Quantitative evaluation of biaxial compressive strain and its impact on proton conduction and diffusion in yttrium-doped barium zirconate epitaxial thin films

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Abstract
Proton-conducting oxides, including 20 mol% yttrium-doped BaZrO$_3$ (BZY20), have attracted considerable attention as electrolytes for environmentally friendly electrochemical cells, such as proton ceramic fuel cells (PCFCs) and proton-conducting solid oxide cells. These oxides exhibit fast proton conduction due to the complex physicochemical phenomena of hydration, chemical lattice expansion, proton migration, proton trapping, and local distortion. Using a proton-conducting oxide as an electrolyte film in electrochemical devices introduces an interface, which thermally and chemically generates mechanical strain. Here, we briefly review the current state of research into proton-conducting oxides in bulk samples and films used in electrochemical devices. We fabricated 18 and 500 nm thick 20 mol% BZY20 epitaxial films on (001) Nb-doped SrTiO$_3$ single-crystal substrates to form a model interface between proton-conductive and non-proton-conductive materials, using pulsed laser deposition, and quantified the mechanical strain, proton concentration, proton conductivity, and diffusivity using thin-film x-ray diffractometry, thermogravimetry, secondary ion mass spectrometry, and AC impedance spectroscopy. Compressive strains of $-2.1\%$ and $-0.85\%$ were measured for the 18 and 500 nm thick films, respectively, and these strains reduced both the proton conduction and diffusion by five and one orders of magnitude, respectively, at 375 $^\circ$C. Analysis based on a simple trapping model revealed that the decrease in proton conduction results from the slower diffusion of mobile protons with a negligible change in the proton trapping contribution. The model shows that the high ohmic resistance reported for a high-performance PCFC with a power density of 740 mW cm$^{-2}$ at 600 $^\circ$C can be solely explained by the estimated compressive strain in the cells. This study shows that minimizing biaxial compressive strain by appropriate choices of the electrolyte–electrode combination and fabrication process is important for maximizing the performance of electrochemical cells.

1. Introduction
Proton-conducting oxides [1–4] have attracted considerable attention as electrolytes for proton ceramic fuel cells (PCFCs) [5–10] and proton-conducting solid oxide cells [11–15] that can be operated at intermediate temperatures in the range of 300 $^\circ$C–600 $^\circ$C. Intermediate-temperature operation could eliminate the need for expensive platinum catalysts and heat-resistant alloys. It could also prolong the lifetime of cells due to the reduced rearrangement of constitutional elements near the triple-phase boundaries between the gas phase, electrode, and electrolyte at the reduced temperature. Reducing the cost of fuel cell systems and the longer lifetime could help accelerate their adoption. The requirements for the electrolytes are fast ionic conduction
and chemical stability under the operating conditions for the cells. The specific requirement for ionic conduction in an electrolyte in fuel cells is more than 0.01 S cm\(^{-1}\) at the operating temperature to attain an area-specific ohmic resistance lower than 0.15 \(\Omega\) cm\(^2\) for a 15 \(\mu\)m thick electrolyte film, which is a typical thickness for reliable manufacture [16]. A 20 mol% yttrium-doped barium zirconate (BZY20) [17] and 60 mol% scandium-doped barium zirconate [18] can meet the requirements for proton conductivity at 450 \(^\circ\)C and 400 \(^\circ\)C, respectively. These oxides also exhibit high chemical stability under reducing and oxidizing conditions on each side of an electrode in electrochemical cells.

Although fast and stable proton conduction is realized in acceptor-doped barium zirconates, the physical chemistry behind it is complex. Proton conduction in oxides requires a hydration reaction, namely, the incorporation of protons into the lattice, and proton diffusion. Hydration occurs in two steps: partial substitution of a host element with acceptors creates oxygen vacancies in the lattice to maintain the electroneutrality of the system [1, 19]. Upon exposure to a moist gas phase containing water molecules, the oxygen vacancies can be filled with hydroxyl groups [4, 20, 21] with an accompanying chemical expansion of the crystal lattice [1, 22–25]. The incorporated protons rotate around an oxygen and hop along the neighboring oxygens [1], overcoming proton trapping near acceptor dopants [26]. \textit{Ab initio} calculations suggest that the origin of proton trapping is strong hydrogen bonding near acceptor dopants accompanied by local lattice distortion [27–29]. The proton-dopant association (trap) energy is experimentally determined to be \(-29\) kJ mol\(^{-1}\) for yttrium dopants [26]. Proton conduction is a macroscopic result of microscopic phenomena, including hydration, chemical lattice expansion, proton migration, proton trapping, and local distortion, which correlate with each other in a complex manner.

Forming a BZY20 electrolyte film introduces an interface, which adds the further complexity of mechanical strain due to lattice mismatch in the conduction behavior of protons. Although proton conduction in acceptor-doped barium zirconate thin films has been reported by many groups [1, 30–40], only one report has investigated mechanical strain at an interface and its influence on bulk proton conduction [34], for various thicknesses of BaZr\(_{0.6}\)Ce\(_{0.4}\)O\(_3\) buffer layers between the BZY20 film (15–87 nm in thickness) and (001) MgO substrate. The measured mechanical strain ranged from +0.7% (tensile, with a 30 nm thick buffer layer) to \(-0.3\%\) (compressive, no buffer layer), where the proton conductivities were measured at 195 \(^\circ\)C–363 \(^\circ\)C in a humidified argon atmosphere. The in-plane proton conductivity at 363 \(^\circ\)C decreased slightly from 0.004 S cm\(^{-1}\) at +0.7% tensile strain to 0.002 S cm\(^{-1}\) without strain, accompanied by an increase in activation energy from 0.39 to 0.44 eV [34]. Consistent with the experimental results, molecular dynamic simulations for 1 mol% (1227 \(^\circ\)C–1727 \(^\circ\)C [41]) and 50 mol% (427 \(^\circ\)C–1027 \(^\circ\)C [34]) yttrium-doped barium zirconates showed that the proton diffusivity in the out-of-plane direction decreased under biaxial compressive strain due to the enlarged jump distances [34, 41]. The complexity of proton-conducting oxides explains the current scarcity of research into the influence of mechanical strain at the interface on the proton conductivity.

In addition to the lattice mismatch, proton-conducting oxides have two other potential sources of mechanical strain induced at elevated temperatures, namely, differences in thermal expansion coefficients and chemical expansion at the interface. While a report by Fluri \textit{et al} [34] detailed the initial investigations into this topic, mechanical strains arising from thermal expansion and chemical expansion at elevated temperatures, at which proton conduction occurs, have not been considered. The consideration of all the factors that influence interfacial mechanical strain is important for developing a fundamental understanding of proton-conducting oxides.

