Experimental visualization of oxide-ion diffusion paths in pyrochlore-type Yb$_2$Ti$_2$O$_7$

Wataru UNO$^1$, Kotaro FUJII$^1$, Eiki NIWA$^1$, Shuki TORII$^2$, Ping MIAO$^{2,†}$, Takashi KAMIYAMA$^2$ and Masatomo YASHIMA$^{1,†}$

$^1$Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1-W4-17 O-okayama, Meguro-ku, Tokyo 152-8551, Japan
$^2$Neutron Science Laboratory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

Crystal structure and neutron scattering length density distribution of a pyrochlore-type ytterbium titanate Yb$_2$Ti$_2$O$_7$ have been investigated by in situ neutron powder diffraction measurements at 293 and 1173 K, Rietveld analysis and maximum-entropy method (MEM). In the MEM neutron scattering length density distributions of Yb$_2$Ti$_2$O$_7$, the oxide ion O$_{48}^-$ bonding to Ti cation was relatively localized at lower temperature of 293 K, while it was largely distributed at a higher temperature of 1173 K. At 1173 K, one oxide-ion diffusion path along the (110) unshared edge of TiO$_6$ octahedron was clearly visualized and the other oxide-ion diffusion path along (100), strictly (2 –8x(O$_{48}$) + 3 8x(O$_{48}$) – 3), shared edge of TiO$_6$ octahedron was also indicated. Here x(O$_{48}$) is the atomic coordinate x of O$_{48}^-$ anion. The MEM neutron scattering length density distribution and difference bond valence sum map at 1173 K strongly suggested that the energy barrier for oxide-ion migration along (110) directions was lower than that along the (100) one. Oxide ions three-dimensionally diffuse through both the (110) and (100) paths across the unit cell.

©2018 The Ceramic Society of Japan. All rights reserved.

Key-words : Pyrochlore, Oxide-Ion conductor, Neutron diffraction, Rietveld analysis, Maximum-entropy method

1. Introduction

Solid oxides with the fluorite-type structure such as zirconia-, ceria- and bismuth oxide-based materials are fast oxide-ion conductors, which enables the use as electrolyte materials for applications to solid oxide fuel cells and gas sensors. To develop better electrolyte materials requires a better understanding of the ion conduction mechanism, and crucial to this is the knowledge of the diffusion paths of mobile ions at high temperatures where the materials work efficiently. Therefore, the structural disorder and oxide-ion diffusion path of fluorite-type and distorted fluorite-type materials have been studied by numerous researchers.$^{1-9}$ These materials exhibit curved diffusion paths along the (100) directions.$^{3,5-7,9}$ The crystal structure of the $Fd\bar{3}m$ pyrochlore-type oxides $A$_2$B$_2$O$_7$ can be regarded as a “vacancy-ordered fluorite-type structure” where A is a larger cation as Yb$^{3+}$ and Gd$^{3+}$ and B is smaller cation as Ti$^{4+}$, Zr$^{4+}$, Hf$^{4+}$. Since some of the $Fd\bar{3}m$ pyrochlore-type oxides exhibit high oxide-ion conductivity,$^{10-13}$ their crystal structures and oxide-ion conduction mechanism have extensively been studied by X-ray and neutron diffraction experiments,$^{1,11-29}$ and by computational calculations.$^{21,22,32}$ However, there have been no reports on the experimental visualization of oxide-ion diffusion pathways in pyrochlore-type oxides. The purpose of this work is the experimental visualization of oxide-ion diffusion paths in pyrochlore-type Yb$_2$Ti$_2$O$_7$. We have chosen the chemical composition Yb$_2$Ti$_2$O$_7$, because Yb$_2$Ti$_2$O$_7$ is one of the highest oxide-ion conductors with the pyrochlore-type structure.$^{13}$ In this work, we apply time-of-flight (TOF) neutron diffraction$^{13}$ and maximum-entropy method$^{3,5-7,34}$ to study the oxide-ion diffusion paths of Yb$_2$Ti$_2$O$_7$. TOF neutron diffraction allows wide d range data to be measured, leading to precise structural parameters and neutron scattering length density distribution,$^{35}$ thus, we are able to visualize the oxide-ion diffusion pathways in oxide-ion conductors.

