Hexagonal perovskite related oxide ion conductor $Ba_3NbMoO_{8.5}$: Phase transition, temperature evolution of the local structure and properties

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Supplementary Information

Table S1. Crystallographic parameters obtained from neutron diffraction Rietveld refinement of $Ba_3NbMoO_{8.40(2)}$ at room temperature. Space group = *R*-3*m* (hexagonal axes); *a* = 5.92805(5) Å; *c* = 21.0910(3) Å; *V* = 641.875(15) Å^3.

Site	Wyckoff	*x*	*y*	*z*	Occupancy	*B* (Å^2)
Ba1	3*a*	0	0	0	1	0.18(4)
Ba2	6*c*	0	0	0.20859(11)	1	1.55(3)
Mo1	6*c*	0	0	0.39780(8)	0.456	0.98(3)
Nb1	6*c*	0	0	0.39780(8)	0.456	0.98(3)
Mo2	6*c*	0	0	0.5255(6)	0.044	0.98(3)
Nb2	6*c*	0	0	0.5255(6)	0.044	0.98(3)
O1	18*h*	0.17210(11)	0.82790(11)	0.10382(4)	1	1.449(19)
O2	9*e*	0.5	0	0	0.457(4)	1.44(6)
O3	36*i*	0.0887(14)	0.0883(13)	0.3203(4)	0.0956(16)	3.4(3)

Table S2. Crystallographic parameters obtained from neutron diffraction Rietveld refinement of $Ba_3NbMoO_{8.42(2)}$ at 600 °C. Space group = *R*-3*m* (hexagonal axes); *a* = 6.00651(6) Å; *c* = 21.2490(4) Å; *V* = 663.917(18) Å^3.

Site	Wyckoff	*x*	*y*	*z*	Occupancy	*B* (Å^2)
Ba1	3*a*	0	0	0	1	1.40(6)
Ba2	6*c*	0	0	0.20567(16)	1	3.27(6)
Mo1	6*c*	0	0	0.39931(9)	0.485	1.80(3)
Nb1	6*c*	0	0	0.39931(9)	0.485	1.80(3)
Mo2	6*c*	0	0	0.526(2)	0.0150(15)	1.80(3)
Nb2	6*c*	0	0	0.526(2)	0.0150(15)	1.80(3)
O1	18*h*	0.17343(12)	0.82657(12)	0.10198(5)	1	2.63(3)
O2	9*e*	0.5	0	0	0.374(5)	3.57(16)
O3	36*i*	0.0883(11)	0.0893(11)	0.3205(2)	0.1085(16)	2.57(2)

Table S3. Crystallographic parameters obtained from neutron diffraction Rietveld refinement of $Ba_3NbMoO_{8.50(3)}$ with M2 sites set to zero occupancy at 600 °C. Space group = *R*-3*m* (hexagonal axes); *a* = 6.00651(6) Å; *c* = 21.2490(4) Å; *V* = 663.917(18) Å^3.

Site	Wyckoff	*x*	*y*	*z*	Occupancy	*B* (Å^2)
Ba1	3*a*	0	0	0	1	1.26(6)
Ba2	6*c*	0	0	0.20560(16)	1	3.24(6)
Mo1	6*c*	0	0	0.39959(9)	0.485	1.96(4)
Nb1	6*c*	0	0	0.39959(9)	0.485	1.96(4)
O1	18*h*	0.17326(12)	0.82674(12)	0.10183(5)	1	2.55(3)
O2	9*e*	0.5	0	0	0.396(6)	3.96(17)
O3	36*i*	0.0872(11)	0.0873(11)	0.3202(2)	0.1100(16)	2.4(2)

