Oxide Ion Conduction of $\text{BaCe}_{0.80}\text{Zr}_{0.10}\text{Y}_{0.10}\text{O}_{3-\delta}$ Thin Film with Oxygen Vacancies

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A $\text{BaCe}_{0.80}\text{Zr}_{0.10}\text{Y}_{0.10}\text{O}_{3-\delta}$ (BCZY) thin film with *a*- and *c*-axes orientations has been deposited on Al_2O_3 (0001) substrates by Radio Frequency magnetron sputtering. The lattice constants of *a*- and *c*-axes decrease with increasing the substrate temperature (T_{sub}) during sputtering deposition. The as-prepared BCZY thin film has the mixed valence states of Ce^{4+} ($4f^0$) and Ce^{3+} ($4f^1$) with oxygen vacancies created by high T_{sub} . The electrical conductivity increases with increasing T_{sub} , but it does not depend on oxygen partial pressure in the intermediate temperature (IMT) region between 400 and 600°C. The Ce^{3+} state at the LUMO level of the BCZY thin film is larger than that of BCZY bulk ceramic in which oxide ion conduction has not been observed. These results indicate that the BCZY thin film with oxygen vacancies has the high oxide ion conduction, which is required for electrolytes of solid oxide fuel cells in IMT region.

Keywords: $\text{BaCe}_{0.80}\text{Zr}_{0.10}\text{Y}_{0.10}\text{O}_{3-\delta}$ (BCZY) thin film, lattice constant, Arrhenius plot, oxide ion conduction, activation energy (E_A), oxygen vacancies

1. INTRODUCTION

Perovskite BaCeO_3 and BaZrO_3 bulk ceramics exhibit proton conduction in water vapor atmosphere at intermediate temperature (IMT) region when the Y^{3+} ions are substituted into Ce^{4+} (or Zr^{4+}) site [1-13]. Protons are adsorbed at the surface by the exchange of proton and oxygen vacancies created by Y^{3+} doping. The proton bound by the oxide ion creates a weak oxygen-proton (O-H) bond between two oxide ions. The proton of the O-H bond migrates between the two oxide ions by the thermal activation process [14,15]. A $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCY) bulk ceramic has proton conductivity of $\sim 1.0 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 400 °C in a wet atmosphere [16]. Furthermore, the $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BZY) bulk ceramic has a high proton conductivity of $\sim 1.0 \times 10^1 \text{ S}\cdot\text{cm}^{-1}$ at 600 °C in a wet atmosphere [17]. Although these proton conduction can use as an electrolyte of solid oxide fuel cells (SOFCs) at IMT region, the chemical stabilities of these bulk ceramics are very low in wet atmosphere due to sintering resistance.

In this manuscript, we have proved the oxide ion conduction of $\text{BaCe}_{0.80}\text{Zr}_{0.10}\text{Y}_{0.10}\text{O}_{3-\delta}$ (BCZY) thin film with oxygen vacancies. The BCZY ceramic is proton conducting material with high chemical stability [18-20]. In recent years, an oxide ion conducting thin film, such as Sm-doped CeO_2 [21-23] and LaGaO_3 [24-25], is refocused as a practical electrolyte of SOFCs at IMT region, although the electricity generation power is not high because the oxide ion conductivity is low at IMT region. If the BCZY thin film has high oxide ion conductivity, the BCZY might be one of useful candidates as an SOFC electrolyte with the high

coefficient against of O_2 gas. However, the oxide ion conduction of BCZY thin film has not been clarified thus far. In order to achieve this subject, we have tried to grow a BCZY thin film using a radio frequency (RF) magnetron sputtering method. The as-deposited thin film can possess a number of oxygen vacancies, which is required for oxide ion conduction, by controlling the substrate temperature during deposition. In this paper, we discuss about the oxide ion conduction of the BCZY thin film in terms of electrical conductivity and electronic structure.

