Oxide-ion conduction in the Dion–Jacobson phase CsBi$_2$Ti$_2$NbO$_{10-\delta}$

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Oxide-ion conductors have found applications in various electrochemical devices, such as solid-oxide fuel cells, gas sensors, and separation membranes. Dion–Jacobson phases are known for their rich magnetic and electrical properties; however, there have been no reports on oxide-ion conduction in this family of materials. Here, for the first time to the best of our knowledge, we show the observation of fast oxygen anionic conducting behavior in CsBi$_2$Ti$_2$NbO$_{10-\delta}$. The bulk ionic conductivity of this Dion–Jacobson phase is $8.9 \times 10^{-2}$ S cm$^{-1}$ at 1073 K, a level that is higher than that of the conventional yttria-stabilized zirconia. The oxygen ion transport is attributable to the large anisotropic thermal motions of oxygen atoms, the presence of oxygen vacancies, and the formation of oxide-ion conducting layers in the crystal structure. The present finding of high oxide-ion conductivity in rare-earth-free CsBi$_2$Ti$_2$NbO$_{10-\delta}$ suggests the potential of Dion–Jacobson phases as a platform to identify superior oxide-ion conductors.
Oxide-ion conductors have attracted much attention because of their extensive applications, including in solid-oxide fuel cells, gas sensors, oxygen separation membranes, and catalysts\(^1\)–\(^9\). Due to the interaction of oxide ions with the cation network, high oxide-ion conductivities have been achieved in a limited number of structure families; for example, the fluorite-type, perovskite-type, melilite-type, and apatite-type structures\(^10\)–\(^17\). Since the limited structure families restrict further development in chemistry and solid-state ionics, the discovery of oxide-ion conductors with new crystal structures is of vital importance for the development of their applications. Various layered perovskites such as BIMEVOX\(^18\)–\(^21\), the Aurivillius phase\(^22\)–\(^25\), the Ruddlesden–Popper phase\(^26\)–\(^29\), the double perovskites\(^30\)–\(^32\), the brownmillerites\(^33\),\(^34\), the hexagonal perovskite derivative (Ba\(_2\)MoNbO\(_8\))\(^35\)–\(^37\), and the BaNdInO\(_4\)-based oxides\(^38\)–\(^40\) were reported to exhibit high oxide-ion conductivities. The Dion–Jacobson phase is an \(A'/A\) cation-ordered layered perovskite with a general formula of \(A'[A_{n-1}B_{n}O_{3n+1}]\) \((A' = \text{Cs, Rb, Li, Ag}; A = \text{La, Ca, Sr, Bi}; B = \text{Ti, Nb, Ta, etc.})\), where \(n\) denotes the number of the BO\(_6\) octahedral layers, and the \(A'\) cation separates the \(A_{n-1}B_{n}O_{3n+1}\) perovskite-like layers\(^41\)–\(^42\). Thus, oxide-ion conduction can be expected in the Dion–Jacobson phases. Numerous studies have been conducted on the electrical properties of the Dion–Jacobson phases, such as ferroelectricity\(^43\), proton\(^44\),\(^45\), lithium-ion\(^46\),\(^47\), sodium-ion\(^47\),\(^48\), and mixed proton–electron conduction\(^49\). However, there are no reports on oxide-ion conduction in the Dion–Jacobson phases. Herein, we report oxide-ion conduction in the Dion–Jacobson phase for the first time.

Here, we have screened 69 Dion–Jacobson phases using available crystallographic data and the bond-valence method (see the details in Supplementary Methods, Supplementary Fig. 1 and Supplementary Table 1\(^12\),\(^13\),\(^16\),\(^17\),\(^37\),\(^38\),\(^40\),\(^50\)–\(^53\)). The chemical composition of CsBi\(_2\)Ti\(_2\)NbO\(_{10}\) is selected because the bond-valence-based energy barrier for the oxide-ion migration, \(E_b\), is relatively low \((E_b = 0.5 \text{ eV})\) and CsBi\(_2\)Ti\(_2\)NbO\(_{10}\) does not contain expensive rare-earth elements. Surprisingly, it is found that the bulk conductivities \((\sigma_b)\) of the Dion–Jacobson phase of CsBi\(_2\)Ti\(_2\)NbO\(_{10}\) are as high as \(8.9 \times 10^{-2} \text{ S cm}^{-1}\) at 1073 K and \(1.5 \times 10^{-2} \text{ S cm}^{-1}\) at 873 K, which are higher than those of the conventional yttria-stabilized zirconia (YSZ). In consideration of the wide compositional space in Dion–Jacobson phases \(A'[A_{n-1}B_{n}O_{3n+1}]\) (where \(A' = \text{Cs, Rb, Li, H}; A = \text{La, Ca, Sr, Bi}; B = \text{Ti, Nb, Ta, etc.}\)), and \(n\) ranges from 2 to 6, and examples are presented in Supplementary Table 1), the present discovery provides new possibilities in the chemistry of oxide-ion conductors.

