Functional properties of pyrochlore-type silver tantalate and fluorite-type silver niobate

Withanage ISURU UDAKARA WITHANAGE¹, Nobuhiko KUMADA²,³, Takahiro TAKEI¹, Sayaka YANAGIDA¹, Kiyoharu TADANAGA², Akira MIURA², Nataly Carolina ROSERO-NAVARRO¹ and Masaki AZUMA³

¹Center for Crystal Science and Technology, University of Yamanashi, 7–32 Miyamae, Kofu 400–8511, Japan
²Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060–8628, Japan
³Laboratory for Materials and Structures, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226–8503, Japan

Key-words: Pyrochlore-type, Ionic conductivity, fluorite-type

©2020 The Ceramic Society of Japan. All rights reserved.

DOI http://doi.org/10.2109/jcersj2.19139

NOTE

1. Introduction

Recently, Ag-based oxides AgMO₃ (M: Nb and Ta),¹⁻³ AgVO₃,⁴ Ag₃PO₄,⁵ AgGaO₂,⁶ etc., have been receiving attention because of their photocatalytic activity for water splitting as well as for the decomposition of organic compounds in water. The AgMO₃ (M: Nb and Ta) compounds have various properties like ion exchange,³⁻⁷ ionic conductivity,⁸ and ferroelectricity,⁹ as well as visible-light-driven photocatalysis. After the discovery of the superionic conductivity of AgI-containing solid electrolytes, the ionic conductivities of Ag-based compounds have been extensively investigated.¹⁰ AgI shows temperature-dependent structural transitions; at low temperatures (147°C), β/γ-AgI transform to α-AgI, owing to the fast ion conductivity.¹¹⁻¹³ However, its application as a solid electrolyte is limited by its low ionic conductivity at room temperature. To ensure its technical applicability, a solid electrolyte must show high ion-mobility at low temperatures. Recently, the ionic conductivity of solid electrolytes has gained much attention for their applications in solid-oxide fuel-cells,¹³⁻¹⁴ gas sensors,¹⁵ oxygen separation membranes,¹⁶ batteries,¹⁷ and catalysts.¹⁸ Much effort has been devoted to obtaining stable structures with high ionic conductivity at low operating temperatures.

Our previous study successfully demonstrated the synthesis of pyrochlore-type Ag₀.₉₃TaO₂.₉₇·₀.₉₄H₂O (AT) and fluorite-type silver niobate Ag₀.₄₁Nb₀.₅₉O₁.₆₈ (AN) by ion-exchange reactions.³ The pyrochlore-type compound is represented by the general formula A₂B₂O₆O and it is considered as a superstructure of the fluorite-type structure which has the general formula AO₂. A larger sized A cation occupied at 16d site is generally an alkali metal, an alkaline earth metal or a rare earth metal,¹⁹,²⁰ a B cation occupied at 16c site is a transition metal while O and O' occupy at 48f and 8b sites respectively.²¹⁻²² The ordered pyrochlore structure can be transformed into the disordered fluorite structure by decreasing the A site cation size²³ which transforms to a face centered cubic system. Furthermore, the tunnel structure of the pyrochlore-type compound and the related fluorite structure provide the possibility of diffusion pathways for the silver ions migration, facilitating the ionic conductivity. In this work, we have successfully investigated the total conductivity of AT and AN by AC impedance measurements as a function of temperature.

2. Experiments

Pyrochlore-type silver tantalate, AT and fluorite-type silver niobate AN were obtained by the reaction of pyrochlore-type (K₀.₅₆H₀.₄₄)TaO₃·1.14H₂O and (K₀.₇₃H₀.²₇)NbO₃·1.72H₂O, respectively, with excess molten AgNO₃ at 300°C for 6 h.³ In-situ high temperature synchrotron X-ray powder diffraction data were collected at the SPring-8 facility in Hyogo Japan, BL02B2 beam line with wavelength λ = 0.413853 Å (1 Å = 0.1 nm), and the samples were loaded in a quartz capillary with a 0.2 mm

