

Local Structure Analysis on Na_{0.5}Bi_{0.5}TiO₃-Based Materials with Perovskite Structure

Naoto Kitamura, Naoya Ishida, Yasushi Idemoto

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Japan

naotok@rs.tus.ac.jp

Perovskite (ABO₃)-type Na_{0.5}Bi_{0.5}TiO₃ where Na and Bi occupy the A site is well known as a piezoelectric material with insulating property. However, some recent works revealed that Na_{0.5}Bi_{0.5}TiO₃-based material with Bi vacancy, i.e. Na_{0.5}Bi_{0.5-x}TiO_{3-□} could show oxide-ion conduction at elevated temperature. Especially, since Na_{0.5}Bi_{0.45}TiO_{3-□} exhibits comparable conductivity to a typical oxide-ion conductor such as yttria-stabilized zirconia, the material is expected highly to be applied for the solid oxide fuel cell (SOFC). It is also found that a sample with Na vacancy had lower conductivity than the Bi-deficient sample, and thus the A site in the materials can be considered to play an important role for oxide-ion behavior. Unfortunately, however, local environments around Na, Bi and their vacancies cannot be clarified by a conventional analytical method for a crystal such as the Rietveld method using Bragg peaks, because the local environments do not have periodicity in the crystals.

In this work, we performed the pair distribution function (PDF) analysis on Na_{0.5}Bi_{0.5}TiO₃-based materials with the perovskite structure. In order to atomic-configuration snapshots from the PDF, the reverse Monte Carlo modelling (RMC) was performed with RMCProfile program. In the modelling, neutron and X-rays structure factors $S(Q)$, reduced pair distribution functions $G^{\text{PDF}}(r)$ as well as the Bragg profiles were used simultaneously. The analysis was carried out under a support of the density functional theory calculation (cp2k) in order to obtain more accurate atomic configurations.

Figure 1 shows a part of a modelling result of Na_{0.5}Bi_{0.5}TiO₃. From the result and a multiple regression analysis using the obtained structural features, it is demonstrated that local environments around Na and Bi are quite different in Na_{0.5}Bi_{0.5}TiO₃ although both the cations occupy the same crystallographic site (A site) of the perovskite structure. In addition, it is suggested that Bi makes O²⁻ conduction path distorted.

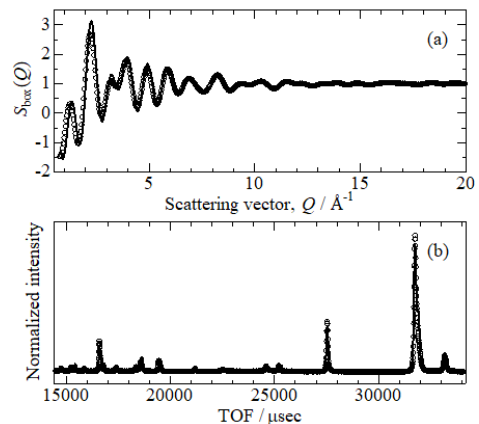


Fig. 1 (a) X-ray structure factor and (b) neutron Bragg profile of Na_{0.5}Bi_{0.5}TiO₃. The circles and the solid line represent the experimental data and RMC model, respectively.