

Powder Neutron Diffraction Studies of Proton-doped and Deuteron-doped $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$: Nuclear Density Map of Hydrogen from Differential Fourier Analysis

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Powder neutron diffraction data have been collected on both the proton-doped and deuteron-doped $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ at room temperature to obtain the nuclear density maps by the differential Fourier synthesis method. In the nuclear density maps, weak negative peaks assigned to hydrogen nuclei were recognized near oxygen atoms as if the proton makes the hydrogen bond with oxygen ion. This result consists with the infrared transmission study which shows the existence of the hydroxyl (O-H bond) in the perovskite-type oxide.

KEYWORDS: proton conductor, $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$, Fourier analysis, nuclear density map

§1. Introduction

Some ABO_3 perovskite-type oxides ($A^{2+} = \text{Sr}, \text{Ba}, \text{Ca}$ and $B^{4+} = \text{Ce}, \text{Zr}$) exhibit proton conduction at high temperature when acceptor ions are heavily doped in the B-atom site.¹⁾ These materials are of special interest because of their potential applications as a solid electrolyte used in fuel cells.²⁾ The proton conduction mechanism for the perovskite-type oxide have not been fully understood yet. It has serious problem that the proton site in these oxides is not exactly known. One cannot discuss how the proton migrates in crystals without knowing where the proton exists.

Neutron diffraction has proved a valuable tool for the structural characterization of both doped and undoped ABO_3 oxides.³⁻⁶⁾ The superior light atom sensitivity of neutrons over X-rays have been allowed the location of the extrinsic oxygen vacancy.⁵⁾ In the case of proton conductors this light atom sensitivity is extended to the proton itself, and neutron diffraction measurements are a vital tool in the structural location of the hydrogen atoms in solids.

Sata *et al.*⁶⁾ performed neutron diffraction measurement using single crystals of H^+ -doped and D^+ -doped $\text{SrTi}_{0.98}\text{Sc}_{0.02}\text{O}_3$, and reported that the proton was determined to be in the site between the O-O ions which consist of an oxygen octahedron, as if it forms the hydrogen bond. As the proton concentration for $\text{SrTi}_{0.98}\text{Sc}_{0.02}\text{O}_3$ is lower than 2 mol%, this structural site is only proposed and additional work will be required for confirmation.

Among the ABO_3 perovskite-type oxides, $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ [abbreviated as BCY10] shows the highest proton concentration as 8.4 mol%.⁷⁾

In the present study, we have performed the powder neutron diffraction measurements on H^+ -doped and D^+ -doped BCY10 and analyzed by the differential Fourier synthesis method to obtain the proton density maps in the crystal lattice. The change in sign of the scattering

length on substituting deuterium ($b = 6.672 \text{ fm}$) for protium ($b = -3.739 \text{ fm}$)⁸⁾ allows more sensitive study on the site determination for the hydrogen atoms.

§2. Experimental

BCY10 samples were prepared by solid state reaction of BaCO_3 , CeO_2 and Y_2O_3 in the correct ratio. The powders were intimately mixed and given an initial firing at 1000 °C in air for 20 h before being milled and re-fired at 1400 °C for 10 h to produce a sample suitable for powder neutron diffraction. Before hydrogenation, the samples were pulverized to <200 mesh. Subsequently, they were loaded with H^+ or D^+ by annealing at 300 ~ 500 °C in H_2O or D_2O vapor which was saturated at a temperature above 90 °C.

Powder neutron diffraction experiments were carried out using approximately 3 cm³ of powder loaded into an 10 mm diameter cylindrical vanadium can on the high efficiency powder diffractometer (HERMES) at JRR-3M reactor of Japan Atomic Energy Research Institute, Tokai. The neutron wave length was 0.18196 nm and the diffraction patterns were recorded over the angular range $10^\circ < 2\theta < 104^\circ$ in a step of 0.1° .

§3. Results and Discussion

Analysis of X-ray and neutron diffraction patterns from the BCY10 have confirmed that the data is consistent with the space group of orthorhombic $Pnma^*$ with lattice constants $a = 0.6215 \text{ nm}$, $b = 0.8759 \text{ nm}$ and $c = 0.6235 \text{ nm}$ as proposed by Knight and Bonanos.³⁾ Table I shows the result of our Rietveld refinements for BaCeO_3 . Crystal structure of BaCeO_3 is shown in Fig. 1.

