High oxide-ion conductivity through the interstitial oxygen site in Ba$_7$Nb$_4$MoO$_{20}$-based hexagonal perovskite related oxides

Masatomo Yashima$^{1,3}$, Takafumi Tsujiguchi$^1$, Yuichi Sakuda$^1$, Yuta Yasui$^1$, Yu Zhou$^2$, Kotaro Fujii$^1$, Shuki Torii$^3$, Takashi Kamiyama$^3$ & Stephen J. Skinner$^2$

Oxide-ion conductors are important in various applications such as solid-oxide fuel cells. Although zirconia-based materials are widely utilized, there remains a strong motivation to discover electrolyte materials with higher conductivity that lowers the working temperature of fuel cells, reducing cost. Oxide-ion conductors with hexagonal perovskite related structures are rare. Herein, we report oxide-ion conductors based on a hexagonal perovskite-related oxide Ba$_7$Nb$_3$.Mo$_{0.1}$O$_{20.05}$. Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ shows a wide stability range and predominantly oxide-ion conduction in an oxygen partial pressure range from $2 \times 10^{-26}$ to 1 atm at 600 °C. Surprisingly, bulk conductivity of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$, $5.8 \times 10^{-4}$ S cm$^{-1}$, is remarkably high at 310 °C, and higher than Bi$_2$O$_3$- and zirconia-based materials. The high conductivity of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ is attributable to the interstitial-O5 oxygen site, providing two-dimensional oxide-ion O1–O5 interstitialcy diffusion through lattice-O1 and interstitial-O5 sites in the oxygen-deficient layer, and low activation energy for oxide-ion conductivity. Present findings demonstrate the ability of hexagonal perovskite related oxides as superior oxide-ion conductors.

$^1$Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1 W4-17 O-okayama, Meguro-ku, Tokyo 152-8551, Japan. $^2$Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK. $^3$Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 203-1 Tokai, Ibaraki 319-1106, Japan. Email: yashima@cms.titech.ac.jp
Oxide-ion conducting ceramic materials have attracted much attention due to their applications in solid-oxide fuel cells (SOFCs), oxygen separation membranes, gas sensors, and catalysts1–24. Yttria stabilized zirconia (YSZ) ceramics have widely been used, but the working temperature is high (700–1000 °C). Thus, there remains a strong motivation to explore oxide-ion conductors with higher conductivities at temperatures below 600 °C. High oxide-ion conductivities have been observed in specific structure families such as the fluoride-type, perovskite-type, melilite-type, and apatite-type structures1–26.

The perovskite and its related materials exhibit interesting physical and chemical properties26 and can be classified into four structural groups of (i) AMX$_2$ perovskite-type, (ii) AMX$_3$-related, (iii) hexagonal perovskite-related and (iv) modular structures26 where A and M are larger and smaller cations, respectively, and X is an anion. A number of perovskite-type materials and perovskite related phases belonging to the groups of (i), (ii) and (iv) have been reported to be oxide-ion conductors. The hexagonal perovskite-related structures (iii) have hexagonal close packing of AX$_x$ layers or sequences of hexagonal (b) and cubic (c) AX$_{1-x}$ (and/ or anion-deficient AX$_x$ (c')) where x is the anion vacancy content) close-packed layers. The hexagonal perovskite related oxides exhibit a variety of crystal structures26–31. However, oxide-ion conductors with hexagonal perovskite-related structures are quite rare. Several mixed ion (oxide-ion and/or proton) and electronic conductors with hexagonal perovskite related structures were reported in the literature32–35. The hexagonal perovskite related oxides Ba$_7$MnMoO$_{20}$ (M = Mo and W; δ is the oxygen deficiency) and their solid solutions exhibit significant oxide-ion conductivities23,30,31,36–39, however, the conductivities are not high at temperatures below 600 °C. The relatively low conductivities are ascribed to relatively high activation energy for conductivity (e.g., 1.2 eV for Ba$_7$MoNbO$_{20.5}$36). Therefore, we have explored oxide-ion conductors with the hexagonal perovskite related structures. Ba$_7$Nb$_3$MoO$_{20}$ is a trigonal P3m1 hexagonal perovskite polytype 7H39,40. Fop et al. found high oxide-ion and proton conductivities of Ba$_7$Nb$_3$MoO$_{20}$40. Herein, we report higher oxide-ion conductivities, crystal structure and oxide-ion diffusion pathways of the solid solution composition Ba$_7$Nb$_4$xMo$_{10}$O$_{20.5}$. Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ is found to exhibit a bulk conductivity of 5.8 $\times$ 10$^{-4}$ S cm$^{-1}$ at 310 °C, which is higher than those of the “best” oxide-ion conductors. The present work also demonstrates the two-dimensional (2D) oxide-ion O1–O5 diffusion through the interstitial octahedral O5 and lattice tetrahedral O1 sites at a high temperature of 800 °C.

