

Crystal Structure Analysis of Novel Ionic Conductors

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Proton and oxide-ion conductors are promising materials with a wide range of potential applications such as proton conducting fuel cells (PCFCs) and solid oxide fuel cells (SOFCs). However, there are no ionic conductors exhibiting both high ionic conductivity and high chemical stability in the ‘Norby gap’ at the intermediate temperatures. Recently, we have discovered several high ionic conductors with the intrinsic oxygen vacancies at intermediate temperatures. Here, the intrinsic oxygen vacancies are oxygen vacancies in a mother material. In these proposals (23613, 23623, 23627), we performed neutron diffraction (ND) measurements using HERMES for several high ionic conductors with intrinsic oxygen vacancies such as $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{13}$ (BEAS).

Figure 1a and 1b show the ND patterns at 5 K of dry and wet $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{13}$, respectively.^[1] Rietveld refinement of the ND data of dry $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{13}$ was successfully carried out using the crystal data of hexagonal $P63/mmc$ $\text{Ba}_5\text{Er}_2\text{Al}_2\text{ZrO}_{12.77}(\text{OH})_{0.46}$ (= $\text{Ba}_5\text{Er}_2\text{Al}_2\text{ZrO}_{13} \cdot 0.23 \text{H}_2\text{O}$)² as initial parameters. The occupancy factor of oxygen atoms at the interstitial O4 site, $g(\text{O}; \text{O}4)$, was 0.02(2), indicating no oxygen atoms at the O4 site. Next, we performed Rietveld analyses of ND data of the deuterated $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{13-5y/2}(\text{OD})_{5y}$ pellets. Here, y is the number of protons per Ba atom. It should be noted that the occupancy factor of oxygen atoms at the interstitial O4 site $g(\text{O}; \text{O}4)$ was 1.08(3), indicating the full occupation of oxygen atoms at the O4 site. The h’ layer of fully hydrated BEAS is not the BaO_3 layer but the BaO_2 layer, indicating that the fully hydrated BEAS is $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{12}(\text{OD})_2$ (= $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{14}\text{D}_2$). Rietveld analyses of hydrated BEAS were performed using 104 models with different D atom positions, which suggested two D sites of D1 closest to the O4 atom and D2 near the O2 atom. The O–D lengths obtained from the refined crystal structure of

$\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{12}(\text{OD})_2$ were 1.10 Å, which agreed with that estimated from the IR data of 0.99(4) Å. The lattice parameters a and c of hydrated BEAS were 0.34% and 0.43% higher than those of dry BEAS at 5 K, respectively, due to the hydration. The bond valence sums of all of the cations and anions at all of the sites were consistent with the formal charges. The proton concentration in $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{13-5y/2}(\text{OD})_{5y}$ calculated from the refined occupancy factors ($y = 0.40$) agreed with that from the TG data ($y = 0.40$). The high proton conductivity of BEAS can be attributed to the full hydration, which was evidenced by neutron diffraction.

[1] K. Matsuzaki, **K. Saito**, *et al.*, *J. Am. Chem. Soc.* **146**, 18544-18555 (2024).

[2] T. Murakami, *et al.*, *J. Am. Chem. Soc.* **142**, 11653-11657 (2020).

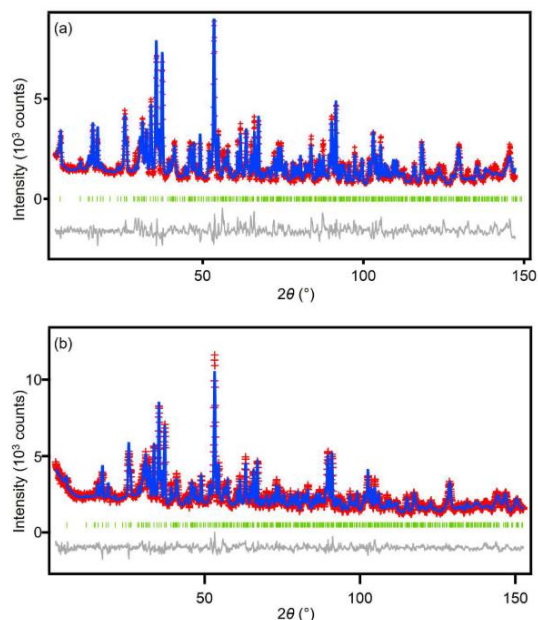


Fig. 1. Rietveld patterns of (a) dry $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{13}$ and (b) hydrated (deuterated) $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{12}(\text{OD})_2$ at 5 K. Red crosses, blue line, and gray line denote observed, calculated, and difference intensities, respectively. Green vertical bars denote calculated Bragg peak positions of the hexagonal phase.