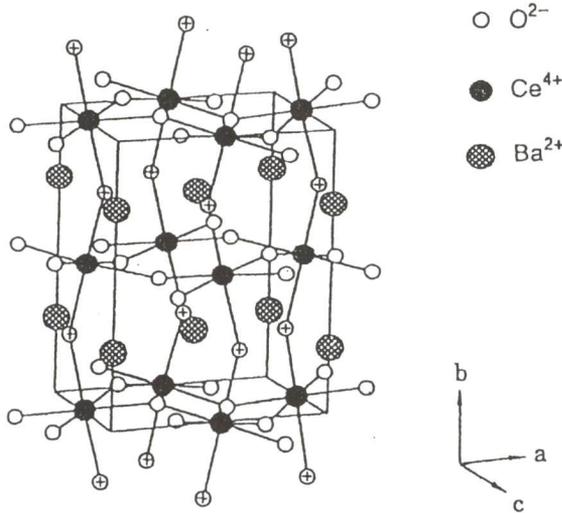
Neutron diffraction patterns obtained from the BaCeO_3 , the H^+ -doped BCY10 and the D^+ -doped

* Knight and Bonanos³⁾ used an alternative setting of the space group, $Pnmc$, with lattice constants $a = 0.8759 \text{ nm}$, $b = 0.6235 \text{ nm}$ and $c = 0.6215 \text{ nm}$. Crystallographically $Pnma$ is equivalent to $Pmnc$ if the axes setting is reversed.

Table I. Structural parameters of BaCeO₃

Element	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (Å ²)
Ba	0.18(1)	0.25	-0.00(2)	0.6(1)
Ce	0.0	0.5	0.0	0.7(1)
O1	0.486	0.25	0.075	0.6(2)
O2	0.2775(9)	0.00391(6)	0.7239(9)	1.1(1)

$$R_P = 5.00, R_{WP} = 7.00, R_E = 3.61, S = 1.9413$$

Fig. 1. Crystal structure of BaCeO₃: O1 is crossed, O2 is uncrossed.

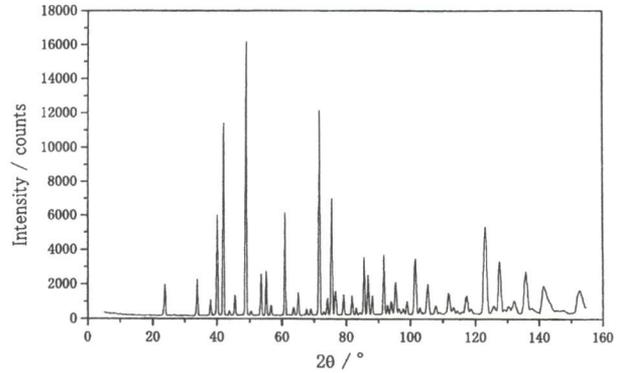
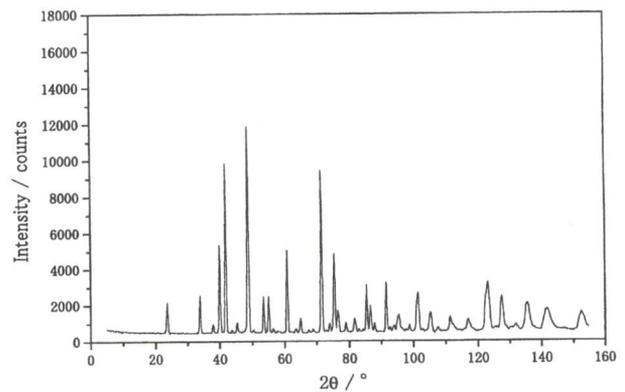
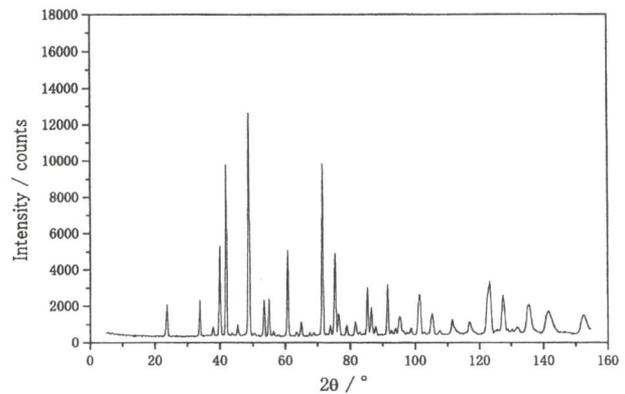
BCY10 samples are shown in Figs. 2-4, respectively. It will be seen from these figures that the intensity of diffraction lines for the non-doped sample changes slightly by the doping and the background intensity for the proton-doped sample increases by the doping due to the large incoherent cross-section of protium to thermal neutrons. The exact proton concentration in the doped sample has not been determined, however the background intensity is used to prove the presence of hydrogen in the doped sample and its absence in the undoped oxide.