Insight into the mechanical strain at interfaces in proton-conducting oxides is also important for the use of such oxides in electrochemical devices. PCFCs have interfaces between the electrolyte and the anode and cathode, where ohmic resistances higher than that expected for bulk samples have been reported for many acceptor-doped barium zirconate electrolytes [6, 10, 42–52], which is problematic with respect to improving the performance of PCFCs. As summarized in figure 1 and table 1 [5–10, 42–76], almost all reports show ohmic resistances higher than 0.15 \(\Omega\) cm\(^2\) at 600 \(^\circ\)C, whereas calculations based on the proton conductivity of bulk samples for different electrolyte thicknesses [6, 7, 17, 18, 77–80] give values lower than 0.15 \(\Omega\) cm\(^2\). Suspected reasons for the higher ohmic resistances are (a) lower proton concentration due to the dissolution of nickel into the electrolyte [81–83] and (b) the resistance at the interface between the electrolyte and the cathode [6, 10]; however, these have not been verified. The lack of information on the interface and its influence on proton conductivity has hindered the development of electrochemical devices such as PCFCs.

In the present study, we quantified the mechanical strain in BZY20 epitaxial films deposited on (001) Nb-doped SrTiO\(_3\) single-crystal substrates to investigate a model interface between proton-conductive and non-proton-conductive materials, with a wide compressive strain range of \(-0.85\%\) to \(-2.1\%\). We determined the influence of misfit, thermal, and chemical strain on proton conductivity and diffusivity in the out-of-plane direction at elevated temperatures. We quantified the proton carrier concentration in the films using secondary ion mass spectrometry (SIMS) to determine the influence of compressive strain on the
Figure 1. Summary of proton conductivities in doped barium zirconate and cerate-based electrolyte films in PCFCs. The y-axis shows the ratio of proton conductivity for electrolyte thin film in anode-supported single cells (σ_{film}) to that for thick and dense pellets. The colors and symbols represent materials used as the electrolyte and anode in the PCFCs. All data are given in table 1.

proton concentration and diffusivity as well as proton trapping in the films. The results provide information on the physicochemical fundamentals of hydration, proton diffusion, and proton trapping under compressive interfacial strain, and show that this strain can explain the ohmic resistance of the high-performance PCFCs reported by Bae et al [66].

1.1. Strain at an interface between proton-conductive and non-proton-conductive materials

Interfaces exist where proton-conductive and non-proton-conductive materials meet in PCFCs, i.e. electrolyte/anode and electrolyte/cathode interfaces, which cause lattice misfit, thermal, and chemical strains. Lattice misfit strain (ε_{in.misfit}) is introduced at the heterointerface due to the difference in atomic spacing between the substrate and film materials. Thermal strain (ε_{in.thermal}) appears when the film and substrate materials possess different linear thermal expansion coefficients. Chemical strain (ε_{in.hyd}) is induced by hydration, a characteristic reaction of proton-conducting oxides, which causes expansion and shrinkage of the crystal lattice. The in-plane strain, ε_{in}, at an elevated temperature at which protons conduct in the oxide may be written as the sum of the three components,

\[ ε_{in}(T; Pt_{12O}) = ε_{in.misfit} + ε_{in.thermal} - ε_{in.hyd} \]

\[ = \left( \sum_i \sum_j f_{ij} \left( d_j - d_i \right) + A \right) + (α_{film} - α_{sub}) \cdot (T - T_0) - bC^β_{HI}. \]  

(1)

Here, \( i \in \{h k l\} \) and \( j \in \{h' k' l'\} \) are the lattice planes of the film and substrate, respectively, that form the interface, \( f_{ij} \) is the fraction of the junction at the interface of the \( i-j \) plane combination, and \( d_i \) and \( d_j \) are the atomic spacings on the \( i \) and \( j \) planes at the thermal-strain-free temperature, \( T_0 \). \( A \) in the misfit strain term is a constant related to the relaxation of the lattice misfit caused by the formation of dislocations and grain boundaries, surface roughness, and the distance from the constrained interface to the relaxed surface. \( α_{film} \) and \( α_{sub} \) are the thermal expansion coefficients for the film and substrate, respectively. \( ε_{hyd} \) is defined as \( (a_{hyd} - a_{dry})/a_{dry} \), where \( a_{dry} \) and \( a_{hyd} \) are the lattice constants under dehydrated and hydrated states, respectively, at a temperature \( T \), and is a function of the proton concentration, \( C_{HI} \), with coefficients \( b \) and \( β \) that express the degree of chemical expansion. When the crystal orientations at the interface between the film and substrate are completely random, i.e. the film is polycrystalline, the macroscopic strain caused by lattice mismatch is averaged to zero. Compressive strain, the subject of this study, is expressed by a negative value of \( ε_{in} \) in equation (1). \( ε_{in.misfit} \) depends on the combination of film–substrate materials and crystal orientations. \( ε_{in.thermal} \) depends on the fabrication process and conditions. \( ε_{in.hyd} \) is a function of temperature, water partial pressure, and the chemical composition of the materials.

2. Results and discussion

BZY20 thin films with 18 and 500 nm thicknesses were prepared on Nb-doped SrTiO$_3$ (001) single-crystal substrates using pulsed laser deposition (PLD). The thicknesses of the two films were determined from the interference fringes of the (002) diffraction peaks (figures 2(a) and S2) and cross-sectional scanning electron
Table 1. Summary of proton conduction in electrolyte film and power densities for PCFCs. Electrolyte materials are doped barium zirconates or cerates. \( R_{\text{ohm}} \), \( R_{\text{bulk}} \), \( R_{\text{total}} \), \( \sigma_{\text{film}} \), \( \sigma_{\text{bulk}} \) and PPD are the ohmic area-specific resistance, expected ohmic area-specific resistance from bulk conductivity and film thickness, total resistance, the total conductivity of electrolyte thin film in single cells, the total conductivity of bulk pellet, and peak power density at 600 °C, respectively.