2. Methods

Yb$_2$Ti$_2$O$_7$ sample was synthesized by solid-state reactions. Starting materials of Yb$_2$O$_3$ (>99.9% purity) and
TiO₂ (>99.9% purity) in a molar ratio of 1:2 were mixed and ground as dried powders and as ethanol slurries using an agate mortar for 30 min. The mixture was calcined in air at 1273 K for 12 h. The calcined material was crushed in a tungsten carbide mortar and ground by the agate mortar for 30 min. Obtained powders were pressed into pellets at 130 MPa and sintered in air at 1673 K for 24 h. White polycrystalline pellets of Yb₂Ti₂O₇ were obtained (Size: 8.4 mm in diameter, 42 mm in height. Density: 5.34 g cm⁻³). The chemical composition of Yb₂Ti₂O₇ sample was confirmed to be Yb:Ti = 2.007(12):1.993(10) by inductively coupled plasma optical emission spectroscopy (ICP-OES), which agreed well with the nominal composition Yb₂Ti₂O₇. Thermogravimetric (TG) analyses of Yb₂Ti₂O₇ were carried out in air and under Ar flow between 373 and 1173 K at the heating and cooling rates of 10 K min⁻¹. The TG measurement was repeated three times to confirm the reproducibility and to negate the influence of absorbed species such as water. The TG results in the second and third heating/cooling processes indicated no significant weight change between 373 and 1173 K. Thus, the oxygen content was constant and no additional oxygen vacancies were formed in Yb₂Ti₂O₇ at high temperatures.

TOF neutron powder diffraction data of Yb₂Ti₂O₇ pellets were measured at 293 and 1173 K. The neutron data were taken using the super-high-resolution diffractometer SuperHRPD 33) installed at the beam line BL-08 of the Materials and Life Science Experimental Facility of the J-PARC center of KEK/JAEA, Tokai, Japan. Rietveld refinements of Yb₂Ti₂O₇ were carried out using the neutron data taken by the backscattering bank of SuperHRPD (d = 0.58–4.0 Å) with computer program Z-code. 36) The absorption correction was performed through the Lohanan empirical formula, 35,37 which is effective to determine accurately the structural parameters and structure factors leading to precise neutron scattering length density distribution.

In order to obtain the neutron scattering length density distribution of Yb₂Ti₂O₇, MEM analysis was performed based on the neutron diffraction data. MEM analysis was carried out using 0th-order single pixel approximation 38) with computer program Dysnomia. 39) The observed structure factors Fobs (d = 0.7–4.0 Å) obtained by the Rietveld refinement were used for the MEM analysis with 96 × 96 × 96 pixels.

Difference bond valence sum (DBVS) 40) map of the test oxide ion was calculated for the refined crystal structure of Yb₂Ti₂O₇ at 1173 K with computer program 3DBVSMAPPER. 40) Spatial resolution in the calculation of DBVS map was set to 0.1 Å. Refined crystal structures, neutron scattering length density distributions and DBVS map of Yb₂Ti₂O₇ were depicted with computer program VESTA. 41)