**Results**

**Phase transition and oxygen content of CsBi\(_2\)Ti\(_2\)NbO\(_{10}\).** CsBi\(_2\)Ti\(_2\)NbO\(_{10}\) was synthesized by the solid-state reactions. The Rietveld refinements of the synchrotron X-ray diffraction data taken in static air and neutron-diffraction data obtained in vacuum were successfully performed using a single orthorhombic \(I\text{ma}2\) structure at 297–813 K and a single tetragonal \(P4/nmm\) structure at 833–1073 K on heating (Fig. 1a, Supplementary Figs. 2, 3a, 4a, 5, and Supplementary Tables 2 and 3). The 002 and 020 peaks and 602 and 620 ones of the orthorhombic phase approached each other and merged at a temperature between 813 and 833 K on heating (Supplementary Fig. 4a). The \(b\)- and \(c\)-axis lengths of the orthorhombic phase continuously approached each other, leading to thermal expansion anomalies (Supplementary Fig. 6), and coincided at a temperature between 813 and 833 K on heating (Fig. 1a and Supplementary Fig. 3b). These results indicate that the orthorhombic-to-tetragonal (o-t) phase transition occurred at a temperature between 813 and 833 K on heating, which is consistent with the literature\(^13\). The reversible t-o transition was observed at a temperature between 793 and 813 K on cooling (Supplementary Fig. 4b), exhibiting a hysteresis of about 20 K. In addition, the reduced lattice volume of CsBi\(_2\)Ti\(_2\)NbO\(_{10}\) discontinuously decreased between the orthorhombic and tetragonal phases (the lattice volume change is \(-0.042\) \((5%)\) (Fig. 1b). The hysteresis and discontinuous decrease indicate that the o-t phase transition is first order. It was found that the o-t transition was accompanied by 0.32 wt% weight loss on heating, as shown in the thermogravimetric (TG) results (black line in Fig. 1c). The weight loss was caused by an increase in the oxygen vacancy concentration (blue squares in Fig. 1c). The presence of oxygen vacancies \((\delta)\) in the high-temperature tetragonal phase of CsBi\(_2\)Ti\(_2\)NbO\(_{10}\) was confirmed by both the oxygen occupancy factors refined using variable temperature neutron-diffraction data and oxygen contents estimated by the

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**Fig. 1 Temperature dependencies of lattice parameters, oxygen content, and conductivities.** Lattice parameters (a) and reduced lattice volume (b) of CsBi\(_2\)Ti\(_2\)NbO\(_{10}\) which were refined using synchrotron X-ray powder diffraction data measured in situ at high temperatures in static air on heating. The subscripts \(o\) and \(t\) denote orthorhombic and tetragonal, respectively. (c) Oxygen contents of CsBi\(_2\)Ti\(_2\)NbO\(_{10}\) on heating, which were obtained by thermogravimetric (TG) analysis in dry air (black line) and calculated from occupancy factors refined using in situ neutron-diffraction (ND) data in vacuum (blue marks). (d) Bulk electrical conductivity \(\sigma_b\) and grain boundary conductivity \(\sigma_{gb}\) of CsBi\(_2\)Ti\(_2\)NbO\(_{10}\) in dry air on heating.
TG analysis (Fig. 1c). The oxygen vacancies are responsible for the high oxide-ion conductivities described later in this paper.