**Results and discussion**

**Preparation and characterization of Ba$_7$Nb$_3$MoO$_{20}$-based oxides.** In this work, we studied the electrical and structural properties of Ba$_7$Nb$_3$MoO$_{20}$-based materials, because (1) the chemical species in Ba$_7$Nb$_3$MoO$_{20}$ are the same as those in the oxide-ion conductor Ba$_7$MoNbO$_{20.5}$–6 (2) Ba$_7$Nb$_3$MoO$_{20}$ has the hexagonal perovskite related structure similar to Ba$_7$MoNbO$_{20.5}$–628,29,38,39 (3) the crystal structure of Ba$_7$Nb$_3$MoO$_{20}$ contains possible oxide-ion conducting Ba–oxygen (c') layers as does the structure of Ba$_7$MoNbO$_{20.5}$–6 and (4) the bond-valence-energy barrier for oxide-ion migration of Ba$_7$Nb$_3$MoO$_{20}$ (0.21 eV) is lower than that of Ba$_7$MoNbO$_{20.5}$ (0.51–0.35 eV, See the details in Supplementary Note 1). Ba$_7$Nb$_3$Mo$_{10}$O$_{20}$ and Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ have the hexagonal perovskite related structure with trigonal P3m1 space group (Supplementary Fig. 1). Arrhenius plots of bulk conductivities ($\sigma_b$) of Ba$_7$Nb$_3$MoO$_{20}$–40, Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$–41 and Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ in dry air are shown in Supplementary Fig. 2. The $\sigma_b$ of Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ is the highest among the three compositions. Thus, we focus on the Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ composition for further detailed studies.

The cation atomic ratio of Ba: Nb: Mo = 7.11 (14): 3.81 (3): 1.26 (14) for Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ determined through X-ray fluorescence (XRF) analyses agreed with that of the nominal composition where the number in parentheses is the standard deviation in the last digit. X-ray photoelectron spectroscopy (XPS) data for the Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ composition indicated that the valences of Ba, Nb and Mo at room temperature (RT) were +2, +5 and +6, respectively (Ba$^{2+}$, Nb$^{5+}$, Mo$^{6+}$, $\sigma_b$ of Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ (Supplementary Fig. 3). Thermogravimetric measurements of Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ in dry air between 400 and 900 °C indicate very little weight loss and oxygen deficiency $\delta$ in Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ at high temperatures (Supplementary Fig. 4).

