

論文内容の要旨

論文題目

First-Principles Simulation of the Ionic Conduction in

Mixed Anion Compounds

(複合アニオン化合物における

イオン伝導の第一原理シミュレーション)

氏名 岡 真悠子

Solid-state ionic conductors are widely used as ionic sensors or electrolytes for fuel cells and secondary batteries. As the performance of such devices heavily relies on the ionic conductivity of these materials, and to expand the application fields of the devices, investigation of new ionic conductive materials is one of the most important issues in the chemical industry. Fluorite with composition of MX_2 is a typical mother structure of ionic conductors. However, there are many kinds of polymorphs of which phase stability depends on the ratio of ionic radii (r_{cation}/r_{anion}), and/or ordering of ions. Doping of aliovalent ions generates compensating cation/anion vacancies, which also affects the crystal structure of compounds. In this thesis, I focused on two materials having fluorite structure, ZrO_2 and $LaOF$. From the first-principles simulation, I discussed the mechanism of ionic conduction and explored the keys to control their properties.

In preceding literatures, several factors were proposed to enhance the ionic conductivity besides the concentration of conducting carrier: mixed bonding character (such as ionicity/covalency) and properties of the mobile and immobile ions (charge, size, polarizability, etc). Recently, epitaxial strain at the interface of multilayer thin film has been intensively studied because of their potential for higher ionic conductivity. In particular, $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ (8YSZ)/ $SrTiO_3$ heteroepitaxial structure has attracted much attention for its anomalously high oxide ion conductivity, although the reproducibility of the phenomenon is still under debate.

In this thesis, I first investigated the mechanism of the ionic conduction in ZrO_2 systems under tensile epitaxial strain. I conducted density functional perturbation theory (DFPT)-based phonon calculations to determine the dynamically stable structure. The cell was expanded along the a - and b -axes to match the lattice constant for $SrTiO_3$ with a 45° rotation (about 7% tensile strain), and thus to reproduce the epitaxial strain in the YSZ/ $SrTiO_3$

multilayer. By tensile epitaxial strain, the oxygen sublattice of pure ZrO_2 was dramatically changed into the zigzag structure, as suggested in the preceding studies. This structure has the space group of $Pbcn$, which was precisely determined by phonon calculation in this study. *Ab initio* MD simulations were performed initiating from the dynamically stable structure. The following models were constructed; (1) 1 oxygen vacancy (V_O) ($\text{Zr}_{72}\text{O}_{143}\square$, where \square denotes V_O); (2) 6V_O and no Y^{3+} dopant ($\text{Zr}_{72}\text{O}_{138}\square_6$); (3) 6V_O and compensating Y^{3+} ions ($\text{Zr}_{60}\text{Y}_{12}\text{O}_{138}\square_6$, represents YSZ). No significant increase in the MSD was observed in 1V_O system when starting from the dynamically stable structure. The ionic conductivity was remarkably increased when the tensile strain and several oxygen vacancies were introduced simultaneously (model (2) or (3)). The conductivity was almost dominated by the number of oxygen vacancies. These oxygen vacancies seemingly deformed the spatial oxygen ordering state, which led to the enhancement of the oxide ion conductivity. The present results indicate that the oxide ion conductivity in ZrO_2 is largely influenced by the oxygen ordering pattern, which sensitively changes with the lattice strain and the number of oxygen vacancies.

In this context, anion doping into anion sublattice of ZrO_2 could also affect the oxide ion conductivity since these dopants will be directly incorporated into the mobile sublattice rather than the cation counterpart. Next, I discussed the effect of N/F-doping into tensile-strained ZrO_2 , particularly focusing on the structural change of oxygen sublattice. The effect of N/F-doping was further analyzed referring to the strengths of Zr–O bonds using Crystal Orbital Hamilton Population (COHP) analysis. Several models with different concentrations of oxygen vacancies were compared; (4) 1V_O and 3 N/F-doping ($\text{Zr}_{72}\text{O}_{140}\text{N}_3\square$ and $\text{Zr}_{72}\text{O}_{140}\text{F}_3\square$); (5) 3V_O and 3 N/F-doping ($\text{Zr}_{72}\text{O}_{138}\text{N}_3\square_3$ and $\text{Zr}_{72}\text{O}_{138}\text{F}_3\square_3$); (6) 6V_O and 3 N/F-doping ($\text{Zr}_{72}\text{O}_{135}\text{N}_3\square_6$ and $\text{Zr}_{72}\text{O}_{135}\text{F}_3\square_6$). The zigzag structure was perturbed by the flipping motion of the lattice at low concentration of dopants or vacancies, and, with increasing the concentration, it was broken into a fluid-like state. Besides, chemical bonding analysis of Zr–O showed that the bonds near the vacancies was weakened by F- or V_O -doping and strengthened by N-doping. Despite the opposite effects on the nearby Zr–O bonds, all doping commonly enhanced the ionic conduction; the doped F[−] or V_O directly weakened the Zr–O bonds in its vicinity, whereas the N^{3-} strengthened the Zr–O bonds in its vicinity but weakened other Zr–O bonds and thus promoted the ionic conduction. Additionally, I observed a peculiar migration mechanism, which is similar to the vacancy mechanism but is mediated by the interstitial position. This migration mechanism *via* interstitial site might be easier to occur in the in-plane direction than in the out-of-plane, since the interstitial site is opened along the in-plane direction by the tensile strain. This novel conduction mechanism involving interstitial sites, which were induced by tensile strain, supposedly contributed to the enhanced ionic conductivity in ZrO_2 systems.

Finally, I explored the ionic conduction mechanism on a mixed anion compounds LaOF, which shows fluoride ion conduction with high selectivity. The anions of LaOF show different ordered structures, a rhombohedral ($R\bar{3}m$, [111] ordering) or tetragonal structure ($P4/nmm$, [001] ordering) depending on its non-stoichiometry, where the latter structure is usually obtained in fluorine-excess condition ($\text{LaO}_{1-x}\text{F}_{1+2x}$, $x > 0$). In general, ionic conduction mechanism can be classified into interstitial, interstitialcy, or vacancy mechanism. Experimental studies suggested that interstitial fluoride ion is the main carrier species in LaOF. However, precise discussion on the selectivity and mechanism of fluoride ion conduction has not been made so far. In this study, I investigated the diffusion mechanism of fluoride ion in LaOF from theoretical perspectives. The formation of F Frenkel pair was more

energetically favored than O Frenkel pair by more than 1.7 eV, which suggests that the F Frenkel pair contributes to the fluoride ion conduction. *Ab initio* MD simulations revealed that the fluoride ion conduction was mainly mediated by the interstitialcy mechanism. Interestingly, such interstitialcy mechanism of interstitial fluoride ion occurred along (001) plane only when its nearest anion sites on the (001) plane are occupied by fluoride ions. The present finding, i.e., dominance of the interstitialcy mechanism under a restricted condition, suggests that the ionic conductivity of mixed anion compounds can be enhanced by controlling the anion ordering.