Structure analysis of novel oxide-ion conductors from neutron powder diffraction data

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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 developments, it is necessary to find new structure families of oxide-ion conductors. According to such background, we are exploring new structure family of oxide-ion conductors. For example, we previously discovered new structural families of oxide-ion conductors $BaNdInO_4$,[1] $Ca_{0.8}Y_{2.4}Sn_{0.8}O_6$,[2] $BaHo_2ZnO_5$, [3] and $Ca_3Ga_4O_9$. [4] Recently, we found several new oxide-ion conductors. 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 these new oxide-ion conductors using high resolution neutron powder diffractometer Echidna installed at the research reactor OPAL, ACNS, ANSTO.

Constant-wavelength neutron powder diffraction data of the prepared samples were measured at 24°C and high temperature (200, 400, 600, and 800 °C). The measurement conditions were wavelength: 1.622652(14) Å step interval: 0.125° in 2θ / step. For the high-temperature measurements, the samples were heated with a vacuum furnace at 10^{-4} Pa during the neutron-diffraction measurements.

We are now analyzing the neutron diffraction data by Rietveld method. Fig. 1(a) shows the preliminary obtained Rietveld plot of the new oxide-ion conductor containing Ba, Ca, Mn, and O. Basically good fitting was obtained but still containing bad fitting for some reflections. To improve the fitting, we are now trying to make better structure model for this compound.

Fig. 1(b) shows neutron diffraction patterns of Ba-Ho-Zn containing new oxide-ion conductor taken at 24, 200, 400, 600, and 800°C. With increasing temperature, lattice volume expansions were observed as the peak position shifts toward lower angle. The data analysis is in progress.

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[3] K. Nakamura et al., J. Ceram. Soc. JPN. 126, 929 (2018).

[4] Y. Yasui et al., Inorg. Chem. 58, 9560 (2019).

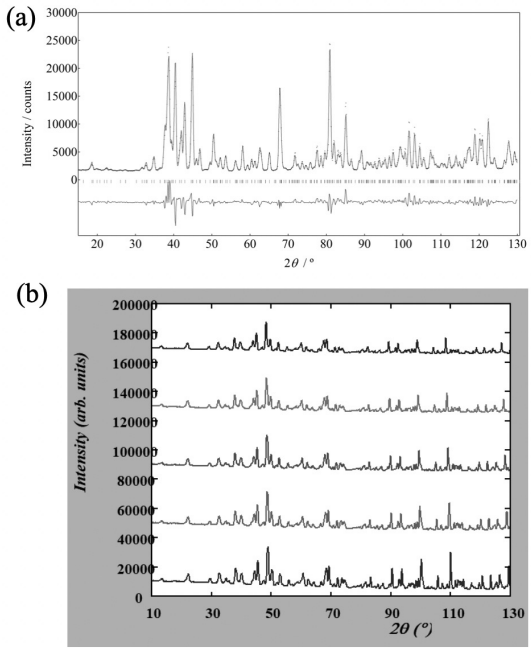

Fig. 1. (a) Rietveld plot of the new oxide-ion conductor containing Ba, Ca, Mn, and O. (b) Neutron diffraction patterns of Ba-Ho-Zn containing new oxide-ion conductor taken at 24, 200, 400, 600, and 800°C (from bottom to top).