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Improved oxide-ion conductivity of NdBaInO₄ by Sr doping†

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The oxide-ion conductivity of NdBaInO₄ has been increased by Sr doping. Nd_{0.9}Sr_{0.1}BaInO_{3.95} showed the highest electrical conductivity among Nd_{1-x}Sr_xBaInO_{4-x/2} ($x = 0.0, 0.1, 0.2, \text{ and } 0.3$). The oxide-ion conductivity σ_{ion} of Nd_{0.9}Sr_{0.1}BaInO_{3.95} ($\sigma_{\text{ion}} = 7.7 \times 10^{-4} \text{ S cm}^{-1}$) is about 20 times higher than that of NdBaInO₄ ($\sigma_{\text{ion}} = 3.6 \times 10^{-5} \text{ S cm}^{-1}$) at 858 °C, and the activation energy of oxide-ion conduction is a little lower for Nd_{0.9}Sr_{0.1}BaInO_{3.95} (0.795(10) eV) than that for NdBaInO₄ (0.91(4) eV). The structure analysis based on neutron powder diffraction data revealed that the Sr exists at the Nd site and oxygen vacancies are observed in Nd_{0.9}Sr_{0.1}BaInO_{3.95}. This result indicates that the increase of the oxide-ion conductivity is mainly due to the increase of the carrier concentration. The bond valence-based energy landscape indicated two-dimensional oxide-ion diffusion in the (Nd,Sr)₂O₃ unit on the *bc*-plane and a decrease of the energy barrier by the substitution of Nd with Sr cations.

Introduction

Oxide-ion conductors, which include pure ionic conductors and mixed oxide-ion and electronic conductors, attract significant interest because of their varied uses in oxygen separation membranes and cathodes for solid-oxide fuel cells (SOFCs).¹ The oxide-ion conductivity is strongly dependent on the crystal structure and particularly the defects. At present, several structures, such as fluorites,^{2,3} perovskites,^{2,4} K₂NiF₄,^{2,5} melli-lites,^{2,6} and apatites,^{2,7} are known to show high oxide-ion conductivities. Further development of oxide-ion conductors involves investigating materials with new types of structures. Recently, we have discovered a new structure family of oxide-ion conductors based on NdBaInO₄, a monoclinic *P*₂₁/*c* perovskite-related phase with a layered structure.⁸ In this study, we have successfully improved the oxide-ion conductivity of NdBaInO₄ by Sr doping at the Nd site, which aims to increase the concentration of oxygen vacancies (*i.e.*, carriers for the oxide-ion conduction) and to lower the activation energy by exchanging Nd³⁺ with the larger Sr²⁺ cation. This study reports on the

electrical conductivity and the crystal structure of Sr-doped NdBaInO₄. The electrical conductivity of NdBaInO₄ was also investigated again for comparison.

Experimental section

Synthesis and characterization of the chemical composition

Nd_{1-x}Sr_xBaInO_{4-x/2} ($x = 0.0, 0.1, 0.2, 0.3, \text{ and } 0.4$) compounds were synthesized by solid-state reactions. Nd₂O₃ (99.95% purity) and BaCO₃ (99.9% purity) from Kanto Chemical Co. Inc., SrCO₃ and In₂O₃ (both 99.9% purity) from Kojundo Chemical Lab. Co., Ltd. were accurately weighed in 1-x : 1 : x : 1 cation molar ratios, and they were mixed and ground using a planetary ball mill (Fritsch, P7) for 30 min. The mixtures were calcined at 1000 °C for 8 h in air for decarbonization. Then, the calcined mixtures were milled again for 30 min and uniaxially pressed into pellets at about 50 MPa. These pellets were sintered in air at 1400 °C for 24 h.

The cation ratio of Nd_{0.9}Sr_{0.1}BaInO_{3.95} was confirmed by inductively coupled plasma optical emission spectrometry (ICP-OES) as Nd : Sr : Ba : In = 0.919(8) : 0.0996(9) : 0.992(3) : 0.989(9), which agreed with the average chemical composition of the starting mixture, Nd : Sr : Ba : In = 0.9 : 0.1 : 1 : 1 within 3 σ . Here, the σ is the standard deviation of the measured chemical composition and the number in the parenthesis is the last digit of σ .

Thermogravimetric analyses (TGA) of NdBaInO₄ and Nd_{0.9}Sr_{0.1}BaInO_{3.95} in Ar flow (50 mL min⁻¹) were conducted using a Bruker-AXS TG-DTA2020SA instrument with heating and cooling rates of 10 °C min⁻¹. The TG measurements were repeated three times to confirm the reproducibility and minimize artefacts from adsorbed species such as water.