Since the concentration of hydrogen ions in the doped samples is low, we performed the difference Fourier analysis to obtain the nuclear density map for the hydrogen ions. In the Fourier synthesis to obtain the nuclear density distribution in unit cell, we used the expression for the *Pnma* symmetry given in the International Table of X-ray crystallography.⁹⁾ The structure factor difference for the *hkl* reflection between hydrogen and deuterium is evaluated by the relation,

$$\Delta f(hkl) = f_H(hkl) - f_D(hkl) = F_H(hkl) - F_D(hkl), \quad (3.1)$$

where $F_H(hkl)$ and $F_D(hkl)$ are the structure factors for the H⁺-doped and D⁺-doped BCY10, respectively.

In order to calculate the nuclear density map from the Fourier analysis method, one must determine the signs of $f(hkl)$ for each reflection since the neutron diffraction measurement gives only the absolute value of the structure factor. In the present analysis the sign of $f(hkl)$ is

Fig. 2. Powder neutron diffraction pattern for BaCeO₃.Fig. 3. Powder neutron diffraction pattern for H⁺ doped BaCe_{0.9}Y_{0.1}O_{2.95}.Fig. 4. Powder neutron diffraction pattern for D⁺ doped BaCe_{0.9}Y_{0.1}O_{2.95}.

assumed to be opposite to the sign of $f_o(hkl)_c$ which are calculated using the structural parameters listed in Table I, because the sign of scattering length for protium is opposite to those for oxygen and deuterium and the hydrogen atoms in the proton conducting oxides may situate near the oxygen atoms forming the O-H bond as reported by Sata *et al.*⁶⁾ and Yugami *et al.*¹⁰⁾ It is supposed, however, that the sign of $f(hkl)$ turns in some cases if the calculated $f_o(hkl)_c$ is nearly zero. But the contribution of this effect is very small, because the $f(hkl)$ at this sit-

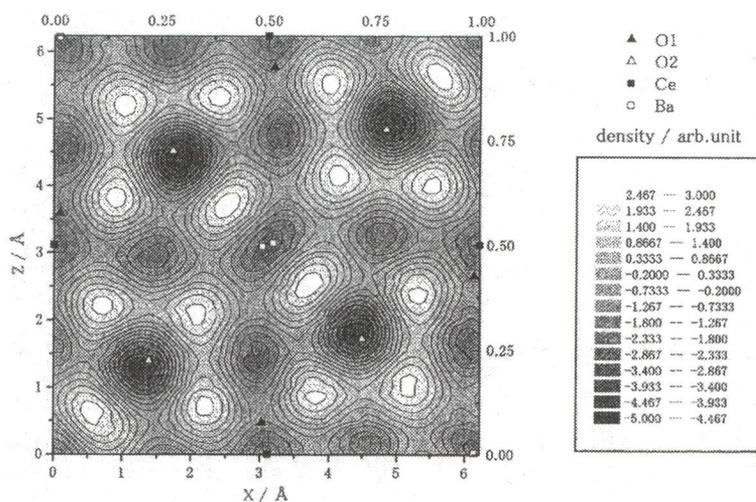


Fig. 5. Nuclear density map for hydrogen for $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ projected on X-Z plane.

uation is very small. For the case of the overlapped reflection, each $f(hkl)$ is evaluated by the assumption that each $f(hkl)$ is proportional to the respective $f_o(hkl)_c$.

Under these assumptions described above, we performed the Fourier synthesis. Figure 5 shows the nuclear density maps projected on X-Z plane. Inspection of these maps shows that weak negative peaks are appeared close to oxygen O2 sites and outside the CeO_6 octahedra. As stated earlier, protium has a negative scattering length and hence these positions will be ascribed to hydrogen. This result consists with the infrared transmission study¹⁰⁾ which shows the existence of the hydroxyl (O-H bond) in the perovskite-type oxides.

Further work is required to locate the structural site of the protons in the proton conducting oxide. Neutron diffraction study at low temperatures will provide the possibility to determine the proton sites since thermal vibrations and proton diffusion, which cause the reduction of diffraction intensity, would freeze out at very low temperatures.

§4. Conclusion

Powder neutron diffraction data are collected on both the proton-doped and the deuterium doped $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ at room temperature to obtain the nuclear density maps by the differential Fourier synthesis

method. In the nuclear density maps, weak negative peaks assigned to hydrogen nuclei are recognized near oxygen O2 site as if the proton makes the hydrogen bond with oxygen ion. Further work is required to locate the proton site in the proton conducting oxides.

Acknowledgements

This work has been supported in part by a Grant-in-Aid for Scientific Research on Priority Area (No.299) from the Ministry of Education, Science, Sports and Culture.

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