Supplementary Information

for

Tuning of the Ionic Conductivity of $Ba_7Nb_4MoO_{20}$ by Pressure: A Neutron Diffraction and Atomistic Modelling Study

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Table S1 Refined atomic parameters, cell parameters and agreement factors for $Ba_7Nb_4MoO_{20}$ from the Rietveld fit to the $P\bar{3}m1$ model from neutron diffraction data collected on the PEARL diffractometer from 0 GPa to 4.9 GPa. Due to their similar scattering lengths, the Mo and Nb cations are distributed on the metal M positions. M= Mo, Nb.

		Pressure	**0 Gpa**	**0.93(5) GPa**	**1.65(5) Gpa**	**3.29(6) Gpa**	**3.56(6) Gpa**	**4.06(8) GPa**	**4.90(8) GPa**
Atom	**Site**	**Parameter**							
Ba1 (0,0,0)	**1*a***	Occupancy	1	1	1	1	1	1	1
		Uiso	0.0074(4)	0.0080(8)	0.0103(8)	0.0069(8)	0.0071(8)	0.0051(9)	0.0040(10)
Ba2 (1/3,2/3, z)	**2*d***	Occupancy	1	1	1	1	1	1	1
		Uiso	0.0074(4)	0.0080(8)	0.0103(8)	0.0069(8)	0.0071(8)	0.0051(9)	0.0040(10)
		z	0.8278(3)	0.8263(5)	0.8265(5)	0.8271(5)	0.8271(5)	0.8248(6)	0.8234 (7)
Ba3 (0,0, z)	**2*c***	Occupancy	1	1	1	1	1	1	1
		Uiso	0.0074(4)	0.0080(8)	0.0103(8)	0.0069(8)	0.0071(8)	0.0051(9)	0.0040(10)
		z	0.2777(3)	0.2784(6)	0.2782(6)	0.2767(8)	0.2771(7)	0.2806(7)	0.2796(9)
Ba4 (1/3, 2/3, z)	**2*d***	Occupancy	1	1	1	1	1	1	1
		Uiso	0.0074(4)	0.0080(8)	0.0103(8)	0.0069(8)	0.0071(8)	0.0051(9)	0.0040(10)
		z	0.5751(4)	0.5740(7)	0.5750(8)	0.5753(8)	0.5765(8)	0.5775(8)	0.5795(9)
M1 (1/3, 2/3, z)	**2*d***	Occupancy	0.877(2)	0.869(4)	0.857(4)	0.869(5)	0.857(5)	0.861(6)	0.851(7)
		Uiso	0.0096(3)	0.0132(7)	0.0103(6)	0.0075(7)	0.0069(7)	0.0112(8)	0.0074(9)
		z	0.0918(3)	0.0918(5)	0.0904(5)	0.0905(6)	0.0912(6)	0.0910(6)	0.0910(8)
M2 (1/3, 2/3, z)	**2*d***	Occupancy	0.123(2)	0.131(4)	0.143(4)	0.131(5)	0.143(5)	0.139(6)	0.149(7)
		Uiso	0.0096(3)	0.0132(7)	0.0103(6)	0.0075(7)	0.0069(7)	0.0112(8)	0.0074(9)
		z	0.2230(18)	0.1935(24)	0.2323(22)	0.2307(28)	0.2297(25)	0.2398(34)	0.2347(31)
M3 (1/3, 2/3, z)	**2*d***	Occupancy	1	1	1	1	1	1	1
		Uiso	0.0096(3)	0.0132(7)	0.0103(6)	0.0075(7)	0.0069(7)	0.0112(8)	0.0074(9)