**Oxide-ion conduction in Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$.** Figure 1a, b shows the typical impedance spectra of Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$, which indicates the bulk, grain boundary and electrode responses. Bulk conductivity ($\sigma_b$), grain-boundary conductivity ($\sigma_{gb}$), and grain-boundary capacitance were obtained by the equivalent circuit fitting (Red lines in Fig. 1a, b, Supplementary Figures 5–9). The $\sigma_b$ and $\sigma_{gb}$ were found to be detailed in Supplementary Table 1. Electronic conductivity was observed in dry O$_2$, dry air and in dry N$_2$ at 295 and 598 °C. They were independent of oxygen partial pressure at these temperatures, which indicates ionic conduction (Supplementary Figure 10). Figure 1c shows the temperature dependencies of the $\sigma_b$ and $\sigma_{gb}$ of Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ on cooling in dry air. The activation energy for $\sigma_b$ was found to be lower than those for $\sigma_{gb}$ and the DC total electrical conductivity, $\sigma_{tot}$. The $\sigma_b$ was higher than $\sigma_{gb}$ at temperatures below 550 °C and higher than $\sigma_{tot}$ at temperatures below 850 °C. The oxide-ion transport number ($f_{ion}$) was investigated using oxygen concentration cell measurements. The $f_{ion}$ values were 1.00 between 700 and 900 °C and 0.99 at 600 °C in air/O$_2$, 0.99 at 800 °C and 1.00 at 900 °C in air/N$_2$, and 0.98 at 600 °C in air/5% H$_2$ in N$_2$ (Fig. 1d). Oxide-ion diffusion in dense Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ was clearly confirmed by the isotope exchange depth profile method41, which calculated a high oxygen tracer diffusion coefficient $D_{O2}$ value of 5.35 $\times$ 10$^{-9}$ cm$^2$ s$^{-1}$ at 700 °C and 7.25 $\times$ 10$^{-9}$ cm$^2$ s$^{-1}$ at 800 °C (Supplementary Figure 11). The diffusion lengths were about 150 μm and the grain sizes of the Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ samples were 1–5 μm (Supplementary Figure 12), thus, the $^{18}$O tracer species encountered a number of grains and grain boundaries. The total DC electrical conductivity ($\sigma_{tot}$) was independent of the oxygen partial pressure $P(O_2)$ between $P(O_2)$ = 7 × 10$^{-2}$ – 1 atm at 300 °C, $P(O_2)$ = 2 × 10$^{-26}$ – 1 atm at 600 °C, and $P(O_2)$ = 5 × 10$^{-18}$ – 1 atm at 900 °C (Fig. 1e). Electronic conductivity was observed in the $P(O_2)$ range of 6 × 10$^{-24}$ – 4 × 10$^{-26}$ atm at 900 °C with the slope of −0.129(19). Therefore, Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ exhibits a wider electrolyte domain compared with Ba$_7$Nb$_3$MoO$_{20}$ as reported by Fop et al.40. To examine the possible proton conduction of this phase, the DC electrical conductivities, $\sigma_{tot}$ of Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ were measured in wet air (H$_2$O partial pressure, $P(H_2O) = 2.3 \times 10^{-2}$ atm) and in dry air ($P(H_2O) < 1.8 \times 10^{-4}$ atm). The contribution of protons to $\sigma_{tot}$ of Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ was small, even in wet air where the proton transport number was 0.03 – 0.12 (Supplementary Fig. 13). Water incorporation behavior was also investigated and the results are shown in Supplementary Fig. 14 and Supplementary Note 2. A significant but small amount of water uptake was observed for Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ compared with Ba$_7$Nb$_3$MoO$_{20}$–42 which is responsible for the lower transport number of protons in Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$. These results indicate that the oxide ion is the dominant charge carrier and that Ba$_7$Nb$_3$Mo$_{11}$O$_{20.5}$ is an...
oxide-ion conductor. No change was observed in the X-ray powder diffraction patterns before and after the oxygen concentration cell measurements (Supplementary Fig. 15), which demonstrates the high phase stability of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ at high temperatures and in the wide $P$(O$_2$) region between $P$(O$_2$) = $1.2 \times 10^{-27}$ and 1 atm. The $\sigma_b$ of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ was found to be higher than those of Ba$_7$Nb$_4$MoO$_{20.04}$ (Fig. 1c) and YSZ, and comparable to those of the best oxide-ion conductors (Fig. 1f). It should be noted that the $\sigma_b$ of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ was higher than the best oxide-ion conductors at temperatures of around 300 °C, due to the low activation energy of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ (0.185-0.454 eV as shown in Fig. 1c). These results indicate the high potential of the hexagonal perovskite related oxide Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ as a superior oxide-ion conductor.

