学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Synthesis, Crystal Structures, and Chloride-ion Conducting Properties of Oxychlorides with Open Borate Frameworks
（ホウ酸塩の開骨格構造を有する酸塩化物の合成と結晶構造及び塩化物イオン伝導特性）

Chloride-ion solid electrolytes have been widely investigated as the core components of membranes, gas sensors, and all-solid-state batteries with high energy densities. Several fast chloride-ion solid electrolytes operating at ambient-to-intermediate temperatures have been reported, ranging from inorganic metal chlorides and metal–organic compounds to complexes. However, these chlorides have the major drawback of being thermally and chemically unstable, and design strategies for chloride-ion conductors have not yet been developed compared with those for cation conducting solids, which restricts their practical applications. In contrast, a layered mixed-anion compound $La_{1-x}Ca_xOCl_{1-x}$ with a tetragonal matlockite-type structure possesses great structural stability against humidity and high temperature. Moreover, $La_{0.8}Ca_{0.2}OCl_{0.8}$ prepared via ball milling exhibited chloride-ion conductivity as high as 7×10^{-4} and 1×10^{-2} S cm^{-1} at 400 and 700 °C, respectively. However, making Cl^- transport dominant in mixed-anion sublattices, where the migration barrier for Cl^- ions tends to be higher than that for O^{2-} ions, remains a major challenge.

On the other hand, open borate frameworks are well known to exhibit a rich variety with 0D–3D dimensionality, which are mainly composed of triangular BO_3 and/or tetrahedral BO_4 units. Diverse open structures can be used to design ion migration pathways, and B–O covalent bonds can increase barriers to O^{2-} ions migration. Currently, compounds with open borate structures based on cationic conduction have been reported, including those with Li^+ and Na^+, but compounds based on Cl^- ions have not yet been reported. This study has explored new oxychloride compounds that show water insolubility and thermal stability, resulting in the discoveries of two types of compounds: $(Ca_{1-x}La_x)_2B_5O_9Cl_{1+2x}$ and $(La_{1-x}M_x)(BO_2)_2Cl_{1-x}$ (M = Ca, Sr) exhibit one-dimensional chloride-ion conduction and possible two-dimensional chloride-ion conduction, respectively. The synthesis, crystal structures, and chloride-ion conducting properties have been discussed.

Chapter 1 provides an overview of the research background, including the ion conductor principles and methods of conductivity calculation.

Chapter 2 mainly presents the experimental techniques used in this research.

Chapter 3 presents the investigation of La-doped $Ca_2B_5O_9Cl$, namely, $(Ca_{1-x}La_x)_2B_5O_9Cl_{1+2x}$, which crystallized in an orthorhombic symmetry with the space group of *Pnn*2. The crystal structure of $Ca_2B_5O_9Cl$ consists of $(BO_3)^{3-}$ triangles and $(BO_4)^{5-}$ tetrahedra. Two $(BO_3)^{3-}$ triangles and three $(BO_4)^{5-}$ tetrahedra are linked together by common vertexes to form $(B_5O_9)^{3-}$ open framework with tunnels filled with Ca^{2+} and Cl^- ions. In particular, the Cl^- ions are independently arranged along the c axis at a distance of 6.3500(3) Å between the nearest neighbour (NN) ions, which is much longer than those of fast chloride ion conductors. Therefore, the introduction of interstitial chloride ions is essential for facilitating Cl^- ion migration. Single crystal structure determination of a La-doped $Ca_2B_5O_9Cl$ with $x = 0.08$ revealed not only a substantial reduction in the

occupancy of the original Cl site but also the presence of interstitial chloride ions within the Cl^- ions channel, resulting in a decrease in the distances between the NN Cl^- ions to lower than 2.10 Å. The $(Ca_{1-x}La_x)_2B_5O_9Cl_{1+2x}$ (x = 0–0.15) solid solutions exhibited the highest conductivity of 1.32×10^{-4} S cm^{-1} at 700 °C when x = 0.05. First-principles molecular dynamics simulations indicated that the predominant chloride-ion conduction is attributed to cooperative diffusion of Cl^- ions through the interstitialcy mechanism.

Chapter 4 presents the investigation of Ca or Sr doped $La(BO_2)_2Cl$, namely, $(La_{1-x}M_x)(BO_2)_2Cl_{1-x}$ (M = Ca, Sr), which crystallizes in a triclinic symmetry with the space group of P–1. $La(BO_2)_2Cl$ consists of zigzag chains of corner-linked $(BO_3)^{3-}$ planar triangles running along the a axis. These one-dimensional chains are separated by La^{3+} ions in the ab plane and Cl^- ions along the c axis. In particular, the Cl^- ions are arranged in the ab plane at distances of 3.45–3.7 Å between the neighbouring ions in the intralayer, which is close to those of fast chloride ion conductors. Single crystal study of Ca/Sr-doped $La(BO_2)_2Cl$ with $x \sim 0.20$ revealed the presence of chloride ion vacancies rather than oxygen vacancies. The $(La_{1-x}M_x)(BO_2)_2Cl_{1-x}$ (M = Ca, Sr, x = 0–0.15) solid solutions exhibited the highest conductivity of 1.84×10^{-4} S cm^{-1} at 700 °C when M = Ca and x = 0.10, and 7.59×10^{-4} S cm^{-1} at 700 °C when M = Sr and x = 0.15, respectively. Notably, the ionic conductivity of the Sr-doped phase was greater than that of La-doped $Ca_2B_5O_9Cl$ over the measured temperature range. The enhanced conductivity suggests possible two-dimensional chloride-ion conduction through the vacancy mechanism.

Chapter 5 presents the overall conclusions and future prospects based on this body of work.