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Electrical conductivity measurements

The electrical conductivities of $\text{Nd}_{1-x}\text{Sr}_x\text{BaInO}_{4-x/2}$ ($x = 0.0, 0.1, 0.2,$ and 0.3) were measured using a DC 4-probe method using sintered pellets (*ca.* 4.4 mm ϕ \times 30 mm with densities in the range of 90–95% of theoretical density) with Pt electrodes over the temperature range from 400 °C to 1200 °C in air. The oxygen partial pressure $P(\text{O}_2)$ dependence of the electrical conductivities of NdBaInO_4 and $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ was measured at 858 °C using N_2/H_2 , N_2/CO_2 , and N_2/O_2 gas mixtures. The $P(\text{O}_2)$ was monitored by an oxygen sensor that was set close to the sample. The oxide-ion conductivities of NdBaInO_4 and $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ were measured from 610 °C to 1100 °C under $P(\text{O}_2) = 3.6 \pm 2.6 \times 10^{-17}$ atm for NdBaInO_4 and $P(\text{O}_2) = 8.8 \pm 6.2 \times 10^{-14}$ atm for $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$.

Neutron and synchrotron X-ray diffraction measurements

Synchrotron X-ray powder diffraction (XRPD) measurements were conducted using a Debye–Scherrer camera with an imaging plate on beam line BL19B2 at SPring-8 (27 °C; wavelength = 0.399662(2) Å).⁹ Room temperature time-of-flight (TOF) neutron powder diffraction (NPD) measurements (24 °C) were performed using the iMATERIA diffractometer of the J-PARC facility, Tokai, Japan.¹⁰ High-temperature angle dispersive-type NPD measurements (800 °C using a vacuum furnace; wavelength = 1.83432(4) Å) were performed using a neutron powder diffractometer HRPD installed at HANARO reactor, KAERI, Korea.¹¹

Results and discussion

XRPD patterns of $\text{Nd}_{1-x}\text{Sr}_x\text{BaInO}_{4-x/2}$ ($x = 0.0, 0.1, 0.2, 0.3,$ and 0.4) identified the final products to be the monoclinic $P2_1/c$ NdBaInO_4 phase, except $x = 0.4$, which showed a different XRPD pattern with additional peaks, indicating possible saturation of the dopant within the NdBaInO_4 structure (Fig. 1a). We found that the total electrical conductivity of $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ is higher than that of NdBaInO_4 , $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{BaInO}_{3.9}$, and $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{BaInO}_{3.85}$ (Fig. 1b). Therefore, we focused on the $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ composition for further detailed studies.

Fig. 2a shows the $P(\text{O}_2)$ dependence of the total electrical conductivity σ_{total} of NdBaInO_4 and $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ at 858 °C. With decreasing $P(\text{O}_2)$, the σ_{total} decreased in the high $P(\text{O}_2)$ range (region [A] and [B] in Fig. 2a), was constant in the intermediate $P(\text{O}_2)$ range (region [C] in Fig. 2a) and increased in the low $P(\text{O}_2)$ range (region [D] in Fig. 2a). The slope of $\log(\sigma_{\text{total}})$ versus $\log(P(\text{O}_2))$ of NdBaInO_4 in the $P(\text{O}_2)$ range from 5.9×10^{-4} to 2.0×10^{-1} atm is 0.215(2) and of $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ in the $P(\text{O}_2)$ range from 5.7×10^{-3} to 2.0×10^{-1} atm is 0.216(6), which indicates that these materials show p-type conductivity in region [A], and mixed oxide-ion and hole conduction in region [B]. The constant conductivities independent of $P(\text{O}_2)$ in region [C] indicate that both NdBaInO_4 and $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ materials show pure oxide-ion conduction.

Fig. 2b shows Arrhenius plots of the total electrical conductivity σ_{total} (circles in Fig. 2b) and oxide-ion conductivity σ_{ion} (triangles in Fig. 2b) of NdBaInO_4 (black) and $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$