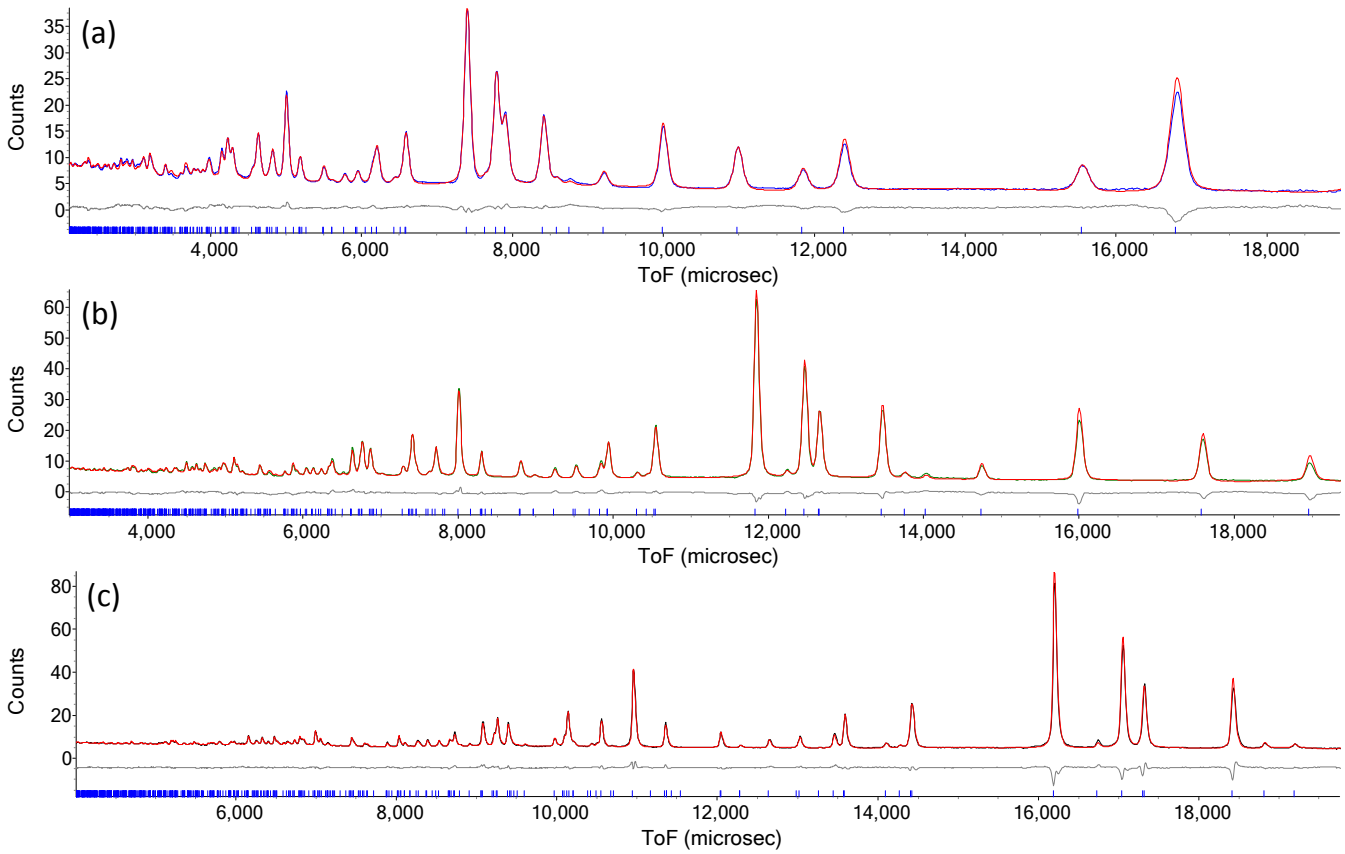

Fig. S1. Rietveld plots of $Ba_3NbMoO_{8.5}$ at room temperature from POLARIS (a) bank 3, R_{wp} = 3.11%, χ^2 = 6.86; (b) bank 4, R_{wp} = 3.32%, χ^2 = 10.167; (c) bank 5, R_{wp} = 2.49%, χ^2 = 4.46. Blue tick marks correspond to reflections arising from $Ba_3NbMoO_{8.5}$.

