

Seeing the Unseen: The Structural Influence of the Lone Pair Electrons in PbWO₄

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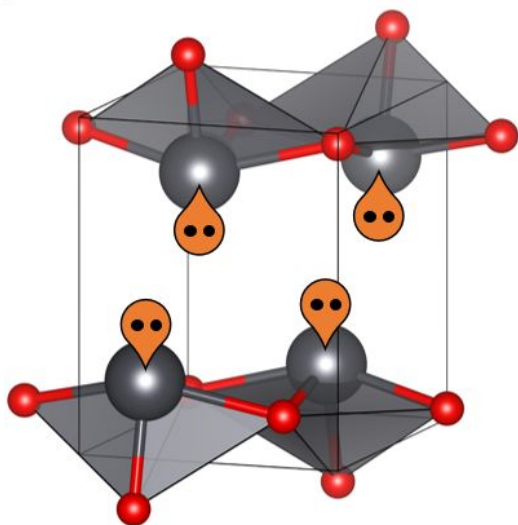
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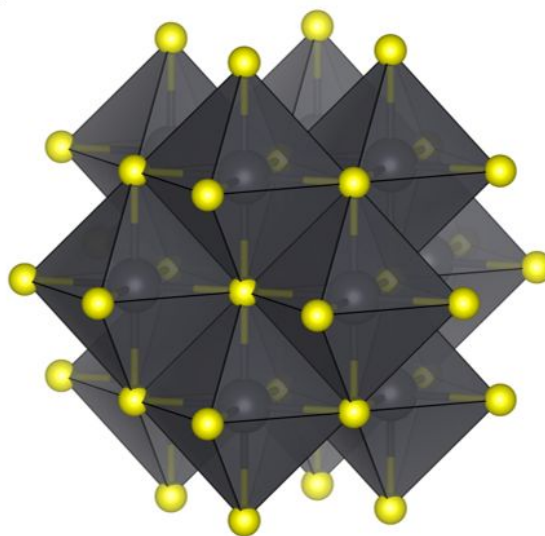


Figure S1: (a) The structure of α -PbO ($Pbcm$). The four short Pb-O bonds reflect the projection of the lone pair electron density in the opposite direction, as shown as an orange lobe. (b) The structure of PbS ($Fm\bar{3}m$). The centrosymmetry of Pb^{2+} in the PbS_6 octahedra, and the six Pb-S bonds of identical length indicate limited lone pair activity. The dark grey, red and yellow spheres correspond to the Pb, O, and S atoms, respectively.

(i) *Neutron Powder Diffraction Data Analysis of PbWO₄ and CaWO₄*

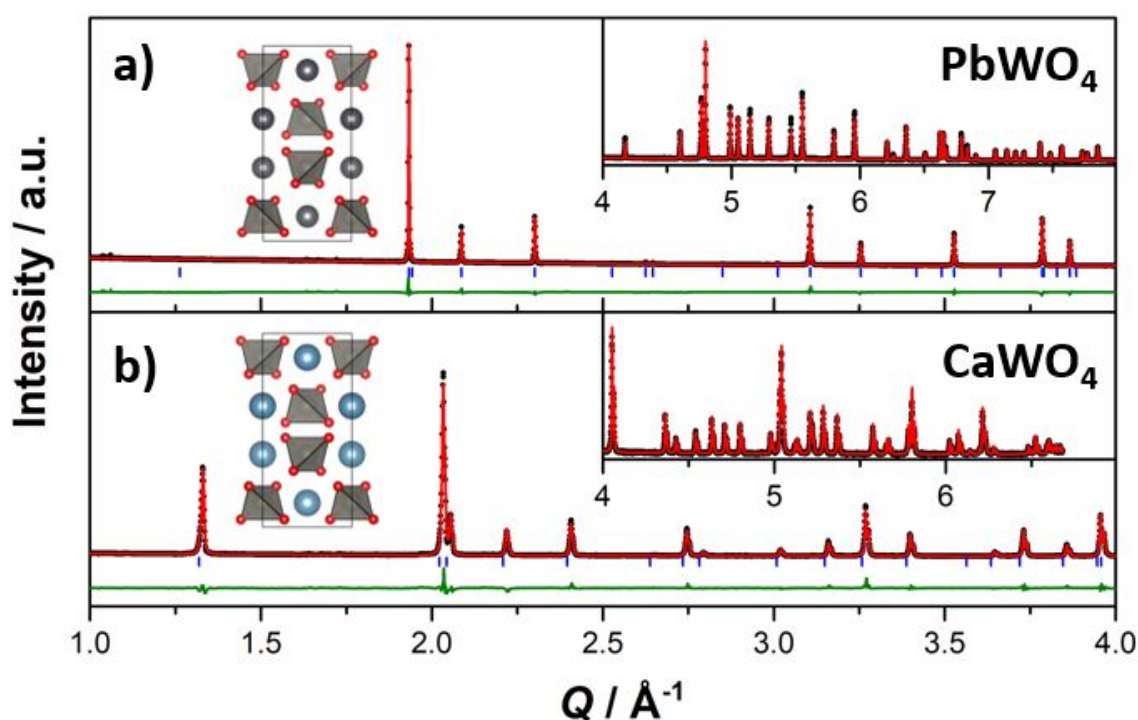


Figure S2: X-ray diffraction data for (a) PbWO₄ collected at the Australian Synchrotron, and (b) CaWO₄ collected on a laboratory Cu-source diffractometer.

Determination of Potential Lone Pair Stereochemical Activity in PbWO₄ and CaWO₄

Since the stereochemistry of the Pb²⁺ cation can be impacted by the 6s² electrons, the possibility of symmetry lowering was explored. The strategy employed to investigate this was as follows: Firstly, the samples were cooled to 3 K to potentially observe static disorder whilst minimizing thermal disorder. The cell metric was then determined using 2.44 Å neutrons, obtained from the 331 reflection of the vertically focusing Ge monochromator. These data were then combined with a dataset measured at 1.30 Å, obtained using the 337 reflection of the same monochromator. The use of the shorter wavelength extended the measured d -range from $d_{\min} = 1.235$ Å to $d_{\min} = 0.66$ Å, providing greater sensitivity to small displacements in the atomic positions leading to more precise structural parameters. Additionally, the longer wavelength neutrons provided greater sensitivity to any subtle deviation from tetragonal symmetry. The wavelength of this second dataset was treated as a variable in the Rietveld refinement, reflecting the greater peak-shape resolution of the 2.44 Å dataset.

Table S1: Selected bond distances and angles for PbWO₄ and CaWO₄ obtained from Rietveld refinements against NPD data using the tetragonal $I4_1/a$ scheelite model.

	Temperature (K)	A-O (Å)	A-O' (Å)	W-O (Å)	O-W-O (°)	O-W-O (°)
PbWO₄	300	2.6358(9)	2.6096(10)	1.7793(9)	112.79(7)	107.84(4)
	3	2.6292(8)	2.5942(8)	1.7891(8)	112.58(5)	107.94(3)
CaWO₄	300	2.4656(8)	2.4377(9)	1.7874(9)	114.00(6)	107.25(3)
	3	2.4714(7)	2.4360(7)	1.7850(7)	113.50(4)	107.494(19)

The results for the Rietveld refinement of PbWO₄ are illustrated in Figure S3 and the refined structural parameters and selected bond distances and angles presented in Tables S1. Data were also obtained for CaWO₄ under identical conditions. The magnitude of the isotropic equivalent ADPs for the Pb²⁺ and Ca²⁺ cations are comparable at both 300 and 3 K. The inclusion of the 1.30 Å dataset in the refinement of the structure at 3 K enabled anisotropic atomic displacement parameters to be obtained, and examination of these provides no evidence of any anomalies.

For both compounds, the shorter A-O distance contracts upon cooling whereas the longer A-O distance expands, leading to increased distortion of the AO₈ dodecahedra that was quantified using the bond distortion index.¹ This is defined as

$$\Delta AO_8 = \frac{1}{8} \sum_{i=1}^8 \frac{|d_{A-O}^i - \langle d_{A-O} \rangle|}{\langle d_{A-O} \rangle}$$

where $\langle d_{A-O} \rangle$ is the average A-O bond distance.

For CaWO₄, this increased by ~20% from 4.8×10^{-2} at 300 K to 5.9×10^{-2} at 3 K and a larger expansion of ~30% was observed for PbWO₄ from 4.1×10^{-2} to 5.3×10^{-2} at 3 K. The former values are comparable to those reported by Culver and Brutchey for CaMoO₄,² noting that these authors missed the $\times 100$ factor in their graph, whilst the latter values are similar to that obtained by Chipaux *et al.*³ That the distortion of the AO₈ dodecahedra is comparable in the two structures suggests that the 6s² electrons do not strongly influence this.