**Fig. 1 High oxide-ion conductivity of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$. a, b Complex impedance plots of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ recorded in dry air at (a) 309 °C and (b) 598 °C. c Arrhenius plots of bulk conductivity $\sigma_b$, grain-boundary conductivity $\sigma_{gb}$ and DC $\sigma_{tot}$ of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ in dry air. Activation energy for $\sigma_b$ of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ decreases with temperature from 0.454 to 0.185 eV as shown by the red numbers in panel c. Green line represents $\sigma_b$ of Ba$_7$Nb$_4$MoO$_{20}$ reported by Fop et al.$^{40}$. d Oxygen transport number of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$. e Oxygen partial pressure $P$(O$_2$) dependence of $\sigma_{tot}$ of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ and other oxide-ion conductors. f Comparison of bulk conductivities of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ and other oxide-ion conductors.**
Structural origin of the high oxide-ion conductivity in Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$. Next, we discuss the structural origin of the high oxide-ion conductivity of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$, based on its refined crystal structure and neutron scattering length density (NSLD) at 800 °C (Fig. 2). In the Rietveld refinements of the neutron-diffraction data, the Mo$^{5+}$ and Nb$^{5+}$ cations were assumed to be disordered, since they have quite similar neutron scattering lengths. By the trigonal $P$3$m$1 hexagonal perovskite polytype 7H (c'hc'hch; Fig. 2a), the crystal structure of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ was successfully refined by Rietveld analyses of the neutron-diffraction data measured in situ at a temperature of 800 °C in vacuum on the super-high-resolution diffractometer, SuperHRPD$^{42,43}$ at J-PARC, Japan (Fig. 3 and Supplementary Table 1). In order to examine the oxide-ion diffusion pathway and to validate the crystal structure of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$, the NSLD was analysed using the maximum-entropy method (MEM) and structure factors obtained through the Rietveld analysis. It is well known that the MEM is a powerful tool to study the structural disorder and ion-diffusion pathways in various ionic conductors.$^{16,19,31}$ Oxygen atoms were found to partially occupy the octahedral interstitial O5 site in the Ba$_1$(O1)$_{2-x}$(O5)$_{0.05+x}$ layer (c'), because (i) the Rietveld fit for the structural model with the O5 atom (weight profile reliability factor $R_{wp} = 2.39\%$) was lower than those without the O5 atom ($R_{wp} = 2.47\%$) and (ii) the MEM NSLD distribution clearly shows the O5 site (Fig. 2b, d). Here the x in Ba$_1$(O1)$_{2-x}$(O5)$_{0.05+x}$ is the vacancy content at the O1 site in the unit cell. We applied the split-atom model for the tetrahedral O1 site, because the atomic displacement parameter was quite high for the non-split-atom model and the Rietveld fit for the split-atom model ($R_{wp} = 2.39\%$) was better than that for the non-split atom model ($R_{wp} = 2.44\%$).

The crystal structure of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ consists of an oxide-ion conducting Ba$_1$(O1)$_{2-x}$(O5)$_{0.05+x}$ layer (c'), two Ba$_2$(O2)$_3$ layers (h), two Ba$_4$(O4)$_3$ layers (h), two Ba$_3$(O3)$_3$ layers (c), and Nb and Mo cations at the Nb/Mo1, Nb/Mo2 and Nb/Mo3 sites (Fig. 2a). A striking feature of the MEM NSLD distribution of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ at 800 °C is the connected oxide-ion diffusional pathway between the tetrahedral O1 and interstitial octahedral O5 sites on the oxide-ion conducting Ba$_1$(O1)$_{2-x}$(O5)$_{0.05+x}$ layer (c') (Fig. 2b, d). The oxide ions two-dimensionally migrate through both lattice O1 and interstitial O5 sites, which indicates the interstitiality mechanism of oxide-ion diffusion. The bond-valence-based energy barriers for oxide-ion migration, $E_{b}$, for the refined crystal structure of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ at 800 °C also supported this 2D feature, because the $E_{b}$ along the ab plane (0.19 eV) is much lower than $E_{b}$ along the c axis (1.54 eV). Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ has an excess oxygen of $x = 0.05$ (O$_{20.05}$ or O$_{0.05}$ in Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$) compared with the mother material Ba$_7$Nb$_3$MoO$_{20}$, which leads to a larger amount of interstitial oxygen and the higher oxide-ion conductivity of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ (Fig. 1c).
In conclusion, we have discovered a structure family of rare-earth-free oxide-ion conductors based on the hexagonal perovskite related oxide Ba$_7$Nb$_3.9$Mo$_1.1$O$_{20.05}$. The bulk conductivity of Ba$_7$Nb$_3.9$Mo$_1.1$O$_{20.05}$ is as high as $5.8 \times 10^{-4}$ S cm$^{-1}$ at 310 °C. This high conductivity is ascribed to the interstitial O$_5$ oxygen, 2D oxide-ion O$^{1-}$O$^{2-}$ diffusion through the lattice tetrahedral O1 and interstitial O5 octahedral oxygen sites on the ab plane at z = 0 and to the low activation energy for oxide-ion conductivity. The (tetrahedral O1)–(octahedral O5) diffusion pathways in Ba$_7$Nb$_3.9$Mo$_1.1$O$_{20.05}$ are along the [110], [120] and [210] directions (Arrows in Fig. 2c), which are the same as those for the (tetrahedral O3)–(octahedral O2) migration paths in the hexagonal perovskite related oxide Ba$_7$MoNbO$_{8.5}$.$^{21}$ This strongly suggests that the (tetrahedral)–(octahedral) oxide-ion migration pathway along the [110], [120] and [210] directions on the oxygen deficient c$^\prime$ layer is a common feature of the oxide-ion conductors with hexagonal perovskite related structures. This feature would be a guide for design of oxide-ion conductors with the hexagonal perovskite-related structures. The present finding of high oxide-ion conductivities in rare-earth-free Ba$_7$Nb$_3.9$Mo$_1.1$O$_{20.05}$ suggests the ability of various hexagonal perovskite related oxides as superior oxide-ion conductors.

