Crystal Structure and Electron Density Distribution Analyses of Nd$_x$Ce$_{1-x}$O$_{2-\delta}$ for Electrolyte by Rietveld/Maximum Entropy Method*

Tomitsugu Taguchi,¹ Naoki Igawa, Atsushi Birumachi, and Hidehito Asaoka
Quantum Beam Science Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

Shuhei Miwa and Masahiko Osaka
Nuclear Science and Engineering Center, Japan Atomic Energy Agency, Oarai, Ibaraki 311-1393, Japan

We carried out the X-ray diffraction studies on the crystal structure and electron density distribution of Nd-doped CeO$_2$ which is considered the candidate material as an electrolyte for solid oxide fuel cell by the combination of Rietveld refinement and maximum entropy method. We determined those crystal structural parameters with the space group, $Fm\bar{3}m$, which is the same as pure CeO$_2$. The Ce and Nd ions randomly occupied the 4a site and O ion preferentially occupied the 8c site in Nd$_x$Ce$_{1-x}$O$_{2-\delta}$. We observed the distribution of the electron conduction pathway through the 4a-8c and 8c-8c sites. [DOI: 10.1380/ejssnt.2015.339]

Keywords: Atom-solid scattering and diffraction; X-ray scattering, diffraction, and reflection; Atom-solid interactions; Diffusion and migration; Maximum entropy method

I. INTRODUCTION

Fuel cells are considered as the attractive green technologies to prevent the global warming by reducing the CO$_2$ emission which is generated by burning of fossil fuel. Rare-earth doped CeO$_2$, RE$_2$Ce$_{1-x}$O$_{2-\delta}$ (RE: rare-earth), is well known to be difficult for using as a solid electrolyte for fuel cells. Many studies on several functional properties such as electrical and thermophysical properties of RE$_2$Ce$_{1-x}$O$_{2-\delta}$ have been reported, and indicated that the non-stoichiometry of RE$_2$Ce$_{1-x}$O$_{2-\delta}$ is significantly affects those properties [1-6]. For example, Li et al. examined the effects of concentration of Nd ion in CeO$_2$ on the ionic conductivity in the temperature range from 450 to 700°C [6]. They found that as the Nd content increases, the ionic conductivity first increased with increasing the Nd content and reached its maximum values at 10% or 15% Nd content, then started to decrease steadily. On the other hand, RE$_2$Ce$_{1-x}$O$_{2-\delta}$ exhibits both ionic and electronic conduction, and those compounds with higher ratio of electronic conduction against ionic conduction is known to be difficult for using as a solid electrolyte for solid oxide fuel cells [7].

The understanding of the relationship between the crystal structure and behaviors of carriers is one of the important keys to improve the conductivity performance. For the crystal structural analyses, the Rietveld method applied to diffraction data is one of the most practical methods because this method can estimate the distributions of electrons and ions, and determine in the interatomic distance with the accuracy within 10⁻⁴ nm. In addition, Yashima [8] reported that the crystal structures, structural disorders, and diffusion paths of mobile ions in several conductors, such as δ-Bi$_2$O$_3$ and (La$_{0.8}$Sr$_{0.2}$)(Ga$_{0.8}$Mg$_{1.5}$Co$_{0.05}$)O$_{2.8}$, can be obtained by a combined technique including Rietveld refinement and maximum entropy method (MEM) applied to the data of neutron or synchrotron X-ray powder diffraction. These results suggest that a combined method with Rietveld refinement and MEM are effective for revealing static and dynamic disorder in crystals. In particular, the maximum entropy method applied to X-ray diffraction is effective for revealing the electron density distributions in crystals. Those distributions are closely related to the electron diffusing pathway which affects the electronic conduction. In this study, to obtain the key to the decrease in the ratio of the electronic to ionic conduction, we investigated the electron density distribution of Nd-doped CeO$_2$ as a function of the content of Nd$_2$O$_3$-dopant.