**Oxide-ion conduction of CsBi$_2$Ti$_2$NbO$_{10}$−δ.** The electrical conductivities of CsBi$_2$Ti$_2$NbO$_{10}$−δ were measured from 573 to 1173 K using AC and DC methods. Figure 2 shows the typical impedance spectra of CsBi$_2$Ti$_2$NbO$_{10}$−δ. The bulk and grain boundary responses were observed (respective capacitance values of $C_b ≈ 0.7 \times 10^{-12}$ F cm$^{-1}$ and $C_{gb} ≈ 7.0 \times 10^{-9}$ F cm$^{-1}$ at 573 K in dry air (Fig. 2a)). The bulk conductivities ($\sigma_b$) were independent of the oxygen partial pressure (dry O$_2$, dry air, and dry N$_2$; Fig. 2b), which indicates ionic conduction in CsBi$_2$Ti$_2$NbO$_{10}$−δ. Figure 1d shows the temperature dependence of the $\sigma_b$ and grain boundary conductivities ($\sigma_{gb}$) of CsBi$_2$Ti$_2$NbO$_{10}$−δ on heating. The $\sigma_b$ abruptly increased between 673 and 873 K on heating, which was attributed to the increase in the carrier (oxygen vacancy) concentration (Fig. 1c) and the o-to-t phase transition (Fig. 1a, b). The total DC electrical conductivity also exhibited an abrupt increase around the o-to-t transition point on heating (Supplementary Fig. 8).

Oxygen concentration cell measurements were performed to determine the oxide-ion transport number ($\nu_{fo}$). The $\nu_{fo}$ values were 1.00–0.98 between 873 and 1173 K in air/O$_2$, 0.97–0.95 between 873 and 1173 K in air/N$_2$, and 0.87 at 873 K in air/5% H$_2$ in N$_2$ (Fig. 3a). The total DC electrical conductivity ($\sigma_{fo}$) at 973 K was almost independent of the oxygen partial pressure $P$(O$_2$) between $P$(O$_2$) = 2.0 × 10$^{-22}$ and 1 atm (Fig. 3b). At the $P$(O$_2$) < 2.0 × 10$^{-22}$ region, an n-type electronic contribution to the total conductivity was observed, which is consistent with the relatively low $\nu_{fo}$ in air/5% H$_2$ in N$_2$. The electronic conduction is attributable to the formation of oxygen vacancies and electronic defects accompanied by reduction of Ti$^{4+}$ and/or Nb$^{5+}$ cations in the reducing atmosphere. No significant proton conduction was observed between 873 and 1173 K because the conductivities measured in dry air (H$_2$O partial pressure, $P$(H$_2$O) < 1.8 × 10$^{-4}$ atm) agreed well with those in wet air ($P$(H$_2$O) = 2.3 × 10$^{-2}$ atm) (Fig. 3c). These results indicate that the oxide ion is the dominant carrier and that CsBi$_2$Ti$_2$NbO$_{10}$−δ is an oxide-ion conductor. No change was observed in the X-ray powder diffraction patterns before and after the impedance spectroscopy and oxygen concentration cell measurements (Supplementary Fig. 9), which demonstrated the high phase stability of CsBi$_2$Ti$_2$NbO$_{10}$−δ at high temperatures and different $P$(O$_2$) values. The $\sigma_b$ of CsBi$_2$Ti$_2$NbO$_{10}$−δ was higher than that of YSZ and comparable with those of the best oxide-ion conductors (Fig. 3d). This indicates the high potential of the Dion–Jacobson phase CsBi$_2$Ti$_2$NbO$_{10}$−δ as a basic composition for oxide-ion conductors.