2. EXPERIMENTAL

The BCZY ceramic target with the chemical composition of $\text{BaCe}_{0.80}\text{Zr}_{0.10}\text{Y}_{0.10}\text{O}_{3-\delta}$ was synthesized by a solid state reaction method, pressed into cylinders, and then sintered in air at 1450 °C for 24 h. The prepared ceramic target was confirmed to be single phase using X-ray diffraction (XRD) analysis with $\text{CuK}\alpha$ using Rigaku Miniflex 600.

The RF magnetron sputtering system was arranged in symmetric configuration with a rotating substrate holder for compositional uniformity. The flow rate of Ar gas and deposition pressure during sputtering deposition were set at 20 sccm and 5.0×10^{-3} Torr, respectively. The substrate temperature (T_{sub}) was changed between 400 and 700°C. The BCZY thin film was deposited on Al_2O_3 (0001) substrate in order to prepare the BCZY thin film of single direction.

The crystal structure of BCZY thin film was confirmed using XRD analysis. The electrical conductivities were measured by the AC impedance method using a frequency response analyzer (Solatron

1260) and amplifier (Solatron 1296) in dry atmosphere in the temperature region from 300 °C to 700 °C. The measurement frequency region was from 0.1 Hz to 32MHz. The interdigital Pt electrode with ~100 nm thickness were deposited on the film surface by RF magnetron sputtering in order to measure the in-plane conductivity. The type of conducting carrier was judged from the slope of the conductivity against of the oxygen gas partial pressure (P_{O_2}), based on defect chemistry analysis.

The electronic structure was characterized by photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS) at BL2A in the Photon Factory (PF) of the High-Energy Accelerator Organization (KEK), Tsukuba in Japan [26]. The XAS spectra were measured in total electron yield mode. The kinetic energy of photoelectron for PES was measured using the Gammadata-Scienta SES-2002 hemispherical analyzer. The energy resolutions of PES and XAS were 100 and 60 meV, respectively, at $h\nu = 700$ eV.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the XRD patterns as a function of T_{sub} for the as-deposited BCZY thin films. These thin films were crystallized without post-annealing. The (002) and (400) peaks of BCZY thin films are observed at $2\theta \sim 27.5^\circ$ and $\sim 40.6^\circ$, respectively. The existence of other phase was not observed in BCZY thin film. Although the intensity of (002) peak decreases with T_{sub} , that of (400) peak increases with T_{sub} . The peak positions of (002) and (400) peaks shifted to the lower diffraction angle side with decreasing T_{sub} .

Figure 1(b) shows the lattice constants of a - and c -axes of the BCZY thin film calculated from the peak position of Fig. 1(a). The lattice constants of the BCZY thin film are larger than those of the BCZY bulk ceramic, whose lattice constants for a - and c - axes are 8.734 Å and 6.216 Å, respectively [18]. Here, the lattice

Fig.1 (a) XRD patterns as a function of T_{sub} for the BCZY thin films. (b) Lattice constants of a - and c -axes as a function of T_{sub} for the BCZY thin films.

Figure 2 PES spectra in the (a) Zr 3d_{5/2} and Ba 4p_{3/2}, (b) Y 3p, and (c) Ce 3d core levels of the BCZY thin film.

mismatch or lattice distortion occur between BCZY and Al_2O_3 . These lattice constants decrease with increasing T_{sub} , although the changes are relaxed above $T_{\text{sub}} = 600^\circ\text{C}$. This would originate to the change of the amount of oxygen vacancies during sputtering deposition.

Figures 2(a) and (b) show the PES spectra in the Zr 3d_{5/2}, Ba 4p_{3/2} and Y 3p core levels, respectively, of the BCZY thin film. The Zr 3d_{5/2} and Ba 4p_{3/2} peak positions correspond to the Zr^{4+} and Ba^{2+} valence states, respectively. The Y 3p PES spectrum consists of 3p_{1/2} and 3p_{3/2} peak structures by spin orbital splitting. This spectral shape and peak position correspond to the Y^{3+} valence state. The existence of these Zr and Y peaks indicate that Zr^{4+} and Y^{3+} are actually doped into BaCeO_3 thin film.

