Electronic Supplementary Material (ESI) for Materials Advances.

Oxide Ion Dynamics in the Hexagonal Perovskite Mixed Conductor $Ba_7Nb_4MoO_{20}$: A Comprehensive Ab Initio Molecular Dynamics Study

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Supplementary Information:

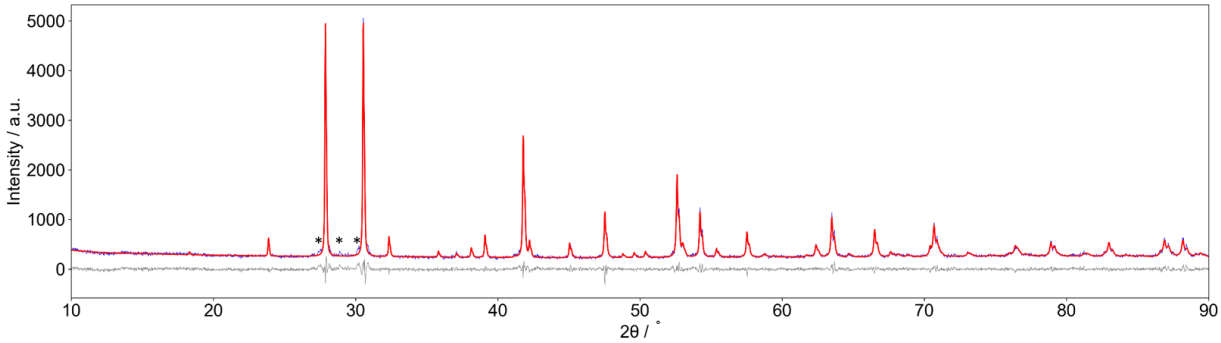

Figure S1. Rietveld plot for $Ba_7Nb_4MoO_{20}$ used for QENS experiments, showing observed data in blue, calculated pattern in red, and the difference in grey. Peaks caused by the presence of $Ba_5Nb_4O_{15}$ and $Ba_3NbMoO_{8.5}$ impurities are marked by *.