II. EXPERIMENTAL

The powder of Nd$_2$O$_3$ and CeO$_2$ was dissolved and mixed in nitric acid. After the mixing, solution was dried out, then heated to remove nitric acid at 500°C. Obtained green powder was calcinated at 1000°C for 10 h. Calcinated powder was pressed into a pellet at 100 MPa and heated at 1400°C for 4h in air. The atomic ratio between Nd and Ce in samples was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, ULTIMA2, HORIBA, Ltd., Kyoto, Japan). The sample preparation for ICP-AES analysis was as follows. After the sulfiting, the solution was dried to remove the excess H$_2$SO$_4$. Then the sample was dissolved in an aqua regia and dried again. Finally the sample was dissolved in 1M HNO$_3$ solution. X-ray powder diffraction measurements were carried out on the Mini-Flex II (Rigaku Corp., Tokyo, Japan) with high speed one-dimensional silicon strip detector system “D/teX Ultra” using CuKα radiation. The X-ray diffraction data was collected in the 2θ range from 20 to 100° with a step of 0.02° at room temperature.

The crystal structure was analyzed by the Rietveld method using the program “RIETAN-FP” [9]. After the Rietveld analysis, the electron density distribution was estimated by the maximum entropy method using the program “Dysnomia” [10]. We partitioned the unit cell into 256 × 256 × 256 pixels in MEM analyses. Three-
III. RESULTS AND DISCUSSIONS

Figure 1 shows the results of the Rietveld analyses of CeO₂ and Ce₀.₈₅Nd₀.₁₅O₁.₈₆. The dot symbols denote the observed intensities and the solid line denotes the refined curve of the best-fit model. The tick marks below the diffraction pattern indicate the calculated peaks of sample. The curve below the tick marks denotes the difference between the observed and refined intensities. For the Rietveld analyses, we applied the following constraints: $B$(Nd) = $B$(Ce), and $g$(Nd) = 1.0 - $g$(Ce) at 4$a$ site ($x = y = z = 0$) where $B$ and $g$ are isotropic atomic displacement parameter and occupancy of atom. The crystal structure of Nd-doped CeO₂ was refined with the space group, $Fm\bar{3}m$, which is the same as undoped ceria (Fig. 2). No reflections of impurities and other phases were observed. The reliability indices, $R_{wp}$, $R_{p}$ and $R_B$ were 4.68%, 3.31%, 1.21% for CeO₂ and 3.26%, 2.14%, 0.95% for Ce₀.₈₅Nd₀.₁₅O₁.₈₆, respectively. In crystal structure of NdₙCe₁₋ₙO₂₋δ (0.05 ≤ $x$ ≤ 0.25), Ce and Nd ions randomly occupied the 4$a$ site and O ion preferentially occupied the 8$c$ site ($x = y = z = 1/4$), and no evidence of the ordering of Ce and Nd ions was observed by the Rietveld refinement.

Figure 3 shows the lattice constant as a function of Nd-dopant content. The lattice constant was proportional to the content of Nd-dopant, and this tendency was agreed with the previous work [12]. Figure 4 shows the occupancy, $g$ of oxygen site as a function of Nd-dopant, $x$. The ratio of $g$(obs.) to $g$(ideal) which is defined as $g$(ideal) = 1 - $x$/4 is also shown in this figure. If the stoichiometry between (Ce⁴⁺ + Nd³⁺) and O²⁻ is equal to 1, the ratio of $g$(obs.) to $g$(ideal) is 1. However those were less than 1; it means that the concentration of oxygen defect was slightly higher than those of the ideal structure. Therefore it indicates that the small amount of Ce⁴⁺ ion was reduced to Ce⁢³⁺ ion including undoped CeO₂ in the present work. Figure 5 shows isotropic atomic displacement parameters, $B$ of O²⁻ and (Ce⁴⁺ and Nd³⁺) ions as a function of the content of Nd-dopant. While calculated error bars are also

FIG. 1. X-ray diffraction patterns and results of a Rietveld refinement of (a) CeO₂ and (b) Ce₀.₈₅Nd₀.₁₅O₁.₈₆.

FIG. 2. Crystal structure of CeO₂. Yellow and red represent Ce and O ions, respectively.

dimensional images of the electron density distributions were drawn using the program “VESTA” [11].
shown in this figure, the errors of (Ce$^{4+}$ and Nd$^{3+}$) ions were too small so drawn within the markers. The isotropic atomic displacement parameter of (Ce$^{4+}$ and Nd$^{3+}$) ions was increased with increasing the Nd content and reached its maximum value at ca. 15% Nd content, then decreased with increasing the Nd content. This phenomenon is very similar to the ionic conductivity of Nd-doped CeO$_2$ reported by Li et al. described above [6]. On the other hand, that of O$^{2-}$ ion was increased with increasing the Nd content.