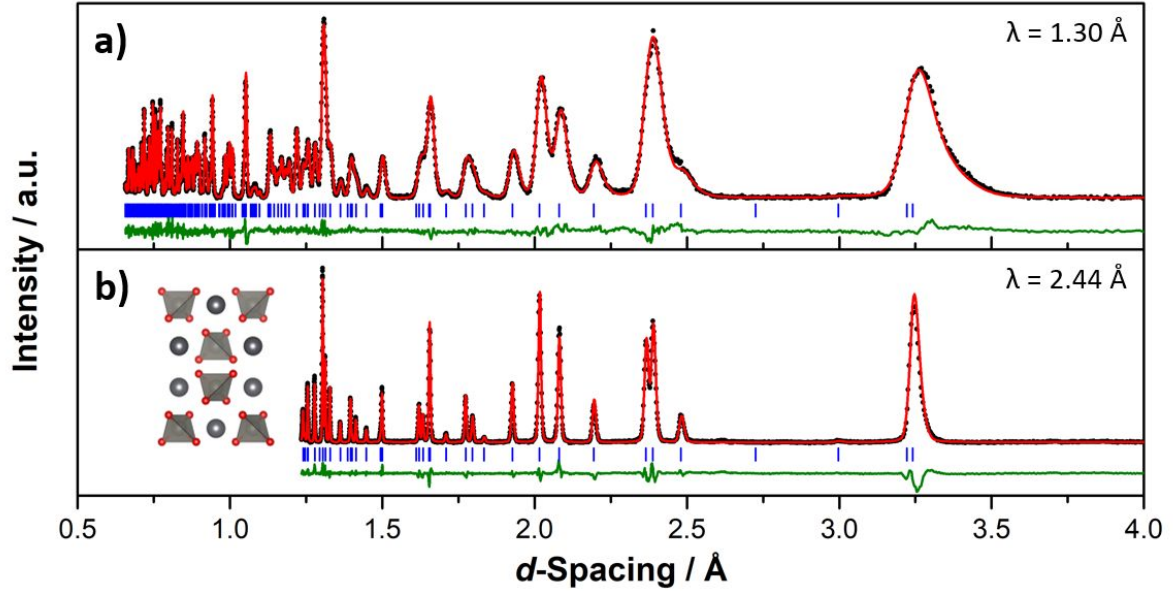


Figure S3: Observed, calculated, and difference neutron diffraction profile for PbWO_4 measured at 3 K using neutrons of wavelength (a) 1.30 and (b) 2.44 Å. The black crosses represent the measured data, the solid red line represents the profile calculated by the Rietveld method, the green line represents the difference between the observed and calculated profiles, and the blue markers show the positions of the space group allowed Bragg reflections.

We next tested a model where the Pb^{2+} was disordered onto the $8e$ ($0, 1/4, 5/8+\delta$) sites, giving it freedom to move in the z direction, similar to that observed for BiVO_4 , against the 3 K data. This resulted in a refined δ value of 0.0041(3) and a comparable χ^2 to the standard model, 3.74 vs. 3.75. The refined ADP for the Pb^{2+} cation in this disordered model was unphysically small $U_{\text{iso}} = 0.007(2)$ Å². A similar displacement was obtained for CaWO_4 , $\delta = 0.0029(7)$, with a more reasonable $U_{\text{iso}} = 0.19(3)$ Å². Finally, we attempted to refine the structures using the monoclinic fergusonite $I2/b$ model. This yielded an identical χ^2 with a metrically tetragonal unit cell $\gamma = 90.000(7)^\circ$ that had only 0.03% difference between the a and b unit cell parameters. The Pb^{2+} cation occupies a $4e$ site in the fergusonite model and the refined positional parameter for Pb^{2+} did not reveal an appreciable displacement from $z = 0.625$ ($5/8$), the refined value being 0.6262(3). The value for $\Delta 4\text{O}_8$ in this monoclinic model was 5.6×10^{-2} that is approximately equal to the distortion estimated for the tetragonal cell, 5.3×10^{-2} .

Table S2: Full Rietveld refinement parameters of PbWO_4 and CaWO_4 taken from the NPD data fitted to the tetragonal $I4_1/a$ model.

	PbWO₄		CaWO₄	
Temperature (K)	300	3	300	3
<i>a</i> (Å)	5.45514(4)	5.45144(4)	5.23569(4)	5.23566(4)
<i>b</i> (Å)	= <i>a</i>	= <i>a</i>	= <i>a</i>	= <i>a</i>
<i>c</i> (Å)	12.0349(3)	11.9894(3)	11.3631(3)	11.3506(2)
Vol. (Å³)	358.140(9)	356.304(10)	311.491	311.143
O(1) <i>x</i>	0.23259(15)	0.23327(13)	0.75760(16)	0.75912(14)
O(1) <i>y</i>	0.10967(12)	0.10817(13)	0.40238(12)	0.40254(11)
O(1) <i>z</i>	0.04317(9)	0.04218(6)	0.03933(8)	0.03878(5)
<i>A</i>-O_S	2.6096	2.5942(8)	2.4377(9)	2.4360(7)
<i>A</i>-O_L	2.6358	2.6292(8)	2.4656(8)	2.4714(7)
W-O	1.7793(9)	1.7891(8)	1.7874(9)	1.7850(7)
AO₈ (Å³)	32.0926	31.6787	26.1495	26.2023
<i>D</i>(AO₈)	0.00499	0.00671	0.00569	0.00720
WO₄ (Å³)	2.8834	2.9324	2.9168	2.9077
BVS (AO₈)	2.01	2.08	2.16	2.15
BVS (WO₄)	5.87	5.71	5.74	5.78

Table S3: Refined unit cell, structural and atomic displacement parameters for PbWO₄ at 3 K obtained using neutron diffraction data measured at 2.44 and 1.30 Å. $a = b = 5.44973(4)$, $c = 11.98569(12)$ Å, Vol. = 355.970(5) Å³, $R_p = 0.049$, $R_{wp} = 0.064$, $\chi^2 = 3.75$.

Atom	Site	x	y	z	U_e (Å ²)
Pb	$4b$	= 0	= 1/4	= 5/8	0.0014*
W	$4a$	= 0	= 1/4	= 1/8	0.0018*
O	$16f$	0.23328(11)	0.10780(11)	0.04204(6)	0.0044*

* Equivalent isotropic value.

Anisotropic displacement parameters (Å²) are:

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.00120(20)	= U^{11}	0.0019(4)	= 0	= 0	= 0
W	0.00027(35)	= U^{11}	0.0050(6)	= 0	= 0	= 0
O	0.00336(25)	0.00469(24)	0.00506(25)	0.00158(25)	0.00262(20)	-0.00007(27)

Table S4: Refined unit cell, structural and atomic displacement parameters for CaWO₄ obtained using neutron diffraction data measured at 2.44 and 1.30 Å. $a = b = 5.23336(4)$, $c = 11.34579(10)$ Å, Vol. = 310.739(4) Å³, $R_p = 0.047$, $R_{wp} = 0.061$, $\chi^2 = 4.01$.

Atom	Site	x	y	z	U_e (Å ²)
Ca	$4b$	= 0	= 1/4	= 5/8	0.0012*
W	$4a$	= 0	= 1/4	= 1/8	0.0014*
O	$16f$	0.24105(12)	0.09769(9)	0.03884(5)	0.0038*

* Equivalent isotropic value.

Anisotropic displacement parameters (Å²) multiplied by 100 are:

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca	0.00192(34)	= U^{11}	-0.0002(5)	= 0	= 0	= 0
W	0.00126(31)	= U^{11}	0.0017(6)	= 0	= 0	= 0
O	0.00249(19)	0.00430(22)	0.00449(18)	0.00080(29)	0.00034(19)	-0.00016(23)

(ii) *Local Structure Analysis Using Pair Distribution Function*

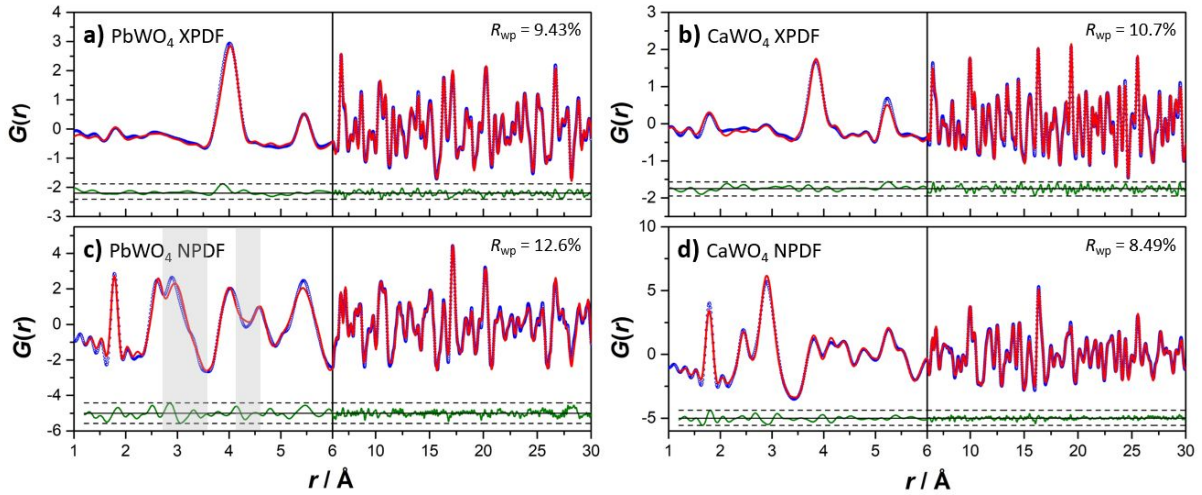


Figure S4: Pair distribution function fits performed over a range of 1.2–30 Å to data obtained at 300 K, fitted to the tetragonal scheelite-type $I4_1/a$ structure. (a) XPDF of PbWO_4 , (b) XPDF of CaWO_4 , (c) NPDF of PbWO_4 , and (d) NPDF of CaWO_4 . In each case, the blue circles represent the data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles. The grey areas highlight the significant misfitting in the NPDF.