		z	0.3536(2)	0.3529(4)	0.3520(4)	0.3531(4)	0.3534(4)	0.3510(5)	0.3517(6)
M4 (0,0, 1/2)	**1*b***	Occupancy	1	1	1	1	1	1	1
		Uiso	0.0096(3)	0.0132(7)	0.0103(6)	0.0075(7)	0.0069(7)	0.0112(8)	0.0074(9)
O1 (x,y,z)	**6*i***	Occupancy	0.243(3)	0.234(5)	0.233(5)	0.230(5)	0.220(5)	0.208(6)	0.180(7)
		Uiso	0.0112(29)	0.0052(42)	0.0015(35)	0.0022(53)	0.0001(43)	0.0010(53)	0.0017(89)
		x	0.3619(10)	0.3652(15)	0.3657 (13)	0.3653 (16)	0.3663 (15)	0.3613(20)	0.3518(47)
		y	0.6381(10)	0.6348(15)	0.6343(13)	0.6347(16)	0.6337(15)	0.6387(20)	0.64822(47)
		z	0.9832(4)	0.9819(7)	0.9830(7)	0.98010(7)	0.9813(7)	0.9824(8)	0.9825(10)
O2 (1/2,0,0)	**3*e***	Occupancy	0.179(5)	0.198(9)	0.200(9)	0.206(10)	0.225(10)	0.249(12)	0.306(14)
		Uiso	0.0179(39)	0.0130(85)	0.0170(89)	0.0015(75)	0.00003(578)	0.0092(83)	0.0351(114)
O3 (x,y,z)	**6*i***	Occupancy	1	1	1	1	1	1	1
		Uiso	0.0167(7)	0.0230(15)	0.0188(13)	0.0127(13)	0.0127(14)	0.0212(18)	0.0112(17)
		x	0.1679(5)	0.1671(9)	0.1662(10)	0.1663(10)	0.1666(11)	0.1684(14)	0.1647(13)
		y	0.8321(5)	0.8329(9)	0.8338(10)	0.8337(10)	0.833386(11)	0.8316 (14)	0.8353(13)
		z	0.1321 (2)	0.1328(4)	0.1331 (4)	0.1333 (4)	0.1331(4)	0.1330(5)	0.1341(5)
O(4) (x,y,z)	**6*i***	Occupancy	1	1	1	1	1	1	1
		Uiso	0.0092(6)	0.0153(13)	0.0164(13)	0.0095(13)	0.0120(13)	0.0274(17)	0.0242(21)
		x	0.4936(4)	0.4930(8)	0.4944(8)	0.4943(8)	0.4964(8)	0.4972(11)	0.4960(11)
		y	0.9873(8)	0.9861(15)	0.9890(15)	0.9887(16)	0.9929(17)	0.9945(22)	0.9921(23)
		z	0.2941(1)	0.2932(2)	0.2929(2)	0.2921(2)	0.2923(2)	0.2926(3)	0.2923 (4)
O5 (x,y,z)	**6*i***	Occupancy	1	1	1	1	1	1	1
		Uiso	0.0049(4)	0.0067(9)	0.0062(10)	0.0033(10)	0.0049(11)	0.0010(9)	0.0027(13)
		x	0.1627(5)	0.1615(8)	0.1609(8)	0.1616(9)	0.1612(9)	0.1606(8)	0.1592(10)
		y	0.8373(5)	0.8385 (8)	0.8391(8)	0.8384 (9)	0.8388(9)	0.8394 (8)	0.8408(10)
		z	0.4316(2)	0.4329(3)	0.4322(4)	0.4319(4)	0.4314(4)	0.4319(4)	0.4328(5)
***a* (Å)**			5.86122(6)	5.84293(9)	5.82887(9)	5.79894(10)	5.79397(10)	5.78531(13)	5.77144(19)
***c* (Å)**			16.5252(3)	16.4680(5)	16.4226(5)	16.3282(6)	16.3136(6)	16.2862(9)	16.2420(12)
V (Å^3)			491.550(9)	486.892(15)	483.216(14)	475.516(16)	474.279(17)	472.068(23)	468.530(34)
χ2			5.336	0.7127	0.725	0.735	0.7854	0.8116	0.7904
R_p(%)			0.0196	0.0189	0.0188	0.0205	0.0214	0.0259	0.031
R_{wp}(%)			0.0228	0.0189	0.0187	0.0201	0.021	0.0245	0.0282