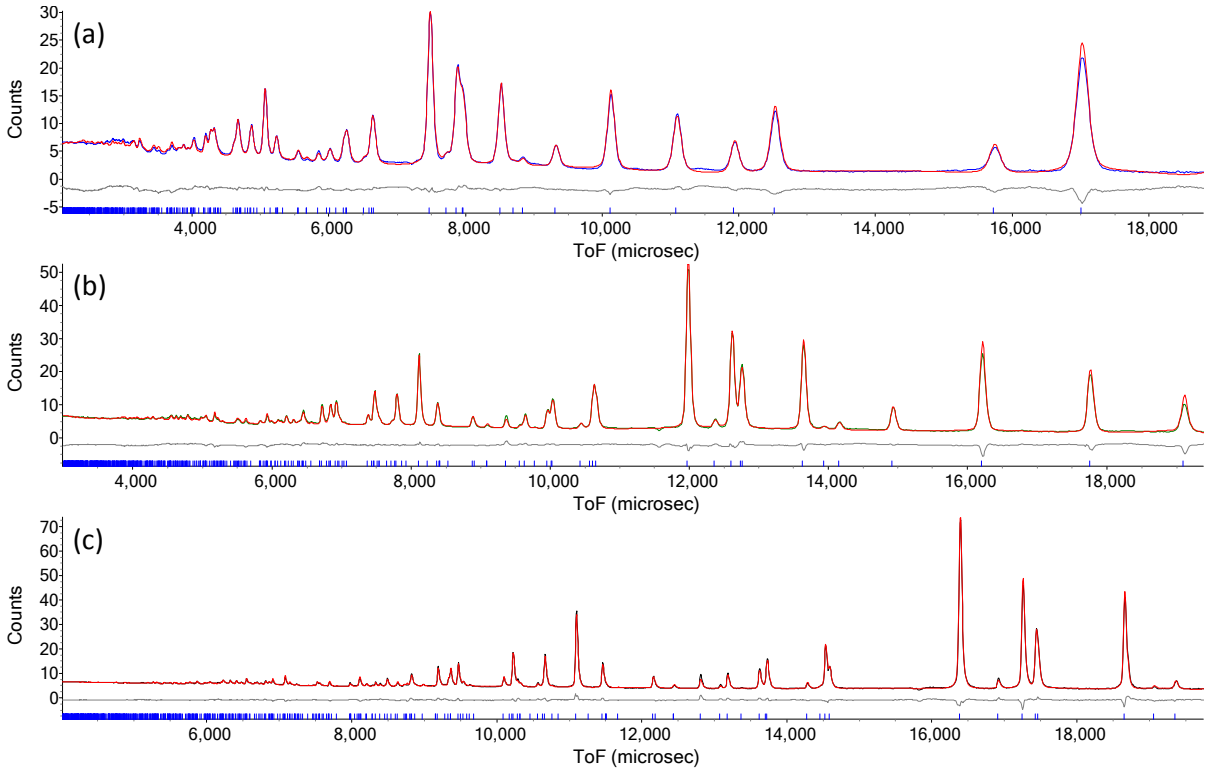

Fig. S2. The Rietveld plots of $Ba_3NbMoO_{8.5}$ at 600 °C from POLARIS (a) bank 3, R_{wp} = 4.84%, χ^2 = 9.25; (b) bank 4, R_{wp} = 4.03%, χ^2 = 11.12; (c) bank 5, R_{wp} = 2.19%, χ^2 = 3.71. Blue tick marks correspond to reflections from $Ba_3NbMoO_{8.5}$.