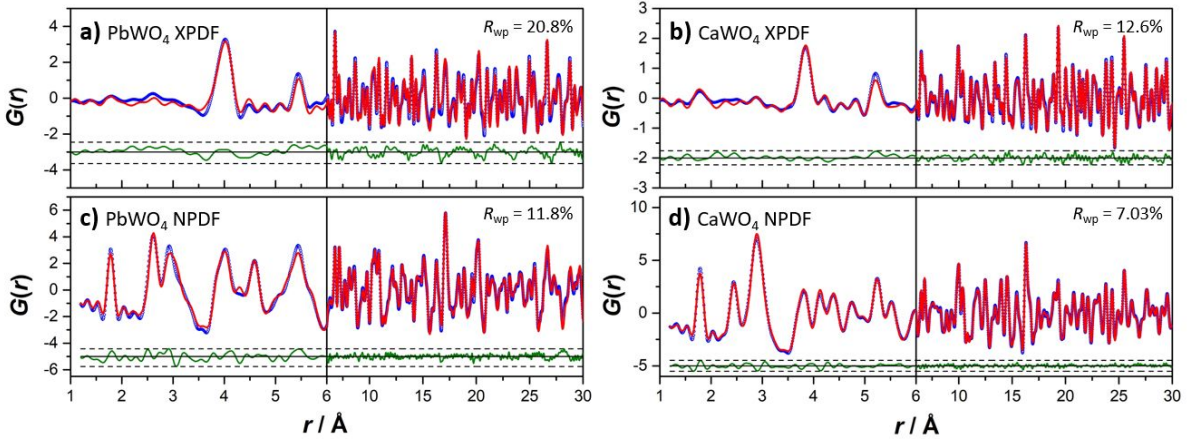


Figure S5: Pair distribution function fits performed over a range of 1.2–30 Å to data obtained at colder temperatures, fitted to the tetragonal scheelite-type $I4_1/a$ structure. (a) XPDF of PbWO_4 at 80 K, (b) XPDF of CaWO_4 at 80 K, (c) NPDF of PbWO_4 at 115 K, and (d) NPDF of CaWO_4 at 100 K. In each case, the blue circles represent the data, the solid red line represents the calculated profile, the green line represents the difference between the observed and calculated profiles. The grey areas highlight the significant misfitting in the NPDF.

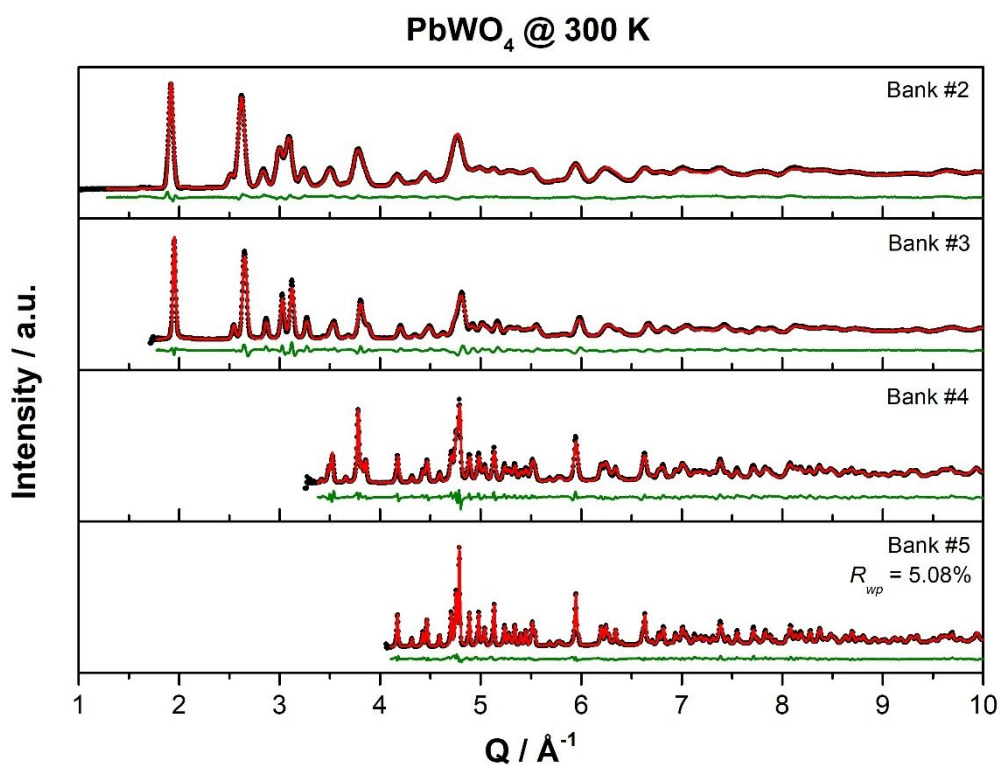


Figure S6: Rietveld refinement of PbWO₄ at 300 K to the tetragonal scheelite $I4_1/a$ model on the NOMAD beamline at Oak Ridge National Laboratory. Data is displayed from the four highest resolution detector banks.

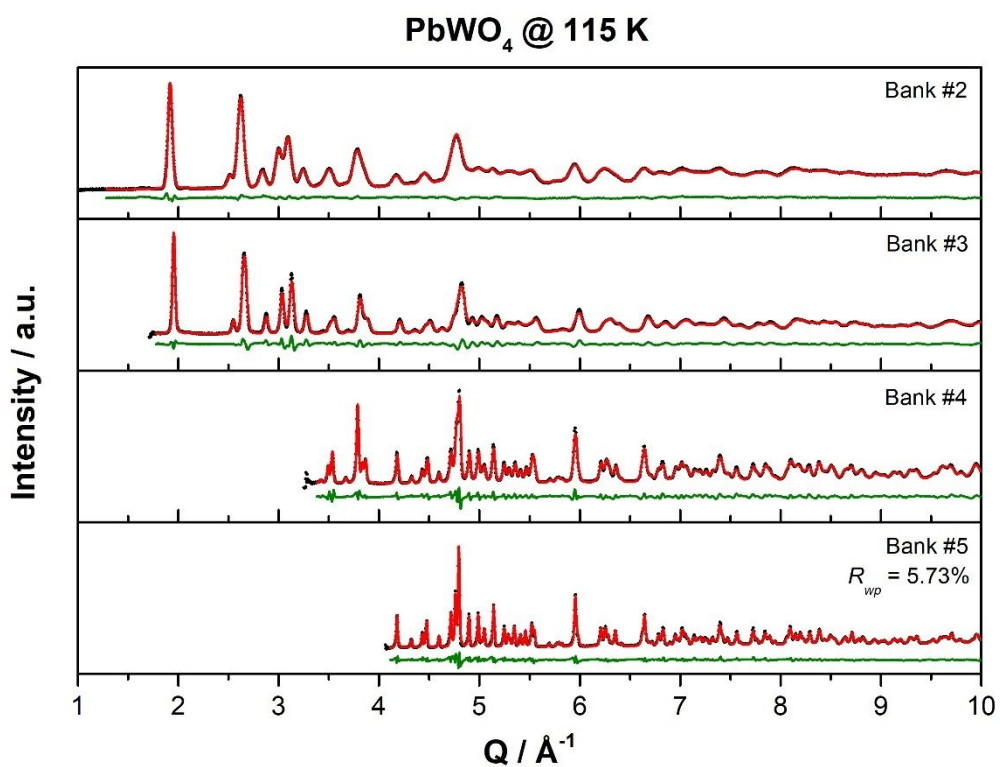


Figure S7: Rietveld refinement of PbWO₄ at 115 K to the tetragonal scheelite $I4_1/a$ model on the NOMAD beamline at Oak Ridge National Laboratory. Data is displayed from the four highest resolution detector banks.

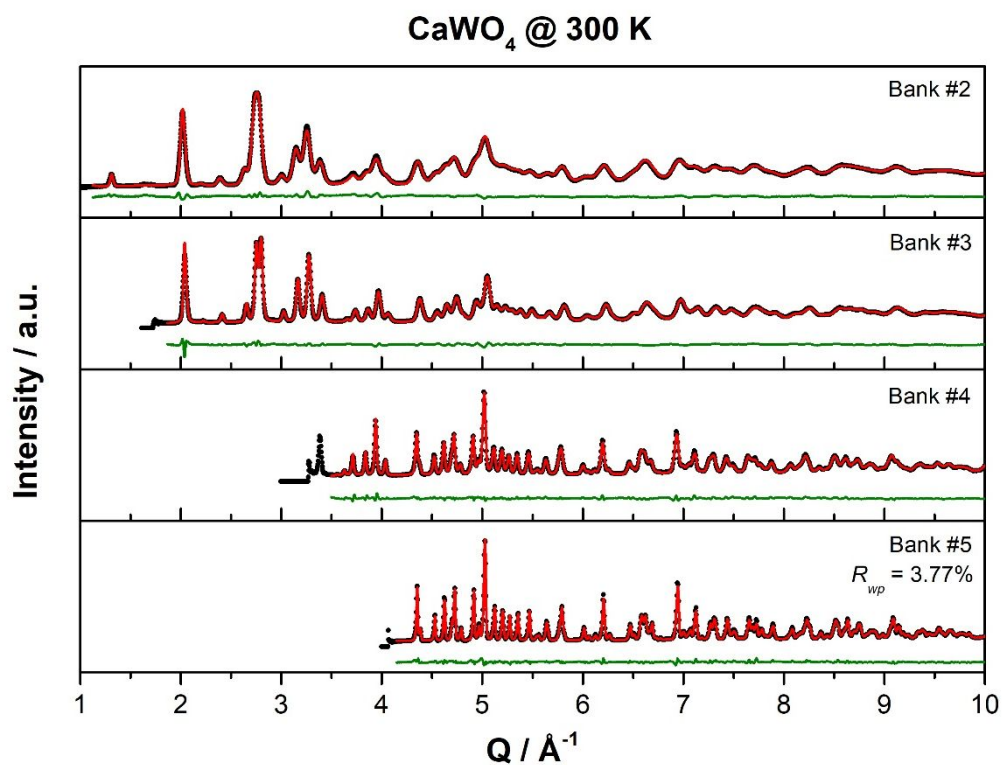


Figure S8: Rietveld refinement of CaWO₄ at 300 K to the tetragonal scheelite $I4_1/a$ model on the NOMAD beamline at Oak Ridge National Laboratory. Data is displayed from the four highest resolution detector banks.

