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Supplementary Information

A Pressure Induced Structural Reversal to the 9R Perovskite in $Ba_3MoNbO_{8.5}$

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Table S1 Refined atomic parameters for $Ba_3MoNbO_{8.5}$ from the Rietveld fit of the high-pressure neutron powder diffraction data recorded on the PEARL diffractometer.

Atom	Wy	Parameter	0.1 MPa	0.9 GPa	1.7 GPa	2.8 GPa	4.3 GPa	4.8 GPa
Ba(1)	**3*a***	**Occupancy**	1.00	1.00	1.00	1.00	1.00	1.00
		$U_{11} = U_{22}$ (Å²)	0.015 (2)	0.010 (1)	0.016 (1)	0.011 (1)	0.010 (1)	0.004 (1)
		U_{33} (Å²)	0.034 (4)	0.023 (3)	0.010 (2)	0.016 (3)	0.001 (2)	0.001 (2)
		U_{12} (Å²)	0.0076 (8)	0.0050 (7)	0.0079 (7)	0.0055 (5)	0.0048 (6)	0.0019 (5)
Ba(2)	**6*c***	***z***	0.2071 (5)	0.2063 (4)	0.2082 (3)	0.2086 (3)	0.2108 (3)	0.211000 (0)
		Occupancy	1.00	1.00	1.00	1.00	1.00	1.00
		$U_{11} = U_{22}$ (Å²)	0.015 (2)	0.010 (1)	0.016 (1)	0.011 (1)	0.010 (1)	0.004 (1)
		U_{33} (Å²)	0.034 (4)	0.023 (3)	0.010 (2)	0.016 (3)	0.001 (2)	0.001 (2)
		U_{12} (Å²)	0.0076 (8)	0.0050 (7)	0.0079 (7)	0.0055 (5)	0.0048 (6)	0.0019 (5)
M(1)	**6*c***	***z***	0.3994 (3)	0.3995 (3)	0.4004 (2)	0.3992 (2)	0.3973 (3)	0.3962 (3)
		Occupancy	0.920 (3)	0.920 (3)	0.926 (4)	0.924 (3)	0.920 (3)	0.904 (3)
		$U_{11} = U_{22}$ (Å²)	0.013 (2)	0.008 (2)	0.002 (1)	0.000 (1)	0.001 (1)	0.003 (1)
		U_{33} (Å²)	0.038 (4)	0.046 (4)	0.051 (3)	0.056 (3)	0.064 (3)	0.056 (3)
		U_{12} (Å²)	0.0065 (8)	0.0038 (8)	0.0010 (5)	0.0002 (5)	0.0007 (5)	0.0015 (5)
M(2)	**6c**	***z***	0.5303 (3)	0.5304 (3)	0.5311 (2)	0.5302 (2)	0.5289 (3)	0.5273 (3)
		Occupancy	0.160 (7)	0.160 (7)	0.148 (8)	0.152 (6)	0.162 (6)	0.194 (4)
		$U_{11} = U_{22}$ (Å²)	0.013 (2)	0.008 (2)	0.002 (1)	0.000 (1)	0.001 (1)	0.003 (1)
		U_{33} (Å²)	0.038 (4)	0.046 (4)	0.051 (3)	0.056 (3)	0.064 (3)	0.056 (3)
		U_{12} (Å²)	0.0065 (8)	0.0038 (8)	0.0010 (5)	0.0002 (5)	0.0007 (5)	0.0015 (5)
O(1)	**18*h***	***x***	0.1711 (3)	0.1716 (3)	0.1705 (3)	0.1702 (3)	0.1706 (1)	0.1717 (1)
		y	0.8289 (3)	0.8284 (3)	0.8295 (3)	0.8298 (3)	0.8294 (1)	0.8283 (1)
		z	0.1033 (1)	0.1037 (1)	0.1036 (1)	0.1035 (1)	0.1039 (1)	0.1050 (1)
		Occupancy	1.00	1.00	1.00	1.00	1.00	1.00
		$U_{11} = U_{22}$ (Å²)	0.030 (1)	0.026 (1)	0.025 (1)	0.0234 (9)	0.0175 (8)	0.0172 (7)
		U_{33} (Å²)	0.012 (1)	0.010 (1)	0.015 (1)	0.016 (1)	0.017 (1)	0.0144 (8)
		U_{12} (Å²)	0.0183 (6)	0.0165 (6)	0.0160 (5)	0.0152 (5)	0.0123 (4)	0.0121 (4)
O(2)	**9*e***	**Occupancy**	0.477 (8)	0.506 (7)	0.510 (6)	0.583 (6)	0.715 (6)	0.789 (6)
		$U_{11} = U_{22}$ (Å²)	0.030 (1)	0.026 (1)	0.025 (1)	0.0234 (9)	0.0175 (8)	0.0172 (7)
		U_{33} (Å²)	0.012 (1)	0.010 (1)	0.015 (1)	0.016 (1)	0.017 (1)	0.0144 (8)
		U_{12} (Å²)	0.0183 (6)	0.0165 (6)	0.0160 (5)	0.0152 (5)	0.0123 (4)	0.0121 (4)
O(3)	**36*i***	***x***	0.082 (5)	0.075 (1)	0.0754 (9)	0.077 (1)	0.0770 (1)	0.0781 (1)
		y	0.094 (4)	0.087 (1)	0.0872 (9)	0.088 (1)	0.0887 (1)	0.0898 (1)
		z	0.327 (1)	0.320 (1)	0.3202 (9)	0.321 (1)	0.3218 (1)	0.3229 (1)
		Occupancy	0.089 (2)	0.082 (2)	0.081 (1)	0.062 (1)	0.029 (2)	0.011 (1)
		U_{iso} (Å²)	0.038 (9)	0.05 (1)	0.054 (9)	0.05 (1)	0.05 (3)	0.03 (5)
χ^2			0.93	0.90	1.17	1.14	0.98	0.86
R_p (%)			3.00	2.69	2.28	2.26	2.49	2.61
R_{wp} (%)			2.77	2.72	2.27	2.12	2.22	2.26

