Electronic Supplementary Information for

Squeezing electrons out of 6s² lone-pairs in perovskite-type oxides

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Details of the high-pressure diffraction experiments

High-pressure synchrotron X-ray powder diffraction (S-XRD) data for all three samples were collected on the PD beamline of the Australian Synchrotron (λ = 0.68787 Å, calibrated against a LaB_6 standard). A diamond-anvil cell (DAC) was used with a 120 μm hole drilled in the gasket, which was then filled with the sample, the pressure-transmitting medium (a standard 4:1 methanol:ethanol mixture), and an Au standard for pressure calibration against the unit cell volume of Au. Data were collected on increasing pressure, with two data sets also successfully collected on reducing pressure for Ba_2BiOsO_6.

High-pressure neutron powder diffraction (NPD) data for Ba_2BiRuO_6 were collected in a Paris-Edinburgh (P-E) press on the Wombat diffractometer at ANSTO's OPAL research reactor (λ = 2.4184). The pressure-transmitting medium was a standard 4:1 methanol:ethanol mixture, and pressures were calibrated against the unit cell volume of a Pb standard.

Table S1. Unit cell parameters for Ba_2BiIrO_6, from Rietveld-refinement against high-pressure synchrotron X-ray powder diffraction data (λ = 0.68787 Å). Space group *Fm*-3*m*. a_{Au} is the unit cell parameter of the Au standard mixed with the sample and used for pressure calibration.

P (GPa)	a_{Au} (Å)	a (Å)	c (Å)	V (Å^3)	R_{wp} (%)
1.43	4.0673(3)	5.9908(5)	14.7275(19)	457.76(10)	5.04
3.45	4.0522(3)	5.9674(6)	14.694(2)	453.13(13)	4.93
4.49	4.0448(5)	5.9424(10)	14.686(4)	449.12(19)	4.78
7.83	4.0225(8)	5.899(3)	14.561(16)	438.9(3)	5.50
10.76	4.0045(8)	5.851(4)	14.50(2)	429.7(4)	5.96
12.82	3.9926(6)	5.787(4)	14.375(18)	416.9(4)	5.32
11.73	3.9988(6)	5.783(5)	14.39(2)	416.6(6)	6.41
14.04	3.9858(6)	5.751(7)	14.38(3)	411.8(8)	6.57

Table S2. Unit cell parameters for Ba_2BiOsO_6, from Rietveld-refinement against high-pressure synchrotron X-ray powder diffraction data (λ = 0.68787 Å). Space group *Fm*-3*m*. a_{Au} is the unit cell parameter of the Au standard mixed with the sample and used for pressure calibration.

P (GPa)	a_{Au} (Å)	a (Å)	c (Å)	V (Å^3)	R_{wp} (%)
0.07	4.0781(4)	6.0008(8)	14.752(3)	460.05(15)	8.01
1.78	4.0646(6)	5.9804(10)	14.705(4)	455.44(18)	11.19
4.55	4.0444(6)	5.9423(11)	14.635(4)	447.6(2)	7.90
5.37	4.0387(7)	5.9240(13)	14.633(4)	444.7(2)	8.69
6.32	4.0323(8)	5.9039(17)	14.639(5)	441.9(3)	9.34
8.19	4.0202(8)	5.8672(19)	14.568(6)	434.3(3)	9.80
10.04	4.0088(6)	5.801(2)	14.495(9)	422.4(4)	6.92
9.36	4.0129(6)	5.805(2)	14.502(8)	423.3(4)	8.36
8.75	4.0167(6)	5.821(2)	14.515(9)	425.9(4)	8.01

Table S3. Unit cell parameters for Ba_2BiRuO_6, from Rietveld-refinement against high-pressure neutron powder diffraction data (λ = 2.4184 Å). Space group *C*2/*c*. a_{Pb} is the unit cell parameter of the Pb standard mixed with the sample and used for pressure calibration.