Table S2 Selected bond lengths for $Ba_7Nb_4MoO_{20}$ determined from the Rietveld fit to the $P\bar{3}m1$ model from neutron diffraction data. Due to their similar scattering lengths, the Mo and Nb cations are distributed on the metal M positions. **M= Mo, Nb.**

Bond distance (Å)	**0 Gpa**	**0.93(5) GPa**	**1.65(5) Gpa**	**3.29(6) Gpa**	**3.56(6) Gpa**	**4.06(8) GPa**	**4.90(8) GPa**
Ba1-O1	3.261(4)	3.241(7)	3.229(6)	3.215(7)	3.207(6)	3.222(8)	3.215(7)
Ba1-O2	2.93061(3)	2.92147(4)	2.91443(4)	2.89947(5)	2.89699(5)	2.89265(7)	2.89947(5)
Ba1-O3	2.770(4)	2.766(7)	2.755(7)	2.744(7)	2.741(8)	2.746(10)	2.744(7)
Ba2-O1	2.585(7)	2.584(13)	2.585(13)	2.533(14)	2.538(13)	2.582(15)	2.533(14)
Ba2-O2	3.311(4)	3.320(7)	3.306(7)	3.281(8)	3.280(7)	3.307(8)	3.281(8)
Ba2-O3	3.0046(11)	2.947(14)	2.9883(23)	2.9705(22)	2.9688(22)	2.9736(27)	2.9705(22)
Ba2-O4	2.672(4)	2.639(8)	2.623(8)	2.605(8)	2.590(8)	2.556(10)	2.605(8)
Ba3-O3	2.949(7)	2.947(14)	2.925(13)	2.876(15)	2.882(14)	2.937(16)	2.876(18)
Ba3–O4	2.9441(6)	2.9319(11)	3.001(11)	2.9112(12)	2.9075(11)	2.8996(10)	2.8933(14)
Ba3-O5	3.032(6)	3.025(11)	3.007(12)	3.009(13)	2.993(12)	2.942(13)	2.954(17)
Ba4-O4	2.785(6)	2.797(11)	2.776(11)	2.772(12)	2.739(11)	2.712(13)	2.697(14)
Ba4-O5	2.936(6) 2.9327(3)	2.907(12) 2.9244(5)	2.919(12) 2.9176(6)	2.909(13) 2.9023(6)	2.930(13) 2.9004(6)	2.937(14) 2.8974(7)	2.954(17) 2.8937(11)
M1-O1	1.818(8)	1.836(14)	1.802(13)	1.816(15)	1.824(15)	1.791(16)	1.786(21)
M1-O2	2.2723(31)	2.266(6)	2.249(6)	2.233(6)	2.239(6)	2.232(6)	2.237(9)
M1-O3	1.807(6)	1.808(11)	1.823(11)	1.818(11)	1.808(11)	1.790(14)	1.827(13)
M2-O3	2.253(20)	1.986(29)	2.282(34)	2.312(32)	2.297(27)	2.400(40)	2.290(40)
M2-O4	2.008(17)	2.270(4)	1.957(28)	1.902(25)	1.931(22)	1.854(25)	1.917(33)
M3-O4	1.902(4)	1.893(8)	1.896(8)	1.900(8)	1.916(8)	1.898(11)	1.892(11)
M3-O5	2.158(5)	2.182(9)	2.179(8)	2.152(9)	2.146(9)	2.175(9)	2.170(11)
M4-O5	2.002(4)	1.972(7)	1.971(7)	1.967(8)	1.967(8)	1.955(7)	1.932(9)

Table S3 Selected bond angles for $Ba_7Nb_4MoO_{20}$ determined from the Rietveld fit to the $P\bar{3}m1$ model from neutron diffraction data. Due to their similar scattering lengths, the Mo and Nb cations are distributed on the metal M positions. **M= Mo, Nb.**

