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Title(English)	Oxide-Ion Conduction in the Dion–Jacobson-Type Layered Perovskites
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論文審査の要旨及び審査員

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論文審査の要旨（2000 字程度）

Materials exhibiting high oxide-ion conductivities have numerous applications in various electrochemical devices, such as solid-oxide fuel cells (SOFCs), separation membranes and gas sensors. Since the high oxide-ion conductivities are achieved in a limited number of structure families, the discovery of oxide-ion conductors with new crystal structures is of vital importance for the development of their applications. In this doctoral thesis, the Dion–Jacobson-type layered perovskites have been found as a new structure family of oxide ion conductors, through the screening by bond valence-based-energy calculations, synthesis, electrochemical measurements, thermogravimetric analyses, and the crystal structure analyses using the high-temperature neutron and synchrotron X-ray diffraction data. $CsBi_2Ti_2NbO_{10-\delta}$ was found to be the first example of the Dion−Jacobson-type oxide-ion conductor where δ represents the oxygen-vacancy content. $CsBi_2Ti_2NbO_{10-\delta}$ showed higher bulk oxide-ion conductivities than those of other widely known oxide-ion conductors such as the conventional yttria-stabilized zirconia (YSZ) and $Na_{0.5}Bi_{0.5}TiO_3$. The oxide-ion conduction was also confirmed in other compositions of the Dion–Jacobson-type layered perovskites. The thesis, entitled “Oxide-Ion Conduction in the Dion–Jacobson-Type Layered Perovskites,” consists of the following four chapters.

In chapter 1, entitled “Introduction,” the background and purpose of this study were explained. First of all, the importance of the research of oxide-ion conductors was described. Secondary, previous researches on the oxide-ion conducting perovskite and perovskite related oxides in the literature were reviewed. Problems of the previous researches and unresolved issues were pointed out. The experimental and calculation methods used in this thesis were also introduced. Mother materials $CsBi_2Ti_2NbO_{10}$ and $CsR_2Ti_2NbO_{10}$ (R = rare earth) were selected, because the bond-valence-based energy barriers for the oxide-ion migration, E_b, were relatively low in the screening of 69 Dion–Jacobson-type layered perovskites.

In chapter 2, entitled “Dion–Jacobson-type $CsBi_2Ti_2NbO_{10}$-based Materials as Oxide-Ion Conductors,” the title compounds were synthesized by the solid-state-reaction method and the crystal structure of $CsBi_2Ti_2NbO_{10-\delta}$ was analyzed using high-temperature neutron and synchrotron X-ray diffraction data. The Rietveld refinements of $CsBi_2Ti_2NbO_{10-\delta}$ were successfully performed using a single orthorhombic *Ima*2 structure at 297–813 K and a single tetragonal *P*4/*mmm* structure at 833–1073 K on heating, showing an orthorhombic-to-tetragonal (o-to-t) phase transition. The presence of oxygen vacancies was confirmed from both the refined occupancy factors of oxygen atoms using variable temperature neutron-diffraction data and the weight loss observed by the thermogravimetric analysis. The existence of oxygen vacancies was responsible for the high oxide-ion conductivities of tetragonal $CsBi_2Ti_2NbO_{10-\delta}$. Electrical conductivities were measured by AC impedance spectroscopy method and by DC 4-probe method in flowing dry air, N_2 and O_2 gases, respectively. The bulk conductivity of $CsBi_2Ti_2NbO_{10-\delta}$ was 8.9×10^{-2} S cm^{-1} at 1073 K. The conductivity abruptly increased between 823 and 873 K on heating, which was attributed to the increase of oxygen vacancy concentration and the o-to-t phase transition. Oxygen concentration-cell measurements were performed to estimate the oxide-ion transport number t_{ion} in $CsBi_2Ti_2NbO_{10-\delta}$. The t_{ion} 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. The bond valence-based energy landscape and neutron scattering length density distribution were used to investigate possible oxide-ion migration paths. The results indicated two-dimensional oxide-ion migration paths along the edges of the octahedron in the oxide-ion conducting inner perovskite layer. A new concept "large bottlenecks for oxide-ion migration by large size of Cs^+ and Bi^{3+} displacement" was proposed to explain the high oxide-ion conductivity of the Dion–Jacobson-type layered perovskite $CsBi_2Ti_2NbO_{10-\delta}$. The oxide-ion conductivity was increased by partial aliovalent cation substitutions for the mother material $CsBi_2Ti_2NbO_{10-\delta}$.

In chapter 3, entitled "Dion–Jacobson-type $CsR_2Ti_2NbO_{10}$-based Materials as Oxide-Ion Conductors (R = Rare earth)," the title compounds were synthesized and their electrical conductivities were measured by DC 4-probe method. $CsLa_2Ti_2NbO_{10-\delta}$ was selected for further study because it showed highest electrical conductivity among the successfully synthesized $CsR_2Ti_2NbO_{10}$ compounds. The oxide-ion conductivity of $CsLa_2Ti_2NbO_{10-\delta}$ was 1.89×10^{-4} S cm^{-1} at 1273 K in air. The t_{ion} estimated using an oxygen concentration cell of $CsLa_2Ti_2NbO_{10-\delta}$ indicated that the dominant charge carrier in $CsLa_2Ti_2NbO_{10-\delta}$ was oxide ion. The Rietveld analyses of variable-temperature neutron and synchrotron X-ray diffraction data of $CsLa_2Ti_2NbO_{10-\delta}$ were successfully performed by the tetragonal *I*4/*mmm* Dion-Jacobson-type structure from room temperature to 1073 K, revealing no phase transition in this temperature range. The bond valence-based energy landscape was used to investigate possible oxide-ion migration path and energy barrier for oxide-ion migration. The landscape showed two-dimensional oxide-ion diffusion along the edges of octahedron in the perovskite layers of $CsLa_2Ti_2NbO_{10-\delta}$. The electrical conductivity was increased by doping for the mother material $CsLa_2Ti_2NbO_{10-\delta}$.

In chapter 4, entitled "Conclusion and Future Work," the results and discussion of this thesis were summarized. The conclusion and impact of this thesis were described. Some future works were proposed on the basis of the results presented in this doctoral thesis.

The present finding of the new structure family of oxide-ion conductors in this doctoral thesis would offer new routes for the design of novel oxide-ion conductors based on the Dion−Jacobson-type layered perovskites and then improve the developments in chemistry, physics, and materials science.