| Electrolyte materials       | Thickness (µm) | \( R_{\text{ohm}} \) (Ω cm²) | \( R_{\text{bulk}} \) (Ω cm²) | \( R_{\text{ohm}} / R_{\text{total}} \) | \( \sigma_{\text{film}} / \sigma_{\text{bulk}} \) | PPD (mW cm⁻²) | Coating method | Sintering temperature (°C) | Year | References (PCFC) | References (σbulk) |
|-----------------------------|----------------|-----------------------------|-----------------------------|--------------------------------|--------------------------------|----------------|----------------|-----------------------------|-----|-------------------|-------------------|
| \( \text{BaZr}_0.0\text{Ce}_0.9\text{Y}_0.2\text{O}_{3-δ} \) | 35             | 1.24                        | 0.63                        | 0.87                          | 0.51                          | 160            | Co-pressing | 1450                        | 2009 | [42]              | [91]              |
| \( \text{BaZr}_0.0\text{Y}_0.2\text{O}_{3-δ} \) | 20             | 1.40                        | 0.09                        | 0.52                          | 0.06                          | 70             | Co-pressing | 1400                        | 2010 | [43]              | [17]              |
| \( \text{BaZr}_{0.7}\text{Y}_{0.3}\text{Yb}_0.1\text{O}_{3-δ} \) | ~15            | 0.55                        | 0.05                        | 0.34                          | 0.10                          | 200            | Co-pressing | 1400                        | 2010 | [44]              | [78]              |
| \( \text{BaZr}_{0.7}\text{Y}_{0.2}\text{O}_{3-δ} \) | ~30            | 0.50                        | 0.16                        | 0.65                          | 0.33                          | 393            | Co-pressing | 1450                        | 2010 | [53]              | [79]              |
| \( \text{BaZr}_0.0\text{Y}_0.1\text{O}_{3-δ} \) | 20             | 0.88                        | 0.09                        | 0.77                          | 0.10                          | 169            | Co-pressing | 1450                        | 2011 | [55]              | [17]              |
| \( \text{BaZr}_{0.7}\text{Y}_{0.1}\text{Yb}_0.1\text{O}_{3-δ} \) | ~15            | 0.36                        | 0.05                        | 0.40                          | 0.15                          | 289            | Co-pressing | 1350                        | 2011 | [56]              | [78]              |
| \( \text{BaZr}_{0.7}\text{Y}_{0.2}\text{O}_{3-δ} \) | 20             | 0.38                        | 0.11                        | 0.52                          | 0.28                          | 350            | Slurry coating | 1400                        | 2011 | [45]              | [79]              |
| \( \text{BaZr}_{0.7}\text{Y}_{0.2}\text{O}_{3-δ} \) | 17.6           | 0.38                        | 0.10                        | 0.74                          | 0.25                          | 747            | Tape casting | 1300                        | 2011 | [46]              | [79]              |
| \( \text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-δ} \) | ~20            | 0.91                        | 0.35                        | 0.74                          | 0.39                          | 194            | Co-pressing | 1400                        | 2012 | [47]              | [91]              |
| \( \text{BaZr}_{0.7}\text{Ce}_0.3\text{Zr}_0.1\text{O}_{3-δ} \) | 12             | 0.46                        | 0.78                        | 0.53                          | 1.69                          | 214            | Slurry coating | 1400                        | 2013 | [57]              | [57]              |
| \( \text{BaZr}_{0.7}\text{Ce}_0.3\text{Zr}_0.1\text{O}_{3-δ} \) | ~60            | 1.60                        | 0.21                        | 0.71                          | 0.13                          | 225            | Slurry coating | 1400                        | 2013 | [58]              | [78]              |
| \( \text{BaZr}_{0.7}\text{Ce}_0.3\text{Zr}_0.1\text{O}_{3-δ} \) | ~10            | 0.20                        | 0.04                        | 0.48                          | 0.18                          | 430            | Slurry coating | 1400                        | 2013 | [59]              | [78]              |
| \( \text{BaZr}_{0.7}\text{Ce}_0.3\text{Zr}_0.1\text{O}_{3-δ} \) | ~20            | 0.45                        | 0.07                        | 0.58                          | 0.14                          | 320            | Co-pressing | 1350                        | 2013 | [48]              | [79]              |
| \( \text{BaZr}_{0.7}\text{Ce}_0.3\text{Zr}_0.1\text{O}_{3-δ} \) | ~15            | 0.73                        | 0.05                        | 0.49                          | 0.07                          | 193            | Co-pressing | 1450                        | 2013 | [60]              | [78]              |
| \( \text{BaZr}_{0.5}\text{Yb}_{0.5}\text{ZrO}_{3-δ} \) | 17.5           | 0.58                        | 0.73                        | 0.54                          | 1.26                          | 221            | Slurry coating | 1400                        | 2014 | [61]              | [61]              |
| \( \text{BaZr}_{0.5}\text{Yb}_{0.5}\text{ZrO}_{3-δ} \) | ~27            | 0.44                        | 0.31                        | 0.69                          | 0.72                          | 396            | Co-pressing | 1400                        | 2014 | [62]              | [62]              |
| \( \text{BaZr}_{0.7}\text{Ce}_0.3\text{Yb}_0.1\text{O}_{3-δ} \) | 14.7           | 0.13                        | 0.05                        | 0.31                          | 0.41                          | 690            | Slurry coating | 1400                        | 2014 | [63]              | [78]              |
| \( \text{BaZr}_{0.7}\text{Ce}_0.3\text{Yb}_0.1\text{O}_{3-δ} \) | 24             | 0.40                        | 0.76                        | 0.88                          | 0.19                          | 600            | Slurry coating | 1400                        | 2015 | [5]                | [17]              |
| \( \text{BaZr}_0.0\text{Y}_0.1\text{O}_{3-δ} \) | 23             | 0.31                        | 0.10                        | 0.84                          | 0.32                          | 460            | Slurry coating | 1400–1450                    | 2015 | [5]                | [17]              |
| \( \text{BaZr}_0.0\text{Y}_0.1\text{O}_{3-δ} \) | ~5             | 0.77                        | 0.09                        | 0.30                          | 0.12                          | 102            | Slurry coating | 1450                        | 2015 | [49]              | [91]              |
| \( \text{BaZr}_{0.7}\text{Ce}_0.3\text{Yb}_0.1\text{O}_{3-δ} \) | 4              | 0.36                        | 0.01                        | 0.57                          | 0.04                          | 418            | Slurry coating | 1300                        | 2016 | [64]              | [78]              |
| \( \text{BaZr}_{0.7}\text{Ce}_0.3\text{Yb}_0.1\text{O}_{3-δ} \) | 25             | 0.32                        | 0.14                        | 0.43                          | 0.42                          | 362            | Co-pressing | 1400                        | 2017 | [67]              | [79]              |

