Crystal structure analysis of high temperature neutron diffraction data of novel oxide-ion conductor SrYbInO4

Kotaro Fujii, Ayaka Fujimoto, 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. According to such background, we are exploring new structure family of oxide-ion conductors. For example, we have discovered a new structural family of oxide-ion conductor $BaNdInO_4$ which has a monoclinic $P2_1/c$ perovskite-related phase with a layered structure, in 2014. More recently, we found novel material, $SrRInO_4$ (R : rare earths) with $CaFe_2O_4$-type structure showed high oxide-ion conductivity compared to the other $CaFe_2O_4$-type materials. In order to understand the mechanism of oxide-ion conduction, it is necessary to precisely determine the crystal structure (particularly position, occupancy factor, and anisotropic displacement parameters of oxygens) at high-temperature because oxide-ion conductors are generally used at high-temperature. In the present study, we investigated the crystal structure of $SrYbInO_4$ at high temperature using high resolution neutron powder diffractometer Echidna installed at the research reactor OPAL, ACNS, ANSTO. The material was prepared by the solid-state reaction. A pure oxide-ion conduction was observed at 1000 °C for $SrYbInO_4$ by electrical conductivity measurements. For the neutron diffraction experiments, the sintered pellets of the reaction products were introduced into a vanadium can and used for the neutron diffraction experiment. The measurements were carried out from room temperature to high temperature (1000 °C) at 200 °C intervals. Each measurement time was few hours. The structural analyses for these data are carried out by Rietveld method using the program RIETAN-FP. The Rietveld structure refinements of the diffraction data of $SrYbInO_4$ taken at the room temperature 23 °C, and 1000 °C using the orthorhombic *Pnma* $CaFe_2O_4$-type structure gave good quality of the fit and the reliability factors (R_{wp} =3.78 %, R_B = 3.82 % for 23 °C data, and R_{wp} = 3.33 %, R_B = 5.04 % for 1000 °C data). The unit-cell parameters and unit-cell volume V of $SrYbInO_4$ at 1000 °C (a = 10.0522(3) Å, b = 3.34702(9) Å, c = 11.7502(3) Å, V = 395.335(18) Å^3) are larger than those at RT (a = 9.920206(15) Å, b = 3.309496(4) Å, c = 11.636340(15) Å, V = 382.0313(9) Å^3), due to the thermal expansion. The bond lengths and equivalent isotropic atomic displacement parameters of $SrYbInO_4$ at 1000 °C are higher than those at RT, which indicates the larger thermal vibration at 1000 °C. The higher equivalent atomic displacement of oxygen atoms at 1000 °C suggests higher oxide-ion conductivity at 1000 °C compared to RT.

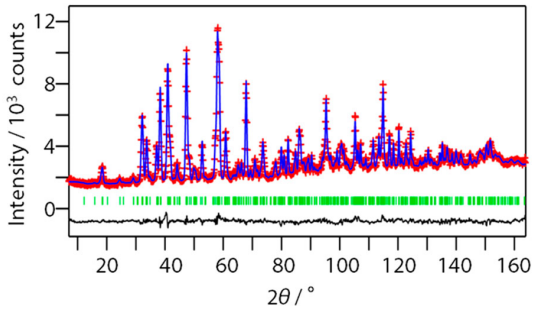

Fig. 1. Rietveld pattern of the neutron diffraction data of SrYbInO4 taken at 1273 K.