### 3. Results and discussion

All the reflections in the neutron powder diffraction data of Yb₂Ti₂O₇ measured at 293 and 1173 K were indexed to a face-centered cubic cell, which indicated the sample to be a single cubic phase at these temperatures. Thus, Rietveld refinements of Yb₂Ti₂O₇ were carried out by a cubic pyrochlore-type structure (space group: Fd³m). In preliminary analyses, it was confirmed that the occupancy factors of Yb atom at the 16c and 16d sites were 1.00 and 0.00, respectively, g(Yb; 16c) = 1.00 and g(Yb; 16d) = 0.00 at 293 and 1173 K, and that the occupancy factors of Ti atom were g(Ti; 16c) = 0.00 and g(Ti; 16d) = 1.00 at these temperatures. Thus, there was no Yb/Ti occupational disordering at the 16c and 16d sites at these temperatures. In other preliminary Rietveld analyses, the refined occupancy factors of oxygen atom were g(O; 8a) = 1.008(2), g(O; 48f) = 1.0033(11) and g(O; 8b) = −0.0005(2) at 293 K and g(O; 8a) = 1.0105(14), g(O; 48f) = 1.010(8), and g(O; 8b) = −0.0005(2) at 1173 K. Thus, there were no interstitial oxygens at the interstitial 8b site at these temperatures. Similarly, there existed no interstitial oxygens at the 32e site (1/4, 1/4, 1/4) at these temperatures. In the final refinements, all the occupancy factors were fixed as shown in Table 1.

**Table 1.** Shows the Rietveld patterns of Yb₂Ti₂O₇ at 293 and 1173 K, which indicates that the observed intensities agree well with the calculated ones. Table 1 lists the refined crystal parameters and reliability factors in the final Rietveld refinements. The refined lattice parameter of Yb₂Ti₂O₇ was 10.034410(4) Å at 293 K, which agree well with the literature value. 20) The refined atomic coordinate x of oxygen atom at the 48f site, x(O48f) at 293 K also agrees with the literature value. 19) Using the bond valence parameters of Brese and O’Keeffe, 42) the bond valence sum (BVSs) of Yb³⁺ and Ti⁴⁺ cations in Yb₂Ti₂O₇ at 293 K were estimated to be 2.90 and 4.14, which agreed well with the formal charges 3 of Yb³⁺ and 4 of Ti⁴⁺, respectively. These results indicate the validity of the refined crystal structure of Yb₂Ti₂O₇.

The lattice parameter of Yb₂Ti₂O₇ at 1173 K, 10.133798(2) Å was higher than that at 293 K, 10.034410(4) Å, due to the thermal expansion. The equivalent isotropic and isotropic atomic displacement parameters Ueq and Uiso of Yb₂Ti₂O₇ at 1173 K were higher than those at 293 K (Table 1), which indicates larger thermal motion at the higher temperature of 1173 K. Equivalent isotropic atomic displacement parameters of O₈[O] Ueq(O₈[O]) was higher than the isotropic atomic displacement parameters of O₈ Uiso(O₈). Therefore, the O₈[O] exhibits larger thermal motion and positional disorder than O₈.

**Figures 2(a) and 3(a)** show the refined crystal structure of Yb₂Ti₂O₇ at 1173 K. The structure consists of TiO₆ octahedra, O₈[O] anions and Yb cations [Figs. 2(a) and 3(a)]. The O₈[O] exhibited highly anisotropic atomic displacements in the directions perpendicular to the Ti–O₈[O] bond, which is consistent with the DBVS map [Fig. 2(c)]. Similar anisotropic atomic displacements were reported for pyrochlore-type and perovskite-type oxide-ion conductors. 1,43–46)

In the MEM neutron scattering length density distributions of Yb₂Ti₂O₇, no significant densities existed at the
Table 1. Refined crystal parameters and reliability factors in Rietveld refinement of TOF neutron powder diffraction data (Fig. 1) of Yb₂Ti₂O₇ measured at 293 and 1173 K

| Composition and temperature | Yb₂Ti₂O₇ at 293 K | Yb₂Ti₂O₇ at 1173 K |
|----------------------------|-------------------|-------------------|
| Lattice parameter          | a/Å               | 10.034410(4)      | 10.133798(2)   |
| Yb at 16c (0, 0, 0)        | U₁₁ = U₂₂ = U₃₃ = 0.00782(6) | U₁₁ = U₂₂ = U₃₃ = 0.02743(8) |
| Ti at 16d (1/2, 1/2, 1/2) | U₁₂ = U₁₃ = U₂₃ = -0.00232(7) | U₁₂ = U₁₃ = U₂₃ = -0.00813(8) |
| O₄₈: O at 8a (1/8, 1/8, 1/8) | 0.00782(6) | 0.02743(8) |
| O₆₈: O at 48f (x, 1/8, 1/8) | 2.90   | 1.28    |
| Reliability factors        | Rwp = 0.00502(13) | 0.01583(14) |