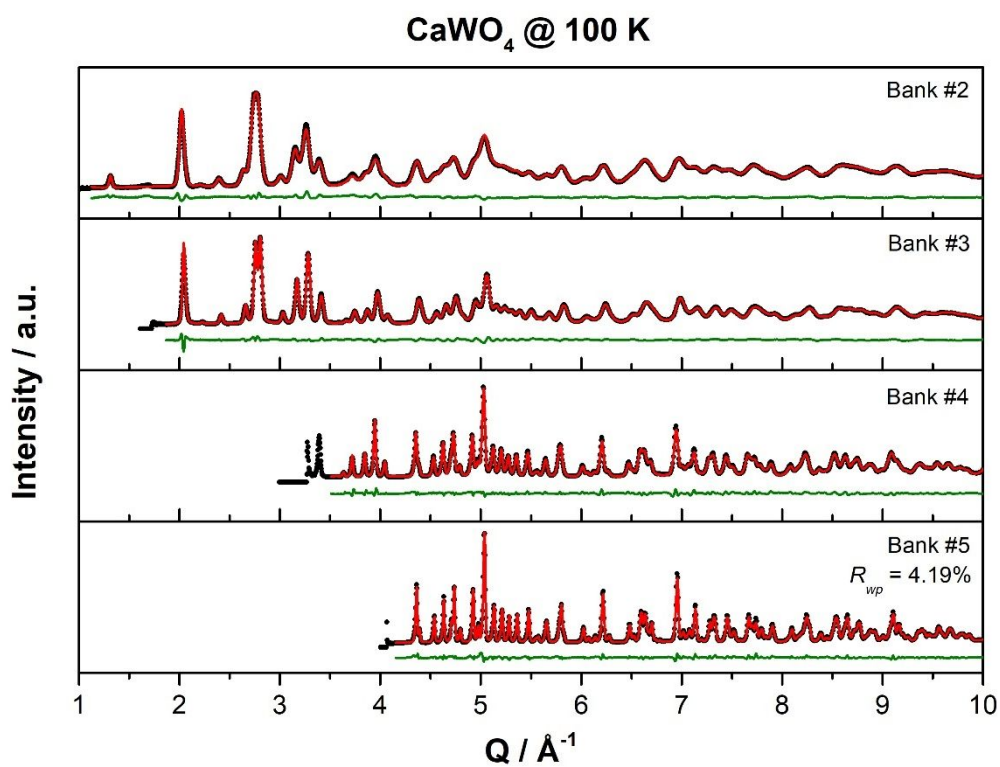


Figure S9: Rietveld refinement of CaWO₄ at 100 K to the tetragonal scheelite $I4_1/a$ model on the NOMAD beamline at Oak Ridge National Laboratory. Data is displayed from the four highest resolution detector banks.

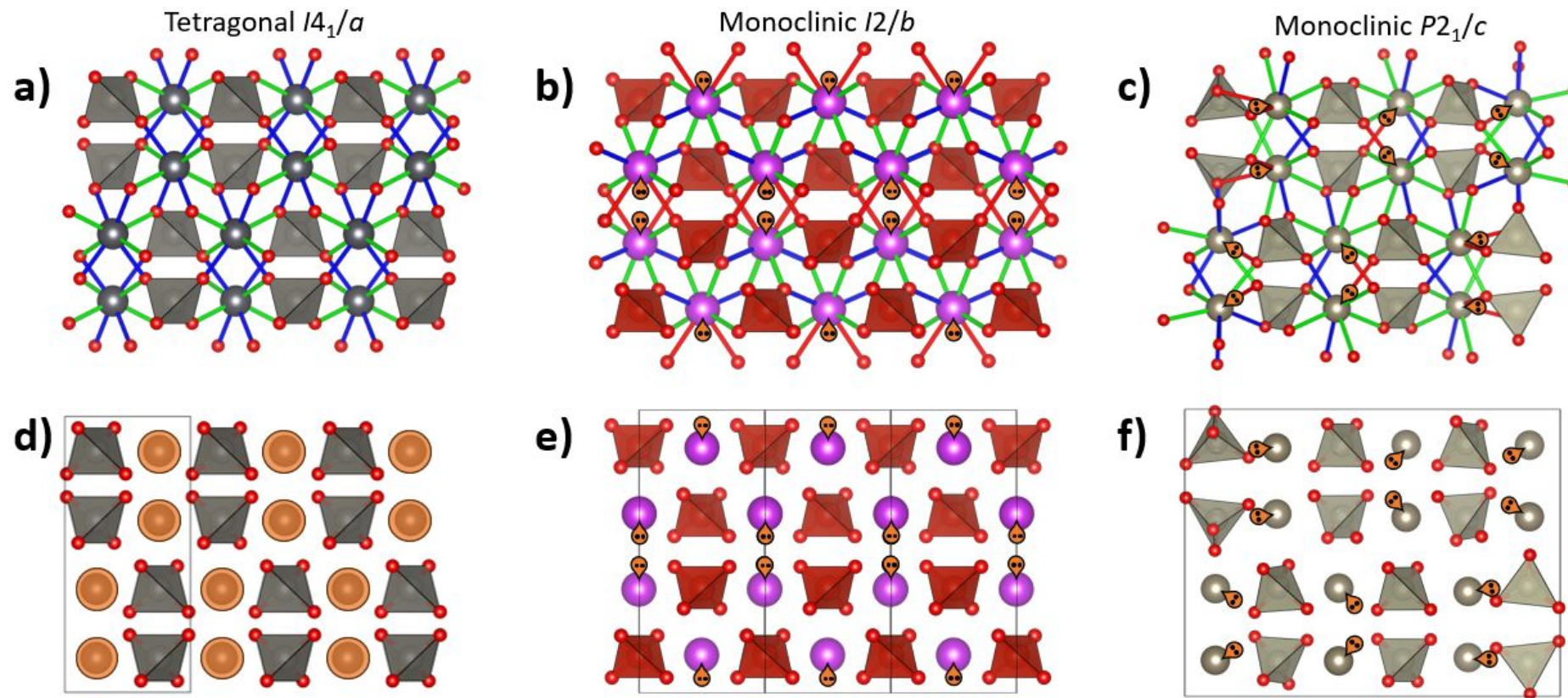


Figure S10: Crystallographic models for (a,d) PbWO_4 $I4_1/a$ (SG #88), (b,e) BiVO_4 $I2/b$ (SG #15), and (c,f) TiReO_4 $P2_1/c$ (SG #14). The top row (a-c) shows the structure with the various A-O bond lengths color-coded in terms of length (blue is short, green is medium, and red is long). The bottom row (d-f) shows the structure with the BO_4 tetrahedra with the lone pairs drawn in orange.

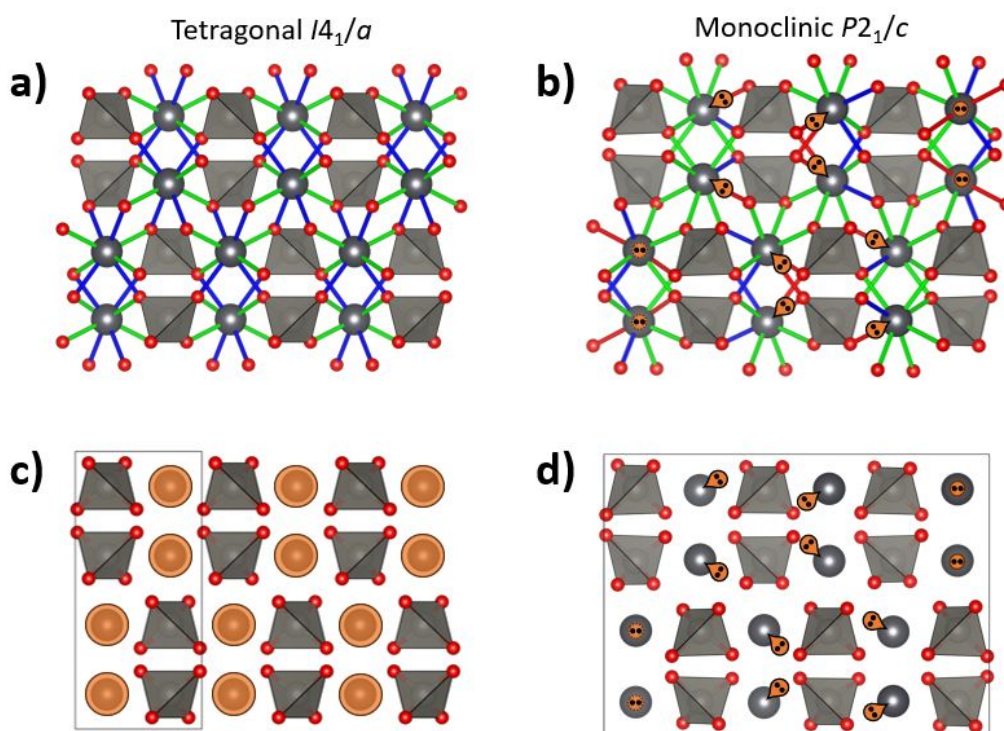


Figure S11: Crystallographic models for PbWO_4 to (a,c) the tetragonal $I4_1/a$ model, and (b,d) the monoclinic $P2_1/c$ model. The top row (a,b) shows the structure with the various A-O bond lengths color-coded in terms of length (blue is short, green is medium, and red is long). The bottom row (c,d) shows the structure with the WO_4 tetrahedra with the lone pairs drawn in orange.