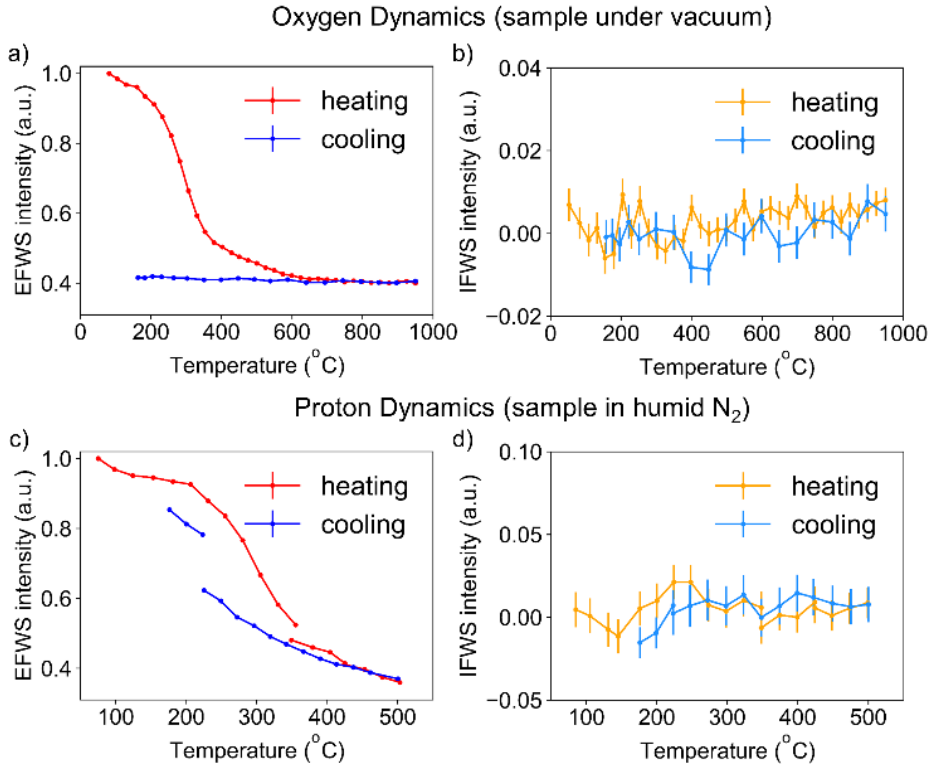

Figure S2. Elastic (a,c) and inelastic (b,d) fixed window scans corrected for residual elastic contribution and summed over all detectors in vacuum (top) and in humid N_2 (bottom). Gaps in curves are caused by QENS measurements performed for several hours between the fixed window scans during which some intensity is gained (if water is reabsorbed on cooling) or lost (if water is lost on heating). IFWS collected on both heating and cooling in vacuum (b) appear to suggest a very slight gradual increase in intensity above 600 °C, however this is too small to be analysed. In the data collected on a separate sample under humid N_2, the decrease in elastic intensity on heating (c) is comparable to that observed under vacuum. The corresponding inelastic intensity (d) shows the appearance of a small peak starting at 150 °C and reaching a maximum at 225 °C. While this peak is indicative of increased proton dynamics in this temperature range, no QENS broadening was observed in data collected at 225 °C and 175 °C on cooling (Figure S5).

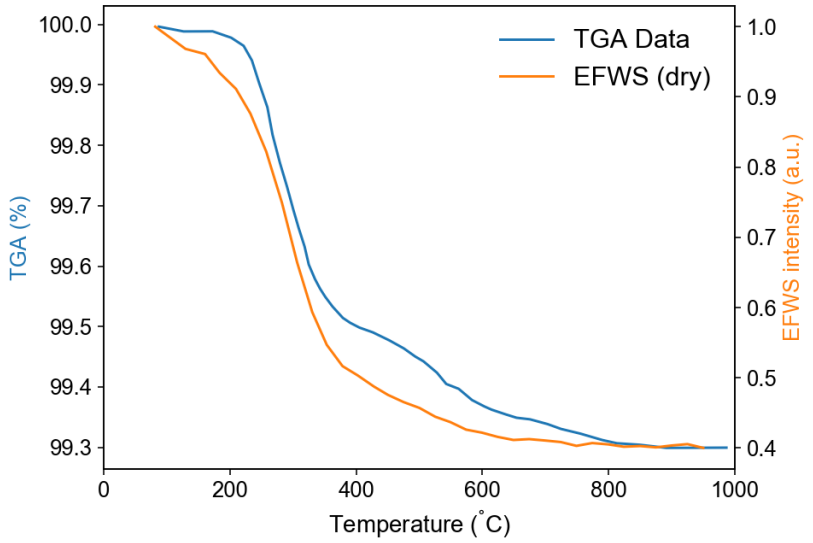

Figure S3. Comparison of EFWS intensity of the dry sample collected on heating (orange, right axis) to the TGA data reported by Fop et al.[1]

[1] Fop, S.; Dawson, J. A.; Fortes, A. D.; Ritter, C.; McLaughlin, A. C. Hydration and Ionic Conduction Mechanisms of Hexagonal Perovskite Derivatives. *Chem. Mater.* **2021**, *33* (12), 4651–4660. DOI: 10.1021/ACS.CHEMMATER.1C01141