**Structural origin of the high oxide-ion conductivity of CsBi$_2$-Ti$_2$NbO$_{10}$−δ.** Next, we discuss the structural origin of the high oxide-ion conductivity using the crystal structure of tetragonal CsBi$_2$Ti$_2$NbO$_{9.80(2)}$ at 973 K (Fig. 4). This structure was obtained by the Rietveld refinement of the neutron-diffraction data measured in situ at 973 K with a super-high-resolution diffractometer, SuperHRPD$^{58,59}$. The tetragonal structure of CsBi$_2$Ti$_2$NbO$_{10}$−δ consists of an oxide-ion conducting inner perovskite Bi-(Ti$_{0.804}$Nb$_{0.196}$)O$_{3−δ}$ layer, two outer perovskite Bi-(Ti$_{0.598}$Nb$_{0.402}$)O$_{3−δ}$ layers, and an insulating CsO$_{1−δ}$ rock-salt layer (Fig. 4a and Supplementary Fig. 5). The refined equivalent isotropic atomic displacement parameters of the equatorial oxygen atom, O$_1$, ($U_{eq}(O1)$) and apical oxygen, O$_2$, ($U_{eq}(O2)$) in the oxide-ion conducting inner perovskite layer were much higher than those of the equatorial O3 and apical O4 atoms in the outer perovskite layers ($U_{eq}(O1) = 0.0879(9)$ Å$^2$, $U_{eq}(O2) = 0.0734(8)$ Å$^2$; $U_{eq}(O3) = 0.0441(5)$ Å$^2$, $U_{eq}(O4) = 0.0382(5)$ Å$^2$). The higher atomic displacement parameters of O1 and O2 were consistent with the results in the literature$^{43}$ and from the synchrotron X-ray diffraction data (Supplementary Table 4).

Therefore, the O1 and O2 atoms in the inner oxide-ion conducting perovskite layer exhibited larger thermal motions than the O3 and O4 atoms in the outer perovskite layer. In particular, the anisotropic atomic displacement parameters ($U_{ij}$) of the O1 and O2 atoms were extremely large: $U_{11}(O1) = 0.0901(19)$ Å$^2$, $U_{33}(O1) = 0.1573(3)$ Å$^2$, and $U_{11}(O2) = 0.1010(11)$ Å$^2$ (see others in Supplementary Table 3). The large $U_{33}(O1)$ and $U_{11}(O2)$ values indicate high anisotropic thermal motions along the $c$ and $a$ axes, respectively, which suggests the O1–O2 oxide-ion diffusion (blue-dotted arrows in Fig. 4a). Similarly, the large $U_{11}(O1)$ means that there are high thermal motions along the $a$ and $b$ axes, indicating the O1–O1 oxide-ion diffusion (the red-dotted arrows in Fig. 4d). The isosurfaces of the neutron scattering length density obtained by the maximum-entropy method (MEM)$^{11,12,14,15,31,37,60,61}$ (yellow isosurfaces in Fig. 4b, e) and bond-valence-based energy landscapes (BVELs, blue isosurfaces in Supplementary Fig. 10) also showed anisotropic thermal motions of O1 and O2 atoms. The O1–O2 and O1–O1 oxide-ion diffusion paths were clearly observed in the BVELs (dotted arrows in Fig. 4c, f). In addition, the O2–O3 diffusion path was observed in the BVELs (the black dotted arrows in Fig. 4c). These results indicate two-dimensional (2D) oxide-ion diffusion along the edges of the Bi(Ti$_{0.804}$Nb$_{0.196}$)O$_{3−δ}$ octahedron in the oxide-ion conducting inner perovskite layer. We attribute the high oxide-ion conductivity of CsBi$_2$Ti$_2$NbO$_{10}$−δ not only to the existence of oxygen vacancies but also to the 2D oxide-ion diffusion and the extremely high $U_{eq}(O1)$, $U_{eq}(O2)$, $U_{11}(O1)$, $U_{33}(O1)$, and
Synthesis and characterization of CsBi$_2$Ti$_2$NbO$_{10.5–δ}$

Cs$_2$Bi$_2$Ti$_2$NbO$_{10.5–δ}$ was synthesized by the solid-state-reaction method. High-purity (>99.9%) Cs$_2$CO$_3$, Bi$_2$O$_3$, TiO$_2$, and Nb$_2$O$_5$ (with molar ratios of Cs, Bi, Ti, and Nb of 1:3:2.0:1.0) were mixed in an agate mortar and then ground to a fine powder. The mixture was then pressed into pellets and sintered at 1100°C for 24 h in an air atmosphere. The pellets were then ground into fine powders, pressed again, and sintered at 1100°C for 24 h in an air atmosphere.

