# Structure analysis of novel proton conductor

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Exploration of novel ceramic materials is important task in the field of the materials science. Recently, our group successfully discovers several novel ionic conductors and mixed anion materials. In the present work, we aim to analyze crystal structures of these materials based on the neutron diffraction data in order to understand relationship between structure and properties. Neutron diffraction techniques enable us to reveal the precise structural information on relatively light elements, such as oxygen and hydrogen. Here, we report our recent research outcome about the novel proton conductor, $Ba_2LuAlO_5$.[1] The crystal structure of $Ba_2LuAlO_5$ in $D_2O$ hydrated condition and dry condition at 5 K has been analyzed using the data taken at the HERMES diffractometer.

The samples were sealed into vanadium holders and cooled down to 5 K using the GM-Cryorefrigerator. Constant-wavelength neutron powder diffraction data were measured at the HERMES diffractometer installed at the JRR-3 reactor of the Japan Atomic Energy Agency with the measurement conditions of wavelength: 1.34171(5) Å, step interval: 0.05° in $2\theta$ / step.

The data were analyzed by Rietveld method. Fig. 1 shows the Rietveld patterns for neutron diffraction patterns of dry $Ba_2LuAlO_5$ and hydrated $Ba_2LuAlO_5{\cdot}0.48\ D_2O$ at 5 K. Rietveld refinements for the hydrated $Ba_2LuAlO_{4.52}(OD)_{0.96}$ were successfully carried out based on the hexagonal $P6_3/mmc$ $Ba_2LuAlO_5$ structure. Structure analyses on the basis of 416 models for the proton positions suggested four deuterium sites D1, D2, D3, and D4, which is consistent with the probability density distribution of protons obtained by the ab initio molecular dynamics (AIMD) simulations. The average OD bond length 0.99(3) Å agrees with those from Raman spectra 0.98(4) Å and IR spectra 0.99(4) Å. The lattice parameters $a$ and $c$ of hydrated $Ba_2LuAlO_{4.52}(OD)_{0.96}$ are 0.26% and 0.82% larger than those of dry $Ba_2LuAlO_5$, respectively, at 5 K, which is attributable to the water incorporation. The final structure refinements yielded good fits and low reliability factors, $R_{wp} = 9.164\%$. The large amount of intrinsic oxygen vacancies in $Ba_2LuAlO_5$ allows higher water uptake of $x = 0.50$ in $Ba_2LuAlO_5{\cdot}xH_2O$ than other typical perovskite and perovskite-related proton conductors, resulting in the high proton conductivity.

[1] R. Morikawa et al., Commun. Mater. **4**, 42 (2023).

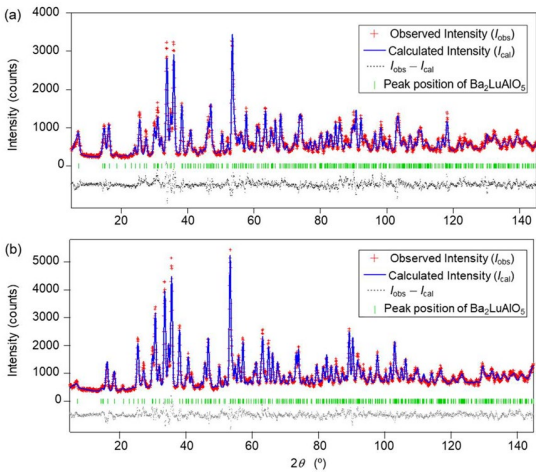


Fig. 1. Rietveld patterns for neutron diffraction data of (a) dry $Ba_2LuAlO_5$ and (b) hydrated $Ba_2LuAlO_5{\cdot}0.48\ D_2O$ at 5 K.

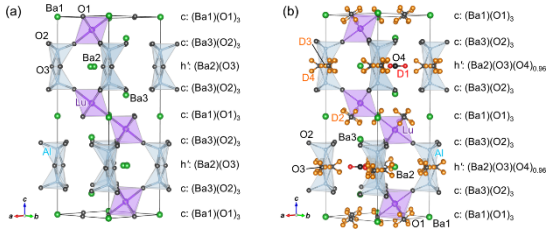


Fig. 2. Refined crystal structures of dry **a** $Ba_2LuAlO_5$ and **b** hydrated $Ba_2LuAlO_5 \cdot 0.48\ D_2O$ at 5 K.