【Grant-in-Aid for Scientific Research (S)】

Creation of High Ion Conductors within the Norby Gap

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Purpose and Background of the Research

●Outline of the Research

Ionic crystals such as NaCl are solids and are composed of ions such as Na^+ and Cl^-. Some compounds exhibit fast ion conduction, even though the compounds are solids. In order to solve the energy, environmental, and information problems, it is necessary to develop high-performance fuel cells, batteries, sensors, catalysts, and so on. To achieve this, we need electrolyte materials that exhibit high electrical conductivity through fast migration of ions such as H^+ and O^{2-}. Namely, it is important to search for high ionic conductors (solid materials with low electrical resistance (= high ionic conductivity)). However, there are no solid materials that exhibit high ionic conductivity and high stability at intermediate temperatures of 200 to 500 °C, which are industrially important. A Norwegian scientist Professor Norby pointed out that when the horizontal axis is the temperature (its reciprocal) and the vertical axis is the ionic conductivity (its logarithm), there is a region where no ionic conductors exist (the so-called Norby gap) (**Figure 1**). Polymer and salt electrolytes are unstable at intermediate temperatures and also require precious metal catalysts. In general, ions cannot diffuse in metals and alloys. In contrast, many ceramic materials are stable at intermediate temperatures. There are numerous chemical compositions of ceramic systems where the formation phases are unknown. The purposes of this research project are (1) to establish a methodology/theory for exploring and discovering new ceramic materials that exhibit high ionic conductivity within the Norby gap at intermediate temperatures; (2) to discover new high ionic conductors; in addition, (3) to elucidate at the atomic level the reasons why ions can migrate in the new materials which we have discovered. Ceramic ionic conductors have been studied for many years, but most of the research has only been improvements of known materials. In this research project, we will design a new structural-type ceramic ion conductor based on the crystal structure (atomic arrangement of the crystal) (**Figure 2**).

The following four original strategies/methods and their combinations will be applied. (1) Screening of hundreds to thousands of known materials (their ionic conduction is unknown) using energy barriers for ion migration, which are simply calculated using interatomic distances and empirical parameters. (2) We will use parent materials with a large amount of vacancies (intrinsic vacancies). (3) We will investigate the ionic conduction of mixed anion compounds containing two or more anion species in a single phase. We expect the interstitialcy (kick-off, push-pull) mechanism for oxygen ion migration. (4) We will search for new materials in the unexplored structure field maps. We will actually synthesize new materials and use X-ray diffraction to study the atomic arrangement of the material. Then, we will measure the ionic conductivity and investigate the chemical stability. For materials with high conductivity, we will investigate their static and dynamic structures using experimental methods such as neutron scattering and spectroscopy, as well as computational methods such as first-principles molecular dynamics simulations, to elucidate why they exhibit fast ion conduction. Students and young researchers will also conduct research abroad.

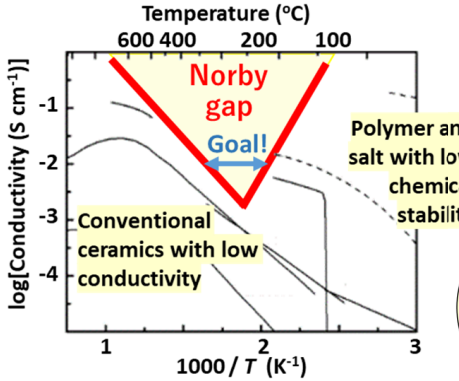

Figure 1. Goal of this project, Norby gap, and problems of conventional ion conductors

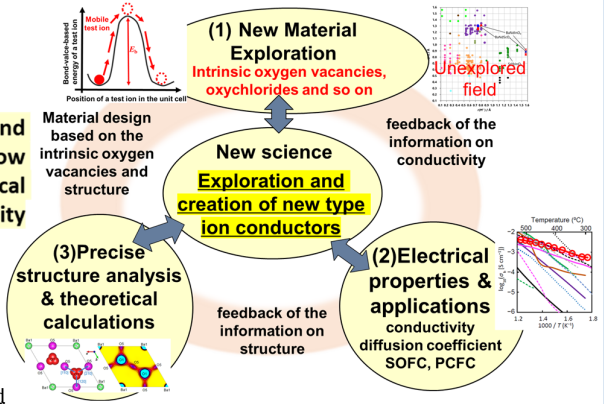

Figure 2. Outline, methods, and strategy of this project

Expected Research Achievements

Through the four strategies, we will achieve high ionic conductivity within the Norby gap in several materials. For this purpose, we will search for new materials. Hundreds of samples will be prepared by solid state reactions and so on. Our goals are very high (**Figure 1**). We will discover new materials with conductivity exceeding 10 mS/cm at intermediate temperatures. In our project, we will utilize the donor doping: a low valence cation such as Sc^{3+} will be replaced by a high valence cation (dopant) such as Mo^{6+}, thus, the effective charge is positive, suppressing proton trapping. We also aim to investigate the ionic conductivity of materials with large amounts of oxygen vacancies. Furthermore, we aim to discover new materials by searching for new oxygen ion conductors via the interstitialcy mechanism. The structures of the discovered high ion conductivitors will be precisely analyzed using not only X-ray diffraction but also multiple probes such as neutron diffraction. In addition to the experimental precise structural analysis (static average structure) at RT to high temperatures, we also investigate dynamic local structures through theoretical calculations based on quantum mechanics (first-principles molecular dynamics calculations) (**Figure 3**). Furthermore, the ion diffusion coefficient *D* will be directly investigated experimentally using secondary ion mass spectrometry (SIMS) (**Figure 4**), and the *D* values estimated from the results of ionic conductivity measurements will be compared with the *D* values obtained from first-principles molecular dynamics calculations (**Figure 5**).

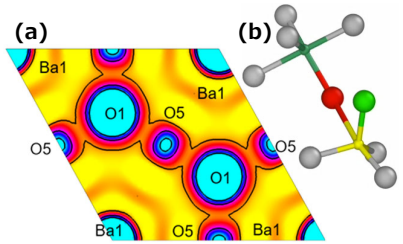

Figure 3. (a) Visualization of the oxide-ion diffusion paths from high-temperature neutron diffraction data and **(b)** the dimer from AIMD simulations (*Chem. Mater.* 2023).

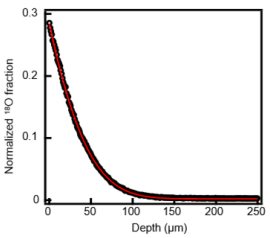

Figure 4. Oxygen diffusion coefficient measurements and depth profile in the SIMS experiments (*Nat. Commun.* 2021)

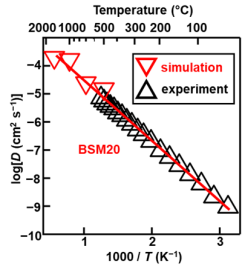

Figure 5. Experimental and theoretical proton diffusion coefficients from the electrical conductivity and TG measurements (△) and AIMD simulations (▽) (*Nat. Commun.* 2023)

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