Bond Angle (°)	**0 GPa**	**0.93(5) GPa**	**1.65(5) Gpa**	**3.29(6) Gpa**	**3.56(6) Gpa**	**4.06(8) GPa**	**4.90(8) GPa**
O1-M1-O3	106.9(2)	106.7(4)	106.9(4)	107.3(4)	106.7(4)	107.8(5)	108.7(9)
O2-M1-O2	80.30(13)	80.26(25)	80.78(25)	80.99(27)	80.64(26)	80.76(28)	80.30(40)
O2-M1-O3	84.28(9) 159.8(2)	84.44(18) 159.9(5)	84.60(18) 160.7(5)	84.77(18) 161.2(5)	84.60(19) 160.6(5)	84.74(24) 160.9(5)	84.44(24) 160.0(7)
O3-M1-O3	107.2(2)	107.0(4)	106.5(4)	106.1(4)	106.6(4)	106.3(4)	107.0(5)
O3-M2-O3	80.4(9)	94.1(18)	79.6(15)	77.9(13)	78.3(12)		79.8(17)
O3-M2-O4	95.06(14) 174.0(13)	94.1(4) 168.0(22)	93.88(31) 171.4(22)	93.1(4) 168.3(21)	93.11(30) 168.8(18)		92.9(4) 170.3(27)

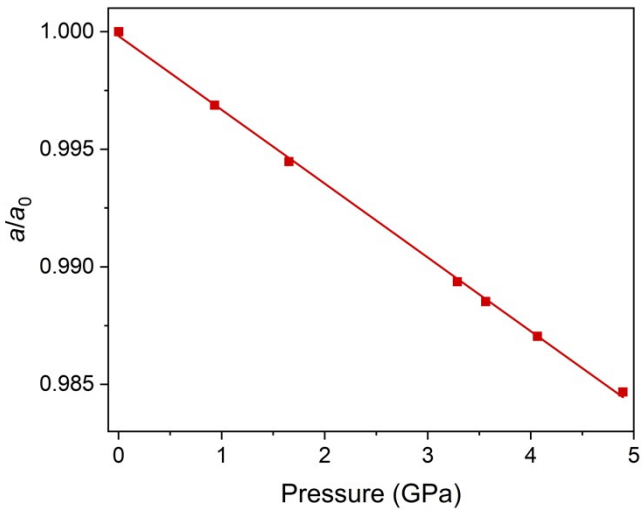

Figure S1 Variation of the normalised unit cell parameter *a* with pressure for $Ba_7Nb_4MoO_{20}$. Axial compressibility of k = 3.14 x 10^{-3} GPa^{-1} was determined from the linear fit of this graph.

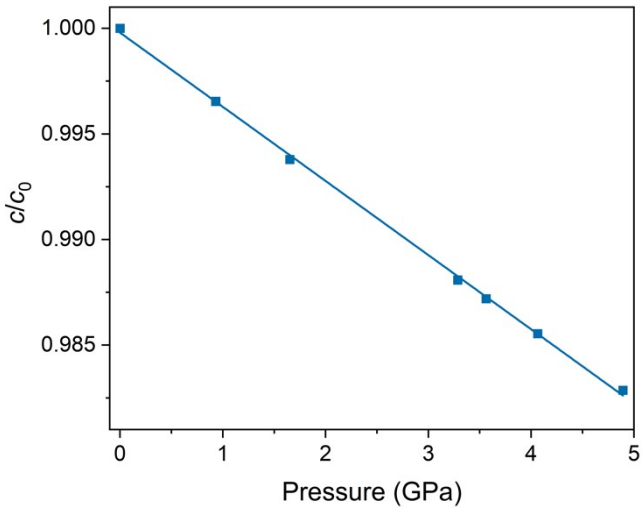

Figure S2 Variation of the normalised unit cell parameter *c* with pressure for $Ba_7Nb_4MoO_{20}$. Axial compressibility of k = 3.51 x 10^{-3} GPa^{-1} was determined from the linear fit of this graph.