Table S2 Bond lengths calculated from the Rietveld refinement of high-pressure powder neutron diffraction data of $Ba_3MoNbO_{8.5}$.

Distance (Å)	0.1 MPa	0.9 GPa	1.7 GPa	2.8 GPa	4.3 GPa	4.8 GPa
Ba(1)–O(1)	2.8022 (3)	2.7971 (3)	2.778 (2)	2.759 (2)	2.743 (2)	2.757 (2)
Ba(1)–O(2)	2.9670 (5)	2.9494 (4)	2.9362 (3)	2.9189 (3)	2.8935 (4)	2.8859 (4)
Ba(1)–O(3)	3.0221 (5)	3.047 (7)	3.034 (6)	3.008 (8)	2.9792 (7)	2.9646 (7)
	3.4086 (5)	3.391 (1)	3.3759 (9)	3.3552 (9)	3.3257 (4)	3.3163 (4)
	3.9172 (6)	3.865 (4)	3.848 (3)	3.830 (4)	3.7980 (6)	3.7922 (6)
Ba(2)–O(1)	2.8108 (3)	2.780 (7)	2.794 (6)	2.785 (6)	2.790 (5)	2.773 (1)
	3.0068 (4)	2.990 (2)	2.971 (1)	2.953 (1)	2.9193 (9)	2.9082 (4)
Ba(2)–O(2)	3.1699 (4)	3.167 (7)	3.122 (6)	3.098 (6)	3.031 (5)	3.0154 (3)
Ba(2)–O(3)	2.5903 (4)	2.44 (2)	2.40 (2)	2.40 (2)	2.341 (6)	2.349 (2)
M(1)–O(1)	1.8435 (2)	1.832 (4)	1.824 (3)	1.827 (3)	1.827 (3)	1.834 (3)
M(1)–O(2)	2.2091 (2)	2.198 (4)	2.202 (3)	2.173 (3)	2.130 (4)	2.108 (4)
M(1)–O(3)	1.6144 (2)	1.74 (2)	1.75 (2)	1.69 (2)	1.632 (6)	1.583 (6)
M(2)–O(1)	2.1384 (2)	2.118 (3)	2.118 (3)	2.111 (2)	2.082 (2)	2.053 (2)

Table S3 Bond angles calculated from the Rietveld refinement of high-pressure powder neutron diffraction data of $Ba_3MoNbO_{8.5}$.