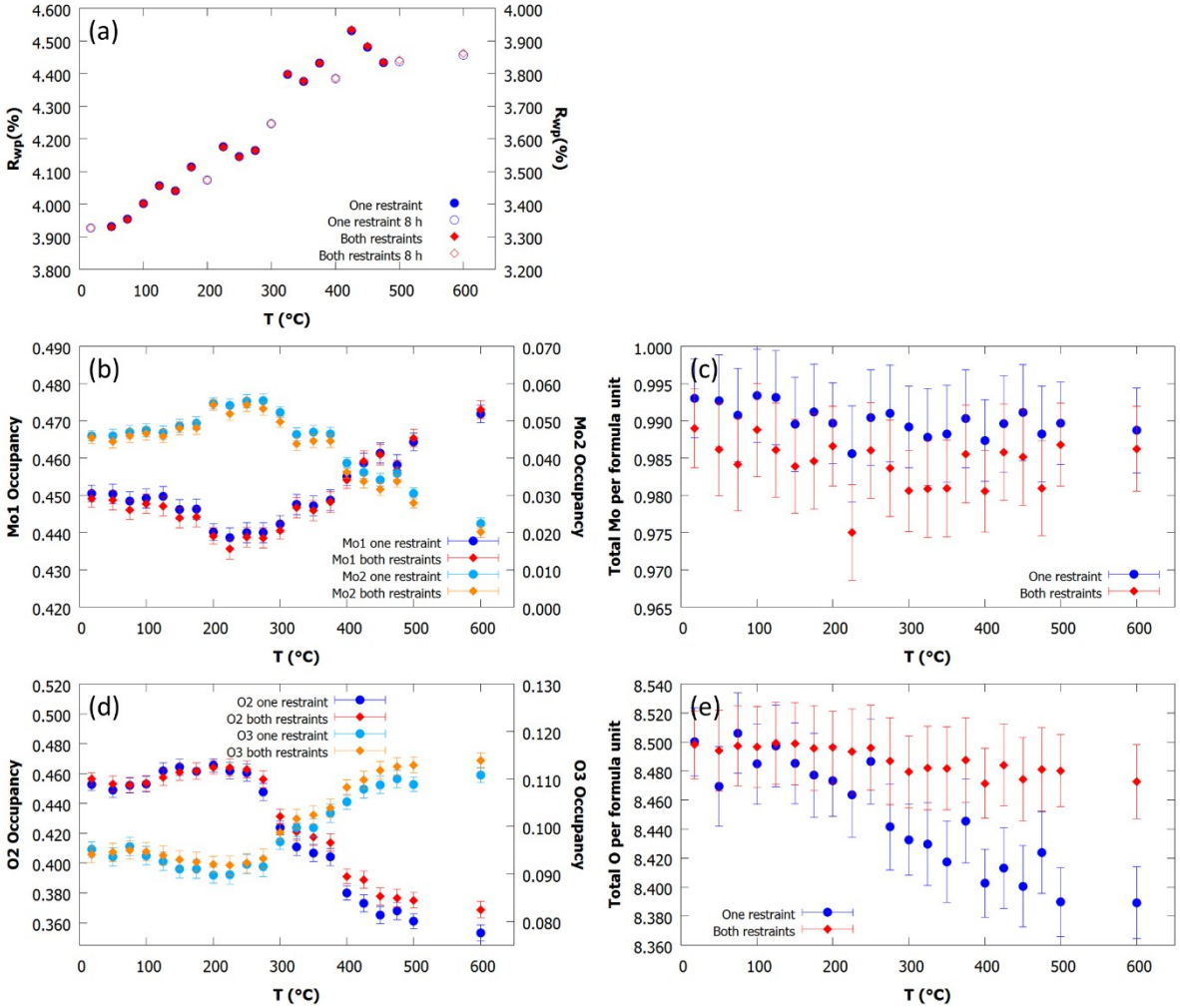

Fig. S3. The thermal evolution of structural parameters of $Ba_3NbMoO_{8.5}$ obtained from neutron diffraction. "One restraint" refers to refinements in which the total M content and Nb:Mo ratios were soft-restrained such that the total metal occupancy over the available sites sums to the expected chemical composition. "Both restraints" refer to refinements in which the overall oxygen content was also soft-restrained to sum to 8.5 per formula unit. Isotropic temperature factors were used