² Corresponding author: N. Kumada; E-mail: kumada@yamanashi.ac.jp

©2020 The Ceramic Society of Japan

This is an Open Access article distributed under the terms of the Creative Commons Attribution License (https://creativecommons.org/licenses/by-nd/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
diameter. The powder diffraction data were refined using the Rietveld method with the RIETAN-FP computer program. The chemical compositions were determined by energy dispersive X-ray spectrometry and the weight losses by thermogravimetry (TG) curves. To measure the total conductivity, pellets (10 mm diameter and 3–4 mm thick) of the pyrochlore and fluorite compounds were obtained at the high pressure of 4 GPa (10 min) using a cubic-anvil-type high-temperature high-pressure apparatus. The total conductivity was determined by AC impedance measurement, as a function of temperature, using an impedance analyzer (SI 1260, Solartron) over the frequency range of 1 Hz to 10 MHz. The electrodes were sputter-coated with gold on both sides of the pellet and connected with a platinum wire using Ag paste. These measurements were performed in the temperature range 25–240°C and the stabilization time before each data point was obtained was approximately 30 min. The ZView software was used to analyze the spectra and calculate the ohmic resistance of the pellets.

3. Results and discussion

3.1 Structure analysis

The Rietveld refinement of AT and AN at room temperature shows in Fig. 1, gave reasonable R-factors ($R_{wp} = 6.61\%$, $R_p = 5.11\%$ for AT and $R_{wp} = 5.37\%$, $R_p = 4.27\%$ for AN); the lattice parameters were determined to be $a = 10.5375(2)\ \text{Å}$ for AT and $a = 5.2134(8)\ \text{Å}$ for AN. The in-situ high-temperature synchrotron X-ray diffraction (SXRD) patterns of AT and AN indicate no phase transition in the temperature range 25–240°C, as shown in Fig. 2. These results imply that AT and AN exhibit good structural stability under air. The temperature dependences of the lattice parameters for AT (a) and AN (b) are shown in Fig. 3. As temperature increased, the lattice parameters of AT decreased, while an increase was observed for those of AN. This negative thermal expansion of AT was caused by the removal of water molecules on the hydrated pyrochlore-type structure. AT was hydrated and the thermogravimetric result in Fig. 4, showed a 4.77% mass loss. On the other hand AN had an anhydrate structure and it showed a very small mass loss (0.81%) caused by the release of absorbed water. The thermal expansion coefficient for AN was calculated to be 0.09 K⁻¹.

3.2 Total conductivity of AT and AN

Impedance spectra give, primarily, the AC impedance of the sample. Charge accumulation can take place within the
bulk, in grain boundaries, or at the interfaces. Therefore, these crystalline samples are usually analogous to a series of two RC-parallel circuits. The overall representation of the AC impedance of AT and AN is contributed from grains and grain-boundaries, as suggested by the Nyquist plot shown in Fig. 5. The first semi-circle shows the total...
conductivity of the sample. The intercept of the first semicircle with the real axis gives the total associated resistance (R) and we consider the total resistance as the contribution from grains and grain-boundaries. The total conductivities of AT and AN reached 4.00 × 10⁻³ and 9.03 × 10⁻⁴ S/cm, respectively, at 240°C. As shown in Fig. 6, the activation energy of AT was 0.61 eV and AN showed non-linear behavior with activation energies of 0.52 eV at temperatures less than 120°C and 0.33 eV at temperatures greater than 120°C. The AN structure refinement shows the change in the atomic displacement parameter for Ag ions (B- 3.4 to 3.7 Å) in the range of 80–120°C and this atomic displacement facilitates the mobility of the silver ions and thus it may increase the total conductivity, reducing the activation energy. The Rietveld refinement of AN showed that the oxygen atom was statistically distributed in the 8c site, and Ag and Nb atoms randomly distributed in the 4a site. The bond valence sum (BVS) of Ag was 1.04 and Ta was 5.26 respectively.

