore, the Rietveld analyses of neutron diffraction data, which were estimated on the basis of

Table 1. The Structure Parameters of Rietveld Analysis of XRD Data for $x = 0.5$

Model I												
Phase	Atom	Sites	Lattice parameter/nm	Occupancy	x	y	z	R_B	R_F	R_{wp}	S	
C phase	M1	8b		1.00	0.25	0.25	0.25					
SG : 206	M2	24d		1.00	-0.011(1)	0.00	0.25					
	O1	48e		1.03(1)	0.382(1)	0.136(1)	0.380(1)					
	O2	16c		0.55(2)	0.361(1)	0.361	0.361					
			1.0988(2)					4.59	5.39	13.63	1.97	
Model II												
Phase	Atom	Sites	Lattice parameter/nm	Occupancy	x	y	z	R_B	R_F	R_{wp}	S	Phase/%
F phase	M11	4a		1.00	0.00	0.00	0.00					
SGr : 225	O11	8c		0.86(1)	0.25	0.25	0.25					
			0.5942(1)					2.08	1.45			66.15
C phase	M21	8b		1.00	0.25	0.25	0.25					
SG : 206	M22	24d		1.00	-0.022(2)	0.00	0.25					
	O21	48e		1.00	0.394(1)	0.145(1)	0.383(2)					
			1.0982(2)					4.30	3.48			33.85
										10.86	1.57	

a split-atom model, shows that the oxygen atoms are distributed at the 8c and 32f sites.

Figure 5 shows the compositional dependence of the fraction of C phase obtained from the Rietveld analysis of the XRD data. The C phase clearly appeared at $x = 0.45$ and then increased with increasing x in the range $x > 0.45$, while the F phase decreased. In particular, for the composition range, $0.5 \leq x \leq 0.7$, the relative amount of the C phase increased linearly. As seen in Fig. 5, it should be noticed that the extrapolation of the straight part of the broken line for $x \geq 0.5$ to the x -axis indicates a composition of between $x = 0.2$ and 0.3 . This fact suggests that the decrease in electrical conductivity may have a close relation with the appearance of the C phase, as well as the F phase, because the onset composition of the decrease in the oxide-ion conductivity agrees with the composition at which the C phase appears. As the C phase derives from the oxygen ordering of the defect fluorite-type structure, the decrease in the conductivity for the heavily Nd-doped CeO_2 must be due to the ordering of the oxygen vacancy.

Figure 6 represents the observed and calculated lattice constants as a function of composition (x) in the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ system, where two kinds of lattice constants for the F and C phases obtained from the Rietveld analyses of XRD data are given. It should be noticed that the lattice parameters of the F and C phases agreed well with each other in the composition range of $0.45 \leq x \leq 0.7$. On the other hand, the calculated values of the lattice constant for a fluorite-type solid-solution system Ce_{1-x}

$\text{Nd}_x\text{O}_{2-x/2}$ are given by the following equation on the basis of the randomly distributed oxygen vacancy model after Hong and Virkar:¹⁷⁾

$$a = \frac{8}{\sqrt{3}} \left[x r_{\text{Nd}} + (1-x) r_{\text{Ce}} + (1-0.25x) r_{\text{O}} + 0.25x r_{\text{Vo}} \right] \times 0.9971 \quad (2)$$

where r_{Nd} , r_{Ce} , r_{O} and r_{Vo} are ionic radii of Nd^{3+} (0.1109 nm for 8 coordination), Ce^{4+} (0.097 nm for 8 coordination), oxide ion (0.138 nm) and oxygen vacancy (0.1164 nm),¹⁸⁾ respectively, and 0.9971 is the multiplication factor in order to fit with the calculated value for that observed for pure CeO_2 . Furthermore, the lattice constants of the F phase given in both Eq. (2) and Fig. 6 are doubled for the direct comparison with the values of C phase. The lattice constant increased with increasing Nd content up to $x = 0.2$ according to Eq. (2). This increase may be reasonable because of the substitution of the larger Nd^{3+} in place of the smaller Ce^{4+} . Thereafter, the lattice constants gradually deviated from Eq. (2) in the composition range, $x \geq 0.3$, where the electrical conductivity decreased. This deviation suggests that the model used in Eq. (2) cannot be applied to the present heavily Nd-doped samples; i.e., the randomly distributed oxygen model cannot be retained. Furthermore, it can be speculated that the decrease in the oxygen coordination number due to the incorporation of oxygen vacancy may play a role as a trigger for the

Fig. 4. Rietveld analysis of neutron powder diffraction data for $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$.

Fig. 5. Compositional dependence of the F and C phase fractions in the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ system.

Table 2. The Structure Parameters of Rietveld Analysis of Neutron Diffraction Data for $x = 0.5$ with Model II

Phase	Atom	Sites	Lattice parameter/nm	Occupancy	x	y	z	R_B	R_F	R_{wp}	S	Phase/%
F	M11	4a		1	0	0	0					
SG :	O11	8c		0.39(9)	0.25	0.25	0.25					
225	O12	32f		0.12(2)	0.276(5)	0.277	0.277					
			0.5943(1)					3.57	3.17			67.99
C	M21	8b		1	0.25	0.25	0.25					
SG :	M22	24d		1	-0.014(1)	0	0.25					
206	O21	48e		0.91(6)	0.381(1)	0.141(1)	0.379(1)					
	O22	16c		0.40(6)	0.389(2)	0.389	0.389					
			1.0990(3)					7.58	6.00			32.01
										6.81	1.89

Fig. 6. Lattice constants of F and C phases in the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ system as a function of composition (x). The values of lattice constant of F phase are doubled for the sake of convenience and the broken line represents the calculated value using Eq. (2).

nucleation of the other phase. In addition, it should be noted that when the lattice constant deviates from the oxygen defect model in the composition range $x > 0.2$, the C phase appears and conductivity decreases, accompanied by an increase in activation energy. In fact, Mori et al.¹²⁾ also found a C structure micro-domain at $x = 0.25$ in the $\text{Ce}_{1-x}\text{M}_x\text{O}_{2-\delta}$ ($\text{M} = \text{Gd}, \text{Yb}, \text{Y}$) systems using TEM observations. Their results concerning the micro-domain may support our speculations. Accordingly, the decrease in the oxide-ion conductivity for the heavily doped CeO_2 can be ascribed to the ordering of oxygen vacancy, rather than the associates of the dopant-oxygen vacancy.

4. Conclusion

The present study concerning the relationship between oxide-ion conductivity and oxygen defect structure in the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ system can be summarized as follows:

The oxide-ion conductivity of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ increased with increasing x , exhibiting the maximum value at $x = 0.2$, and then decreased with increasing x .

It appears from the Rietveld analyses of XRD and neutron diffraction data that the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ ($0.40 \leq x \leq 0.7$) are composed of oxygen deficient fluorite and rare-earth C phases, and that the

fraction of the C phase increased with increasing x . Therefore, the decrease in oxide-ion conductivity has a close relation with the presence of the C phase, which derives from the oxygen ordering of the defect fluorite-type structure.

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