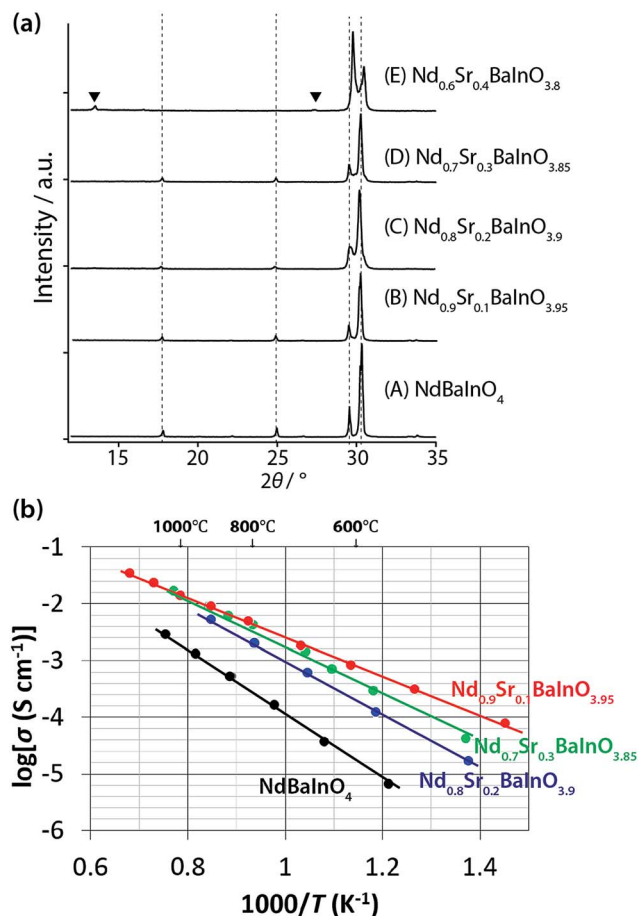


Fig. 1 (a) X-ray powder diffraction patterns of (A) NdBaInO_4 , (B) $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$, (C) $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{BaInO}_{3.9}$, (D) $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{BaInO}_{3.85}$, and (E) $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{BaInO}_{3.8}$. The dashed lines indicate the peak positions of the pure NdBaInO_4 phase. The black triangles show additional peaks that only appeared in $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{BaInO}_{3.8}$. (b) Total electrical conductivities of NdBaInO_4 (black), $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ (red), $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{BaInO}_{3.9}$ (blue), and $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{BaInO}_{3.85}$ (green) measured in air.

(red). Over the entire temperature range, the total electrical conductivity σ_{total} and oxide-ion conductivity σ_{ion} of $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ are higher than those of NdBaInO_4 . For example, the σ_{total} and σ_{ion} of $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ at 858 °C were 7.3×10^{-3} S cm^{-1} and 7.7×10^{-4} S cm^{-1} , respectively, are higher than those of NdBaInO_4 1.0×10^{-3} S cm^{-1} and 3.6×10^{-5} S cm^{-1} , respectively. The hole conductivities of $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ and NdBaInO_4 were calculated to be 6.5×10^{-3} and 9.6×10^{-4} S cm^{-1} , respectively, at 858 °C. The activation energies of total, oxide-ion, and hole conductivities of $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ were 0.685(7), 0.795(10), and 0.673 eV, which are lower than those of NdBaInO_4 (0.952(13), 0.91(4), and 0.953 eV). Therefore, 10 mol% Sr doping into NdBaInO_4 improves the oxide-ion conductivity and lowers its activation energy.

To investigate the structure changes in NdBaInO_4 by 10 mol% Sr doping, Rietveld analysis was conducted for $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ based on the synchrotron XRPD and NPD data using RIETAN-FP¹² and Z-Code.¹³ $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ is isostructural with NdBaInO_4 (space group $P2_1/c$) and has seven



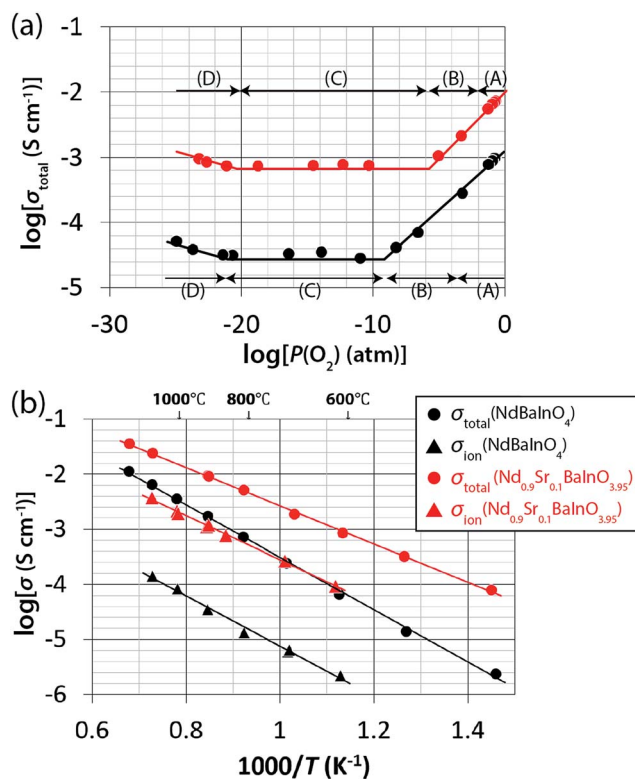


Fig. 2 (a) Partial oxygen pressure $P(\text{O}_2)$ dependence of the total electrical conductivity σ_{total} (858 °C) of NdBaInO₄ (black) and Nd_{0.9}Sr_{0.1}BaInO_{3.95} (red). The dominant carriers are electron holes in [P(O₂) region [A], oxide ions and electron holes in [B], oxide ions in [C], and the oxide ions and electrons in [D]. (b) Arrhenius plots of the total conductivity σ_{total} (circles) and ionic conductivity σ_{ion} (triangles) of NdBaInO₄ (black) and Nd_{0.9}Sr_{0.1}BaInO_{3.95} (red). σ_{total} values were measured in air and σ_{ion} values were measured under $P(\text{O}_2) = 3.6 \pm 2.6 \times 10^{-17}$ atm for NdBaInO₄ and $P(\text{O}_2) = 8.8 \pm 6.2 \times 10^{-14}$ atm for Nd_{0.9}Sr_{0.1}BaInO_{3.95}.