throughout. Parameters plotted are: (a) The R_{wp} obtained for each of the fits at different temperatures; (b) Mo1 and Mo2 occupancies (Nb1 = Mo1, Nb2 = Mo2); (c) Total Mo content per formula unit; (d) O2 and O3 occupancies; (e) Total O content per formula unit. In panel (a), R_{wp} for longer (8 h) data collections are plotted on right-hand ordinate axis with open symbols.

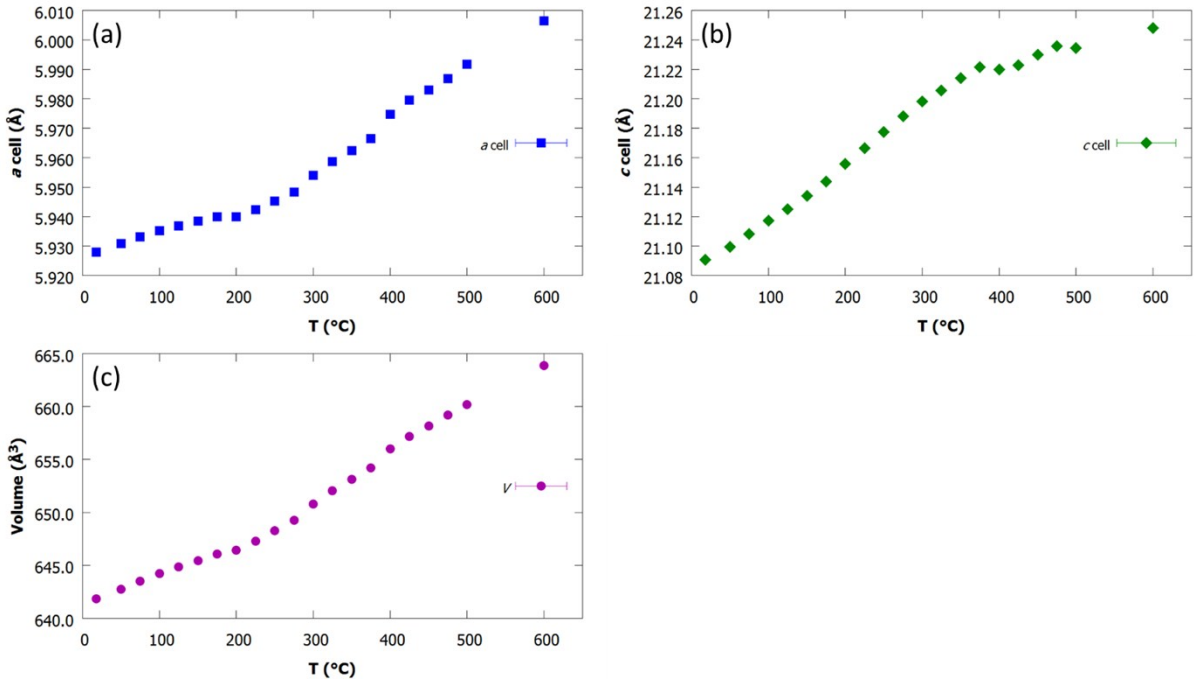

Fig. S4. Temperature evolution of the cell parameters of $Ba_3NbMoO_{8.5}$ obtained from neutron diffraction.