Angle (°)	0.1 MPa	0.9 GPa	1.7 GPa	2.8 GPa	4.3 GPa	4.8 GPa
O(1)–M(1)–O(1)	103.113 (6)	102.8 (2)	103.7 (2)	102.9 (2)	101.2 (2)	99.5 (2)
O(1)–M(1)–O(2)	85.343 (7)	85.59 (9)	85.30 (8)	85.46 (7)	85.96 (7)	86.62 (7)
O(1)–M(1)–O(3)	99.576 (8)	102.4 (3)	101.8 (3)	101.8 (4)	102.7 (1)	103.4 (1)
	111.688 (6)	112.5 (2)	111.9 (2)	112.3 (2)	113.5 (2)	114.6 (2)
	132.390 (1)	130.2 (4)	129.3 (4)	130.5 (5)	132.4 (3)	134.4 (3)
O(2)–M(1)–O(2)	84.371 (9)	84.3 (2)	83.6 (1)	84.4 (2)	85.6 (2)	86.4 (2)
O(1)–M(2)–O(1)	84.939 (9)	85.1 (1)	85.21 (9)	85.21 (9)	85.43 (4)	85.94 (4)
	95.061 (9)	95.0 (1)	94.79 (9)	94.79 (9)	94.57 (4)	94.06 (4)

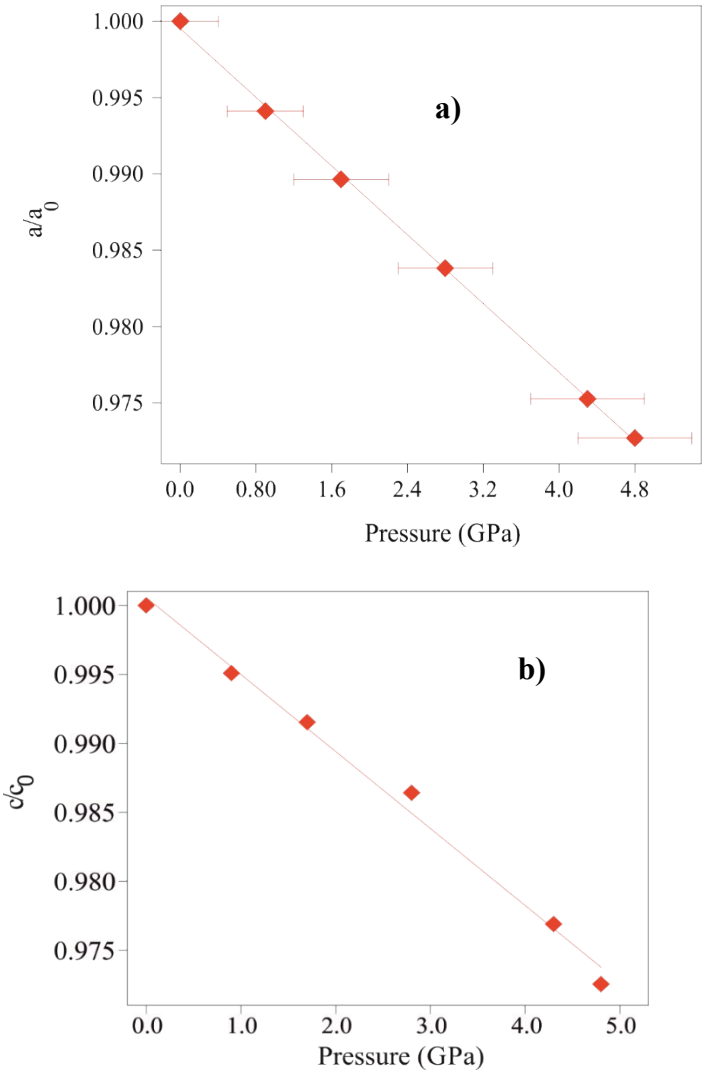

Figure S1 Variation of normalised unit cell parameter *a* (a) and *c* (b) with pressure for $Ba_3MoNbO_{8.5}$. The error arising from the Pb pressure marker is shown in a). Both axes undergo an axial compressibility of $k = 5.6 \times 10^{-3}$ GPa^{-1} which was determined from the linear fit.

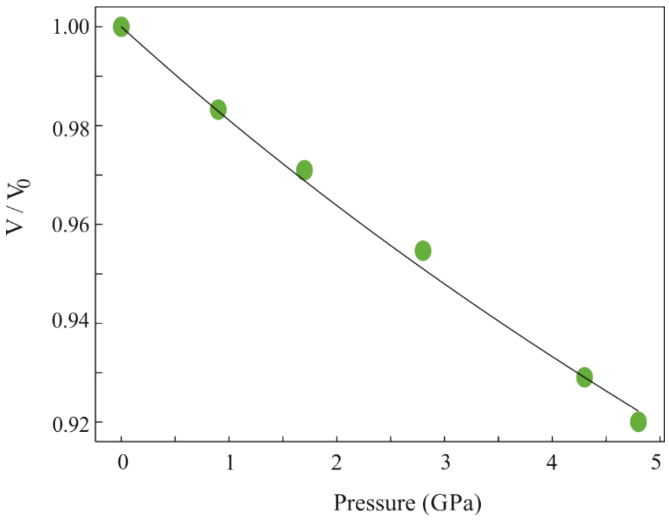

Figure S2 Variation of normalised unit cell volume with pressure for $Ba_3MoNbO_{8.5}$. The data is fit with a second order Birch-Murnaghan fit revealing a bulk modulus (K_0) of 50(1) GPa for the refined V_0 value of 644.8(6) $Å^3$.