independent sites at the general position, Nd, Ba, In, O1, O2, O3, and O4 (Table 2).⁸ The site preference of Sr was investigated in a preliminary analysis that gave the best reliable factors, R_{wp} and R_{B} , in the case that Sr exists at the Nd site (Table S2 in (ESI†)). Here, R_{wp} is the weighted reliability factor of profile intensity and R_{B} is the reliability factor based on integrated intensities. Therefore, the occupancy factors were fixed to $g(\text{Nd}, \text{Nd}) = 0.9$ and $g(\text{Sr}, \text{Nd}) = 0.1$ in the final refinement. Here, $g(Y, X)$ represents the occupancy factor of atom Y at the X site. The refinement of the occupancy factors of the oxygen atoms using common values for all oxygen atoms yields 0.9842(10), which clearly indicates the existence of oxygen vacancies. The value agrees with the expected value of 0.9875 calculated from the charge balance. In the final refinement, the occupancy factors of oxygen atoms were fixed to 0.9875. The TGA of Nd_{0.9}Sr_{0.1}BaInO_{3.95} showed 0.18% weight loss between 50 and 800 °C, which corresponds to $\delta = 0.05$ of Nd_{0.9}Sr_{0.1}BaInO_{3.95- δ} (Fig. 3). Here, $(0.05 + \delta)$ is the amount of oxygen vacancies. Thus, the occupancy factors of oxygen atoms were fixed to 0.975 for the high-temperature (800 °C) data. The final Rietveld patterns are shown in Fig. 4a and b. The final refined atomic coordinates are shown in Table 1 for the TOF neutrons data and Table S1 in the ESI† for the synchrotron X-ray and the angle dispersive type neutron data.

Comparing the unit-cell parameters between 24 °C and 800 °C, the a -, b - and c -axes increased and the β -angle decreased with increasing temperature. The average thermal expansion coefficients between 24 °C and 800 °C were found to be $\alpha_a = 1.23(4) \times 10^{-5} \text{ K}^{-1}$, $\alpha_b = 1.07(3) \times 10^{-5} \text{ K}^{-1}$, $\alpha_c = 0.72(4) \times 10^{-5} \text{ K}^{-1}$, $\alpha_\beta = -3.73(17) \times 10^{-5} \text{ K}^{-1}$, and $\bar{\alpha} = 1.06(2) \times 10^{-5} \text{ K}^{-1}$ (the definition of these coefficients are described in section D of the ESI†). These average thermal expansion coefficients of Nd_{0.9}Sr_{0.1}BaInO_{3.95} are similar to those of NdBaInO₄ between 20 °C and 1000 °C ($\alpha_a = 1.42(2) \times 10^{-5} \text{ K}^{-1}$, $\alpha_b = 1.176(14) \times 10^{-5} \text{ K}^{-1}$, $\alpha_c = 0.77(3) \times 10^{-5} \text{ K}^{-1}$, $\alpha_\beta = -3.81(4) \times 10^{-5} \text{ K}^{-1}$,

Table 1 Crystallographic data of Nd_{0.9}Sr_{0.1}BaInO_{3.95- δ} . Comparison with NdBaInO₄

Source and facility	TOF ^a Neutron iMATERIA, J-PARC	Synchrotron BL19B2, SPring-8	Neutron HRPD, HANARO	Ref. 8
Chemical formula	Nd _{0.9} Sr _{0.1} BaInO _{3.95}	Nd _{0.9} Sr _{0.1} BaInO _{3.95}	Nd _{0.9} Sr _{0.1} BaInO _{3.90}	NdBaInO _{4.00}
Formula weight	453.92	453.92	453.20	460.39
Temperature / °C	24	27	800	20
Wavelength / Å	Time of flight ($d = 0.494\text{--}5.223$ Å)	0.399662(2)	1.83432(4)	
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	9.106468(17)	9.10285(12)	9.2060(17)	9.09538(3)
b / Å	6.050490(11)	6.04769(5)	6.0999(11)	6.04934(2)
c / Å	8.268786(19)	8.26670(9)	8.2984(17)	8.25620(2)
β / Å	103.40613(14)	103.3924(9)	103.057(12)	103.4041(3)
Unit-cell volume / Å ³	443.184(2)	442.716(8)	453.95(15)	441.89(2)
Z	4	4	4	4
Calculated density / Mg m ⁻³	6.81	6.81	6.64	6.92
R_{wp}	0.0458	0.0230	0.0362	
R_{p}	0.0334	0.0150	0.0280	—
Goodness of fit	2.994	1.000	1.860	—
R_{B}	0.0534	0.0139	0.0297	—
R_{F}	0.0295	0.0117	0.0156	—

^a TOF: Time-of-Flight.