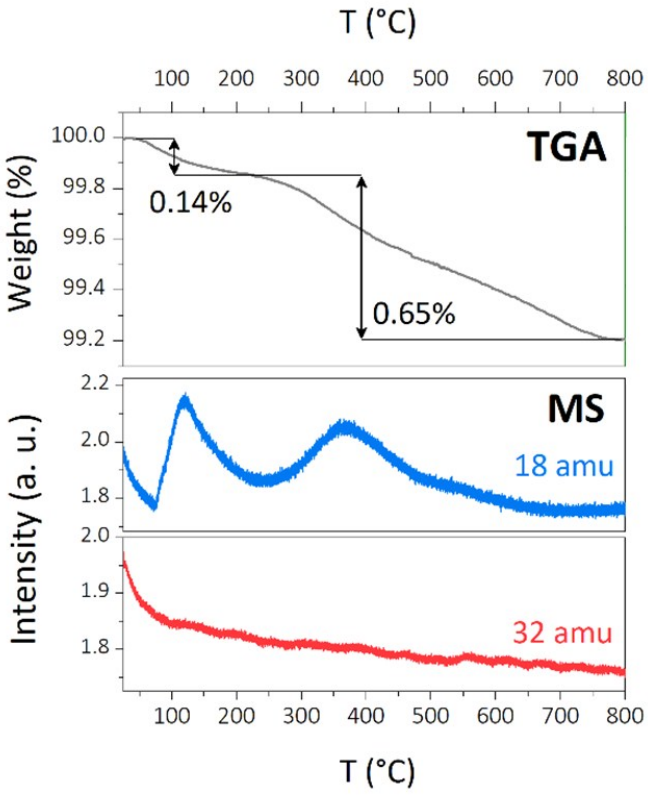

Fig. S5. (a) Results of TGA-MS analysis on a $Ba_3NbMoO_{8.5}$ sample under air. The top panel shows the thermogravimetric (TGA) diagram, while the bottom ones show mass spectrometry results at 18 amu (H_2O) and 32 amu (O_2)..