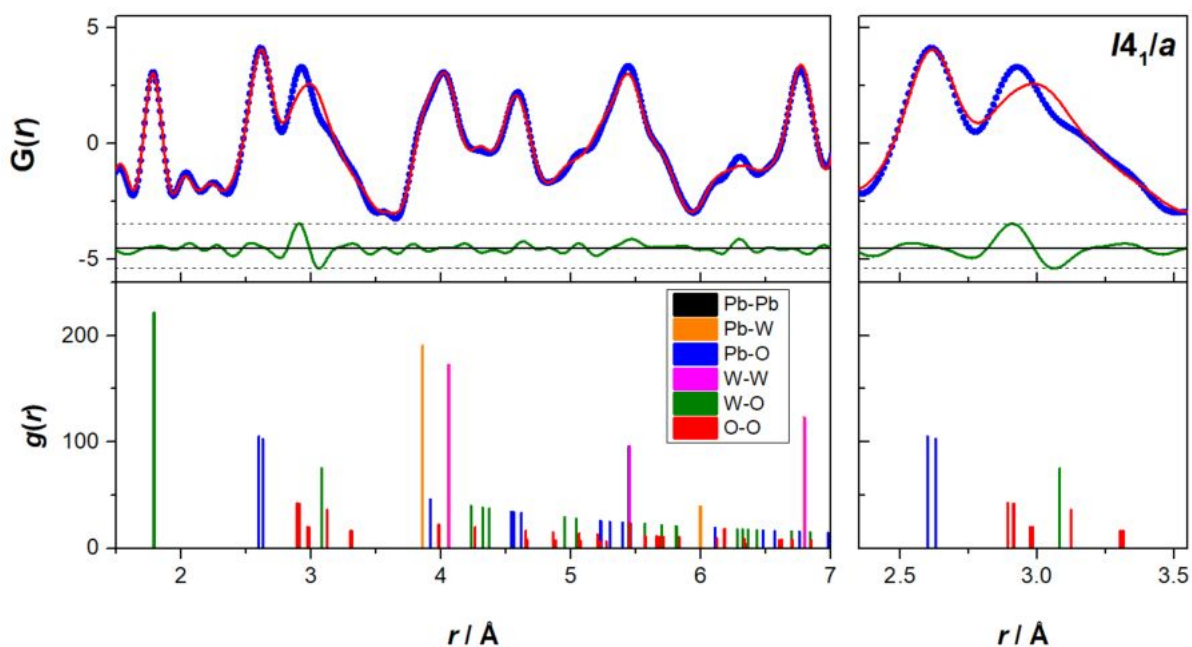


Figure S12: Partial NPDFs plotted for PbWO_4 at 115 K using the $I4_1/a$ model, fitted using a 1-30 Å range. Two different ranges are displayed: (a) 1-7 Å, and (b) 2.35-3.55 Å.

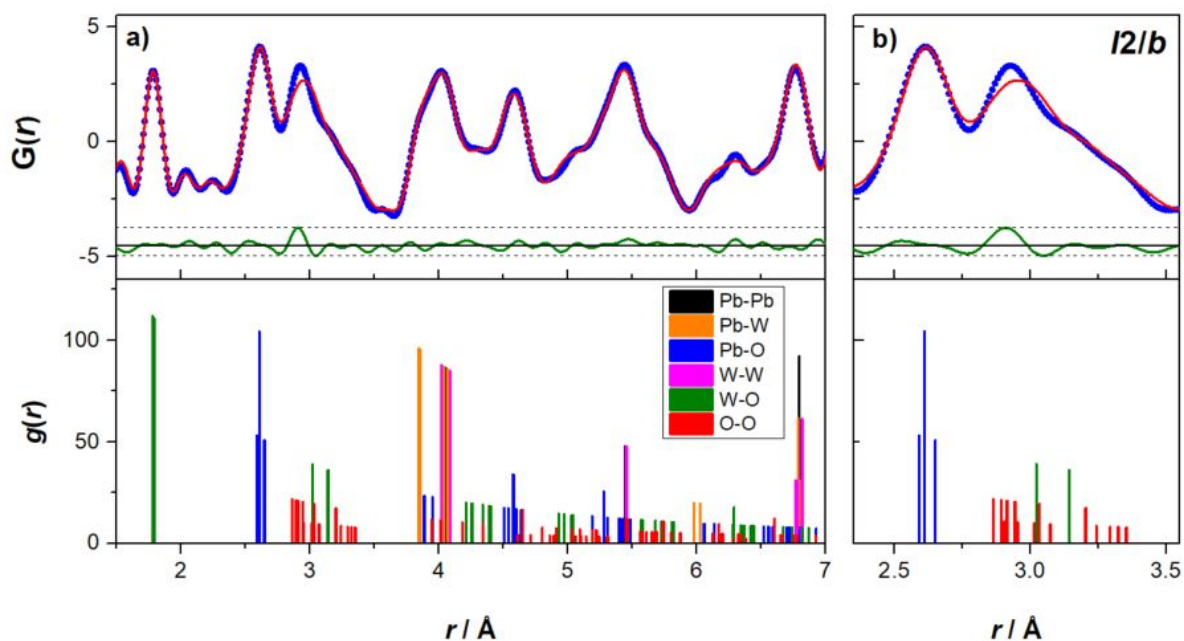


Figure S13: Partial NPDFs plotted for PbWO_4 at 115 K using the $I2/b$ model, fitted using a 1-30 Å range. Two different ranges are displayed: (a) 1-7 Å, and (b) 2.35-3.55 Å.

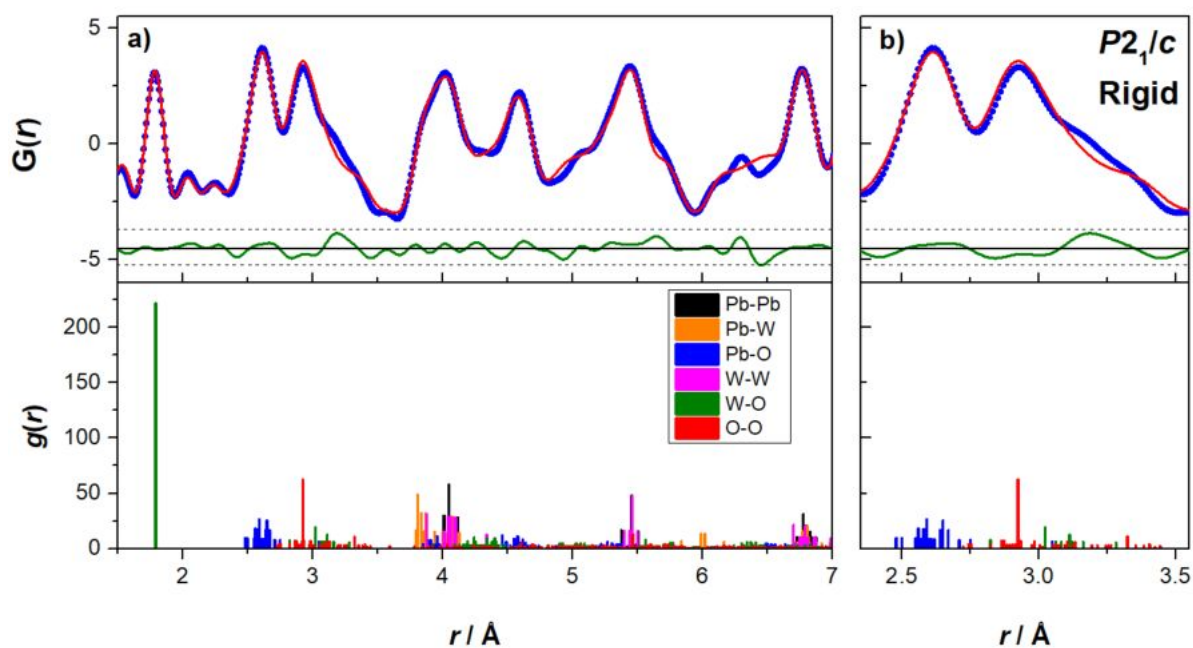


Figure S14: Partial NPDFs plotted for PbWO_4 at 115 K using the $P2_1/c$ model with rigid WO_4 tetrahedra, fitted using a 1-30 Å range. Two different ranges are displayed: (a) 1-7 Å, and (b) 2.35-3.55 Å.