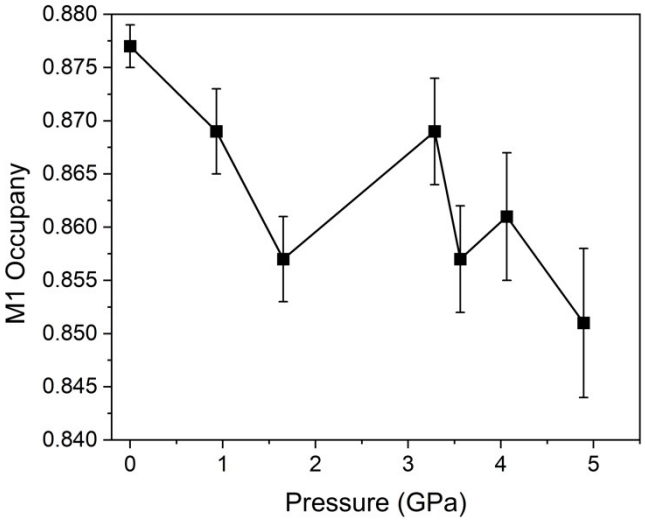

Figure S3 Variation of the M1 fractional occupancy with pressure for $Ba_7Nb_4MoO_{20}$

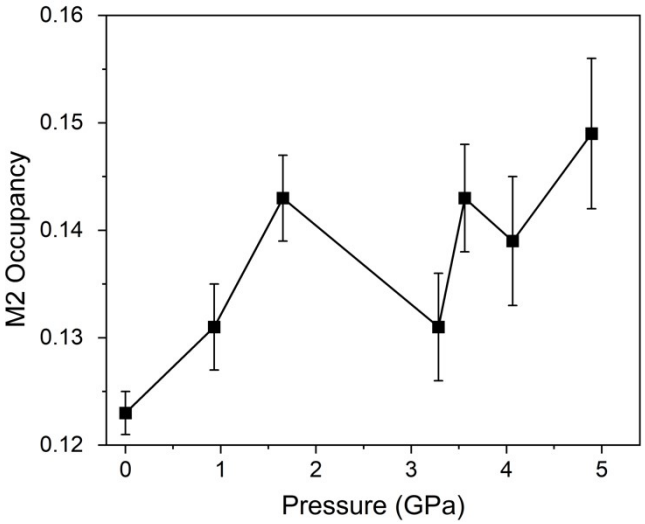

Figure S4 Variation of the M2 fractional occupancy with pressure for $Ba_7Nb_4MoO_{20}$.

Table S4 Minimum bounding ellipsoid data calculated by the PIEFACE software package for $M1O_4$ tetrahedra. R1, R2 and R3 are the principal ellipsoid radii, <R> is the mean radius, σ(R) is a measure of the polyhedral distortion, S is the ellipsoidal shape parameter and *d* is the centre cation displacement.

Pressure	*R1* (Å)	*R2* (Å)	*R3* (Å)	*<R>* (Å)	σ*(R)* (Å)	S	*d*
0	1.85845	1.78442	1.78442	1.80910	0.03490	0.03983	0.03881
0.93(5)	1.87929	1.78781	1.78781	1.81830	0.04313	0.04868	0.03881
1.65(5)	1.86427	1.79326	1.79326	1.81693	0.03348	0.03809	0.06955
3.29(6)	1.88084	1.78310	1.78310	1.81568	0.04608	0.05197	0.06212
3.56(6)	1.87450	1.77799	1.77799	1.81016	0.04550	0.05149	0.04841
4.06(8)	1.85168	1.75636	1.75636	1.78813	0.04493	0.05147	0.05976
4.90(8)	1.85202	1.78878	1.78878	1.80986	0.02981	0.03415	0.07972

Table S5 Minimum bounding ellipsoid data calculated by the PIEFACE software package for $M1O_6$ octahedra. R1, R2 and R3 are the principal ellipsoid radii, <R> is the mean radius, σ(R) is a measure of the polyhedral distortion, S is the ellipsoidal shape parameter and *d* is the centre cation displacement.