*Space group: FdÅm, g(Yb; 16c): occupancy factor of Yb atom at the 16c site. g(Ti; 16d): occupancy factor of Ti atom at the 16d site. g(O; 8a): occupancy factor of O atom at the 8a site. g(O; 48f): occupancy factor of O atom at the 48f site. These occupancy factors were fixed to unity: g(Yb; 16c) = g(Ti; 16d) = g(O; 8a) = g(O; 48f) = 1, in the final refinements.

vacant 8b site at 293 and 1173 K [Figs. S1 and S2 in the Supporting Information (SI)], which strongly suggests that the 8b site little contributes to the oxide-ion diffusion. The O₆₈ was localized and isolated at these temperatures (Figs. S1 and S2 in SI), which indicates that the O₆₈ also little contributes to the oxide-ion diffusion. On the contrary, the O₄₈ oxide ion bonding to a Ti cation had much larger spatial distribution at the higher temperature 1173 K [Fig. 2(d)]. The larger distribution at 1173 K [Fig. 2(d)] compared with that at 293 K [Fig. 2(b)] is consistent with higher oxide-ion conductivity at a higher temperature.16 It should be noted that there existed a connected density distribution between the second nearest neighbor O₄₈ ions in the ⟨110⟩ direction, which clearly indicated the oxide-ion diffusion path in Yb₂Ti₂O₇. Figure 2(d) strongly suggests the other oxide-ion diffusion path between the nearest neighbor O₆₈ and O₄₈ anions in the...
Fig. 3. (a) A part of the refined crystal structure and (b) equi-density surface of the MEM neutron scattering length density distribution of Yb$_2$Ti$_2$O$_7$ at 1173 K at 0.002 fm Å$^{-3}$.

The (100) direction of Yb$_2$Ti$_2$O$_7$. Here the exact direction of (100) is [1 1 5.6] = [8x(O$_{8f}$) − 3 8x(O$_{8g}$) − 3 2] in Fig. 2. The minimum neutron scattering length density on the (110) diffusion path (0.056 fm Å$^{-3}$) of Yb$_2$Ti$_2$O$_7$ was much higher than that on the (100) one (0.003 fm Å$^{-3}$). Therefore, it is suggested that the energy barrier for oxide-ion migration along the (110) path was lower than that along the (100) one in Yb$_2$Ti$_2$O$_7$. The (110) and (100) diffusion paths in Figs. 2(d) and 3(b) are the first examples of experimental visualization of oxide-ion diffusion in pyrochlore-type oxides. The (110) and (100) diffusion paths were supported also by the DBVS map [Fig. 2(c)]: the maximum DBVS along (110) (0.10 vu) was much lower than that along (100) (0.51 vu) in Yb$_2$Ti$_2$O$_7$. An important question is why the (110) path has lower energy barrier compared with that on (100) one. The (110) path is along the unshared edge between the Ti and vacant 8b sites, while the (100) path is along the shared edge between the Ti and Yb cations. Therefore, the (110) path has lower energy barrier compared with the (100) one. Figure 3(b) shows the equi-density surface of MEM neutron scattering length density distribution of Yb$_2$Ti$_2$O$_7$, which indicates the long-range diffusion paths across the unit cell. An oxide ion in Yb$_2$Ti$_2$O$_7$ is able to migrate in the (100) directions through both (110) and (100) diffusion paths across the unit cell. Thus, the pyrochlore-type Yb$_2$Ti$_2$O$_7$ exhibits the three-dimensional network of oxide-ion diffusion paths.