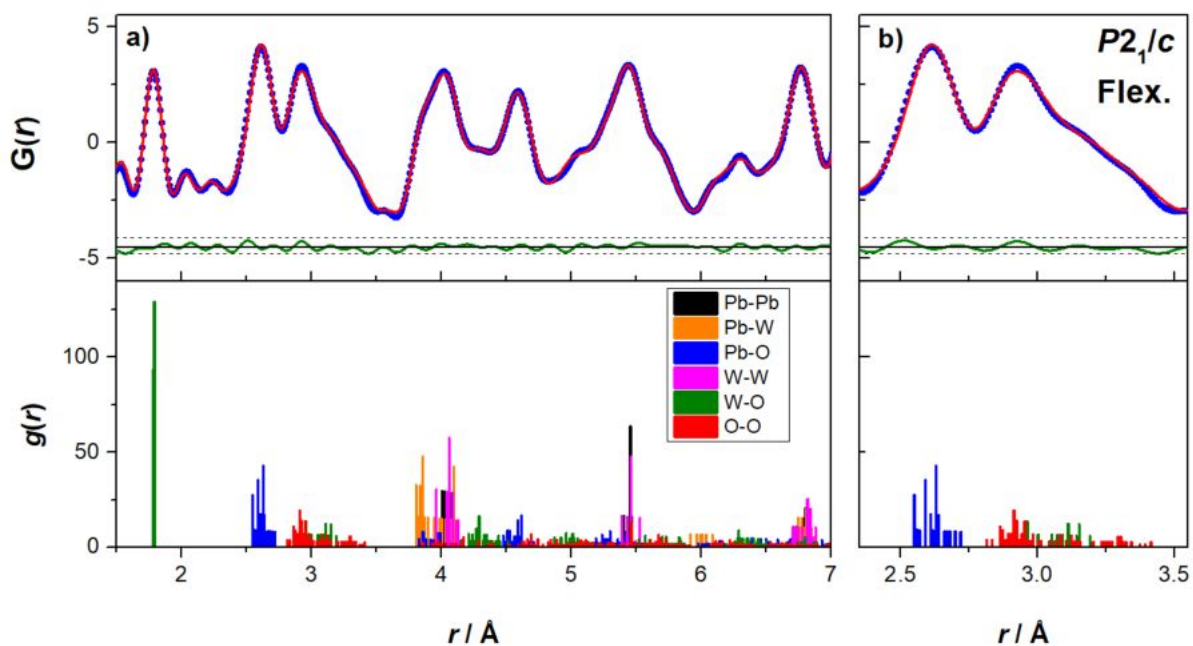


Figure S15: Partial NPDFs plotted for PbWO_4 at 115 K using the $P2_1/c$ model with flexible WO_4 tetrahedra, fitted using a 1-30 Å range. Two different ranges are displayed: (a) 1-7 Å, and (b) 2.35-3.55 Å.

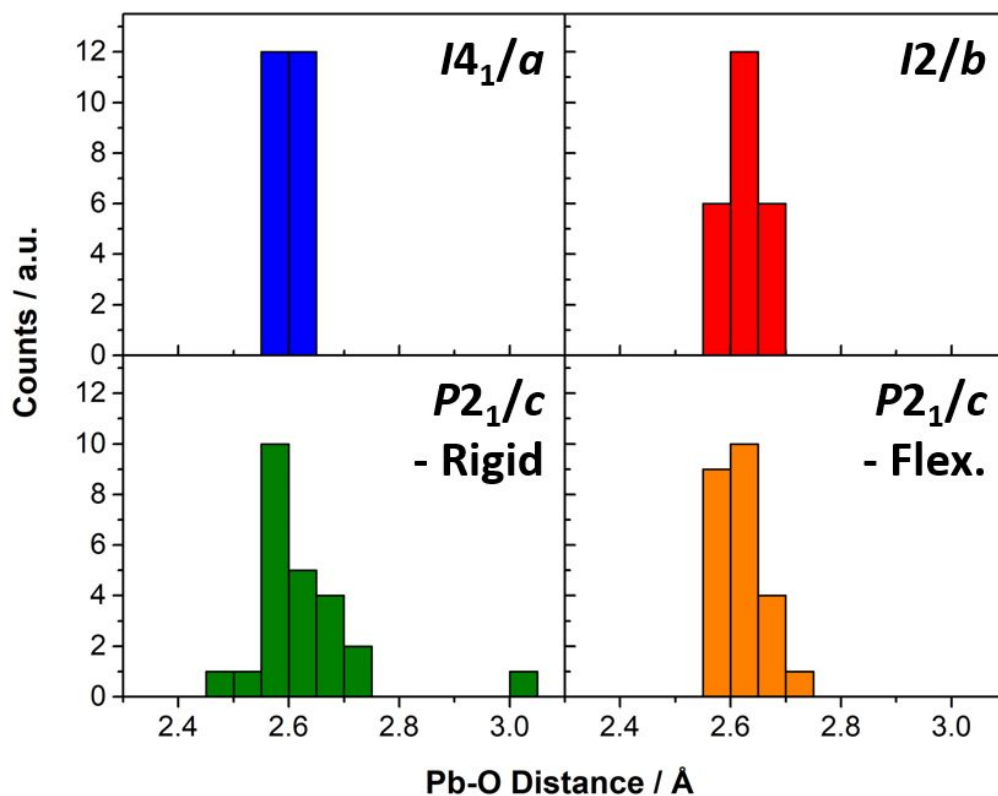


Figure S16: Histogram of Pb-O bonds from the NPDF refinements for (a) the $I4_1/a$, (b) the $I2/b$, (c) the $P2_1/c$ with rigid tetrahedra, and (d) the $P2_1/c$ with flexible tetrahedra.

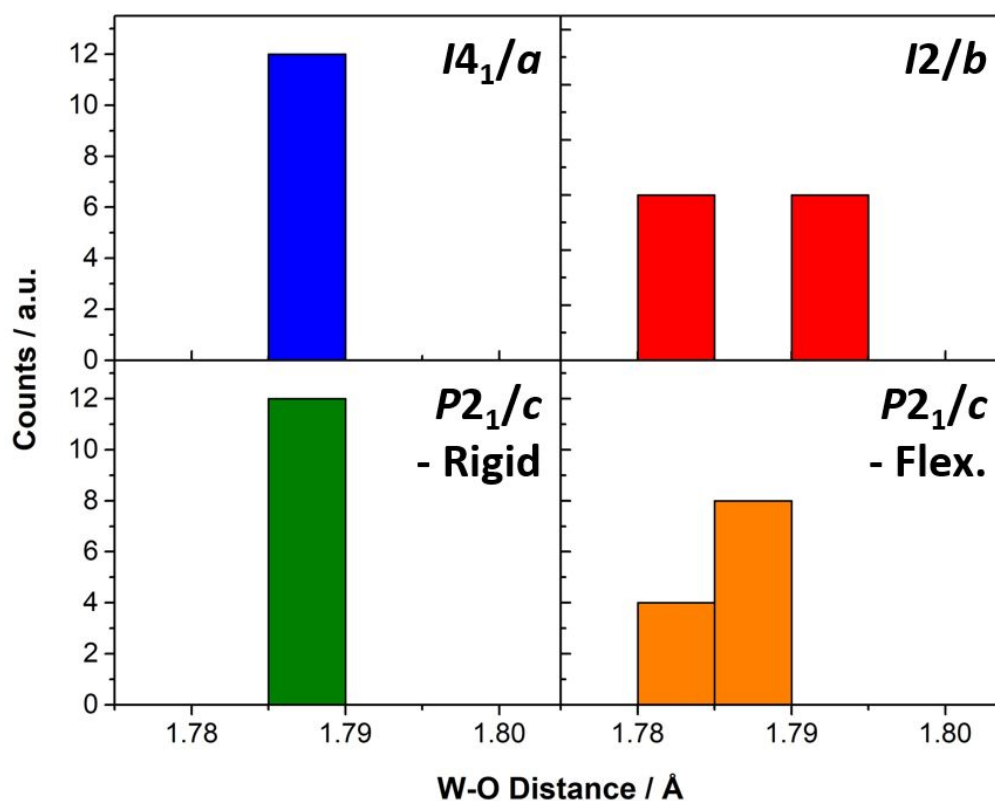


Figure S17: Histogram of W-O bonds from the NPDF refinements for (a) the $I4_1/a$, (b) the $I2/b$, (c) the $P2_1/c$ with rigid tetrahedra, and (d) the $P2_1/c$ with flexible tetrahedra.

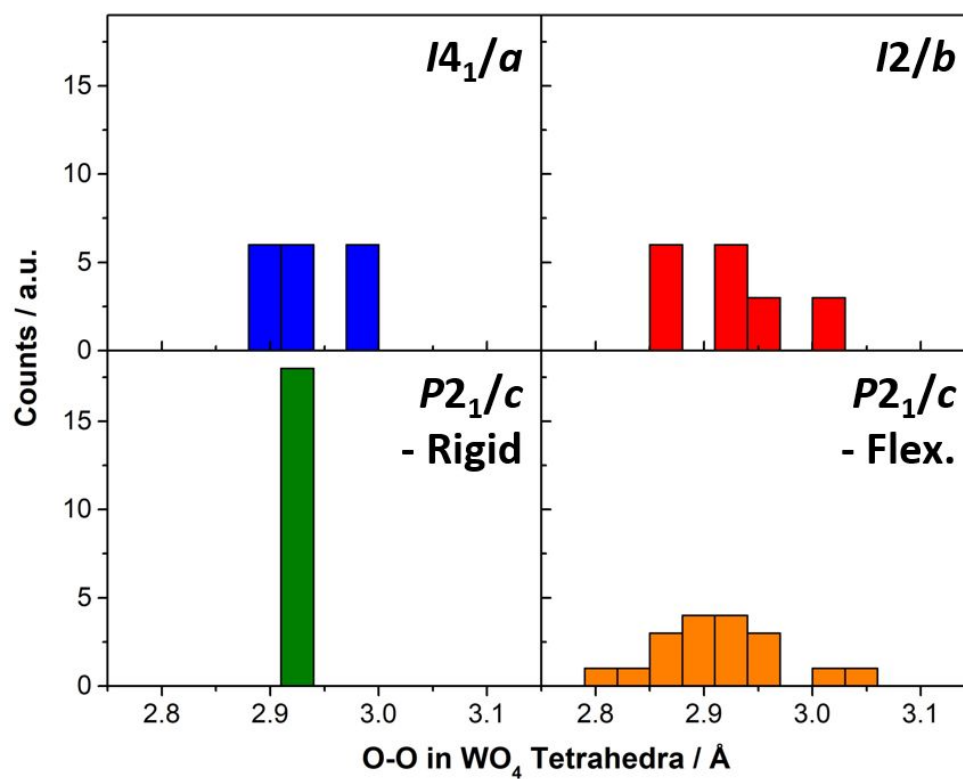


Figure S18: Histogram of O-O distances across the WO_4 tetrahedra from the NPDF refinements for (a) the $I4_1/a$, (b) the $I2/b$, (c) the $P2_1/c$ with rigid tetrahedra, and (d) the $P2_1/c$ with flexible tetrahedra.