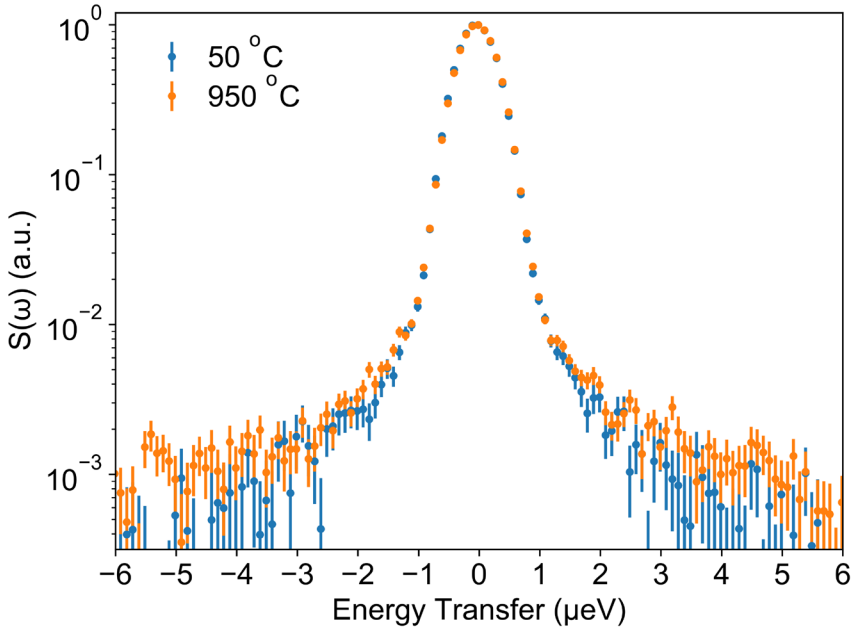

Figure S4. IN16b data collected on dry $Ba_7Nb_4MoO_{20}$ and summed over all detectors at 50 and 950 °C, showing no sign of QENS broadening.

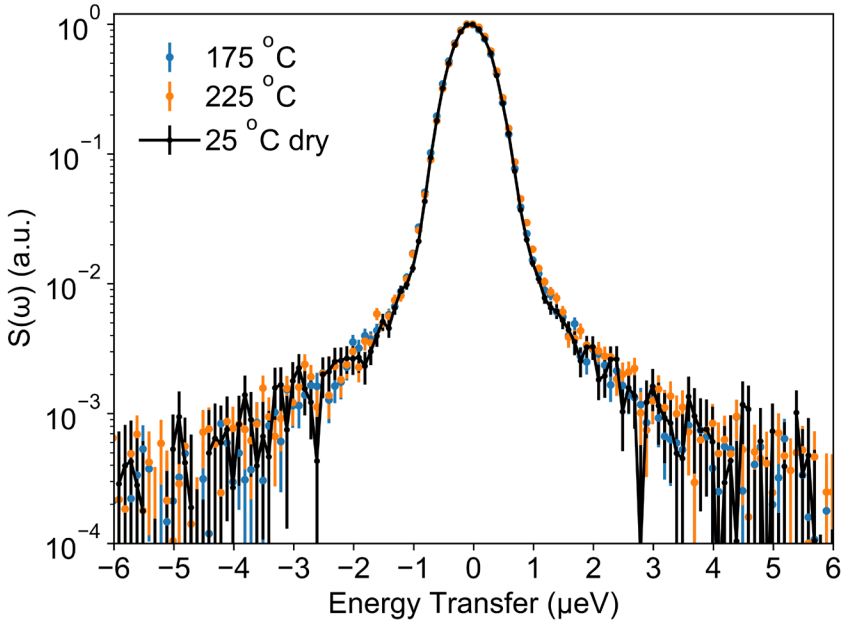

Figure S5. IN16b data collected on humid $Ba_7Nb_4MoO_{20}$ and summed over all at 175 and 225 °C, showing no sign of QENS broadening at the temperature where a small peak was observed in the IFWS. The QENS data measured at 50 °C on the dry sample is given for reference.

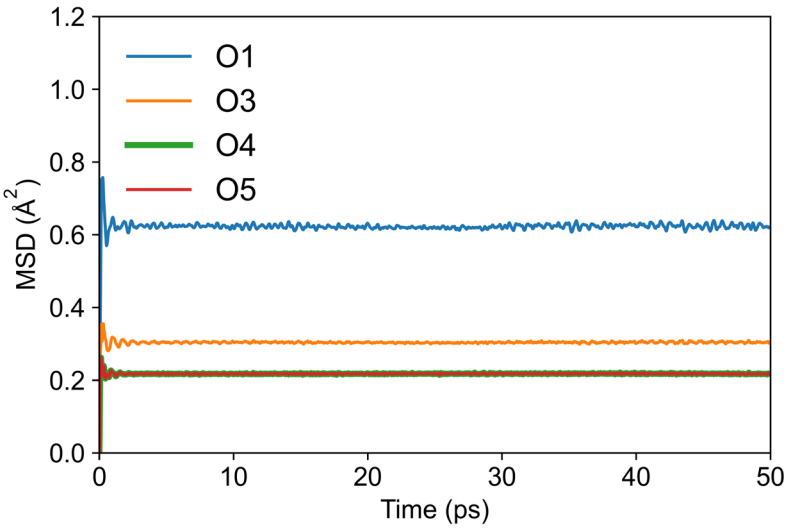

Figure S6. Contribution of the individual oxygen sites to the MSD in the simulation performed at 1000 °C.