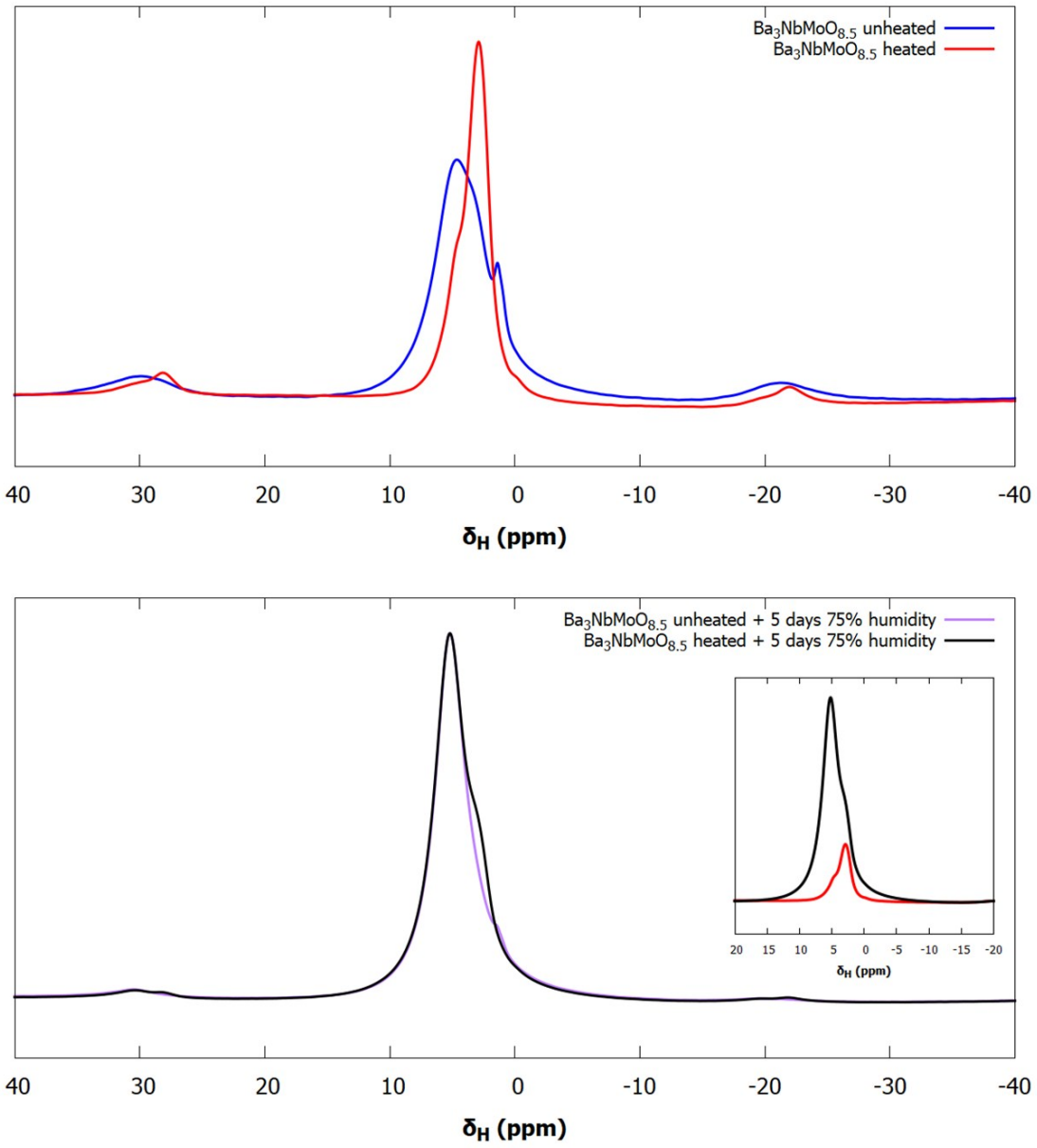

Fig. S6. (a) ^{1}H NMR recorded on a sample that had been heated to 600 °C during neutron diffraction experiments then stored in a vial before (unheated) and after (heated) re-heating to 600 °C. A weak ^{1}H signal is observed in both samples, with relative areas ~1.2:1 suggesting that they take up water from the atmosphere on cooling to room temperature. (b) Data on each sample after holding for 5 days at 75% relative humidity confirming further water uptake. Insert shows the heated sample before and after humidity treatment; colours as in main plots.

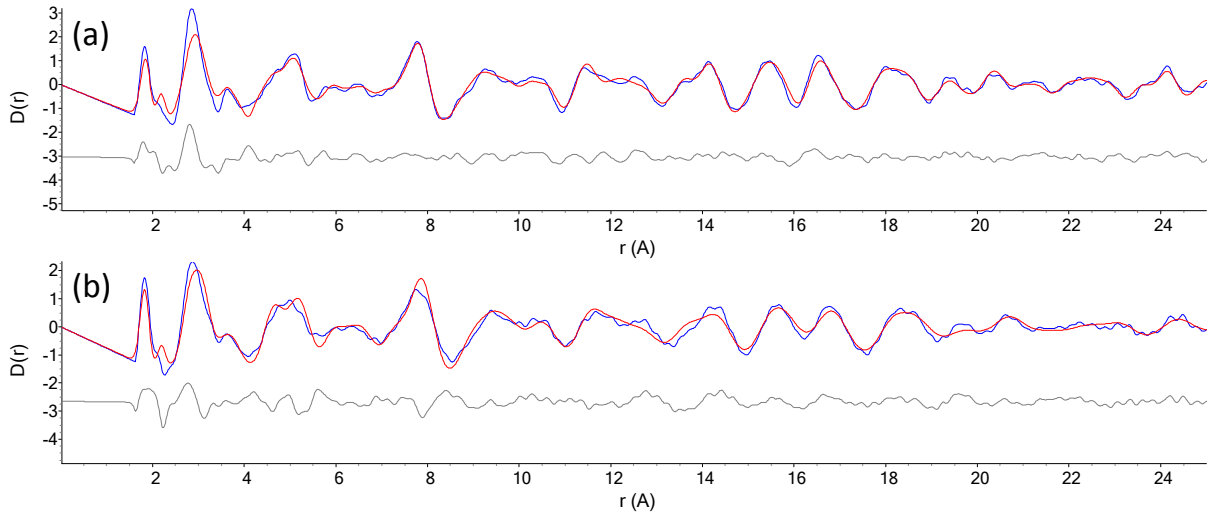

Fig. S7. Small-box neutron PDF fit of $Ba_3NbMoO_{8.5}$ at (a) room temperature (b) 600 °C.