P (GPa)	a_{Pb} (Å)	a (Å)	b (Å)	c (Å)	V (Å^3)	R_{wp} (%)
0.00	4.9506(8)	6.0374(29)	10.342(5)	20.298(14)	1267.3(12)	6.41
0.08	4.9475(4)	6.0378(16)	10.349(3)	20.307(9)	1269.0(7)	3.38
0.66	4.9255(4)	6.0236(15)	10.324(3)	20.260(6)	1259.9(6)	3.23
1.81	4.8860(3)	6.0031(14)	10.277(3)	20.213(6)	1247.1(6)	2.55
3.10	4.8479(3)	5.9703(15)	10.221(3)	20.177(8)	1231.3(7)	2.79
3.09	4.8480(3)	5.9680(14)	10.218(3)	20.182(7)	1230.6(6)	2.83
4.08	4.8216(3)	5.9479(13)	10.168(3)	20.128(9)	1217.2(7)	2.38
4.11	4.8209(3)	5.9487(13)	10.165(3)	20.092(6)	1214.9(6)	2.40
5.29	4.7923(4)	5.9311(14)	10.119(3)	20.043(8)	1202.9(6)	2.91
6.51	4.7654(4)	5.8353(8)	10.022(3)	19.540(7)	11427(6)	1.98

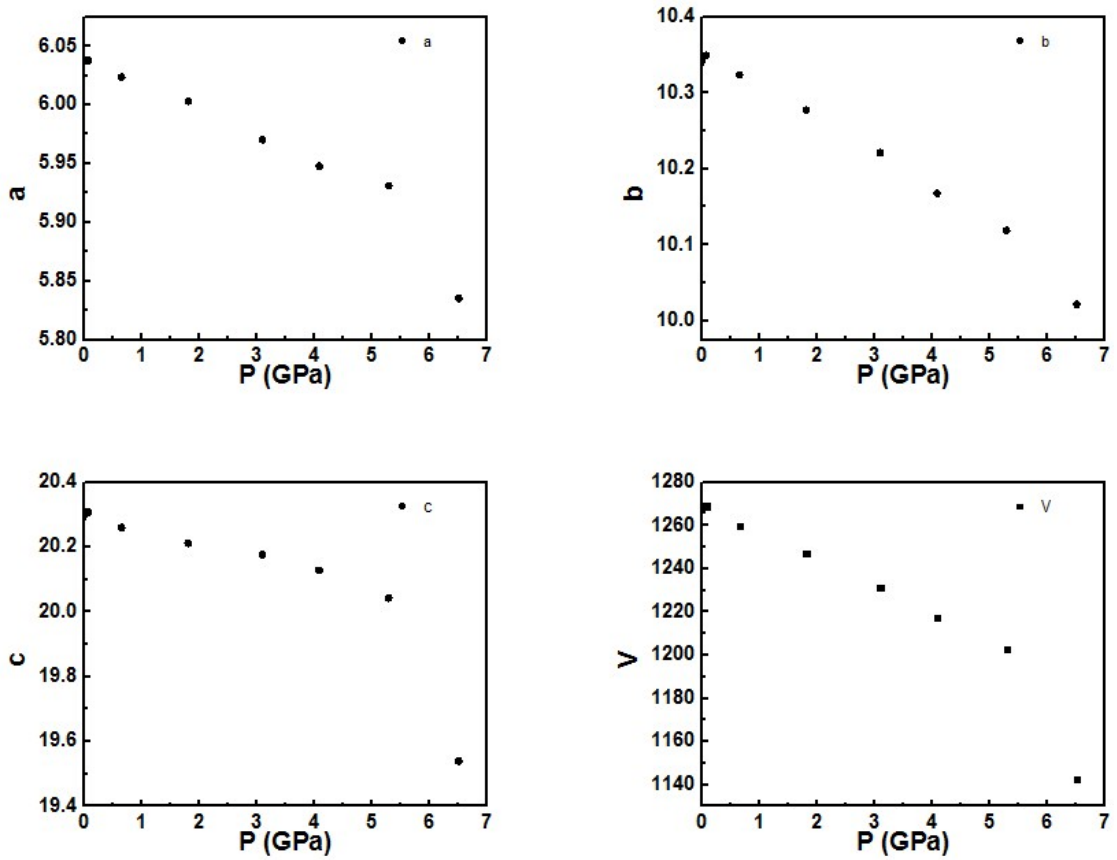

Figure S1. Unit cell parameters for Ba_2BiRuO_6, from Rietveld-refinement against high-pressure neutron powder diffraction data. Where not apparent, error bars are smaller than symbols.