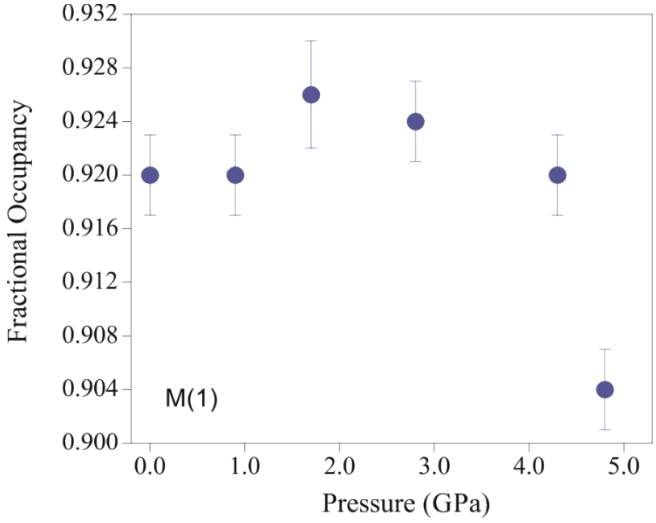

Figure S3 Variation of the M(1) site fractional occupancy of $Ba_3MoNbO_{8.5}$ with pressure.

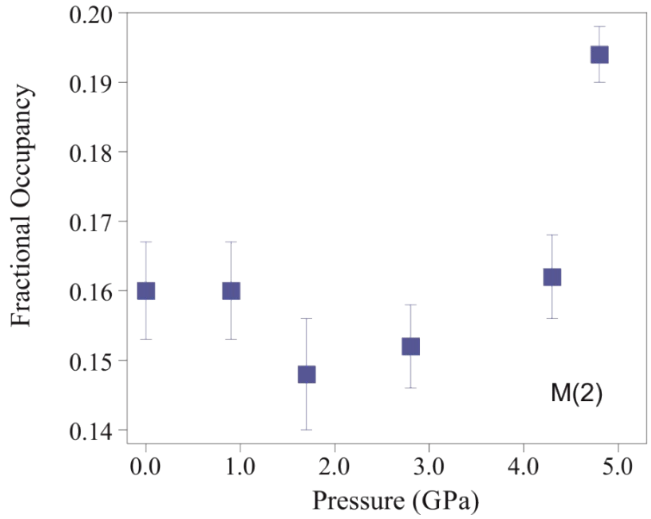

Figure S4 Variation of the M(2) site fractional occupancy of $Ba_3MoNbO_{8.5}$ with pressure.

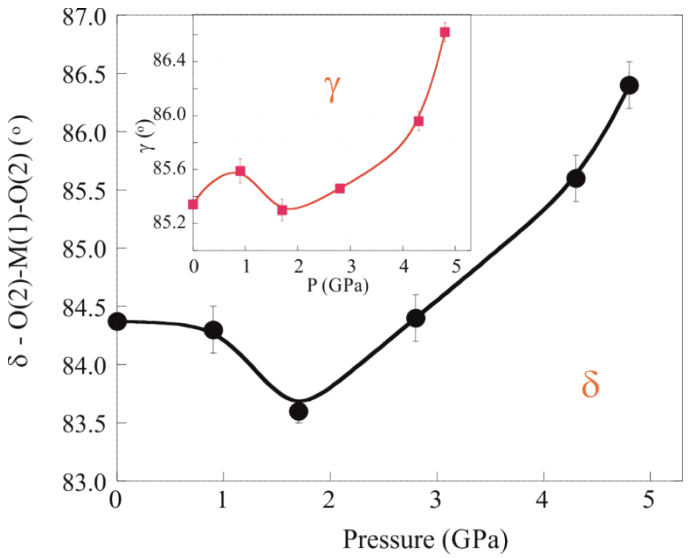

Figure S5 Pressure dependency of δ – O(2)-M(1)-O(2) and γ – O(1)-M(1)-O(2) angles for the M(1) polyhedra.