Pressure	*R1* (Å)	*R2* (Å)	*R3* (Å)	*<R>* (Å)	σ*(R)* (Å)	S	*d*
0	2.06469	2.06469	1.89089	2.00675	0.08193	-0.08417	0.43319
0.93(5)	2.06292	2.06292	1.89423	2.00669	0.07952	-0.08177	0.42100
1.65(5)	2.06353	2.06353	1.89356	2.00687	0.08012	-0.08237	0.38882
3.29(6)	2.05243	2.05243	1.88522	1.99670	0.07882	-0.08147	0.38661
3.56(7)	2.04846	2.04846	1.88100	1.99264	0.07894	-0.08175	0.40166
4.06(9)	2.03522	2.03522	1.87605	1.98216	0.07503	-0.07820	0.40919
4.90(9)	2.05249	2.052491	1.88643	1.99714	0.07828	-0.08091	0.37632

Table S6 Minimum bounding ellipsoid data calculated by the PIEFACE software package for $M2O_6$ octahedra. R1, R2 and R3 are the principal ellipsoid radii, <R> is the mean radius, σ(R) is a measure of the polyhedral distortion, S is the ellipsoidal shape parameter and *d* is the centre cation displacement.

Pressure	*R1* (Å)	*R2* (Å)	*R3* (Å)	<*R*> (Å)	σ*(R)* (Å)	S	*d*
0	2.31728	2.026417	2.026416	2.123371	0.137114	0.125518	0.204895
0.93(5)	2.285496	2.021889	2.021887	2.109757	0.124266	0.115338	0.268666
1.65(5)	2.270681	2.031085	2.031084	2.11095	0.112947	0.105516	0.363238
3.29(6)	2.243334	2.019446	2.019444	2.094075	0.105542	0.099801	0.341188
3.56(6)	2.248237	2.027345	2.029788	2.094578	0.10413	0.087389	0.304334
4.06(8)	2.250569	2.018324	2.018322	2.095738	0.109482	0.103193	0.448155
4.90(8)	2.224157	2.029789	2.029788	2.094578	0.091626	0.087389	0.393607

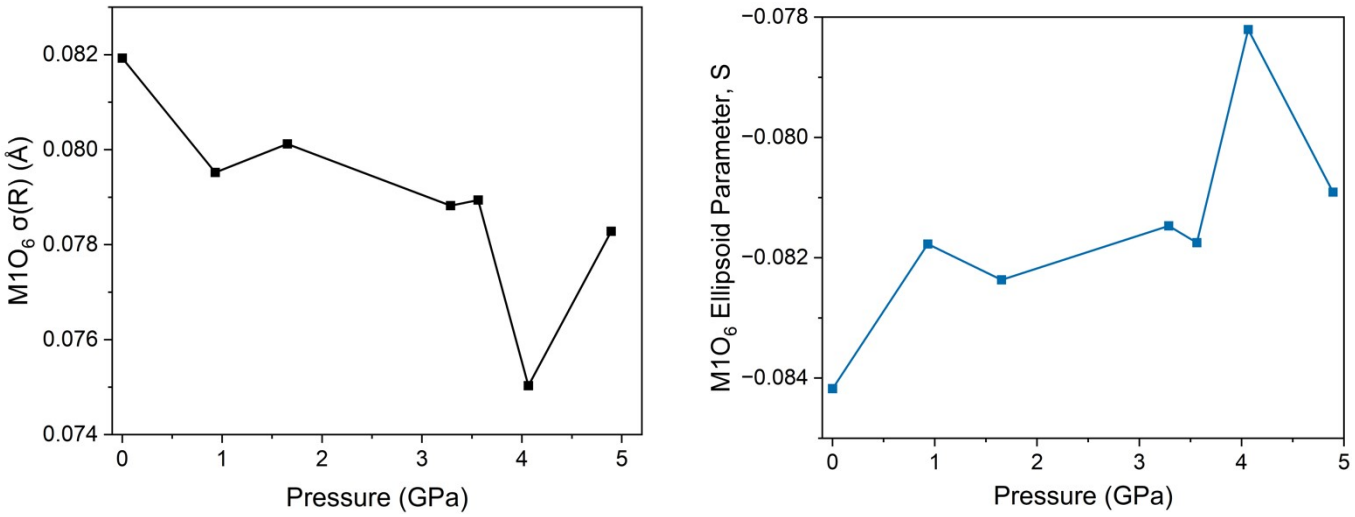

Figure S5 Variation of the polyhedral distortion, σ(R), for the $M1O_6$ octahedra (left). Variation of ellipsoid shape parameter, S, for the $M1O_6$ octahedra for $Ba_7Nb_4MoO_{20}$ (right).