Table 2 Occupancy factors, atomic coordinates and atomic displacement parameters of Nd_{0.9}Sr_{0.1}BaInO_{3.95} obtained from the time-of-flight neutron powder diffraction data (iMATERIA, J-PARC) measured at 24 °C

Site label X	Atom Y	$g(Y,X)^a$	x	y	z	U^b (Å ²)
Nd	Nd	0.9	0.45269(5)	0.74731(11)	0.10734(6)	0.00819 (U_{eq}) ^c
	Sr	0.1				
Ba	Ba	1	0.14825(7)	0.25034(18)	0.0328(11)	0.00933 (U_{eq})
In	In	1	0.83211(9)	0.2545(2)	0.20649(14)	0.0030(19)
O1	O	0.9875	0.18155(8)	0.80285(9)	0.04782(12)	0.01422 (U_{eq})
O2	O	0.9875	0.98669(11)	0.98872(17)	0.26951(12)	0.00988 (U_{eq})
O3	O	0.9875	0.38341(9)	0.5429(13)	0.32909(11)	0.01730 (U_{eq})
O4	O	0.9875	0.65046(8)	0.50812(15)	0.12937(11)	0.01549 (U_{eq})

Site label X	U_{11}^d (Å ²)	U_{22} (Å ²)	U_{33} (Å ²)	U_{12} (Å ²)	U_{13} (Å ²)	U_{23} (Å ²)
Nd	0.0065(3)	0.0051(2)	0.0063(3)	0.0001(3)	-0.0008(2)	0.0020(3)
Ba	0.0078(3)	0.0018(3)	0.0106(4)	0.0010(5)	0.0032(3)	0.0019(5)
O1	0.0170 (4)	0.0148(5)	0.0094(3)	0.0055(4)	0.0064(3)	0.0077(5)
O2	0.0048(3)	0.0090(3)	0.0148(5)	0.0056(3)	-0.0000(3)	0.0048(5)
O3	0.01516(5)	0.0194(5)	0.0131(5)	0.0059(4)	0.0016(4)	0.0032(5)
O4	0.0091(4)	0.0142(5)	0.0220(5)	0.0060(4)	-0.0041(4)	-0.007(4)

^a $g(Y,X)$: occupancy factor of atom Y at the X site. ^b Atomic displacement parameter. ^c Equivalent isotropic atomic displacement parameter. ^d U_{ij} : anisotropic atomic displacement parameter.

and $\bar{\alpha} = 1.176(15) \times 10^{-5} \text{ K}^{-1}$). There was an anisotropy observed in the thermal expansion. The average thermal expansion coefficients are similar for the *a*- and *b*-axes, whereas that of the *c*-axis is lower than the others. The average linear thermal expansion coefficients $\bar{\alpha}$ of Nd_{0.9}Sr_{0.1}BaInO_{3.95} ($1.06(2) \times 10^{-5} \text{ K}^{-1}$) and NdBaInO₄ ($1.176(15) \times 10^{-5} \text{ K}^{-1}$) are close to that of yttria stabilized zirconia (YSZ), which is favourable for using this material as a cathode in SOFC applications. The average thermal expansion coefficients of 3 and 8 mol% Y₂O₃-ZrO₂ between 20 and 1000 °C were reported to be 1.08×10^{-5} and $1.05 \times 10^{-5} \text{ K}^{-1}$, respectively.¹⁴

The crystal structure of Nd_{0.9}Sr_{0.1}BaInO_{3.95} at 24 °C comprises the A rare earth structure A₂O₃ ((Nd,Sr)₂O₃) and the perovskite

(A,A')BO₃ ((Nd,Sr)_{2/8}Ba_{6/8}InO₃) units (Fig. 4c) which belongs to the same structural family as NdBaInO₄.⁸ Here, A and A' are relatively large cations and B is a smaller cation. The unit-cell volume at 24 °C of Nd_{0.9}Sr_{0.1}BaInO_{3.95} ($443.184(2) \text{ \AA}^3$) is slightly larger than that of NdBaInO₄ ($441.8905(3) \text{ \AA}^3$). The larger volume is ascribed to the larger ionic radius¹⁵ of Sr²⁺ (1.21 Å for coordination number (CN) of 7) than that of Nd³⁺ (1.046 Å for CN = 7). The calculated bond valence sums (BVSs)¹⁶ from the bond lengths are 1.77 for Ba, 2.85 for (Nd_{0.9}Sr_{0.1}) and 2.99 for In sites in Nd_{0.9}Sr_{0.1}BaInO_{3.95}. These values are consistent with their formal charges 2, 2.9, and 3, respectively, which indicates the validity of the refined crystal structure of Nd_{0.9}Sr_{0.1}BaInO_{3.95}.