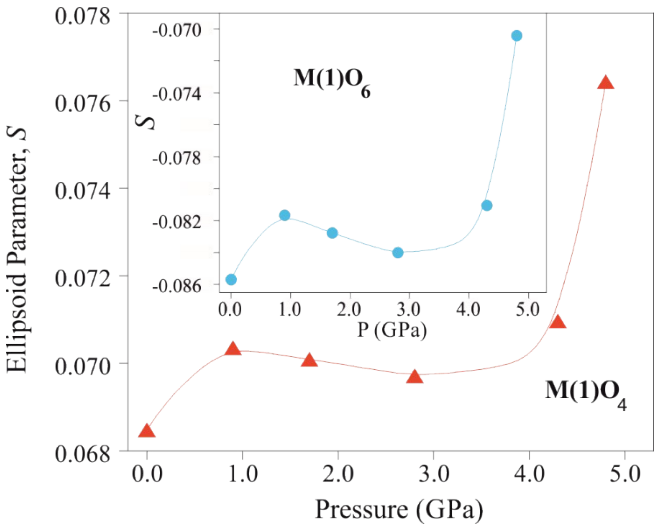

Figure S6 Pressure dependency of the ellipsoid shape parameter, *S*, for the $M(1)O_6$ and $M(1)O_4$ polyhedra.

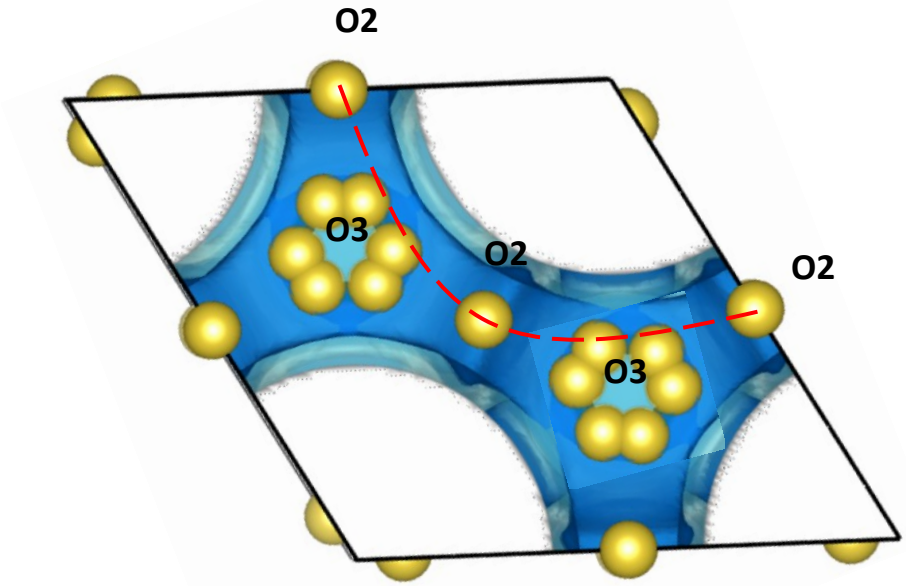

Figure S7 Bond valence site energy map and view of the 2-dimensional diffusion pathway, as seen along the *c* axis. The dashed red line shows the connectivity between O2/O3 sites.

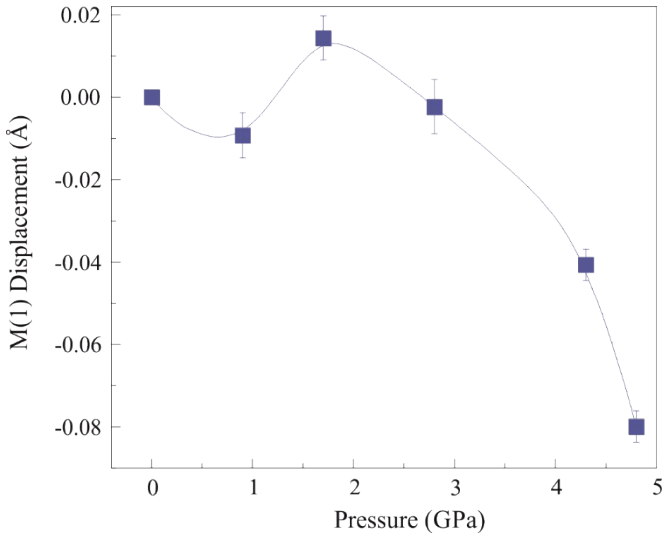

Figure S8 Variation of the M(1) displacement with pressure.