Table S5: Mean and standard deviation of the Pb-O bonds, as well as the O-O distances across the WO₄ tetrahedra of PbWO₄. The Bragg data was refined from NPD data.

	<i>I</i> 4 ₁ / <i>a</i>	<i>I</i> 2/ <i>b</i>	<i>P</i> 2 ₁ / <i>c</i> - Rigid	<i>P</i> 2 ₁ / <i>c</i> – Flex.	<i>I</i> 4 ₁ / <i>a</i> (Bragg RT)	<i>I</i> 4 ₁ / <i>a</i> (Bragg 3 K)
Mean (°)	109.47	109.47	109.47	109.47	109.47	109.47
Std (°)	2.39	2.94	0.00	3.20	2.54	2.35
Mean (Pb-O)	2.62	2.62	2.63	2.62	2.62	2.61
Std (Pb-O)	0.023	0.025	0.108	0.047	0.013	0.017
Mean (O-O tetra.)	2.93	2.92	2.92	2.91	2.91	2.92
Std (O-O tetra.)	0.041	0.055	0.00	0.057	0.041	0.038

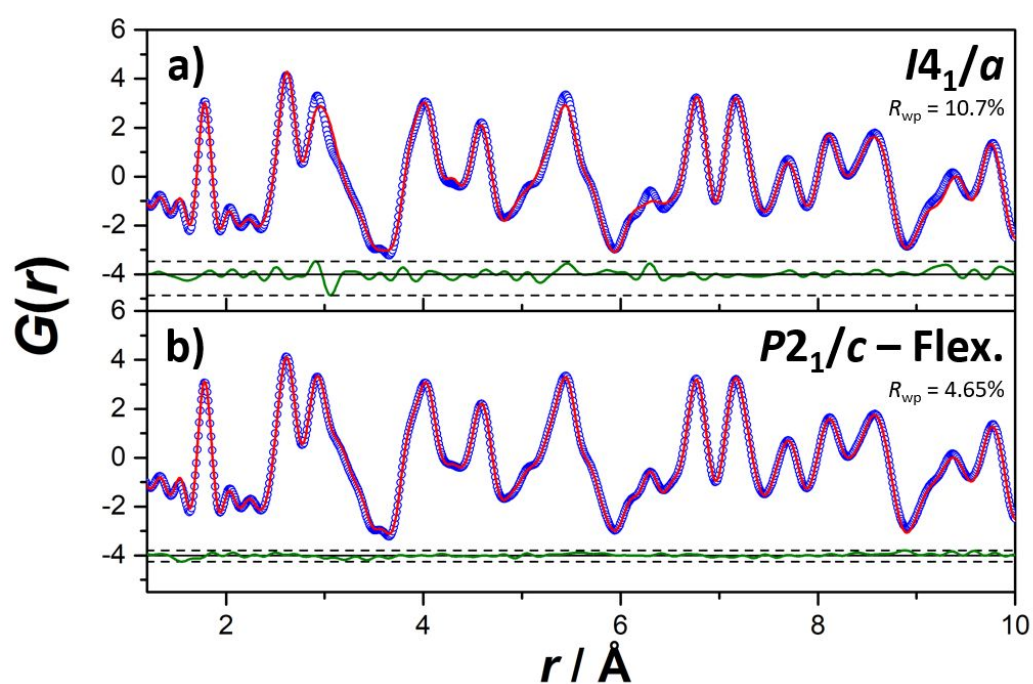


Figure S19: NPDF fits to PbWO₄ at 115 K for (a) tetragonal-scheelite *I*4₁/*a*, and (b) monoclinic *P*2₁/*c* with flexible WO₄ tetrahedra. The data is fitted over a range of 1.2-10 Å. The blue dots represent the data, the solid red line represents the calculated profile, the solid green line represents the difference between the observed and calculated profiles.

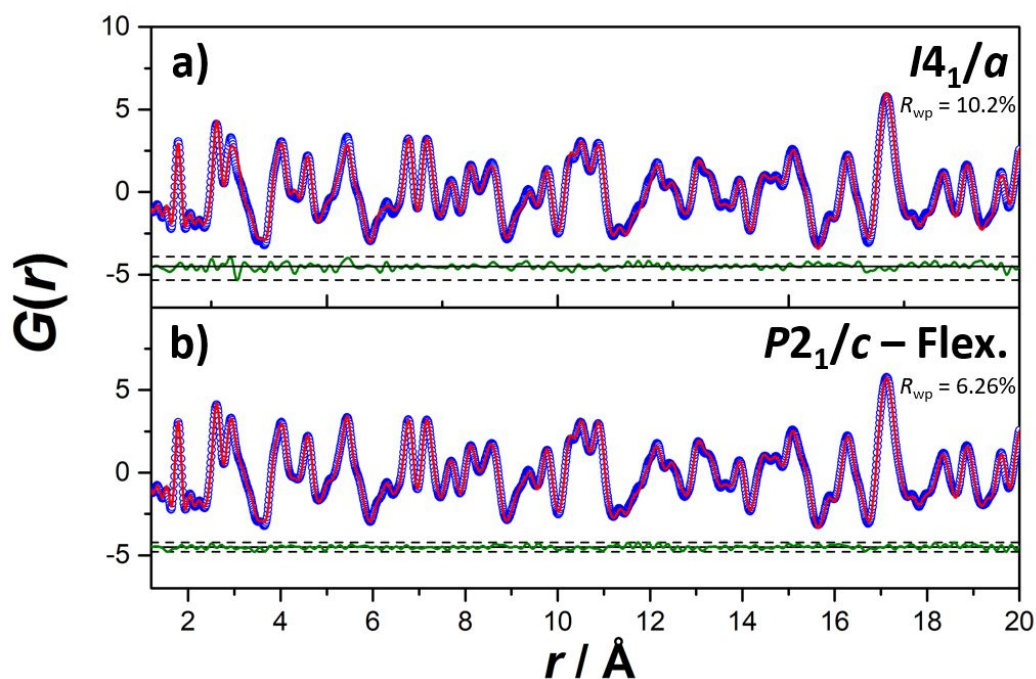


Figure S20: NPDF fits to PbWO₄ at 115 K for (a) tetragonal-scheelite $I4_1/a$, and (b) monoclinic $P2_1/c$ with flexible WO₄ tetrahedra. The data is fitted over a range of 1.2-20 Å. The blue dots represent the data, the solid red line represents the calculated profile, the solid green line represents the difference between the observed and calculated profiles.

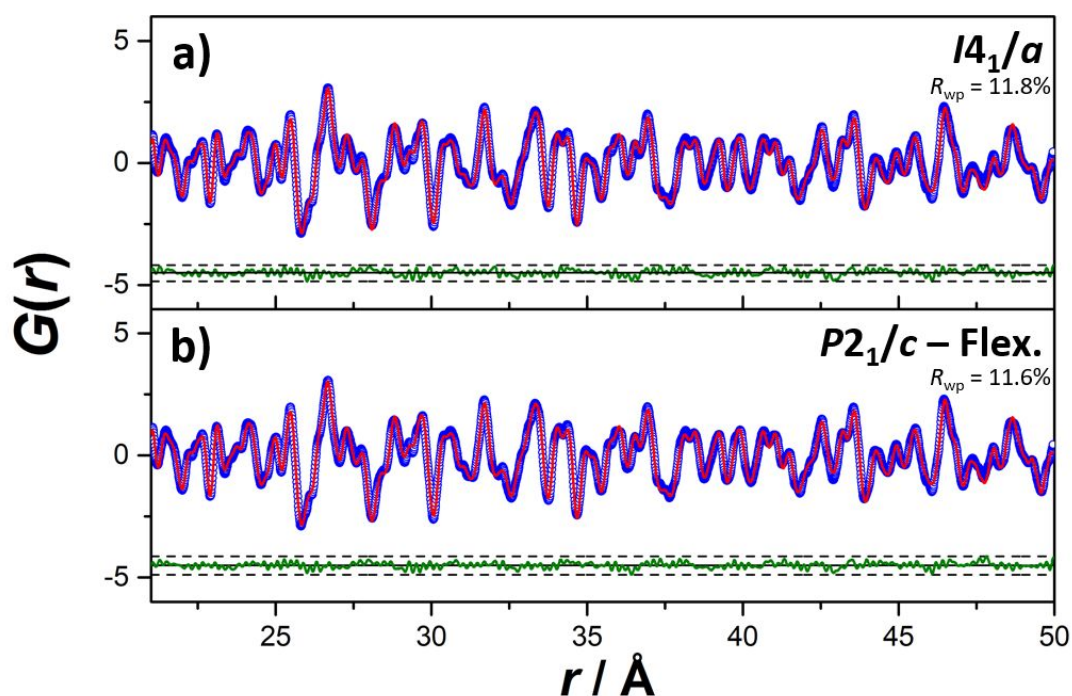


Figure S21: NPDF fits to PbWO₄ at 115 K for (a) tetragonal-scheelite $I4_1/a$, and (b) monoclinic $P2_1/c$ with flexible WO₄ tetrahedra. The data is fitted over a range of 21-50 Å. The blue dots represent the data, the solid red line represents the calculated profile, the solid green line represents the difference between the observed and calculated profiles.