As described above, Nd_{0.9}Sr_{0.1}BaInO_{3.95} contains oxygen vacancies, while there are no significant oxygen vacancies within the 3σ of refined occupancy in NdBaInO₄ at room temperature, where σ is the estimated standard deviation.⁸ Considering that Nd_{0.9}Sr_{0.1}BaInO_{3.95} has a much higher oxide-ion conductivity than NdBaInO₄, the dominant carrier for the oxide-ion conduction in Nd_{0.9}Sr_{0.1}BaInO_{3.95} is the oxygen vacancy. The activation energy of the oxide-ion conduction is a little lower for Nd_{0.9}Sr_{0.1}BaInO_{3.95} (0.795(10) eV) than that for NdBaInO₄ (0.91(4) eV). The lower activation energy of Nd_{0.9}Sr_{0.1}BaInO_{3.95} is attributable to the larger bottleneck size for the oxide-ion diffusion in Nd_{0.9}Sr_{0.1}BaInO_{3.95} compared with NdBaInO₄. TGA of NdBaInO₄, and Nd_{0.9}Sr_{0.1}BaInO_{3.95} showed little weight loss (around 0.02%) above 600 °C. Therefore, the effect of the carrier concentrations on the activation energy is thought to be negligible.

Diffusion pathways of oxide ions in the crystal structure of Nd_{0.9}Sr_{0.1}BaInO_{3.95} and NdBaInO₄ were investigated by the bond valence based energy (BVE)¹⁷ using the program

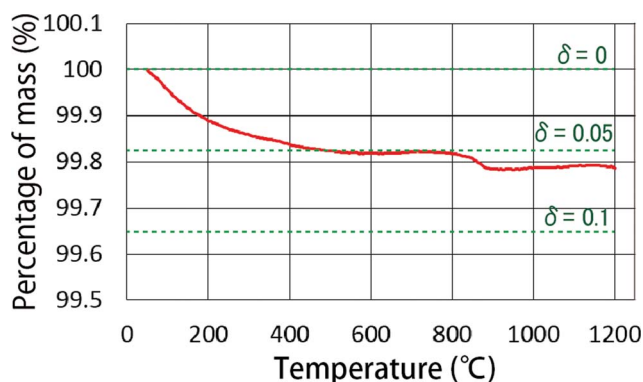


Fig. 3 TGA curve of Nd_{0.9}Sr_{0.1}BaInO_{3.95- δ} measured in Ar. This figure shows the second cycle (first and third cycles are shown in the ESI†). The green dash lines indicate the δ of Nd_{0.9}Sr_{0.1}BaInO_{3.95- δ} . The weight loss from 50 to 800 °C was 0.18 wt%, which corresponds to the increase in the oxygen vacancy content $\delta = +0.05$.



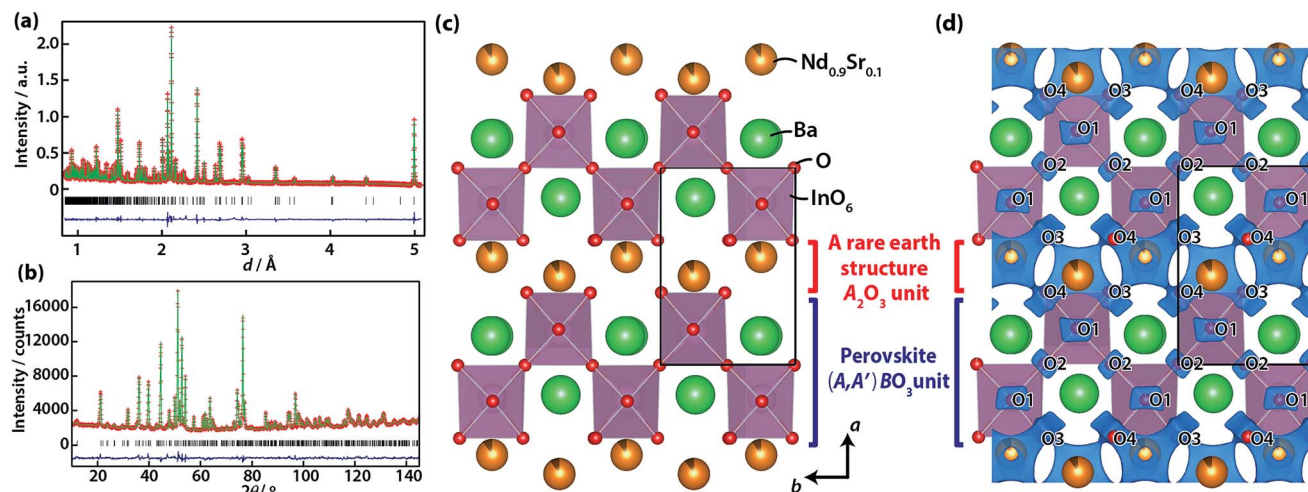


Fig. 4 Rietveld patterns for NPD data of (a) $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ taken at 24 °C (iMATERIA) and of (b) $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.90}$ at 800 °C (HRPD), showing the experimental (red + marks), calculated (green solid line) and difference (blue lower line) plots. Black tick marks indicate the calculated Bragg peak positions. (c) Refined crystal structure of $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ at 24 °C viewed along the c -axis. The solid lines represent the unit cell. (d) Bond valence-based energy (BVE) landscape for an oxide ion with an isovalue at 1.6 eV in $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.90}$ at 800 °C. Here, A and A' are relatively large cations ((Nd,Sr) and Ba in this case) and B is a smaller cation (In in this case).