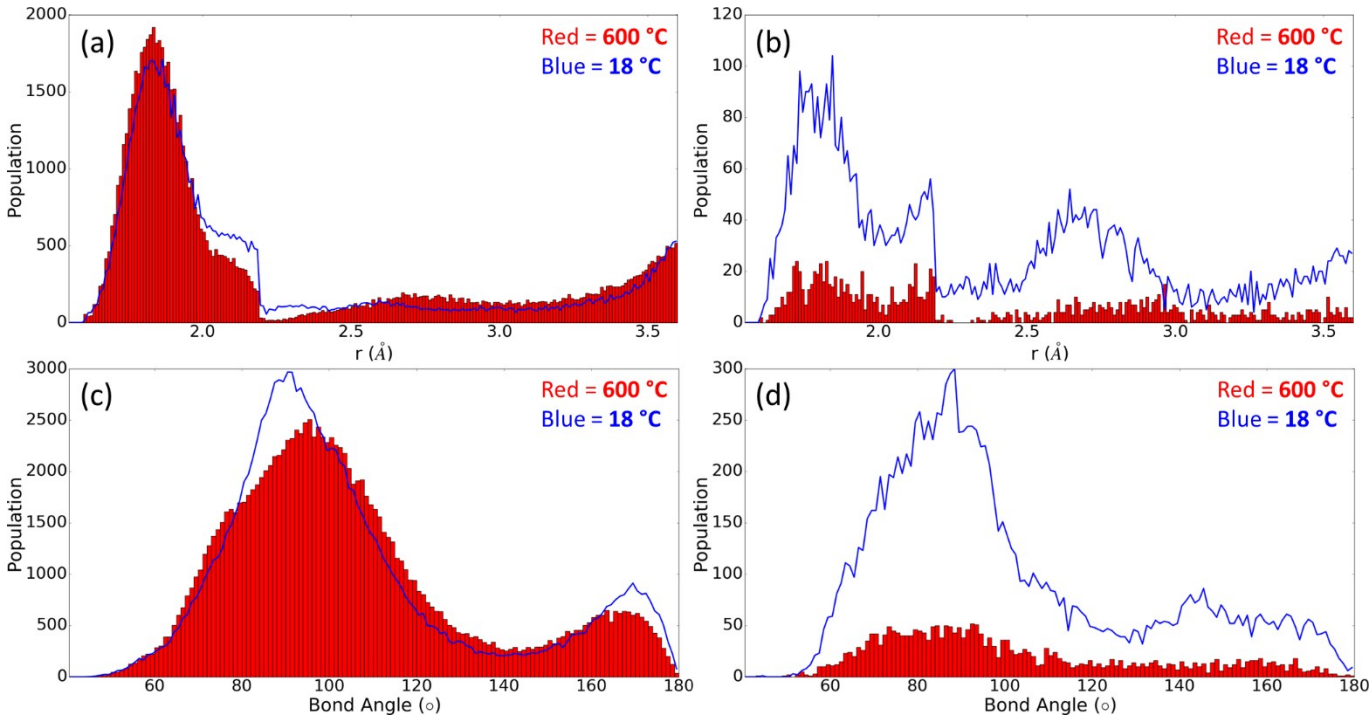

Fig. S8. Histograms of bond distances and angles from RMCProfile models at room (blue line) and 600 °C (red bars): (a) Mo1–O distances; (b) Mo2–O distances; (c) O–Mo1–O bond angles; (d) O–Mo2–O bond angles