Methods

Synthesis and characterization. Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ and Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ were prepared by the solid-state reactions. High-purity (> 99.9%) BaCO$_3$, Nb$_2$O$_5$, and MoO$_3$ were mixed and ground using an agate mortar and pestle as ethanol slurries and dry powders repeatedly for 0.5–2 h. The obtained mixtures were calcined at 900 °C for 10–12 h in static air. The calcined samples were crushed and ground using an agate mortar and pestle as ethanol slurries and dry powders repeatedly for 0.5–2 h. The powders thus obtained were uniaxially pressed into pellets (2 mm in diameter, 4.5 mm in height, and relative density of 100–98%) attached to an alumina tube with a glass seal. One side of the pellet was exposed to flowing dry air and the other side to flowing dry O$_2$ (AirO$_2$), N$_2$ (AirN$_2$), or 5% H$_2$ in N$_2$ (Air5%H$_2$) gases at high temperatures. The electromotive forces of the concentration cell were recorded with a Keithley model 617 electrometer. The following Nernst equation was utilized to estimate the i$_{ion}$:

$$E = \left( \frac{R}{4F} \right) \ln \left( \frac{\rho(O_2)}{\rho(O_2)} \right)$$

$$\sigma = \frac{A}{d} \exp \left( \frac{E}{kT} \right)$$

where $A$, $k$, and $T$ are the pre-exponential factor, Boltzmann constant, and absolute temperature, respectively. Oxidation concentration cell measurements were conducted to investigate the oxygen transport number $i_{ion}$ using a sintered pellet (20 mm in diameter, 0.2 mm in thickness, relative density of 100–98%) attached to an alumina tube with a glass seal. One side of the pellet was exposed to flowing dry air and the other side to flowing dry O$_2$ (AirO$_2$), N$_2$ (AirN$_2$), or 5% H$_2$ in N$_2$ (Air5%H$_2$) gases at high temperatures. The electromotive forces of the concentration cell were recorded with a Keithley model 617 electrometer. The following Nernst equation was utilized to estimate the $i_{ion}$:

$$E = \left( \frac{R}{4F} \right) \ln \left( \frac{\rho(O_2)}{\rho(O_2)} \right)$$

The total electrical conductivity $\sigma$ of the Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ pellet (relative density: 95%) was measured by a DC-4 probe method using Pt electrodes at various oxygen partial pressure $p(O_2)$. The $p(O_2)$ was controlled using a mixture of O$_2$, N$_2$, and 5% H$_2$ in N$_2$ and $p(O_2)$ was monitored by an oxygen sensor. $^{18}$O tracer diffusion measurements of dense Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ pellets (relative density of 98–100%) were carried out using the line scan method by secondary ion mass spectrometry (SIMS)$^{41}$. Each sample was prepared by polishing with diamond spray media down to a thickness of 0.25 µm. Samples were pre-annealed in dry research grade oxygen (BOC 99.996%) of natural isotopic abundance for a duration of 10 times that of the isotopic exchange. The samples were subsequently annealed for 2 h in $^{18}$O-enriched gas at a pressure of 0.02 mbar. After the exchange anneal, the samples were cut perpendicular to the original surface and the exposed cross-sections polished to 0.25 µm finish, as above. The oxygen diffusion profiles were measured by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) using a ToF-SIMS 5 instrument (IONTOF GmbH) using Bi$^+$ ions at 25 keV energy. Values of oxygen self-diffusion, $D^*$, and surface exchange, $k$, coefficients were obtained by fitting the experimental data to Crank’s solution of Fick’s 2nd law of diffusion$^{1,4,44}$ using the TraceAX software$^{45}$. The microstructure of the Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ pellet used for the $^{18}$O tracer diffusion measurements was observed by a scanning electron microscope (KEYENCE VE-8800).