(Continued.)
| Electrolyte materials | Thickness (µm) | $R_{\text{ohm}}$ (Ω cm$^2$) | $R_{\text{bulk}}$ (Ω cm$^2$) | $R_{\text{ohm}}/R_{\text{bulk}}$ | $\sigma_{\text{film}}/\sigma_{\text{bulk}}$ | PPD (mW cm$^{-2}$) | Coating method | Sintering temperature (°C) | Year | References (PCFC) | References (σ$_{\text{bulk}}$) |
|-----------------------|---------------|-----------------|-----------------|------------------|------------------|------------------|----------------|----------------------|------|----------------|---------------------|
| BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$Yb$_{0.1-\delta}$ | 11 | 0.38 | 0.04 | 0.41 | 0.10 | 258 | Slurry coating | 1350 | 2017 | [68] | [78] |
| BaCe$_{0.5}$Zr$_{0.5}$Y$_{0.15}$O$_{1-\delta}$ | 5 | 0.09 | 0.04 | 0.49 | 0.45 | 1302 | Slurry coating | 1350 | 2018 | [7] | [7] |
| BaCe$_{0.5}$Zr$_{0.5}$Y$_{0.15}$O$_{1-\delta}$ | ~15 | 0.16 | 0.02 | 0.55 | 0.15 | 1098 | Slurry coating | 1500–1550 | 2018 | [6] | [6] |
| BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{1-\delta}$ | ~12 | 0.22 | 0.06 | 0.70 | 0.30 | 841 | Co-pressing | 1350 | 2019 | [70] | [79] |
| BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{1-\delta}$ | ~18 | 0.26 | 0.10 | 0.60 | 0.37 | 643 | Co-pressing | 1320 | 2019 | [71] | [79] |
| BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{1-\delta}$ | ~10 | 0.76 | 0.03 | 0.72 | 0.05 | 243 | Slurry coating | 1350 | 2019 | [72] | [78] |
| BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{1-\delta}$ | ~30 | 0.89 | 0.06 | 0.37 | 0.07 | 74 | Tape casting | 1450 | 2020 | [73] | [80] |
| BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{1-\delta}$ | ~10 | 0.11 | 0.03 | 0.38 | 0.31 | 1060 | Tape casting | 1400 | 2021 | [74] | [78] |
| BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{1-\delta}$ | 10 | 0.38 | 0.08 | 0.60 | 0.21 | 417 | Co-pressing | 1350 | 2021 | [75] | [79] |
| BaCe$_{0.4}$Y$_{0.1}$Yb$_{0.1}$O$_{1-\delta}$ | 7 | 0.07 | 0.01 | 0.23 | 0.16 | 1474 | Slurry coating | 1500 | 2021 | [9] | [6] |
| BaCe$_{0.4}$Y$_{0.1}$Yb$_{0.1}$O$_{1-\delta}$ | 15 | 0.17 | 0.05 | 0.72 | 0.31 | 1160 | Slurry coating | 1450 | 2021 | [8] | [78] |
| BaCe$_{0.4}$Y$_{0.1}$Yb$_{0.1}$O$_{1-\delta}$ | ~22 | 0.071 | 0.069 | 0.63 | 0.97 | 1184 | Tape casting | 1400 | 2022 | [10] | [10] |
| BaCe$_{0.4}$Y$_{0.1}$O$_{1-\delta}$ | 0.7 | 0.08 | 0.003 | 0.42 | 0.04 | 1400 | PLD | n/a | 2005 | [50] | [77] |
| BaZr$_{0.1}$Y$_{0.2}$O$_{1-\delta}$ | 4 | 1.90 | 0.02 | 0.77 | 0.009 | 110 | PLD | 800 | 2010 | [54] | [17] |
| BaCe$_{0.5}$Zr$_{0.5}$Y$_{0.15}$O$_{1-\delta}$ | 1.5 | 0.15 | 0.02 | 0.38 | 0.12 | 508 | PLD | 1200 (post annealing) | 2016 | [51] | [7] |
| BaCe$_{0.4}$Y$_{0.1}$O$_{1-\delta}$ | 1 | 0.26 | 0.004 | 0.67 | 0.02 | 1050 | RF sputtering | 700 (post annealing) | 2016 | [52] | [77] |
| BaZr$_{0.1}$Y$_{0.2}$O$_{1-\delta}$ | 0.075 | 0.12 (400 °C) | 0.001 | 0.04 (400 °C) | 0.01 (400 °C) | 274 (400 °C) | PLD | 800 | 2016 | [65] | [17] |
| BaZr$_{0.1}$Y$_{0.2}$O$_{1-\delta}$ | 2.5 | 0.09 | 0.01 | 0.36 | 0.12 | 740 | PLD | 1200 (post annealing) | 2017 | [66] | [17] |
| BaCe$_{0.5}$Zr$_{0.5}$Y$_{0.15}$O$_{1-\delta}$ | 1 | 0.06 | 0.01 | 0.22 | 0.19 | 1100 | PLD | 1200 (post annealing) | 2018 | [69] | [7] |
| BaZr$_{0.1}$Sc$_{0.3}$O$_{1-\delta}$ | 1 | 0.08 (500 °C) | 0.008 | 0.30 (500 °C) | 0.10 (500 °C) | 931 (500 °C) | PLD | 700 | 2021 | [76] | [18]$^b$ |

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$^a$ The total conductivity is assumed to be the same as that for BaZr$_{0.1}$Y$_{0.2}$O$_{1-\delta}$.

$^b$ Data for BaZr$_{0.4}$Sc$_{0.6}$O$_{1-\delta}$ used as reference.

n/a: not available.
microscopy (SEM) images (figure S3). The two films are much thicker than 5 nm, the thickness at which dislocations are intensively formed at the interface with the substrate [36, 84]. By performing electrochemical measurements in the out-of-plane direction, the influence of fast ionic conduction along the dislocations on the total conductivity was minimized.

The two films were found to be epitaxially grown on the (001) single-crystal substrates. The $2\theta - \theta$ profiles determined using x-ray diffractometry show peaks that correspond to (00l) planes for both the BZY20 films and the Nb-SrTiO$_3$ substrates, as shown in figure 2(a). This shows that the BZY20 films are oriented perpendicular to the (001) substrates. The pole figures for the (110) plane exhibit poles with four-fold symmetry at $\Psi = 45^\circ$ in figures 2(b) and (c), where the positions are equivalent to those for the (001) Nb-SrTiO$_3$ single-crystal substrate in figure 2(d). These results indicate cube-on-cube epitaxy on the substrate.

A quantitative analysis of the in-plane lattice constant revealed that biaxial compressive strain was induced in the as-prepared BZY20 thin films. The asymmetric 103 reflection was used for reciprocal space mapping (RSM) to gain in-plane and out-of-plane information for the films, as shown in figures 3(a) and (b). Here, $q_x$ and $q_z$ show the reciprocal spaces horizontal and vertical, respectively, to the direction of the x-rays at an incidence angle of $\omega = 0$, defined as $q_{x,z} = 1/d_{hkl}$ where $d_{hkl}$ is the (hkl) lattice spacing. The large spots at the bottom of figures 3(a) and (b) represent diffraction from the (103) planes in the BZY20 films. The in-plane and out-of-plane lattice parameters, $a_{in}$ and $a_{out}$, respectively, obtained from $q_x$ and $q_z$ using the (103) spots with correlations $q_x = 1/d_{100} = 1/a_{in}$ and $q_z = 1/d_{003} = 3/a_{out}$ are plotted against the sample thickness and compared with that of the bulk BZY20 sample in figure 3(c). The in-plane lattice constant ($a_{in}$) decreases with the decreasing sample thickness, showing that the in-plane compression is stronger close to the substrate. The biaxial strain induced by the in-plane compression is $-2.1\%$ and $-0.85\%$ for the 18 and 500 nm thick films, respectively. These results suggest that the compressive strain in the films is mechanically introduced by the substrate.

