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Local structure and vibrational dynamics of proton conducting $Ba_2In_2O_5(H_2O)_x$

(Supplementary Information)

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1 X-ray powder diffraction

Fig. S1 shows the X-ray powder diffraction (XRPD) pattern measured on the as-sintered $Ba_2In_2O_5$ powder at room temperature using a Bruker AXS D8 ADVANCE VARIO powder diffractometer ($CuK_{\alpha,1} = 1.54056$ Å) and a solid-state LynxEye detector. Phases were identified with the DIFFRACplusEVA software package using the PDF (ICDD, 2019) database.

The diffractogram contains contributions from the sample (top marks, red) and the aluminium sample holder (bottom marks, blue). The position of the most intense peak of the $BaCO_3$ impurity is marked with (∗), which shows that the amount of $BaCO_3$, residual from the synthesis, is negligible.

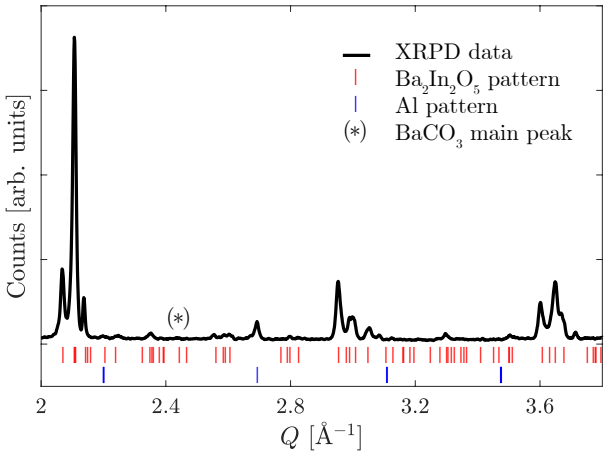

Fig. S1 XRPD pattern of the as-sintered sample (black). Top tick marks correspond to the positions of the peaks associated with the $Ba_2In_2O_5$ pattern. Bottom tick marks correspond to peaks associated with the Al pattern. The position of the most intense $BaCO_3$ peak is marked with (∗).

2 Debye-Waller factors

The relationship between momentum and energy transfer of the indirect-geometry spectrometer IN1 Lagrange is calculated and shown in Fig. S2(a). The calculation considers a range of scattering angles of 33.73–69.36° between the incident wavevector, k_i, and the final wavevector, k_f. The Debye-Waller factors used for the computation of $S(Q,\hbar\omega)$ from $G(\hbar\omega)$, calculated from the AIMD trajectories of the $x = 1$ model, are shown in Fig. S2(b).

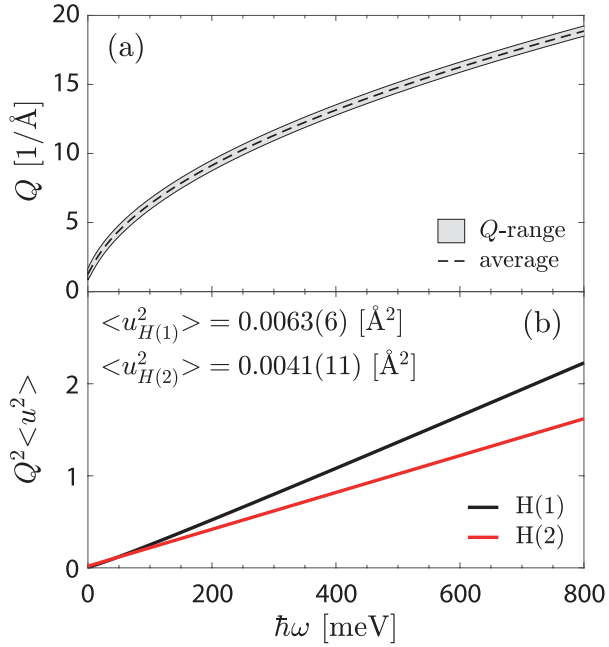

Fig. S2 (a) Calculated Q-profile of the IN1 Lagrange spectrometer (grey). The average (dashed line) is used for calculation of the Debye-Waller factors. (b) Debye-Waller factors of the H(1) (black) and H(2) (red) protons obtained from the mean-square displacements from the AIMD trajectories of the fully-hydrated model, $x = 1$.