Neutron-diffraction measurements of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ at 800 °C. Rietveld and MEM analyses. High-temperature neutron-diffraction measurements of Ba$_7$Nb$_{3.9}$Mo$_{1.1}$O$_{20.05}$ pellets (8.7 mm in diameter, 43 mm in height) in a Ti-Zr alloy holder were carried out in vacuum using a super-high-resolution time-of-flight (TOF) neutron diffractometer (SuperHRPD) installed at the Materials and Life Science Experimental Facility of J-PARC, Japan$^{41}$. The absorption correction was performed using the method given by Rouse and Cooper$^{46}$. The diffraction data were analysed by the Rietveld method using the Z-Rietveld program$^{47}$. The neutron scattering length density distribution was investigated using the MEM. The MEM analysis was carried out with computer program, Dysnoma$^{48}$, using the structural model obtained in the Rietveld refinement of the neutron diffraction data at 800 °C. The MEM calculations were performed with the unit cell divided into $60 \times 60 \times 168$ pixels.
Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Received: 16 March 2020; Accepted: 21 December 2020;
Published online: 25 January 2021

References

1. Abraham, F., Boivin, J. C., Maressa, G. & Nowogrodzki, G. The BIMEVOX series: a new family of high performances oxide ion conductors. Solid State Ion. 40–41, 934–937 (1990).
2. Goodenough, J. B., Ruiz-Diaz, J. E. & Zhen, Y. S. Oxide-ion conduction in BaInO4 and BaInMoO6 (M = Ce, Hf, or Zr). Solid State Ion. 44, 21–31 (1990).
3. Ishihara, T., Matsuda, H. & Takita, Y. Doped LaGaO3 perovskite type oxide as a new oxide ion conductor. J. Am. Chem. Soc. 116, 3801–3803 (1994).
4. Nakayama, S., Kageyama, T., Aono, H. & Sadaoka, Y. Ionic conductivity of lanthanoid silicates, Ln2O3SiO4 (Ln = La, Nd, Sm, Gd, Dy, Y, Ho, Er and Yb). J. Mater. Chem. 5, 1801–1805 (1995).
5. Nakayama, S. & Sakamoto, M. Electrical properties of new high type oxide ion conductor RE2(SiO3)2 (RE = La, Pr, Nd, Sm, Gd, Dy). J. Eur. Ceram. Soc. 15, 1413–1418 (1998).
6. Huang, K., Feng, M. & Goodenough, J. B. Synthesis and electrical properties of dense Cs2GeO3O9 ceramics. J. Am. Ceram. Soc. 81, 357–362 (1998).
7. Lacorre, P., Goutenoire, F., Bohne, O., Retoux, R. & Laligant, Y. Designing fast oxide-ion conductors based on La2MoO8. Nature 404, 856–858 (2000).
8. Skinner, S. J. & Kilner, J. A. Oxygen diffusion and surface reaction in La2–xSr2xNiO4. Solid State Ion. 135, 709–712 (2000).
9. Kilner, J. A. Fast oxygen transport in acceptor doped oxides. Solid State Ion. 129, 13–23 (2000).
10. Esaka, T. Ionic conduction in substituted scheelite-type oxides. Solid State Ion. 136–137, 1–9 (2000).
11. Imamura, N., Kamijima, M. & Adachi, G. Y. A carbon dioxide gas sensor by combination of multivalent cation and anion conductors with a water-insoluble oxycarbonate-based auxiliary electrode. Anal. Chem. 74, 4800–4804 (2002).
12. Huang, K., Tichy, R. S. & Goodenough, J. B. Superior perovskite oxide ion conductor: strontium- and magnesium-doped La2O3. I. Phase relationships and electrical properties. J. Am. Ceram. Soc. 81, 2565–2575 (2005).
13. León-Reina, L. et al. High oxide ion conductivity in Al-doped germanium oxide. Chem. Mater. 17, 596–600 (2005).
14. Kwon, O. H. & Choi, G. M. Electrical conductivity of thick film YSZ. Solid State Ion. 177, 3057–3062 (2006).