Grins et al., 25) the K ion migration in pyrochlore type 
K\textsubscript{1+x}Ta\textsubscript{1+y}W\textsubscript{1−z}O\textsubscript{6}·nH\textsubscript{2}O compound. The activation energy of AT obtained was 0.61 eV which is almost similar (0.65 eV) to the data achieved in Grins et al. (Fig. 6). Furthermore Isasi et al. 26) reported that Rb ionic conductivity of defect pyrochlore type anhydrate structure (Fig. 6) which had shown 0.70 eV activation energy. Although Rakesh et al. 27) has previously reported dielectric properties, to our knowledge there has been no reports of conductivity for pyrochlore-type silver tantalate and fluoride-niobate structures. To compare with previously results we thought that the total conductivity of AN and AT is mostly correlated with migration of Ag⁺ ions as well as oxygen ions or protons of the water molecules in the pyrochlore compounds. 28), 29)

### Table 1. Room temperature crystallographic data and atomic parameters of AT and AN

| Space group | AT | AN |
|-------------|----|----|
| Fd-3m (#227) | Fm-3m (#225) |
| \(a\) (Å) | 10.5375(2) | 5.2134(8) |
| Cell Volume \((\text{Å}^3)\) | 1170.09(4) | 141.69(3) |
| \(z\) | 16 | 4 |
| \(R\)-factor \(R_{wp}\) | 6.61% | 5.11% | 5.37% | 4.27% |
| \(R_{ref}\) | 9.71% | 6.25% | 18.77% | 13.35% |

| Atomic parameters Ag\textsubscript{0.93}TaO\textsubscript{2.97}·0.94H\textsubscript{2}O |
|-----------------|-----|--|-----|
| Atom | Site | \(g\) | \(x\) | \(y\) | \(z\) | \(B\) \((\text{Å}^2)\) | BVS |
| Ta | 16c | 1.036 | 0 | 0 | 0 | 1.7(5) | 5.26 |
| Ag | 16d | 0.785 | 1/2 | 1/2 | 1/2 | 6.6(2) | 1.04 |
| O1 | 48f | 1.000 | 0.335(1) | 1/8 | 1/8 | 1.0* |
| O2 | 8b | 3.675 | 0.375 | \(=x\) | \(=x\) | 65.1(4) |

| Atomic parameters Ag\textsubscript{0.41}Nb\textsubscript{0.59}O\textsubscript{1.68} |
|-----------------|-----|--|-----|
| Atom | Site | \(g\) | \(x\) | \(y\) | \(z\) | \(B\) \((\text{Å}^2)\) | BVS |
| Ag/Nb | 4a | 1 | 0 | 0 | 0 | 3.0(1) | 3.00 |
| O | 8c | 2.3(4) | 1/4 | 1/4 | 1/4 | 32(4) |

*: Fixed parameter.

### 4. Conclusions

Pyrochlore-type Ag\textsubscript{0.93}TaO\textsubscript{2.97}·0.94H\textsubscript{2}O and fluorite-type Ag\textsubscript{0.41}Nb\textsubscript{0.59}O\textsubscript{1.68} were prepared by ion-exchange reactions. Their structural and electrical properties were investigated. The impedance measurement of total conductivity, at 240°C reached the order of \(10^{-3}\) and \(10^{-4}\) S/cm for tantalate and niobate, respectively. The calculated activation energy of AT was 0.61 eV and AN showed non-linear behavior with activation energies of 0.52 eV at temperatures less than 120°C and 0.33 eV at temperatures greater than 120°C. The activation energy of AN was smaller than K ion migration in hydrated pyrochlore-type compound and Rb ion migration of dehydrated defect pyrochlore compound. The AN structure refinement shows the change in the atomic displacement parameter for Ag ions (B- 3.4 to 3.7 Å), in the range of 80–120°C; this atomic displacement facilitates the mobility of Ag ions and, consequently, it may increase the total conductivity, reducing the activation energy.

