Crystal structure analysis of high temperature neutron diffraction data of novel oxide-ion conductor HoGaTi2O7

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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, $SrYbInO_4$ with $CaFe_2O_4$-type structure, showed higher 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 $HoGaTi_2O_7$ 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. 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). Each measurement took about 6 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 $HoGaTi_2O_7$ taken at the room temperature 23 °C, and 1000 °C using the orthorhombic *Pbcn* $GdGaTi_2O_7$-type structure gave good quality of the fit and the reliability factors (R_{wp} =2.31 %, R_B = 1.48 % for 23 °C data, and R_{wp} = 2.07 %, R_B = 2.44 % for 1000 °C data). The unit-cell parameters and unit-cell volume V of $HoGaTi_2O_7$ at 1000 °C (a = 9.8658(3) Å, b = 7.4117(2) Å, c = 13.6497(4) Å, V = 998.09(5) Å^3) are larger than those at RT (a = 9.77095(16) Å, b = 7.35349(13) Å, c = 13.5334(2) Å, V = 972.38(3) Å^3), due to the thermal expansion. The bond lengths and equivalent isotropic atomic displacement parameters of $HoGaTi_2O_7$ 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.

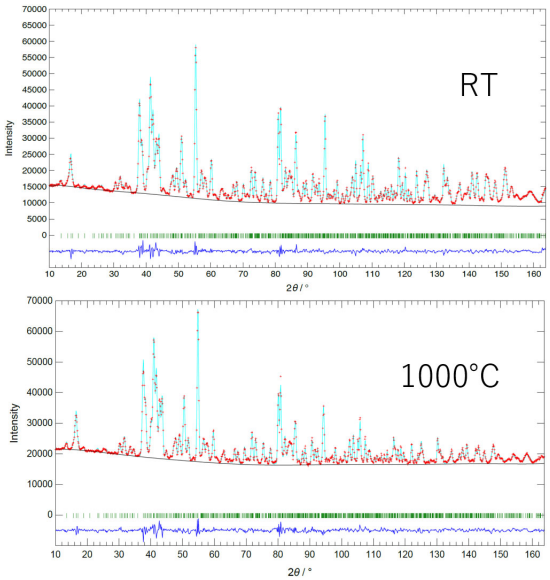

Fig. 1. Results of Rietveld refinement