3DBVSMAPPER¹⁸ based on the crystal structure at 800 °C. The blue surfaces in Fig. 4d represent the isosurfaces where the BVE for an oxide ion is +1.6 eV. In this landscape, the most stable position (at O4) was set to 0 eV. BVE isosurfaces around O1 and O2 sites are localized, while those around O3 and O4 sites spread in the A rare earth structure A_2O_3 ((Nd,Sr) $_2O_3$) unit and are connected with each other along both the b - and c -axes. The lowest energy path for oxide-ion conduction in $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ was found to be along the b -axis with an energy barrier of 1.42 eV. The energy barriers of the path along the a - and c -axes were calculated to be 2.72 and 1.47 eV for $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$. The paths along the b - and c -axes have similar energy barriers and the path along the a -axis has significantly higher energy barriers than the others. Thus, the oxide-ion conduction in $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ would be two dimensional.

BVE barriers of $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ have lower values than those of NdBaInO_4 along the oxide-ion diffusion paths. The energy barriers along the a -, b - and c -axes calculated based on the crystal structures at 24 °C are 1.47, 2.88, and 1.69 eV for $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ and 1.72, 3.95, and 2.01 eV for NdBaInO_4 . These results are consistent with the experimental data that showed that $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ has a lower activation energy of oxide-ion diffusion than NdBaInO_4 . The highest BVE point along the possible oxide-ion diffusion path is surrounded by two (Nd or (Nd,Sr)) and one Ba cations, which forms a cation triangle bottleneck. The areas of the triangles were calculated to be 6.889(5) Å² for NdBaInO_4 and 6.911(3) Å² for $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$. Thus, the substitution of Nd with Sr increases this bottleneck area, and hence, lowers the activation energy of oxide-ion conduction.

Conclusions

The oxide-ion conductivity has been increased and the activation energy of oxide-ion conduction has been lowered by the

substitution of Nd with Sr cations in NdBaInO_4 . $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ showed the highest electrical conductivity among $\text{Nd}_{1-x}\text{Sr}_x\text{BaInO}_{4-x/2}$ ($x = 0.0, 0.1, 0.2$ and 0.3). The oxide-ion conductivity σ_{ion} of $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ was $7.7 \times 10^{-4} \text{ S cm}^{-1}$ at 858 °C, which is higher than that of NdBaInO_4 ($\sigma_{\text{ion}} = 3.6 \times 10^{-5} \text{ S cm}^{-1}$ at 858 °C). The crystal structure of $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ has been analysed, and we have confirmed that Sr exists at the Nd site. $\text{Nd}_{0.9}\text{Sr}_{0.1}\text{BaInO}_{3.95}$ contains oxygen vacancies, which were not observed for NdBaInO_4 at room temperature. Thus, the increase of the oxide-ion conductivity is mainly attributed to the increase of the carrier concentration. BVE calculations indicated two-dimensional oxide-ion diffusion in the A_2O_3 ((Nd,Sr) $_2O_3$) unit on the bc -plane and a decrease of the energy barrier by the substitution of Nd with Sr cations.