Figure 2(c) shows the PES spectrum in the Ce 3d core level of the BCZY thin film. The Ce 3d PES spectrum consists of 3d_{3/2} and 3d_{5/2} structures. Furthermore, each spectrum splits to three structures of 3d⁹4f⁰ (Ce^{4+}), 3d⁹4f¹ (Ce^{3+}) and 3d⁹4f² $\bar{L}$ (satellite) [27]. Here, $\bar{L}$ denotes the hole in the valence band, which is mainly composed of the O 2p state. The existence of hole state at the top of the valence band has been already observed in BCY by O 1s-XAS [27-29]. The satellite structure is caused by the charge transfer from the O 2p orbital to the Ce 4f orbital in the intermediate state for the PES, indicating that the Ce 4f state hybridizes with the O 2p state in the valence band. The Ce^{3+} state is created by oxygen vacancies in the as-deposited thin film. Such a situation has been reported in CeO_2 and $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ with oxygen vacancies [23,30].

Figure 3 Electrical conductivities as a function of the P_{O_2} of the BCZY thin film of $T_{sub} = 700$ °C measured at 400 and 600 °C.

Figure 4 Arrhenius plots of the electrical conductivities as a function of T_{sub} for the BCZY thin films

Figure 3 shows the conductivity as a function of the P_{O_2} of the BCZY thin film measured at 400 and 600 °C. When the conductivities are independent of P_{O_2} , the slopes of conductivities against P_{O_2} reflect ion conduction in terms of defect chemistry analysis. As seen in Fig. 3, the conductivities are almost independent of P_{O_2} , and this behavior is similar to Sm-doped CeO_2 with high oxide ion conduction in IMT region [20]. This suggests that the BCZY thin film has oxide ion conduction, which has not been reported thus far. In addition, we found that the oxide ion conductivity of the BCZY thin film is higher than that of Sm-doped CeO_2 [20].

Figure 4 shows the Arrhenius plots of the electrical conductivities as a function of T_{sub} for the BCZY thin films in dry atmosphere. In general, ion conductivity (σ) are given as follows:

$$\sigma T = A \exp(-E_A/kT),$$

where E_A is the activation energy of carrier migration, A is the pre-exponential factor, and k is Boltzmann constant, where the axis of ordinates is σT . These conductivities exhibit the thermal activation-type

Fig.5 (a) Ce 3d XAS spectrum of the dry BCZY thin film. (b) Resonant-PES (RPES) spectra in the Ce 3d $\rightarrow$ 4f energy region of the dry BCZY thin film.

behavior. The oxide ion conductivity of BCZY thin film is higher than proton conductivity of BCZY bulk ceramic. The conductivity increases with increasing T_{sub} . The activation energies (E_A) of $T_{sub} = 400, 500, 600$, and 700 °C are estimated to be 0.69, 0.58, 0.65, and 0.50 eV, respectively. The changes of the conductivity and E_A for T_{sub} may contribute to the change of the amount of oxygen vacancies of BCZY thin film, as indicated in Fig. 1. The high E_A of BCZY thin films originate the increase in the O-O bond length, where the lattice constant is longer.

Figure 5(a) shows the Ce 3d XAS spectrum of the BCZY thin film. The spectrum corresponds to the transition from Ce 3d_{5/2} core level to the unoccupied Ce 4f state. The spectral shape and peak position is similar to those of CeO_2 and $BaCe_{0.90}Y_{0.10}O_{3-\delta}$ [28,31]. Two peaks at 881 and 883.3 eV correspond to Ce^{3+} (on1) and Ce^{4+} (on2), respectively. A broad peak at ~889 eV is satellite structure. This is also an additional evidence that the BCZY thin film has the mixed valence states of Ce^{3+} and Ce^{4+} , as shown in Fig. 2(c).