The out-of-plane lattice constant ($a_{out}$) indicates that the mechanical stress in the BZY20 films is almost fully relaxed, consistent with an elastic body with respect to Poisson’s ratio. The values of $a_{out}$ increase slightly with the decreasing film thickness in figure 3(c), consistent with previous reports on yttrium-doped barium zirconate films [31, 36]. The blue line in figure 3(c) shows the degree of expansion in the out-of-plane
Figure 3. Lattice distortion in BZY20 thin films. (a) and (b) RSM for 103 reflection for samples with different thicknesses. (c) Estimated in-plane and out-of-plane lattice constants. (d) Estimated lattice volume as a function of film thickness. The lattice constants for the bulk sample and Nb-SrTiO$_3$ (Nb-STO) substrate are shown as black and blue dashed lines, respectively.

Table 2. Chemical composition and material properties for BZY20 bulk and film samples. The relative dielectric constant ($\varepsilon_\gamma$) and apparent activation energy ($Q_{\text{app}}$) were determined from the bulk proton conductivity.

| Thickness | Composition (f.u.$^{-1}$) | $\varepsilon_\gamma$ (unitless) | $Q_{\text{app}}$ (kJ mol$^{-1}$) | Temperature range for $Q$ ($^\circ$C) |
|-----------|---------------------------|-------------------------------|---------------------------------|-----------------------------------|
| 18 nm     | Ba: $0.96 \pm 0.19$ Zr: $0.73 \pm 0.15$ Y: $0.20 \pm 0.04$ H: $0.091 \pm 0.018$ | 118 $\pm$ 16 | 111 $\pm$ 2 | 168–399 |
| 500 nm    | Ba: $0.99 \pm 0.03$ Zr: $0.71 \pm 0.15$ Y: $0.20 \pm 0.04$ H: $0.12 \pm 0.03$ | 28 $\pm$ 5 | 54 $\pm$ 1 | 29–163 |
| 0.5 mm    | Ba: $1.0$ Zr: $0.75$ Y: $0.21$ O: $3-\delta$ | 55 $\pm$ 1 | 50 $\pm$ 1 | 30–196 |

*The chemical compositions in parentheses are the results from EDS. The chemical compositions without parenthesis were determined using SIMS in the depth regions of 5–15 nm and 100–400 nm for the 18 and 500 nm thick films, respectively. The BZY20 bulk sample was used as a reference for converting the SIMS signals to chemical compositions.

direction for an elastic body with a Poisson’s ratio of $\nu = 0.237$ for non-doped barium zirconate [85]. The blue line matches well with the experimentally determined lattice parameters in the out-of-plane direction, which confirms that the two films are elastic bodies. We therefore do not need to consider out-of-plane stress because it is fully relaxed. As expected for a Poisson’s ratio smaller than 0.5, the apparent lattice volume, $V = a_{\text{in}} a_{\text{out}}$, is smaller for thinner samples, as shown in figure 3(d).

A SIMS analysis showed that the chemical compositions of the films are very close to BZY20. Using energy-dispersive x-ray spectrometry (EDS), the chemical composition of the PLD target sample was determined to be Ba$_{1.0}$Zr$_{0.75}$Y$_{0.21}$O$_{3-\delta}$ (EDS, table 2). This was used as a reference for determining the chemical compositions of the films using SIMS. The chemical compositions determined using SIMS near the surface and heterointerface are highly uncertain due to differences in ionization yields, and these regions, highlighted in gray in figures 4(a) and (b), were excluded from the chemical analyses. The average chemical compositions thus determined in the thinner and thicker films were found to be Ba$_{0.96 \pm 0.19}$Zr$_{0.73 \pm 0.15}$ Y$_{0.20 \pm 0.04}$O$_{3-\delta}$ and Ba$_{0.99 \pm 0.03}$Zr$_{0.71 \pm 0.15}$ Y$_{0.20 \pm 0.03}$O$_{3-\delta}$, respectively, both of which are almost equivalent to that of the bulk sample, Ba$_{1.0}$Zr$_{0.75}$Y$_{0.21}$O$_{3-\delta}$.

The Ba, Zr, and Y cations in the 500 nm thick film were uniformly distributed in the depth direction. As shown in figure 4(b), the depth profiles of the cations were almost constant. Sharp drops in the signals for
Figure 4. Chemical compositions of BZY20 thin films determined by SIMS. (a) A 18 and (b) 500 nm thick films. (c) Proton concentration ($C_H$) in films and bulk sample. The left and right axes in (a) and (b) correspond to the chemical compositions of the films and the secondary ion mass signals for elements observed from the Nb-doped SrTiO$_3$ substrate, respectively. The gray vertical bands in (a) and (b) represent uncertain regions in the quantification based on ionization yields at the surface and heterointerface differences from the bulk domain. The error bars in (c) show the range of reproducibility for the two measurements. The raw thermogravimetry data for the bulk sample are given in figure S6.

Strontium and titanium near the interface suggest that the elements in the substrate did not significantly diffuse into the BZY20 layer. Although it was difficult to determine the cation concentration for the 18 nm thick film (figure 4(a)) due to the large uncertainties near the surfaces and interfaces, the homogeneity for the 500 nm thick film implies that the 18 nm thick film is likely also homogeneous.

The proton concentrations for the thick and thin films determined by SIMS are equivalent to that for bulk BZY20. The films were hydrated at 400 °C for 24 h under a flow of humidified air at $p_{H_2O} \sim 0.02$ atm. Thermogravimetry results for a SIMS pellet standard are given in figure S4 and those for a powder sample are given in figure S5. The proton concentrations determined by averaging the SIMS signals (red lines) for the 18 and 500 nm thick films in figures 4(a) and (b), excluding the near-surface and interface regions, are $0.091 \pm 0.018$ and $0.12 \pm 0.03$ per formula unit, respectively, as shown in figure 4(c). The thinner film had a slightly smaller concentration than the bulk BZY20, by $\sim 40\%$ at most, whereas the thicker film had a concentration that was equivalent to that for the bulk BZY20.