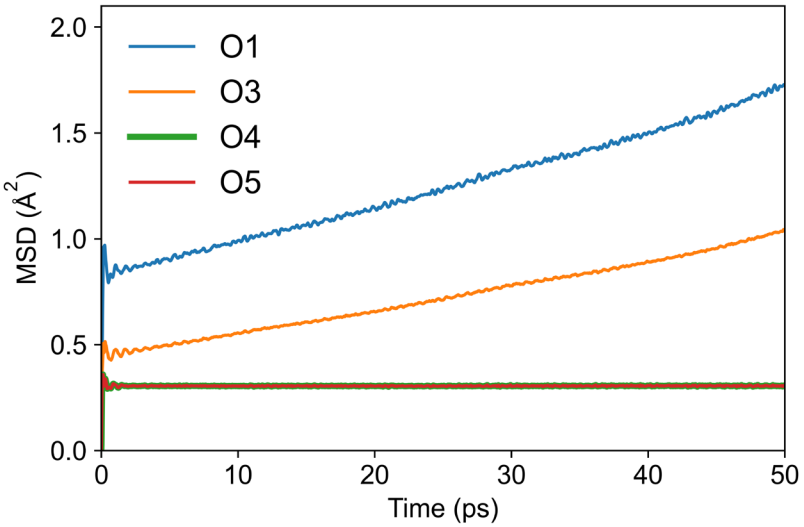

Figure S7. Contribution of the individual oxygen sites to the MSD in the simulation performed at 1500 °C.

Table S1. Table summarising all jumps occurring during the simulations at 1500 and 2000 °C

	1500 °C (50 ps)		1500 °C (100 ps)		2000 °C (100 ps)		2000 °C (200 ps)	
	O1	O3	O1	O3	O1	O3	O1	O3
total jumps	2	4	3	6	11	28	25	60
% of total jumps	33.3	66.7	33.3	66.7	28.2	71.8	29.4	70.6

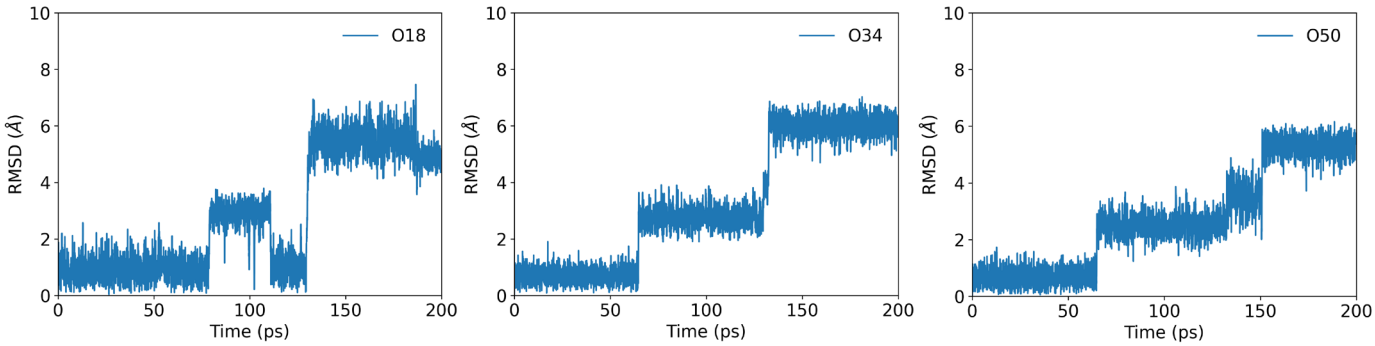

Figure S8. Root mean square deviation (RMSD) of three oxygen atoms during the simulation at 2000 °C, showing the distance the atoms moved away from the starting position during the simulation.