Figure 5 (b) shows the resonant-PES (RPES) spectra in the Ce 3d $\rightarrow$ 4f energy region of the wet BCZY thin film. The PES reflects the electronic structure in the surface state since the mean free path of photoelectron is very short. The off-resonance spectrum corresponds to the O 2p DOS in the valence band. The peaks A and B are resonantly enhanced by excitation energies corresponding to on1 and on2, respectively, in Fig. 5(a). Therefore, the peak A at the top of the valence band corresponds to Ce^{3+} ($4f^1\bar{L}$) state and the peak B in the valence band is due to Ce^{4+} ($4f^0$) state. The peak C is considered to be Ce 5d state, as reported in ref [30]. These results indicate that the valence band of $BaCeO_3$

is mainly composed of the O 2p state hybridized with the Ce 4f and Ce 5d states. Similar situation has been reported in Sm-doped CeO_2 and $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ [23,30], which has same electronic configuration of BCZY.

The intensity of peak A (Ce^{3+}) in BCZY thin film is stronger than that of Ce oxide such as CeO_2 and BaCeO_3 . The Ce^{3+} state is created by oxygen vacancies in Ce oxide. When the contribution of Ce^{3+} state is large, the Ce oxide has a lot of oxygen vacancies in Ce oxide [30]. On the other hand, the energy separation between the top of Ce^{3+} state and the Fermi level (E_F) does not accord with E_A of the conductivity. This indicates that the main carrier of BCZY thin film is not electron or hole. Although the contribution of Zr 4d DOS is not clarified in this study, the high oxide ion conduction contributes to the oxygen vacancies created by Y^{3+} doping and sputtering deposition.

4. CONCLUSION

We have prepared the BCZY thin films on Al_2O_3 (0001) substrates by RF magnetron sputtering. The BCZY thin films exhibited (002) and (400) peaks on Al_2O_3 substrate. The lattice constants of the *a*- and *c*-axes decrease with increasing T_{sub} . The valence states of Y^{3+} and Zr^{4+} are confirmed by PES. The Ce 3d PES and RPES spectra exhibit the mixed valence states of Ce^{4+} and Ce^{3+} . The electrical conductivities at 400 and 600°C are independent of P_{O_2} , indicating the existence of oxide ion conduction. The oxide ion conductivity increases with increasing T_{sub} . Although the E_A of BCZY thin films are larger than that of ceramic, the oxide ion conductivity of BCZY thin film is higher than that of Sm-doped CeO_2 , which is a practical electrolyte of SOFC in IMT region. This result is due to a lot of oxygen vacancies created by Y^{3+} doping and high T_{sub} during sputtering deposition.