3 Peak fit analysis

The model of seven Gaussian functions for the peak fit analysis of the INS spectra is based on the following peak assignment and constraints:

(1) the two low-energy shoulders at about 70 meV (P_1) and 80 meV (P_2), identified as being phonon-related (riding modes, or hybrid modes from phonon/δ(O-H(1)) coupling), have the same full width at half maximum (FWHM),

(2) the two δ(O-H(1)) modes, at about 95 meV (B1) and 110 meV (B2) have the same integrated intensity (the same constraint is used for the δ(O-H(2)) modes, (C1) and (C2)),

(3) the FWHM of the $p = 2$ multiphonon term of the δ(O-H(1)) band, at about 190 meV (D), is fixed to 50 meV.

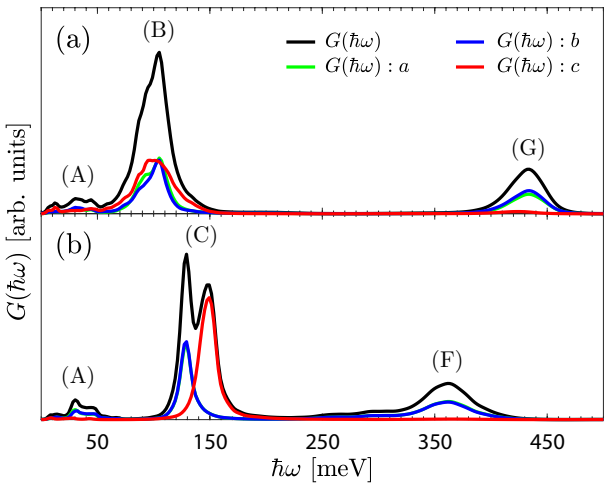

Fig. S3 Projected $G(\hbar\omega)$ of H(1) (a) and H(2) (b) on the Cartesian coordinates (a, b, and c). The spectra are calculated from the AIMD trajectories for the $x = 1$ model.

One may note that the inclusion of Lorentzian components improves the overall fit of the BIO30 and BIO76 spectra, but that the increased number of degrees of freedom makes the fitted parameters too unreliable to be compared.

4 Bond length distribution

The parameters extracted from the fit of the hydrogen bond length distributions, obtained by statistical analysis of the AIMD trajectories, are reported in Table S1.

5 Partial density of states

The projection of the $G(\hbar\omega)$ of H(1) and H(2) protons on the Cartesian coordinates (a, b, c-axes) is shown in Fig. S3.

Table S1 Parameters from the fit of the hydrogen bond length distributions, calculated from the AIMD trajectories, for all hydration levels. The widths of the Gaussian functions μ_1 and μ_2 are constrained to be identical. The parameter Fraction μ_1/H(1) represents the relative weight of the μ_1 component over the H(1) site, (μ_1+μ_2). The Gaussian function μ_3 models the distribution of the H(2) protons. Numbers in parenthesis represent standard error of the fit. The uncertainty of the data set is estimated to be 1 to 2 orders of magnitude higher than the standard error, based on the dispersion of the fitted parameters

Hydration level x	Fraction μ_1/H(1)	Centre μ_1 (Å)	Centre μ_2 (Å)	Width μ_1/μ_2 (Å)	Centre μ_3 (Å)	Width μ_3 (Å)
8/8	0.663(1)	1.890(1)	2.130(1)	0.130(1)	1.708(1)	0.125(1)
7/8	0.581(1)	1.863(1)	2.081(1)	0.117(1)	1.716(1)	0.122(1)
6/8	0.697(1)	1.915(1)	2.172(1)	0.142(1)	1.703(1)	0.130(1)
7/8	0.583(1)	1.871(1)	2.109(1)	0.127(1)	1.692(1)	0.137(1)
4/8	0.443(1)	1.971(1)	2.175(1)	0.139(1)	1.678(1)	0.115(1)
3/8	0.377(1)	1.872(1)	2.081(1)	0.118(1)	1.717(1)	0.115(1)
2/8	0.369(1)	1.926(1)	2.163(1)	0.121(1)	1.716(1)	0.108(1)
1/8	0.414(1)	1.883(1)	2.120(1)	0.121(1)	1.757(1)	0.120(1)