### Reference

1) H. Kato, H. Kobayashi and A. Kudo, *J. Phys. Chem. B*, 106, 12441–12447 (2002).
2) D. Arney, C. Hardy, B. Greve and P. A. Maggard, *J. Photoch. Photobio. A*, 214, 54–60 (2010).
3) I. Withanage, N. Kumada, T. Takei, S. Yanagida, Y. Kuroiwa and C. Moriyoshi, *J. Ceram. Soc. Jpn.*, 125, 776–778 (2017).
4) R. Konta, H. Kato, H. Kobayashi and A. Kudo, *Phys. Chem.*, 5, 3061–3065 (2003).
5) X. Yang, H. Cui, Y. Li, J. Qin, R. Zhang and H. Tang, *ACS Catal.*, 3, 363–369 (2013).
6) Y. Maruyama, H. Irie and K. Hashimoto, *J. Phys. Chem. B*, 110, 23274–23278 (2006).
7) W. I. U. Withanage, S. Yanagida, T. Takei and N. Kumada, *J. Ceram. Soc. Jpn.*, 125, 776–778 (2017).
8) R. Konta, H. Kato, H. Kobayashi and A. Kudo, *Phys. Chem.*, 5, 3061–3065 (2003).
9) X. Yang, H. Cui, Y. Li, J. Qin, R. Zhang and H. Tang, *ACS Catal.*, 3, 363–369 (2013).
10) C. Tubandt and E. Lorenz, *Z. Phys. Chem.*, 87, 513–542 (1914).
11) R. Makiura, T. Yonemura, T. Yamada, M. Yamauchi, R. Ikeda, H. Kitagawa, K. Kato and M. Takata, *Nat. Mater.*, 8, 476–480 (2009).
12) M. Tatsumisago, Y. Shinkuma and T. Minami, *Nature*, 354, 217–218 (1991).
13) J. C. Boivin and G. Mairesse, *Chem. Mater.*, 10, 2870–2888 (1998).
14) O. Smirnova, N. Kumada, Y. Yonesaki and N. Kinomura, *Electrochem. Commun.*, 10, 485–487 (2008).
15) H. M. M. Arachchige, D. Zappa, N. Poli, N. Gunawardhana and E. Comini, *Sensor Actuat. B-Chem.*, 269, 331–339 (2018).
16) J. Sunarso, S. Baumann, J. M. Serra, W. A. Meulenberg, S. Liu, Y. S. Lin and J. C. Diniz da Costa, *J. Membrane Sci.*, 320, 13–41 (2008).
17) Y. Ren, Y. Shen, Y. Lin and C. Nan, *Electrochem. Commun.*, 57, 27–30 (2015).
18) M. Salazar, D. A. Berry, T. H. Gardner, D. Shekhawat and D. Floyd, *Appl. Catal. A-Gen.*, 310, 54–60 (2006).
19) A. V. Shlyakhtina, K. S. Pigalskiy, D. A. Belov, N. V. Lyskov, E. P. Kharitonova, I. V. Kolbanean, A. B. Borunova, O. K. Karyagina, E. M. Sadowskaya, V. A. Sadykov and N. F. Eremeev, *Dalton T.*, 47, 2376–2392 (2018).
20) A. V. Shlyakhtina, D. A. Belov, K. S. Pigalskiy, A. N. Shechegolikhin, I. V. Kolbanean and O. K. Karyagina, *Mater. Res. Bull.*, 49, 625–632 (2014).
21) L. Minervini, R. W. Grimes and K. E. Sickafus, *J. Am. Ceram. Soc.*, 83, 1873–1878 (2000).
22) M. Saiduzzaman, T. Takei, S. Yanagida, N. Kumada, H. Das, H. Kyokane, S. Wakazaki, M. Azuma, C. Moriyoshi and Y. Kuroiwa, *Inorg. Chem.*, 58, 1759–1763 (2019).
23) J. Lian, L. Wang, J. Chen, K. Sun, R. C. Ewing, J. M. Farmer and L. A. Boatner, *Acta Materialia*, 51, 1493–1502 (2003).
24) F. Izumi and K. Momma, *Solid State Phenom.*, 130, 15–20 (2007).
25) J. Grins, M. Nygren and T. Wallin, *Mater. Res. Bull.*, 15, 53–61 (1980).
26) J. Isasi, M. L. Lopez, M. L. Veiga and C. Pica, *Solid State Ionics*, 89, 321–326 (1996).
27) R. Muduli, R. Pattanayak, S. Kumar, S. K. Kar, P. Kumar, S. Panigrahi and R. K. Panda, *J. Alloy. Compd.*, 656, 33–44 (2016).
28) J. B. Goodenough, H. Y. Hong and J. A. Kafalas, *Mater. Res. Bull.*, 11, 203–220 (1976).
29) A. D. English, A. W. Sleight, J. L. Fourquet and R. De Pape, *Mater. Res. Bull.*, 15, 1727–1735 (1980).