The proton conductivity for the hydrated BZY20 films was significantly reduced compared to that for the bulk sample, more significantly for the thinner film, which exhibited more compressive strain. At about 375 °C, for example, the proton conductivities for the 500 and 18 nm thick films were, respectively, about one and five orders of magnitude smaller than those for the bulk, as shown in figure 5(a), with representative Nyquist plots and fits given in figure S6. The conductivity data for the BZY20 bulk sample are consistent with the literature [17]. A plot against biaxial strain shows a gradual decrease in the proton conductivity by five orders of magnitude (figure 5(c)), and a gradual increase in apparent activation energy for proton conduction, $Q_{app}$, from 50 $\pm$ 1 to 111 $\pm$ 2 kJ mol$^{-1}$ (figure 5(d)) with the increasing compressive strain to $-2.1\%$. The influence of biaxial strain on the activation energy for proton conduction in BZY20 films has...
Figure 5. Proton conductivities in BZY20 thin films. (a) Arrhenius plots of bulk proton conductivities, (b) H/D isotope effects, (c) influence of misfit strain on proton conductivities at 375 °C, (d) influence of misfit strain on apparent activation energies for proton conductivities. The red line in (a) shows data from [17]. The solid lines in (b) are guides for the eye, while the dashed line in (b) is the theoretical value. The negative values on the x-axis in (c) and (d) represent compressive strain. Data from [34] are shown in (c) and (d). The solid line in (d) is a result of fitting to a parabolic function, suggested by [34], using all the data including [34].

been previously reported [34], and our data show a smooth extension from the literature data with a parabolic relation, as has been suggested [34] (solid line in figure 5(d)), demonstrating good agreement.

The isotope effect between H and D supports proton conduction in BZY20 films. An ideal harmonic oscillator affecting the vibrational frequency [86] would, in theory, give $\sigma_H/\sigma_D = 1.41$. Such isotope effects are apparent for all bulk and film samples (figures 5(a) and (b)), although the values of $\sigma_H/\sigma_D$ increase from 1.4 to 4 with the decreasing temperature. The reason for this is related to the difference in the ground-state energy for H and D, which increases at lower temperatures [86]. The relative dielectric constants for the 18 and 500 nm thick films of 118 ± 16 and 28 ± 5, respectively, also agree with the value of 55 ± 1 for the bulk sample, and the literature values [17]. In summary, all the results support protons being the major conduction carriers in the BZY20 films.

A reduction in proton diffusion significantly reduces the proton conductivity in BZY20 films. As expected from the close equivalence of the proton concentration (40% difference at most), the apparent proton diffusivity, $D_{H,app}$, obtained by inputting the proton concentration for bulk BZY20 (black line in figure 4(c)) into the Nernst–Einstein relationship is one and five orders of magnitude smaller for the 500 and 18 nm thick films, respectively, than those for the bulk samples in this work and the literature [26] for the whole temperature range in figure 6(a), noting that the results for bulk BZY20 in this work and the literature are consistent. The apparent proton diffusivity for the 500 nm thick film shows a downward curvature, a
Figure 6. Influence of in-plane strain, \( \varepsilon_{\text{in}} \), on proton diffusion behavior in BZY20 thin films. (a) Arrhenius plots of apparent proton diffusivities, \( D_{\text{H.app}} \), (b) parameters for mobile proton diffusion and proton trapping, and (c) mobile proton diffusivity and mobile proton concentration at 375 \( ^\circ \)C. The green dashed line in (a) shows data from [26]. The negative values on the x-axes of \( \varepsilon_{\text{in}} \) in (b) and (c) represent compressive strains. The solid lines in (a) and (b) show the results of fitting the obtained data using equation (4). The temperature dependence of \( \varepsilon_{\text{in.hyd}} \) given in figure S7 for the 500 nm thick film is considered for solid lines in (b) and (c), which increases the compressive strain from \(-0.85\%\) into green area (details and resulting parameters are given in supporting information and table S1, respectively). The yellow and orange regions in (c) represent the contributions of \( D_0 \) and \( E_a \), respectively, to the retarded mobile proton diffusivity (\( D_{\text{H.m.}} \)).

feature of proton trapping [26], and is one order of magnitude smaller than that for the bulk sample, whereas that for the 18 nm thick film shows a linear decrease by up to five orders of magnitude.

To investigate slow proton diffusion in the films, a simple proton trapping model is introduced, similar to that for hydrogen trapping in metals [87], where mobile and trapped protons in a solid are locally in equilibrium,

\[
\text{OH}^\bullet_{\text{O.m}} \overset{K_{\text{trap}}}{\leftrightarrow} \text{OH}^\bullet_{\text{O.trap}}.
\]  

(2)

Here, the left and right sides of the equation represent mobile and trapped protons, respectively, and \( K_{\text{trap}} \) is the equilibrium constant for proton trapping. The phenomenological equilibrium model is used without specifying the position of protons because of the lack of information on how the compressive strain changes the position of protons associated with the dopant under the biaxial compressive strain. The concentration of mobile protons is expressed as

\[
[\text{OH}^\bullet_{\text{O.m}}] = \frac{[\text{OH}^\bullet_{\text{O.total}}]}{1 + K_{\text{trap}}} = \frac{[\text{OH}^\bullet_{\text{O.total}}]}{1 + B \exp(-E_{\text{trap}}/RT)}
\]  

(3)

where the brackets denote the concentration of the respective species, and \( R, T, E_{\text{trap}} \), and \( B \) are the universal gas constant, absolute temperature, proton trapping energy, and pre-exponential factor for proton trapping, respectively (see the full description in the supporting information). The apparent proton diffusivity, \( D_{\text{H.app}} \), for macroscopic proton transport is the product of the diffusivity of mobile protons, \( D_{\text{H.m.}} \), and the fraction of mobile protons relative to the total number of protons,

\[
D_{\text{H.app}} = D_{\text{H.m.}} \frac{[\text{OH}^\bullet_{\text{O.m}}]}{[\text{OH}^\bullet_{\text{O.total}}]},
\]

\[
= D_0 \exp \left(-\frac{E_a}{RT} \right) \frac{[\text{OH}^\bullet_{\text{O.m}}]}{[\text{OH}^\bullet_{\text{O.total}}]}
\]  

(4)

where \( D_0 \) is a pre-exponential factor and \( E_a \) is the migration energy for the diffusion of mobile protons.

The model independently returns the parameters that describe the impact of mobile proton diffusion and proton trapping on proton diffusivity. The parameters obtained without considering \( \varepsilon_{\text{in.hyd}} \) are listed in...
Table 3. Parameters for proton diffusivity in proton trapping model. These values are obtained for a 500 nm thick film and bulk samples with constant $\varepsilon_{in}$. Those dependent on $\varepsilon_{in}$ are listed in table S1.

| Thickness | $D_0$ ($10^{-5}$ cm$^2$ s$^{-1}$) | $E_a$ (kJ mol$^{-1}$) | $B$ (unitless) | $E_{trap}$ (kJ mol$^{-1}$) |
|-----------|---------------------------------|----------------------|----------------|------------------------|
| 500 nm    | 2.6 ± 0.8                       | 28 ± 1               | (1.8 ± 0.9) × 10$^{-3}$ | −28 ± 2              |
| 0.5 mm    | 10 ± 3                          | 23 ± 1               | (5.6 ± 2.1) × 10$^{-4}$ | −30 ± 1              |