Discussion

Here, we propose a new concept: large bottlenecks for oxide-ion migration by the large size of Cs$^+$ and Bi$^{3+}$ displacement. The bottlenecks of CsBi$_2$Ti$_2$NbO$_{10.5–δ}$ are the Bi–Bi–Ti triangles (the yellow and pink triangles in Fig. 5a–c). The large bottlenecks of CsBi$_2$Ti$_2$NbO$_{10.5–δ}$ can be explained using the new concept, as described below. Cs$^+$ expands the Bi–Bi distance along the $b$ axis (the orange arrows in Fig. 5a) due to the occupaional ordering of the large Cs$^+$ and small Bi$^{3+}$ cations. Bi$^{3+}$ is displaced along the $c$ axis apart from the Ti/Nb/O1 layer (the blue arrows in Fig. 5a), by electrostatic forces (Supplementary Note 1 and Supplementary Fig. 11). The Bi$^{3+}$ displacement increases the Bi–Bi distance along the $c$ axis. The increase in the Bi–Bi distances along both the $b$ and $c$ axes leads to large bottlenecks for the O1–O2 (the yellow areas) and O1–O1 (the pink areas) oxide-ion diffusion (Fig. 5b–d). Since the bottleneck of CsBi$_2$Ti$_2$NbO$_{10.5–δ}$ is the Bi–Bi–Ti triangle, it is interesting to compare the bottleneck sizes (critical radii) and oxide-ion conductivities of CsBi$_2$Ti$_2$NbO$_{10.5–δ}$ with those of layered perovskites with Bi–Bi–Ti bottleneck triangles, BaBi$_4$Ti$_4$O$_{15}$, Bi$_2$Ti$_3$O$_{12}$, and Bi$_2$Sr$_2$TiNb$_2$O$_{12}$. The oxide-ion conductivity of CsBi$_2$Ti$_2$NbO$_{10.5–δ}$ was much higher than those of these materials, which is attributable to the larger bottlenecks (Supplementary Table 7).

In summary, we have discovered the first example of the Dion–Jacobson-type oxide-ion conductor (CsBi$_2$Ti$_2$NbO$_{10.5–δ}$). It was found that CsBi$_2$Ti$_2$NbO$_{10.5–δ}$ exhibits a high $σ_0$ of $8.9 \times 10^{-2}$ S cm$^{-1}$ at 1073 K and high phase stability at high temperatures and different $P(O_2)$ values. The conductivity abruptly increased between 673 and 873 K on heating, which is ascribed to the increase in oxygen vacancy concentration and the o-to-t phase transition. The high oxide-ion conductivities of Cs/Bi-cation-ordered CsBi$_2$Ti$_2$NbO$_{10.5–δ}$ are attributable to (i) the large anisotropic thermal motions of the oxygen atoms in the inner oxide-ion conducting perovskite layer, (ii) the 2D O1–O2 and O1–O1 oxide-ion diffusion, (iii) the existence of oxygen vacancies and (iv) the large bottlenecks. We have also proposed a concept: large bottlenecks for oxide-ion migration by large size of Cs$^+$ and Bi$^{3+}$ displacement. The oxide-ion conductivity is expected to be improved by doping and/or modification of the chemical composition of the basic material CsBi$_2$Ti$_2$NbO$_{10.5–δ}$. The present finding of high oxide-ion conductivities in the new structure family, Dion–Jacobson-type CsBi$_2$Ti$_2$NbO$_{10.5–δ}$ and the concept would facilitate the design of novel oxide-ion conductors based on the Dion–Jacobson phases.
Fig. 4 Crystal structure and oxide-ion diffusion pathway of tetragonal CsBi₂Ti₂NbO₉.₈₀(2) at 973 K. a, d Refined crystal structure of CsBi₂Ti₂NbO₉.₈₀(2) at 973 K, which was obtained by Rietveld analysis of in situ neutron-diffraction data. b, e Yellow isosurfaces of the neutron scattering length density at 1.0 fm Å⁻³ with the structure (973 K). c, f Blue isosurfaces of the bond-valence-based energy for an oxide ion at 0.6 eV for the structure at 973 K. Blue, red, and black dotted lines with arrows denote the possible O₁–O₂, O₁–O₁, and O₂–O₃ diffusion pathways of oxide ion, respectively. The solid lines with arrows in a and d stand for the directions of anisotropic thermal motions of O₁ and O₂ oxygen atoms. Thermal ellipsoids are drawn at the 50% probability level. Regions of a–c −1/2 ≤ x, y, z ≤ 1/2 and of d–f −1/2 ≤ x, y ≤ 3/2, 0 ≤ z ≤ 0.1.