Figure 6 shows the typical 3-dimensional electron density distribution maps of Ce$_{0.85}$Nd$_{0.15}$O$_{1.86}$ with isosurface levels of (a) 10 and (b) 0.4 Å$^{-3}$. The cross sections of the density on {100} planes are also shown in these figures; the lower and higher densities of cross sections are represented by blue and red. Figure 6 (a) indicates that the O$^{2-}$ and (Ce$^{4+}$ and Nd$^{3+}$) ions essentially located their original sites, which was in agreement with the result of Rietveld refinement. On the other hand, Fig. 6 (b) shows that the electron densities of the O$^{2-}$ and (Ce$^{4+}$ and Nd$^{3+}$) ions at 0.4 Å$^{-3}$ widely distributed and overlapped each other. Those phenomena were observed in all specimens of Nd$_x$Ce$_{1-x}$O$_{2-δ}$ (0.05 ≤ x ≤ 0.25).

Figure 7 shows the 2-dimensional electron density distribution of Ce$_{0.85}$Nd$_{0.15}$O$_{1.86}$ on (110) plane at room temperature. The highest electron density is at 8c site (point D, oxygen occupied position) and we can observe the paths between 8c sites (point E). The values of electron densities at the points D and E are also drawn. The black lines of isosurface levels from 0 to 5 Å$^{-3}$ with the contour interval of 0.2 Å$^{-3}$ are also drawn.

Figure 8 shows the maximum values of electron density at the point of A (red circles), B (blue diamonds) and C (green squares) on (110) of Nd$_x$Ce$_{1-x}$O$_{2-δ}$ in Fig. 9 as a function of the content of Nd-dopant, x. The highest values of electron densities at the points A, B and C as a function of content of Nd-dopant, x, are drawn in Fig. 8. Those highest electron densities at the points A, B and C decreased with increasing x. Figure 9 shows the 2-dimensional electron density distribution of Ce$_{0.85}$Nd$_{0.15}$O$_{1.86}$ on (400) plane at room temperature. The highest electron density is at 8c site (point D, oxygen occupied position) and we can observe the paths between 8c sites (point E).

The value of electron density at the point D was decreased with increasing x. It is the similar tendency that the occupancy of oxygen decreased with increasing x (see in Fig. 4), therefore it is indicated that the value at the point D is directly affected of the occupancy of O$^{2-}$ ion. On
FIG. 9. 2-D-image of electron density distribution of \( \text{Ce}_{0.85}\text{Nd}_{0.15}\text{O}_{1.86} \) on (400) plane at room temperature. The lower density is represented by blue (0 Å\(^3\)) and the higher changes into red (over 0.3 Å\(^3\)) in color. The black lines of isosurface levels from 0 to 30 Å\(^3\) with the contour interval of 2 Å\(^3\) are also drawn.

FIG. 10. Maximum values of electron density at the point of D (red circles) and E (blue squares) on (400) plane of \( \text{Nd}_{x}\text{Ce}_{1-x}\text{O}_{2-x} \) in Fig. 9 as a function of the content of Nd-dopant, \( x \).

IV. CONCLUSIONS

The crystal structure and electron density distribution of \( \text{Nd}_{x}\text{Ce}_{1-x}\text{O}_{2-x} \) (0.05 \( \leq x \) \( \leq 0.25 \)) were analyzed by the combination of Rietveld method and MEM applying to X-ray diffraction data. The crystal structure of \( \text{Nd}_{x}\text{Ce}_{1-x}\text{O}_{2-x} \) was refined with the space group, \( Fm\overline{3}m \), which is the same as undoped \( \text{CeO}_2 \). \( \text{Ce} \) and \( \text{Nd} \) ions randomly occupied the 4\( a \) site and O ion preferentially occupied the 8\( c \) site in the unit cell. According to the analyzed 3D- and 2D-electron density distribution maps, it indicated that the electron conduction pathway was distributed through 4\( a-8c \) and 8\( c-8c \) sites.

ACKNOWLEDGMENTS

We thank Drs. F. Izumi and K. Momma for developing the program RIETAN-FP for the Rietveld refinement, Dynomia for the MEM, and VESTA for the visualizer. This study is partly supported by a Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Culture, Sports, Science and Technology in Japan (No. 23360431).