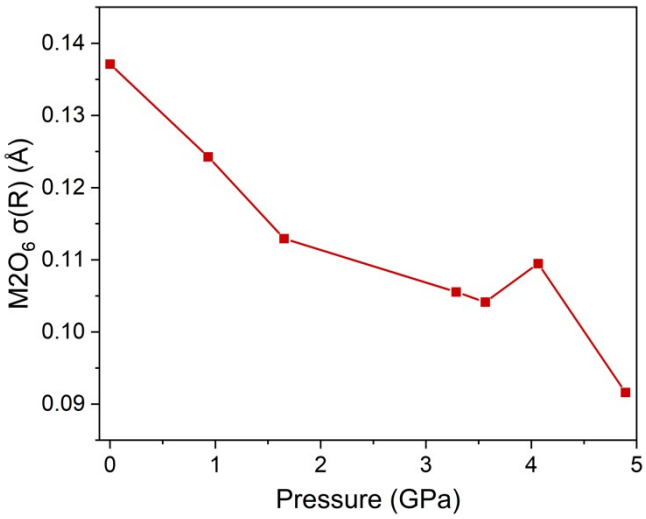

Figure S6 Variation of the polyhedral distortion, σ(R), for the $M2O_6$ octahedra.

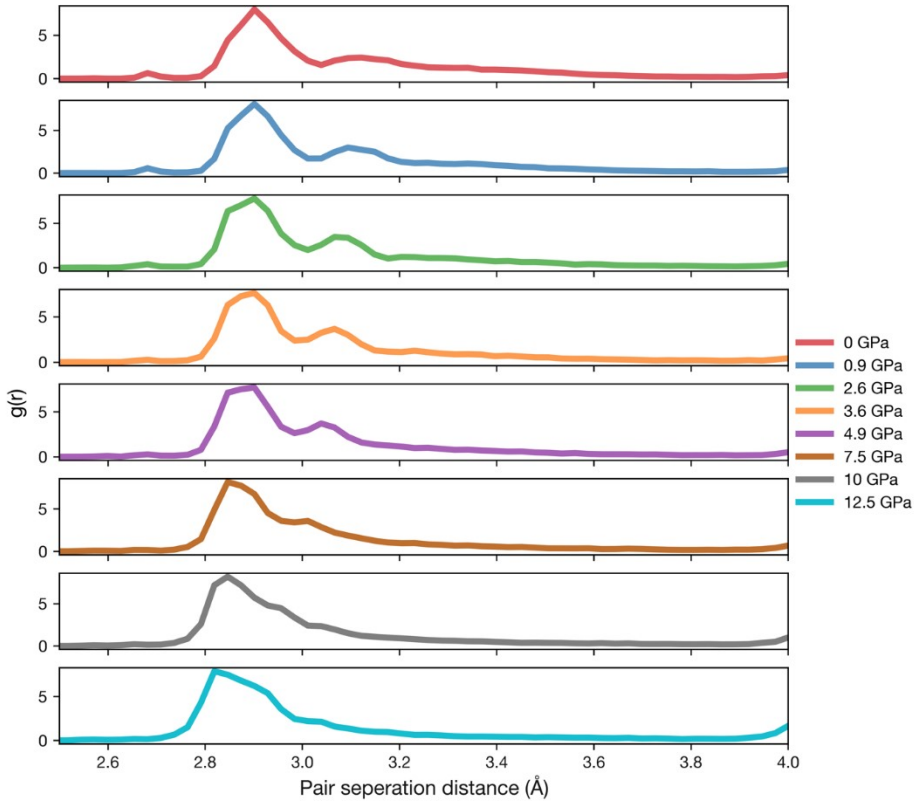

Figure S7 O–O radial distribution functions from molecular dynamics simulations as a function of pressure.