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REFERENCES

- [1] H. Iwahara, T. Esaka, H. Uchida and N. Maeda, *Solid State Ionics*, **3/4** (1981) 359.
- [2] H. Iwahara, T. Yajima, T. Hibino, K. Ozaki and H. Suzuki, *Solid State Ionics* **61** (1993) 65.
- [3] K.D. Kreuer, Th. Dippel, Y.M. Baikov and, J. Maier, *Solid State Ionics*, **86–88** (1996) 613.
- [4] H. Matsumoto, T. Shimura, T. Higuchi, H. Tanaka, K. Katahira, T. Otake, T. Kudo, K. Yashiro, A. Kaimai, T. Kawada and J. Mizusaki, *J. Electrochem. Soc.*, **152** (2005) A488.
- [5] N. Ito, M. Iijima, K. Kimura and S. Iguchi, *J. Power Sources* **152** (2005) 200.
- [6] Kreuer, K. D. , *Solid State Ionics*. **125** (1999) 285.
- [7] K. D. Kreuer, *Annu. Rev. Mater. Res.* **33** (2003) 333.
- [8] F. Iguchi, T. Yamada, N. Sata, T. Tsurui and H. Yugami, *Solid State Ionics* **177** (2006) 2381.
- [9] F. Iguchi, T. Tsurui, N. Sata, Y. Nagao and H. Yugami, *Solid State Ionics* **180** (2009) 563.
- [10] Y. Yamazaki, R.H-Sanchez and S.M. Haile, *Chem. Mater.* **21** (2009) 2755.
- [11] E. Fabbri, D. Pergolesi, E. Traversa, *Chem. Soc. Rev.* **39** (2010) 4355.
- [12] F. Iguchi, Y. Nagao, N. Sata and H. Yugami, *Solid State Ionics* **192** (2011) 97.
- [13] Y. Yamazaki, F. Blanc, Y. Okuyama, L. Buannic, J.C. L-Vega, C. P. Grey & S. M. Haile, *Nature Mater.* **12** (2013) 647.
- [14] F. Shimojo, K. Hoshino, and H. Okazaki, *J. Phys. Soc. Jpn* **67** (1998) 2008
- [15] R. Glöckner, M. S. Islam, and T. Norby, *Solid State Ionics* **122**, (1999) 145.
- [16] T. Hibino, A. Hashimoto, M. Suzuki, and M. Sano, *J. Phys. Chem. B* **105** (2001) 11399
- [17] S.B.C. Duval, P. Holtappels, U. F. Vogt, E. Pomjakushina, K. Conder, U. Stimming, and T. Graule *Solid State Ionics* **178** (2007) 1437
- [18] K. H. Ryu and S. M. Haile, *Solid State Ionics* **125** (1999) 355.
- [19] K. Katahira, Y. Kohchi, T. Shimura and H. Iwahara, *Solid State Ionics* **138** (2000) 91.
- [20] D. Pergolesi, E. Fabbri, A. D'Epifanio, E. Di Bartolomeo, A. Tebano, S. Sanna, S. Licocchia, G. Balestrino & E. Traversa : *Nature Mater.* **9** (2010) 846.
- [21] H. Yahiro, Y. Eguchi, K. Eguchi, and H. Arai, *J. Appl. Electrochem.* **18** (1988) 527.
- [22] S. W. Zha, C. Xia, G. Meng, *J. Power Sources* **115** (2003) 44.
- [23] S. Yamaguchi, Y. Tasaki, M. Kobayashi, K. Horiba, H. Kumigashira and T. Higuchi, *Jpn. J. Appl. Phys.* **54** (2015) 06FJ04.
- [24] T. Ishihara, T. Ishihara, H. Matsuda and Y. Takita, *J. Am. Chem. Soc.*, **116** (1994) 3801.
- [25] T. Ishihara, J. Tabuchi, S. Ishikawa, J-W. Yan, M. Enoki and H. Matsumoto, *Solid State Ionics* **177** (2006) 1949.
- [26] K. Horiba, H. Ohguchi, H. Kumigashira, and M. Oshima, K. Ono, N. Nakagawa and M. Lippmaa, M. Kawasaki and H. Koinuma, *Rev. Sci. Instrum.* **74** (2003) 3406.
- [27] A. Pfau, K.D. Schierbaum, *Surf. Sci.* **321** (1994) 71
- [28] M. Matsumoto, K. Soda, K. Ichikawa, S. Tanaka, Y. Taguchi, K. Jouda, O. Aita, Y. Tezuka, and S. Shin *Phys. Rev. B* **50** (1994) 11340.
- [29] D. R. Mullins, S.H Overbury and D.R Huntley *Surf. Sci.* **409** (1998) 307
- [30] T. Higuchi, T. Owaku, Y. Iida, E. Sakai, M. Kobayashi and H. Kumigashira, *Solid State Ionics* **270** (2015) 1.
- [31] T. Higuchi, T. Yamashita, T. Owaku, Y. Shimazu, H. Kato, M. Kobayashi, and H. Kumigashira, *Trans. Mater. Res. Soc. Jpn.* **40**, (2015) 429