4. Conclusions

In this work, we have demonstrated the first example of experimental visualization of oxide-ion diffusion paths of the pyrochlore-type oxide-ion conductor. The combined technique of in situ TOF neutron powder diffraction measurements at high temperatures and maximum-entropy method enabled to obtain reliable neutron scattering length density distribution, indicating the experimental oxide-ion diffusion pathways. It was found that there exist two kinds of oxide-ion diffusion paths along (110) and (100) (strictly, (2 − 8x(O$_{8g}$) + 3 8x(O$_{8f}$) − 3) directions. The minimum neutron scattering length density on the (110) path was higher than that on (100), and DBVS on the (110) was lower than DBVS on (100). These results strongly suggest that the energy barrier for (110) oxide-ion migration is lower than that for (100). Furthermore the present study has clearly indicated that an oxide ion three-dimensionally diffuses through both the (100) and (110) paths.

Acknowledgment The neutron diffraction measurements by SuperHRPD were performed with the approval (2013B0198, 2014B0233, 2015A0190, 2016A0175, 2017A0111, 2017L1300). The ICP-OES analyses were kindly performed by Daiichi-Kigenso Co. This study was partly supported by a Grant-in-Aid for Scientific Research (KAKENHI, Nos. JP15H02291, JP25630365, JP26870190, JP16H08884, JP16H06293, JP16H06440, JP16H06438, JP16H06438, JP17H06222) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and JSPS Core-to-Core Program, A. Advanced Research Networks (Solid Oxide Interfaces for Faster Ion Transport).

