Structure analysis of the oxide-ion conductor which belongs to the new structure family

Kotaro Fujii, Masahiro Shiraiwa, Yuichi Esaki, Masatomo Yashima
Tokyo Institute of Technology

Oxide-ion conductors, which include pure ionic conductors and mixed oxide-ion and electronic conductors, attract significant interest because of their varied uses in oxygen separation membranes and cathodes for solid-oxide fuel cells (SOFCs). The oxide-ion conductivity is strongly dependent on the crystal structure. At present, several structures, such as fluorites, perovskites, K_2NiF_4, mellilites, and apatites, are known to show high oxide-ion conductivities. For further development of oxide-ion conductors is investigating materials with new types of structures. Recently, we have discovered a new structural family of oxide-ion conductor based on $NdBaInO_4$, a monoclinic $P2_1/c$ perovskite-related phase with a layered structure. In this study, we have successfully improved the oxide-ion conductivity of $NdBaInO_4$ by Ba substitution at the Nd site, and its crystal structure was investigated from high-temperature neutron diffraction data.

The target materials ($Nd_{1-x}Ba_{1+x}InO_{4-\delta}$) were prepared by the solid-state reactions. Well ground and mixed starting materials of Nd_2O_3, $BaCO_3$ and In_2O_3 were pressed into pellet and sintered at 1400 °C for several hours. The obtained samples were used for the neutron diffraction experiments.

High-temperature angle dispersive-type powder neutron diffraction measurements of $Nd_{1-x}Ba_{1+x}InO_{4-\delta}$ were using a vacuum furnace. The obtained neutron diffraction data were analyzed by Rietveld method using the program RIETAN-FP. The final result of the Rietveld refinement of $Nd_{1-x}Ba_{1+x}InO_{4-\delta}$ at the room temperature gave good fitting (Rwp = 5.64 %).

The crystal structure of $Nd_{1-x}Ba_{1+x}InO_{4-\delta}$ comprises the A rare earth structure A_2O_3 ((Nd,Ba) $_2O_3$) and the perovskite $(A,A')BO_3$ ((Nd,Ba)InO_3) units (Figure) which belongs to the same structural family as $NdBaInO_4$. Here, A and A' are relatively larger cations and B is a smaller cation. The unit-cell volumes of $Nd_{1-x}Ba_{1+x}InO_{4-\delta}$ were confirmed to be larger than that of the original non-substituted material $NdBaInO_4$. The larger volume is ascribed to the larger ionic radius of Ba^{2+} (1.38 Åfor coordination number of 7) than that of Nd^{3+} (1.046 Åfor CN = 7). Now the structure analysis of the high-temperature data are being carried out.

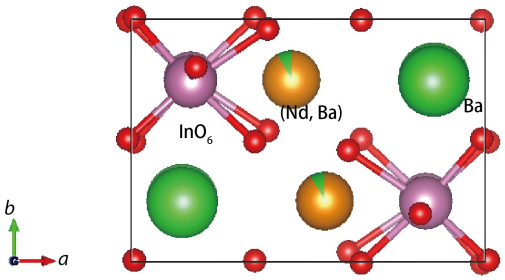

Fig. 1. Crystal structure of Nd1-xBa1+xInO4-d