Table 3 and plotted as circles against the in-plane strain in figure 6(b). The compressive strain decreases and increases $D_0$ and $E_a$, respectively, the parameters for the diffusivity of mobile protons. Both contribute almost equally to a significant decrease in $D_{Hlm}$ of more than one order of magnitude at $\varepsilon_{in} = −1.12\%$ compared with $\varepsilon_{in} = 0$ at 375 °C in figure 6(c). The increase in $E_a$ observed under biaxial compression is in good agreement with the results of molecular dynamics simulations [41]. In contrast, $E_{trap}$ and $B$, the parameters for proton trapping (figure 6(b)) and $C_{Hlm}$ (figure 6(c)) have a negligible influence from a compressive strain of −1% considering uncertainties in the experiments and fitting. Since $E_{trap}$ quantitatively correlates with the hydration enthalpy, a parameter describing the proton concentration, $C_{Hlm}$ [88], it is reasonable that both $C_{Hlm}$ in figure 4(c) and $E_{trap}$ in figure 4(b) have an almost negligible influence from compressive strain. An influence due to compressive strain on mobile proton diffusion and proton trapping is observed over the whole temperature range examined in figure S8. All the results consistently support the idea that biaxial compressive strain mainly suppresses the diffusivity of mobile protons in the film.

The larger activation energy for mobile proton diffusion, $E_a$, and the lower $D_0$ under a −1% compressive strain are related to the shrinkage of the perovskite structure and anisotropic deformation of BO$_6$ octahedra. The activation energy for mobile proton diffusion represents the energy needed to overcome the saddle point from the initial state [89]. The smaller lattice volume in the BYZ20 thin film in figure 3(d) requires more energy than for the bulk sample. Anisotropically deformed BO$_6$ octahedra under compressive strain break the even energy landscape around oxygen sites that are important for fast proton diffusion with lower activation energy in a cubic structure, leading to a lower local crystal symmetry with a larger activation energy. A greater variety of proton sites under compressive strain causes higher entropy in the initial and final states before and after proton diffusion, respectively, which reduces the change in the configurational entropy between the initial and transition states. Similarly, the change in vibrational entropy, related to the vibrational frequencies of protons affected by the local environment in the solid, is lowered for the resulting lower $D_0$. Mobile proton diffusion behavior for larger $E_a$ and lower $D_0$ in a biaxially compressed film can be consistently understood in terms of the physicochemical fundamentals of diffusion in solids.

The negligible influence of compressive strain on proton trapping shows that the hydrogen bond angle around YO$_6$ octahedra, considered to be trapping sites [27, 29], is not altered by the strain. A compressive strain of −1% slightly alters the shape of YO$_6$ octahedra, but trapped protons bonded to the apex of YO$_6$ octahedra have enough freedom to maintain the initial hydrogen bond angle. This could be the reason why compressive strain does not have a large influence on proton trapping.

The mechanical strain accumulated in the electrolyte of a PCFC can be estimated using equation (1). A PCFC with a high power density of 740 mW cm$^{-2}$ at 600 °C, composed of a BaZr$_{0.75}$Y$_{0.15}$O$_{3-δ}$ and nickel cermet anode, a 2.5 μm thick BaZr$_{0.25}$Y$_{0.15}$O$_{3-δ}$ polycrystalline electrolyte, and a La$_{0.6}$Sr$_{0.4}$CoO$_{3-δ}$ cathode [66], was selected for the evaluation. The parameters $\varepsilon_{in,mistfit}$, $\alpha_{BY20}$, $\alpha_{NiO}$, $T_0$, and $\varepsilon_{in,hyd}$ for the PCFC were 0 (polycrystalline), 1200 °C (maximum temperature that the cell experienced in the fabrication process), 9.05 × 10$^{-6}$ K$^{-1}$ (median of reported values [1, 22–25]), 13.08 × 10$^{-6}$ K$^{-1}$ (median of reported values of 11.23 − 14.93 × 10$^{-6}$ K$^{-1}$ [90]), and 8.47 × 10$^{-3}$ × $C_{Hlm}$ [25], respectively. It is noted that $\alpha$ for nickel, 13 × 10$^{-6}$ K$^{-1}$ [24], is equivalent to that for NiO, so there will be a negligible difference between nickel metal and its oxide in the evaluation of strain. By inserting these material parameters for the high-performance PCFC into equation (1), we obtain the temperature dependence of the in-plane thermal and chemical strain shown in figure 7(a). For the estimate of $\varepsilon_{in,hyd}$, it is assumed that the proton concentration in the electrolyte in the fuel cell, $C_{Hlm}$, is identical to that for the bulk sample (black line in figure 4(c)). Lowering the temperature increases both the thermal and chemical strain in the electrolyte of PCFCs to −0.5% and −0.3%, respectively, thus −0.8% in total, at room temperature (figure 7(a)).

The estimate of the mechanical strain combined with the quantitative model for proton conduction under compressive strain constructed in this work reveal why proton conductivity in the electrolyte of actual fuel cells is much lower than that for the constituent materials. The estimated mechanical strain gives values for the four diffusion parameters $D_0$, $E_a$, $B$, and $E_{trap}$ in the model, which simulates the proton conductivity in the electrolyte of a high-performance PCFC (red line in figure 7(b)). The simulation quantitatively agrees with the values (red circles) reported for a high-performance PCFC [66] and the degree of suppression of the proton conductivity, $\sigma_{film}/\sigma_{bulk}$, by a factor of 0.22–0.36, in the literature (table 1). Although the contact
resistance [6, 10] and/or interdiffusion of nickel with electrolytes [81, 82] have been considered, the biaxial compressive strain would be a significant contributor to the enlarged ohmic resistance in the reported PCFCs. Our analysis emphasizes that minimizing the biaxial compressive strain in PCFCs by appropriate choices of the electrolyte–electrode combinations and the fabrication process are critical for maximizing the potential of proton-conducting oxides for use in environmentally friendly electrochemical devices.

3. Conclusions

Biaxial in-plane strain, proton concentration, proton conductivities, and proton/deuteron isotope effects in high-quality epitaxial BZY20 films, 18 and 500 nm in thickness, grown on Nb-doped SrTiO$_3$ single crystal substrates by PLD, were quantitatively evaluated in the temperature range between 28 $^\circ$C and 604 $^\circ$C (400 $^\circ$C for proton concentration) and compared with those for a compositionally equivalent bulk sample. Thin-film X-ray diffractometry, SIMS, SEM-EDS, thermogravimetry, and AC impedance spectroscopy were used. Both films showed epitaxial growth on Nb-doped SrTiO$_3$ (001) single-crystal substrates. The chemical compositions of the films were almost equivalent to that of the bulk sample. The biaxial compressive misfit strains introduced into the 500 and 18 nm thick films were $-0.85\%$ and $-2.1\%$, respectively. The proton concentration for the 500 nm thick film hydrated at 400 $^\circ$C for 24 h at $p_{H_2O}$ $\sim 0.02$ atm was almost equivalent to that for the bulk sample, while that for the 18 nm thick film was slightly smaller, by $\sim 40\%$ at most. The compressive misfit strains of $-0.85\%$ and $-2.1\%$ in the 500 and 18 nm thick films inhibit both proton conduction and proton diffusion by one and five orders of magnitude, respectively, at 375 $^\circ$C.

