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Dissertation Outline

Proton and Oxide-ion Conduction, and Crystal Structure of $BaNdIn_{1-x}Sc_xO_4$

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Chapter 1 Introduction

Developments of proton and oxide-ion conductors are very important for many applications such as membranes, sensor, fuel cells, and batteries. Critical to the development of clean energy applications is the study of new proton and oxide-ion conductors. This thesis reports the crystal structure, proton and oxide-ion conduction of $BaNdInO_4$-based materials, $BaNdScO_4$-based oxides and their related materials.

Chapter 2 Crystal Structure and Oxide-Ion Conductivity of $Ba_{1+x}Nd_{1-x}InO_{4-x/2}$

I have investigated oxide-ion conduction and crystal structure of $Ba_{1.1}Nd_{0.9}InO_{3.95}$. The oxide-ion conductivity of $Ba_{1.1}Nd_{0.9}InO_{3.95}$ is about 12 times higher than that of $BaNdInO_4$ at 858 °C. $Ba_{1.1}Nd_{0.9}InO_{3.95}$ exhibits a little lower activation energy (0.86 eV) than $BaNdInO_4$ (0.91 eV). Crystal structure analyses have indicated that the excess Ba^{2+} substitutes for Nd^{3+} and that oxygen vacancies exist in $Ba_{1.1}Nd_{0.9}InO_{3.95}$, which leads to the formation of the carrier and higher oxide-ion conductivity of $Ba_{1.1}Nd_{0.9}InO_{3.95}$ in comparison with $BaNdInO_4$. The bond-valence-based energy landscapes have shown two-dimensional oxide-ion diffusion along the *bc* plane in the A-type rare earth oxide-like $(Nd,Ba)_2O_3$ unit of $Ba_{1.1}Nd_{0.9}InO_{3.95}$. $Ba_{1.1}Nd_{0.9}InO_{3.95}$ has a larger bottleneck size for oxide-ion migration in comparison with $BaNdInO_4$, which leads to the lower activation energy for oxide-ion conduction. The present work described in this chapter was published in Ref. [1].

Chapter 3 $BaNdScO_4$ as a New Structure-Type Proton Conductor

I have discovered new structure-type proton conductors $BaNd_{1-x}Ca_xScO_{4-x/2}$ (x =

0 and 0.2). Electrical conductivity measurements of $BaNd_{1-x}Ca_xScO_{4-x/2}$ showed that the proton conductivity of $BaNd_{0.8}Ca_{0.2}ScO_{3.9}$ is approximately 30 times higher than that of $BaNdScO_4$. Rietveld analysis using neutron-diffraction data of $BaNd_{0.8}Ca_{0.2}ScO_{3.9}$ have indicated that there exist proton and oxygen vacancies, which has been supported by the structural optimization by density functional theory (DFT) calculations. Due to the higher oxygen vacancy concentration in $BaNd_{0.8}Ca_{0.2}ScO_{3.9}$ compared with the mother material, the carrier (proton) concentration in $BaNd_{0.8}Ca_{0.2}ScO_{3.9}$ is also higher compared with the mother material, leading to higher proton conductivity of $BaNd_{0.8}Ca_{0.2}ScO_{3.9}$. Oxide-ion conduction is also confirmed in $BaNd_{1-x}Ca_xScO_{4-x/2}$ compounds. The present work described in this chapter was published in Ref. [2].

Chapter 4 Proton Conductivity and Composition Dependence of Lattice Parameters of $BaNdInO_4$ Related Materials

I have investigated the electrical conductivity of $BaNdInO_4$-related materials. It was found that a solid solution shows higher proton conductivity than that of $BaNdInO_4$. Using the high-angular-resolution synchrotron X-ray powder diffractometry, I have examined the existing phases and lattice parameters of the $BaNdInO_4$-related materials.

Chapter 5 Conclusions

In this work, the crystal structure and oxide-ion conduction of $Ba_{1.1}Nd_{0.9}InO_{3.95}$ are revealed for the first time. This investigation of the structural origin of oxide-ion conduction will accelerate further developments of the $BaNdInO_4$-based materials. I have discovered a new structure-type proton conductors $BaNd_{1-x}Ca_xScO_{4-x/2}$ (x = 0 and 0.2). This thesis would greatly contribute to the science of crystal structure and proton/oxide-ion conduction of (110) layered perovskites.

Achievements and references

[1] Masahiro Shiraiwa, Kotaro Fujii, Yuichi Esaki, Su Jae Kim, Seongsu Lee and Masatomo Yashima "Crystal Structure and Oxide-Ion Conductivity of $Ba_{1+x}Nd_{1-x}InO_{4-x/2}$" *Journal of the Electrochemical Society*, **164**, (13) F1392-F1399 (2017).

[2] Masahiro Shiraiwa, Takafusa Kido, Kotaro Fujii, Masatomo Yashima, "High-temperature proton conductors based on the (110) layered perovskite $BaNdScO_4$", *Journal of Materials Chemistry*, **7**, (2021) DOI: 10.1039/D0TA11573H.