15. Kuang, X. et al. Intertitial oxide ion conductivity in the layered tetrahedral network melilite structure. Nat. Mater. 7, 498–504 (2008).
16. Yoshima, M. Diffusion pathway of mobile ions and crystal structure of and mixed conductors: a brief review. J. Ceram. Soc. Jpn. 117, 1055–1059 (2009).
17. Malavasi, L., Fisher, C. A. J. & Islam, M. S. Oxide-ion and proton conducting electrolyte materials for clean energy applications: structural and mechanistic features. Chem. Soc. Rev. 39, 4370–4387 (2010).
18. Jung, D. W., Duncan, K. L. & Wachsmann, E. D. Effect of total dopant concentration and dopant ratio on conductivity of (DyO1.25)0.25–x(BO1.25)0.25–x (BO3)1.25–x, Acta Mater. 58, 355–363 (2010).
19. Yoshima, M., Srirakuda, N. & Ishihara, T. Crystal structure, diffusion path and oxygen permeability of a Pr2NiO4-based mixed conductor. (Pr0.4La0.6)0.45Ni0.55O2–x, J. Am. Chem. Soc. 132, 2385–2392 (2010).
20. Li, M. et al. A family of oxide ion conductors based on the ferroelectric perovskite Na2Bi3Ti2O8. Nat. Mater. 13, 31–35 (2014).
21. López, C. A., Pedregosa, J. C., Lamas, D. G. & Alonso, J. A. The strongly defective perovskite Sr1–xMoxO3. Crystal structure in relation to oxide ion conductivity. J. Appl. Crystallogr. 47, 1395–1401 (2014).
22. Fujii, K. et al. New perovskite-related structure family of oxide-ion conducting materials Nb5BaNiO6. Chem. Mater. 26, 2488–2491 (2014).
23. Fop, S. et al. Oxygen ion conductivity in the hexagonal perovskite derivative Ba4Mg2NiO8.5. J. Am. Chem. Soc. 135, 16764–16769 (2013).
the experiments/analyses. We would like to acknowledge to Kojundo Chemical Laboratory Co. Ltd. for arrangements of the XPS and ICP measurements. We thank the Ookayama Materials Analysis Division of Tokyo Institute of Technology for their assistance in the XRF measurements. The neutron-diffraction measurements were carried out by the project approval (J-PARC MLF Proposal No. 2017A0111 and 2017L1301). This study was partly supported by Grants-in-Aid for Scientific Research (Kakenhi, No. JP15H02291, JP16H00884, JP16H06293, JP16H06440, JP16H06441, JP16H06438, JP16K21724, JP17K17717, JP17H06222, and JP19H00821) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, Adaptable and Seamless Technology transfer Program through Target-driven R&D (A-STEP) No. JPMJTM19AY from Japan Science and Technology Agency (JST) and JSPS Core-to-Core Program, A. Advanced Research Networks (Solid Oxide Interfaces for Faster Ion Transport).

Author contributions
M.Y. and T.T. designed research. K.F., S.T., T.T. and T.K. measured the neutron data. Y.Y. and Y.Z. carried out the oxygen diffusion measurements based on the supervision by S.J.S. T.T., Y.S. and Y.Y. prepared the samples and measured the X-ray diffraction data, electrical conductivity, TG data, and transport number. T.T., Y.S., Y.Y. and K.F. analyzed the data and made figures and Tables. M.Y. wrote and edited the manuscript and response to the referees’ comments. All the authors read the manuscript. Funding acquisition and supervision: M.Y. and S.J.S.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-20859-w.

Correspondence and requests for materials should be addressed to M.Y.

Peer review information Nature Communications thanks Peter Slater and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2021