An analysis based on a simple proton trapping model quantified the influence of biaxial compressive strain on four parameters related to proton diffusion, namely the pre-exponential factor and activation energy for mobile protons, and the pre-exponential factor and energy for proton trapping. The analysis revealed that the retardation of proton diffusion in the film did not result from the contribution of proton trapping but from the slower diffusion of mobile protons. A biaxial compressive misfit strain of $-0.85\%$ increased the activation energy for mobile protons from 23 to 28 kJ mol$^{-1}$ and decreased the pre-exponential factor from $1.0 \times 10^{-4}$ to $2.6 \times 10^{-3}$ cm$^2$ s$^{-1}$, resulting in a more than one order of magnitude retardation at 375 $^\circ$C. The retarded mobile proton diffusion with larger $E_a$ and lower $D_0$ in the biaxially compressed film is understood to be related to the non-uniform energy states of protons due to anisotropic deformation of BO$_6$ octahedra in the compressed perovskite lattice.

The model allows us to estimate the proton conductivity in the electrolyte of PCFC devices considering thermally and chemically introduced biaxial strain, and the results agree well with the reported values in the
literature. Mechanical compressive strain could be the origin of the large ohmic resistance observed in PCFCs, so minimizing biaxial compressive strain in PCFCs with an appropriate choice of electrolyte–electrode combinations and optimizing the fabrication process for single cells are critical for maximizing the potential applications of proton-conducting oxides as electrolytes in environmentally friendly electrochemical devices. The insights obtained in this study should help in the design of high-performance proton-based electrochemical devices.

4. Experimental methods

4.1. Thin-film preparation

BaZr$_{0.8}$Y$_{0.2}$O$_{3−δ}$ thin films were prepared by the PLD method on Nb-doped SrTiO$_3$ (001) single-crystal substrates (a = 3.905 Å, commercially available from Crystal Base Co., Ltd., Japan) using BaZr$_{0.75}$Y$_{0.21}$O$_{3−δ}$ bulk target (lattice constant, a = 4.224 Å). The details of the BZY20 target synthesis are given in the supporting information. The PLD system (PLAD-247, AOV Co. Ltd) was operated with a KrF excimer laser (COMPex Pro 102F, Coherent Inc.) emitting at 248 nm and an energy of 2 J cm$^2$ with a repetition rate of 1 Hz. During the ablation process, the substrate temperature and oxygen partial pressure were maintained at 700 °C and 1 Pa, respectively. The film thickness was controlled by varying the deposition time (10–100 min for the two films, respectively). After deposition, the samples were annealed in the deposition chamber for 5 min to crystallize the deposited films. The chemical composition of the films was measured using EDS in conjunction with SEM (SU3500, Hitachi High-Technologies Co.) and SIMS, as described below. Because the X-ray signal intensity was lower than the detection limit, the chemical composition of the 18 nm thick film could not be determined using EDS.

4.2. Chemical composition analysis by SIMS

The chemical composition of the deposited BZY20 films was measured by SIMS (SC-Ultra, Cameca) using primary 1 keV Cs$^+$ ions. Positive ion signals corresponding to the mass of the CsM$^+$ matrix (M = H, Ti, Sr, Nb, Zr, Y, and Ba) were recorded. To quantify the Ba, Zr, Sr, and H elements in the film, a hydrated BZY20 bulk sample (BaZr$_{0.75}$Y$_{0.21}$O$_{2.89}$H$_{0.15}$) was used as a reference. The sputtering rate was determined by analyzing the depth of craters for the 500 nm thick sample after a depth profile measurement with a surface profiler (P-16+, KLA-Tencor). We note that it is difficult to distinguish between Nb and Zr–H in our SIMS system equipped with a quadrupole mass spectrometer.

4.3. Crystal structure analysis

The crystal structure of the dehydrated thin films was analyzed using a line focus x-ray source (D8 DISCOVER, Bruker AXS). The 20 – θ profiles were obtained, and RSM was performed using a monochromatic Cu–K$_α$ line with a one-dimensional detector (LYNXEYE, Bruker AXS). The in-plane and out-of-plane lattice constants were estimated from the RSM results for the 103 peak. For pole figure measurements, a collimated x-ray beam with a diameter of 0.5 mm and a two-dimensional detector (VÀNTEC 500, Bruker AXS) were used. Pole figures for the (110) planes in the deposited BZY20 thin films were recorded with a rotation angle (Φ) step size of 3° and tilt angles (Ψ) of 35° and 75° along the normal direction of the x-rays.

4.4. Conductivity measurements

The electrical conductivity of BZY20 thin films in the vertical direction was determined using AC impedance spectroscopy. The configuration of the BZY20 thin-film sample for AC impedance spectroscopy is schematically given in figure S9. A silver layer with a thickness of 650 nm was deposited onto the surfaces of the thin film and Nb–SrTiO$_3$ substrate using DC sputtering (SC-701HMC II, Sanyu Electron Co., Ltd). The areas of silver electrode for the 18 nm and 500 nm film samples were measured to be 0.37 and 0.15 cm$^2$, respectively, using a standard scale. A current collector made of silver mesh (Nilaco Corporation) was pasted on the silver layer using silver paste (TR-3025, Tanaka Kikinzoku Kogyo), and connected to an AC impedance spectrometer via gold wires. For adhesion, the sample specimens were heated at 750 °C for 2 h before the electrochemical measurements. AC impedance spectroscopy was performed in the temperature range of 28 °C–604 °C in an argon atmosphere saturated with H$_2$O and D$_2$O at 17.5 °C and 20 °C, respectively (P$_{H_2O} = P_{D_2O} = 0.02$ atm) with a flow rate of 100 ml min$^{-1}$. The AC impedance was recorded by sweeping the frequency from 10$^{-1}$ to 10$^6$ Hz with a voltage amplitude of 10–50 mV (Biologic, VSP-300). The Nyquist plots were fitted with results for an equivalent circuit comprising a parallel structure of RC components in the grain interior and electrode regions. Here, R is an ideal resistor with $Z_r = R$ and C is a constant-phase element with $Z_C = Y(j\omega)^n$ $^{-1}$, where $j$ is $\sqrt{-1}$, $\omega$ is the frequency, and $Y$ and $n$ are constants with 0 $\leq n \leq 1$. The results of impedance measurements below 141 °C for the 18 nm thick film were not
used in this work because no obvious semicircles were observed due to an overlap of the response frequencies for the bulk and electrode (figures S6(d) and (h)).

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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