Reference
1) T. Moriga, A. Yoshiasa, F. Kanamaru, K. Koto, M. Yoshimura and S. Somiya, Solid State Ionics, 31, 319–328 (1989).
2) J. C. Boivin and G. Mairesse, Chem. Mater., 10, 2870–2888 (1998).
3) M. Yashima and D. Ishimura, Chem. Phys. Lett., 378, 395–399 (2003).
4) S. Hull, Rep. Prog. Phys., 67, 1233–1314 (2004).
5) M. Yashima and D. Ishimura, Appl. Phys. Lett., 87, 221909 (2005).
6) M. Yashima, S. Kobayashi and T. Yasui, Faraday Discuss., 134, 369–376 (2007).
7) M. Yashima, J. Ceram. Soc. Jpn., 117, 1055–1059 (2009).
8) A. Orera and P. R. Slater, Chem. Mater., 22, 675–690 (2010).
9) M. Yashima, Catal. Today, 253, 3–19 (2015).
10) M. P. van Dijk, K. J. de Vries and A. J. Burggraaf, Solid State Ionics, 9, 913–919 (1980).
11) B. J. Wuensch, K. W. Eberman, C. Heremans, E. M. Ku, P. Onnerud, E. M. Yeo, S. M. Haile, J. K. Stalick and J. D. Jorgensen, Solid State Ionics, 129, 111–133 (2000).
12) H. Yamamura, H. Nishino, K. Kakinuma and K. Nomura, Solid State Ionics, 158, 359–365 (2003).
13) A. V. Shlyakhtina and L. G. Shecherbakova, Russ. J. Electrochem., 48, 1–25 (2012).
14) O. Knop, F. Brisse and L. Castelliz, Can. J. Chem., 47, 971–990 (1969).
15) M. A. Subramanian, G. Aravamudan and G. V. Subba Rao, Prog. Solid State Ch., 15, 55–143 (1983).
16) A. V. Shlyakhtina, P. Fedtke, A. Busch, I. V. Kolbanean, T. Barfels, M. Wienecke, A. E. Sokolov, V. A. Ulianov, V. A. Trounov and L. G. Shcherbakova, Solid State Ionics, 179, 1004–1008 (2008).
17) T. Hagiwara, H. Yamamura and H. Nishino, IOP Conf. Ser.: Mater. Sci. Eng., 18, 132003 (2011).
18) K. A. Ross, T. Profen, H. A. Dabkowska, J. A. Quilliam, L. R. Yaraskavitch, J. B. Kycia and B. D. Gaulin, Phys. Rev. B, 86, 174424 (2012).
19) J. M. Farmer, L. A. Boatner, B. C. Chakoumakos, M.-H. Du, M. J. Lance, C. J. Rawn and J. C. Bryan, J. Alloy. Compd., 605, 63–70 (2014).
20) K. Baroudi, B. D. Gaulin, S. H. Lapidus, J. Gaudet and R. J. Cava, Phys. Rev. B, 92, 24110 (2015).
21) K. Nakamura, M. Mori, T. Itoh and T. Ohnuma, AIP Adv., 6, 115003 (2016).
22) T. Hagiwara, K. Nomura and H. Kageyama, J. Ceram. Soc. Jpn., 125, 65–70 (2017).
23) M. Pirzada, R. W. Grimes, L. Minervini, J. F. Maguire and K. E. Sickafus, Solid State Ionics, 140, 201–208 (2001).
24) C. R. Stanek, L. Minervini and R. W. Grimes, J. Am. Ceram. Soc., 85, 2792–2798 (2002).
25) M. Pirzada, R. W. Grimes and J. F. Maguire, Solid State Ionics, 161, 81–91 (2003).
26) W. R. Panero, L. Stixrude and R. C. Ewing, Phys. Rev. B, 70, 54110 (2004).
27) H. Y. Xiao, X. T. Zu, F. Gao and W. J. Weber, J. Appl. Phys., 104, 73503 (2008).
28) J. Wang, F. Zhang, J. Lian, R. C. Ewing and U. Becker, Acta. Mater., 59, 1607–1618 (2011).
29) X. J. Wang, H. Y. Xiao, X. T. Zu, Y. Zhang and W. J. Weber, J. Mater. Chem. C, 1, 1665–1673 (2013).
30) H. Y. Xiao, W. J. Weber, Y. Zhang and X. T. Zu, Acta. Mater., 87, 273–282 (2015).
31) S. Torii, M. Yonemura, T. Yulius Surya Panca Putra, J. Zhang, P. Miao, T. Muroya, R. Tomiyasu, T. Morishima, S. Sato, H. Sagehashi, Y. Noda and T. Kamiyama, J. Phys. Soc. Jpn., 80, SB020 (2011).
32) M. Sakata, T. Uno, M. Takata and C. H. Howard, J. Appl. Crystallogr., 28, 159–165 (1995).
33) A. Fujimoto, M. Yashima, K. Fuji and J. R. Hester, J. Phys. Chem. C, 121, 21272–21280 (2017).
34) R. Oishi, M. Yonemura, T. Nishimaki, S. Torii, A. Hoshikawa, T. Ishigaki, T. Morishima, K. Mori and T. Kamiyama, Nucl. Instrum. Meth. A, 600, 94–96 (2009).
35) N. N. Lobanov and L. Alde da Veiga, 6th Eur. Powder Diffr. Conf. Abstr., (1988) P12–16.
36) M. Kumazawa, M. Takata and M. Sakata, Acta Crystallogr. A, 51, 47–53 (1995).
37) K. Momma, T. Ikeda, A. A. Belik and F. Izumi, Powder Diff., 28, 184–193 (2013).
38) M. Sale and M. Avdeev, J. Appl. Crystallogr., 45, 1054–1056 (2012).
39) K. Momma and F. Izumi, J. Appl. Crystallogr., 44, 1272–1276 (2011).
40) N. E. Brese and M. O’Keeffe, Acta Crystallogr. B, 47, 192–197 (1991).
41) M. Yashima, K. Nomura, H. Kageyama, Y. Miyazaki, N. Chitose and K. Adachi, Chem. Phys. Lett., 380, 391–396 (2003).
42) M. Yashima and T. Tsuji, J. Appl. Crystallogr., 40, 1166–1168 (2007).
43) M. Yashima and T. Kamioka, Solid State Ionics, 179, 1939–1943 (2008).
44) Y.-C. Chen, M. Yashima, T. Ohta, K. Ohoyama and S. Yamamoto, J. Phys. Chem. C, 116, 5246–5254 (2012).