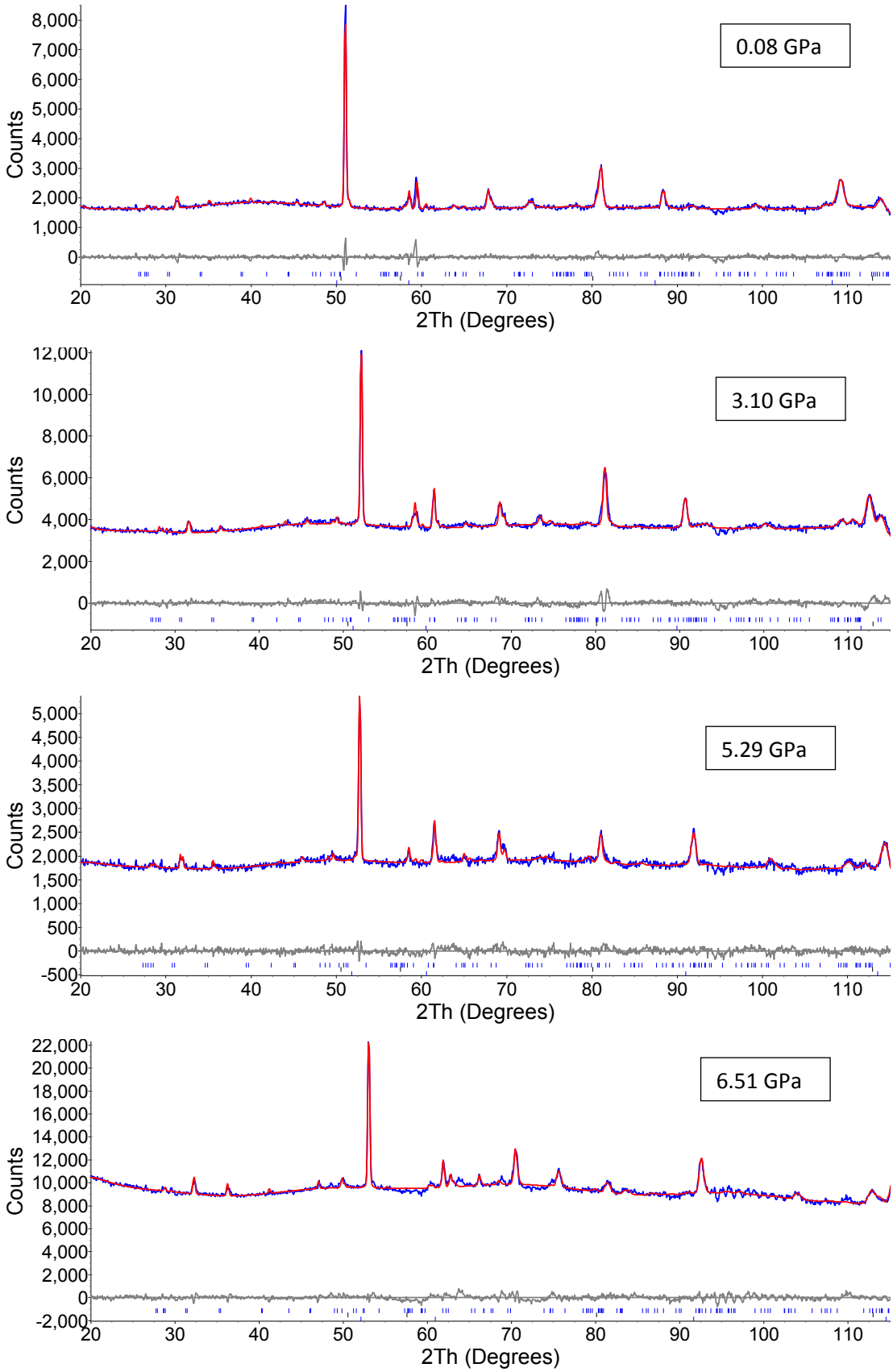

Figure S2. Example Rietveld fits of the structural model for Ba_2BiRuO_6 to high-pressure neutron powder diffraction data (λ = 2.4184 Å). Observed data are blue, the fits is red, and the difference profile is grey. The lower row of reflection markers refers to the Pb standard mixed with the sample and used for pressure calibration.