Fig. 5 New concept of enlarged bottlenecks for oxide-ion migration by large size of Cs⁺ and Bi³⁺ displacement. a New concept of enlarged bottlenecks for oxide-ion migration created by large size of Cs⁺ and Bi³⁺ displacement in Dion–Jacobson-type Cs/Bi-cation-ordered CsBi₂Ti₂NbO₁₀₋δ (−1/2 ≤ x, y, z ≤ 1/2). Yellow and pink Bi–Bi–Ti triangles stand for the areas of bottlenecks for O₁–O₂ and O₁–O₁ oxide-ion migration, respectively. Oxygen atoms are omitted for simplicity in a. b Refined structure and Bi–Bi–Ti/Nb₁ triangle bottleneck of CsBi₂Ti₂NbO₉.₈₀(2) at 973 K (−1/2 ≤ x, y, z ≤ 1/2). A part of the structure (c) and corresponding bond-valence-based energy landscape (BVEL) with the isosurface at 0.6 eV (d), showing the O₁–O₂ and O₁–O₁ oxide-ion diffusion paths. Blue and red-dotted lines with arrows denote the possible O₁–O₂ and O₁–O₁ diffusion pathways of oxide ion, respectively.
were mixed and ground using an agate mortar and a pestle for 30 min as ethanol slurries, where an excess amount of Cs$_2$CO$_3$ (30 mol%) was added to compensate for the diffusion of the volatilisation of the Cs species during sintering. The mixture was dried on a hot plate (with a setting temperature of 373 K) and then ground into powder in the mortar for 30 min. This mixing, drying, and grinding processes were repeated a few times. The obtained mixtures were uniaxially pressed into pellets at about 100 MPa and subsequently sintered in static air at 1173 K for 12 h at heating and cooling rates of 5 K min$^{-1}$. The grinding, pressing, and sintering processes were repeated a few times until a single phase of Cs$_{2-x}$Bi$_2$Ti$_2$Nb$_{0.8}$O$_{10}$-$\delta$ was obtained. Parts of the sintered pellets were crushed and ground into powders to carry out X-ray powder diffraction, synchrotron X-ray powder diffraction, transmission electron microscopy (TEM, H-9000, Hitachi), and scanning electron microscopy (SEM, Hitachi S-4800) analyses.

The existing phase of Cs$_{2-x}$Bi$_2$Ti$_2$Nb$_{0.8}$O$_{10}$-$\delta$ was examined with an X-ray powder diffractometer (RINT-2500, Cu Kα radiation, 2θ range: 5–100°, Step interval: 0.02°). The AAS and ICP-OES results indicated that the cation molar ratios of Cs$_2$Bi$_2$Ti$_2$Nb$_{0.8}$O$_{10}$-$\delta$ were Cs:Bi:Ti:Nb = 1:2:1:2, which is consistent with the nominal composition. TG analysis was carried out from 297 to 1073 K using a Bruker-AXS 2020SA instrument at heating and cooling rates of 1 K min$^{-1}$. The measurements between 473 and 1073 K were repeated three times to negate the influence of absorbed species, such as water, and also to confirm the reproducibility. The TG data on the third heating in dry air were plotted in Fig. 1c. The TG data in dry air agreed well with those in static air. The sample did not decompose during the TG measurements, which was confirmed by X-ray powder diffraction measurements of the sample after the TG measurements.

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Author contributions
M.Y. and W.Z. designed research. W.Z., K.F., M.H., and T.K. measured the neutron data. W.Z. prepared the samples and measured the X-ray diffraction data, electrical conductivity, TG data and transport number. E.N. advised W.Z. in the oxygen concentration cell measurements. W.Z. analyzed the data and made figures and tables. W.Z. and M.Y. wrote and edited the manuscript and response to the referees’ comments. All the authors read the manuscript and gave comments. Funding acquisition and supervision: M.Y. M.Y. created the new concept with W.Z.

Competing interests
The authors declare no competing interests.

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