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Notes and references

- (a) J. B. Goodenough, *Nature*, 2000, **404**, 821; (b) J. B. Goodenough, *Annu. Rev. Mater. Res.*, 2003, **33**, 91; (c) V. Thangadurai and W. Weppner, *Ionics*, 2006, **12**, 81; (d) D. J. L. Brett, A. Atkinson, N. P. Brandon and S. J. Skinner, *Chem. Soc. Rev.*, 2008, **37**, 1568; (e) L. Malavasi, C. A. J. Fisher and M. S. Islam, *Chem. Soc. Rev.*, 2010, **39**, 4370; (f) S. Y. Istomin and E. V. Antipov, *Russ. Chem. Rev.*, 2013, **82**, 686; (g) A. B. Muñoz-García, A. M. Ritzmann, M. Pavone, J. A. Keith and E. A. Carter, *Acc. Chem. Res.*, 2014, **47**, 3340.
- (a) J. C. Boivin and G. Mairesse, *Chem. Mater.*, 1998, **10**, 2870; (b) J. A. Kilner and M. Burriel, *Annu. Rev. Mater. Res.*, 2014, **44**, 365.
- (a) M. Mogensen, D. Lybye, N. Bonanos, P. V. Hendriksen and F. W. Poulsen, *Solid State Ionics*, 2004, **174**, 279; (b) M. Yashima, *Solid State Ionics*, 2008, **179**, 797.
- (a) A. S. Bhalla, R. Guo and R. Roy, *Mater. Res. Innovations*, 2000, **4**, 3; (b) R. E. Schaak and T. E. Mallouk, *Chem. Mater.*, 2002, **14**, 1455; (c) S. Stølen, E. Bakken and C. E. Mohn, *Phys. Chem. Chem. Phys.*, 2006, **8**, 428; (d) M. Yashima, *J. Ceram. Soc. Jpn.*, 2009, **117**, 1055.
- (a) V. V. Kharton, A. P. Viskup, E. N. Naumovkh and F. M. B. Marques, *J. Mater. Chem.*, 1999, **9**, 2623; (b) S. Miyoshi, T. Furuno, O. Sangoanruang, H. Matsumoto and T. Ishihara, *J. Electrochem. Soc.*, 2007, **154**, B57; (c) T. Ishihara, K. Nakashima, S. Okada, M. Enoki and H. Matsumoto, *Solid State Ionics*, 2008, **179**, 1367; (d) M. Yashima, M. Enoki, T. Wakita, R. Ali, Y. Matsushita, F. Izumi and T. Ishihara, *J. Am. Chem. Soc.*, 2008, **130**, 2762; (e) M. Yashima, N. Sirikanda and T. Ishihara, *J. Am. Chem. Soc.*, 2010, **132**, 2379; (f) M. Yashima, H. Yamada, S. Nuansaeng and T. Ishihara, *Chem. Mater.*, 2012, **24**, 4100; (g) K. Kawamura, M. Yashima, K. Fujii, K. Omoto, K. Hibino, S. Yamada, J. R. Hester, M. Avdeev, P. Miao, S. Torii and T. Kamiyama, *Inorg. Chem.*, 2015, **54**, 3896.
- X. Kuang, M. A. Green, H. Niu, P. Zajdel, C. Dickson, J. B. Claridge, L. Jantsky and M. J. Rosseinsky, *Nat. Mater.*, 2008, **7**, 498.
- (a) S. Nakayama and M. Sakamoto, *J. Eur. Ceram. Soc.*, 1998, **18**, 1413; (b) M. Higuchi, Y. Masubuchi, S. Nakayama, S. Kikkawa and K. Kodaira, *Solid State Ionics*, 2004, **174**, 73; (c) R. Ali, M. Yashima, Y. Matsushita, H. Yoshioka, K. Ohoyama and F. Izumi, *Chem. Mater.*, 2008, **20**, 5203.
- K. Fujii, Y. Esaki, K. Omoto, M. Yashima, A. Hoshikawa, T. Ishigaki and J. R. Hester, *Chem. Mater.*, 2014, **26**, 2488.
- http://www.spring8.or.jp/wkg/BL19B2/instrument/lang-en/INS-0000000300/instrument_summary_view.
- T. Ishigaki, A. Hoshikawa, M. Yonemura, T. Morishima, T. Kamiyama, R. Oishi, T. Sakuma, Y. Tomota, M. Arai, M. Hayashi, K. Ebata, Y. Takano, H. Asano, Y. Takano and T. Kasao, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 2009, **600**, 189.
- <http://hanaro.kaeri.re.kr:444/NB/sub02/sub02.do>.
- F. Izumi and K. Momma, *Solid State Phenom.*, 2007, **130**, 15.
- (a) R. Oishi, M. Yonemura, Y. Nishimaki, S. Torii, A. Hoshikawa, T. Ishigaki, T. Morishima, K. Mori and T. Kamiyama, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 2009, **600**, 94; (b) R. Oishi-Tomiyasu, M. Yonemura, T. Morishima, A. Hoshikawa, S. Torii, T. Ishigaki and T. Kamiyama, *J. Appl. Crystallogr.*, 2012, **45**, 299.
- I. Yasuda and M. Hishinuma, *Electrochemistry*, 2000, **68**, 526.
- R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.*, 1976, **32**, 751.
- R. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1991, **47**, 192.
- (a) S. Adams, *Solid State Ionics*, 2000, **136**, 1351; (b) S. Adams, *Struct. Bonding*, 2014, **158**, 91; (c) M. Avdeev, M. Sale, S. Adams and R. P. Rao, *Solid State Ionics*, 2011, **225**, 43.
- (a) M. Sale and M. Avdeev, *J. Appl. Crystallogr.*, 2012, **45**, 1054; (b) M. Yashima, N. Kubo, K. Omoto, H. Fujimori, K. Fujii and K. Ohoyama, *J. Phys. Chem. C*, 2014, **118**, 5180; (c) M. Yashima, T. Sekikawa, D. Sato, H. Nakano and K. Omoto, *Cryst. Growth Des.*, 2013, **13**, 829; (d) M. Yashima, Invited Review: Some recent developments in the atomic-scale characterization of structural and transport properties of ceria-based catalysts and ionic conductors, *Catal. Today*, 2015, DOI: 10.1016/j.cattod.2015.03.034, in press.