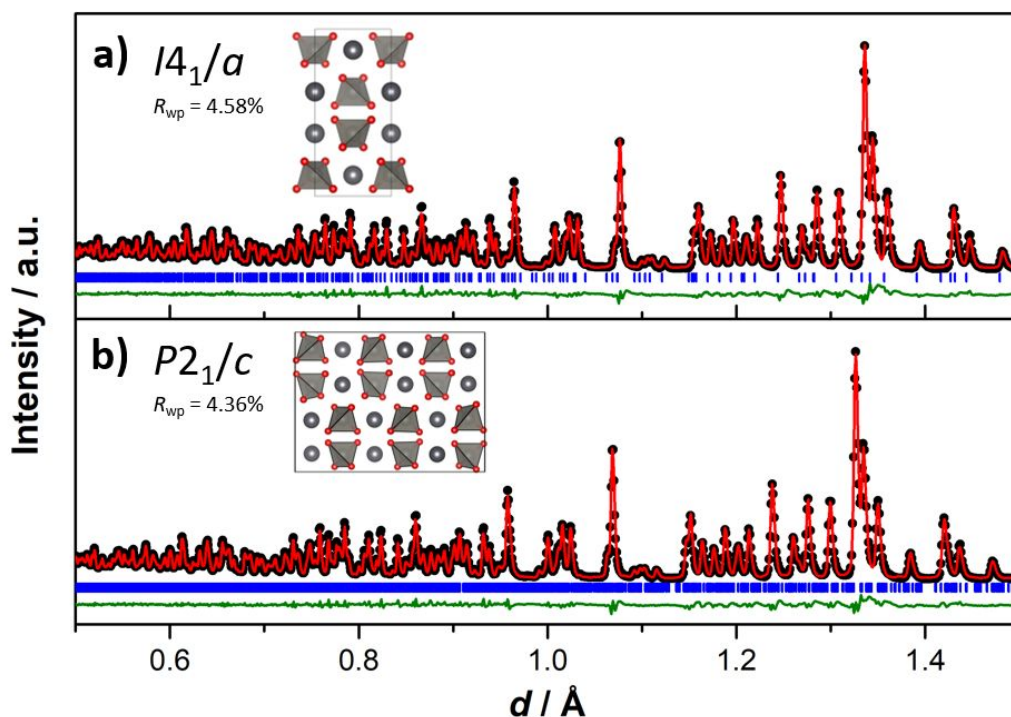


Figure S22: Rietveld refinements of PbWO_4 at 115 K to (a) tetragonal $I4_1/a$ and (b) monoclinic $P2_1/c$ using the highest resolution bank at the Nanoscale-Ordered Materials Diffractometer (NOMAD).

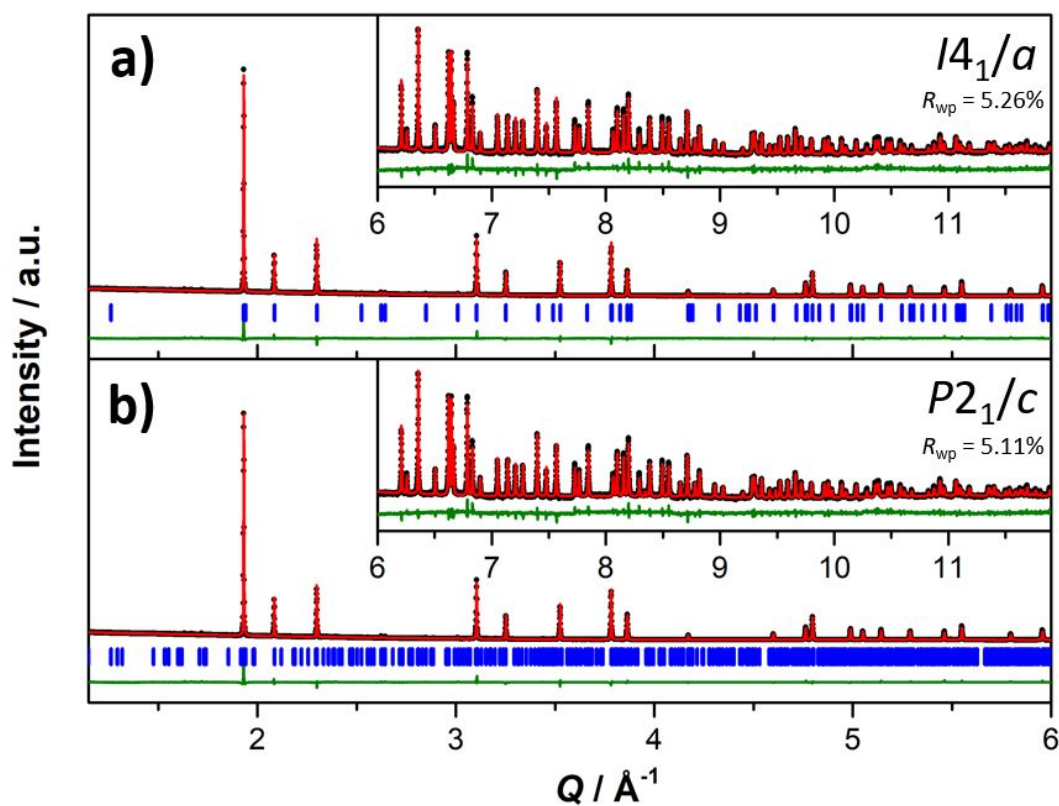


Figure S23: Rietveld refinements of PbWO_4 at 300 K to (a) tetragonal $I4_1/a$ and (b) monoclinic $P2_1/c$ using data collected on the Powder Diffraction beamline at the Australian Synchrotron.

(iii) Ground State Energy Calculations of PbWO_4 and CaWO_4

Calculations Relating to PbWO_4

Table S6: Comparison of the ground state energy calculation of the PbWO_4 structures using different functionals.

Ground State Energy (eV)	$I4_1/a$	$I2/b$	$P2_1/c$
PBE	-191.84123871	-191.88288916	-191.88339513
PBEsol	-200.43221999	-200.45794581	-200.45849094
AM05	-195.55951041	-195.58727773	-195.58776976

Table S7: Comparison of the atomic coordinates of PbWO_4 fitted to the tetragonal $I4_1/a$ space group from neutron total scattering data fitted at 115 K with density functional theory calculations using different functionals.

Atoms	Method	x	y	z
Pb	Experimental	= 0	= 1/4	= 5/8
	PBE	= 0	= 1/4	= 5/8
	PBEsol	= 0	= 1/4	= 5/8
	AM05	= 0	= 1/4	= 5/8
W	Experimental	= 0	= 1/4	= 1/8
	PBE	= 0	= 1/4	= 1/8
	PBEsol	= 0	= 1/4	= 1/8
	AM05	= 0	= 1/4	= 1/8
O	Experimental	0.24130	0.09889	0.03889
	PBE	0.23463	0.10954	0.04304
	PBEsol	0.23329	0.10261	0.04105
	AM05	0.23385	0.10583	0.04193

Table S8: Comparison of the atomic coordinates of PbWO₄ fitted to the monoclinic *I2/b* space group from neutron total scattering data fitted at 115 K with density functional theory calculations using different functionals.

Atoms	Method	<i>x</i>	<i>y</i>	<i>z</i>
Pb	Experimental	= 0	= 1/4	0.62470
	PBE	= 0	= 1/4	0.62500
	PBEsol	= 0	= 1/4	0.62499
	AM05	= 0	= 1/4	0.62500
W	Experimental	= 0	= 1/4	0.12630
	PBE	= 0	= 1/4	0.12500
	PBEsol	= 0	= 1/4	0.12505
	AM05	= 0	= 1/4	0.12494
O(1)	Experimental	0.14330	0.47690	0.21058
	PBE	0.14029	0.48466	0.20690
	PBEsol	0.14725	0.48337	0.20890
	AM05	0.14395	0.48392	0.20794
O(2)	Experimental	0.26150	0.39000	0.45420
	PBE	0.26535	0.39023	0.45685
	PBEsol	0.26662	0.39715	0.45883
	AM05	0.26607	0.39404	0.45801

Table S9: Comparison of the unit cell parameters of PbWO₄ to the monoclinic *I2/b* model obtained by Rietveld refinement against NPD data measured at 3 K or NPDF data measured at 115 K with those obtained using DFT calculations.

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>γ</i> (°)	Volume (Å ³)	Δ <i>V</i> (%)
NPD 3 K	5.45167(18)	5.44777(18)	11.98573(12)	90.018(5)	355.969(7)	-0.343
NPDF 115 K	5.45406(14)	5.45406(14)	12.0078(5)	90.02(2)	357.193(8)	--
DFT PBE	5.519	5.519	12.196	89.99	371.569	+4.02
DFT PBEsol	5.441	5.441	11.874	89.99	351.621	-1.56
DFT AM05	5.461	5.46	11.971	90.004	356.97	-0.062

Table S10: Comparison of the atomic coordinates of PbWO₄ fitted to the monoclinic $P2_1/c$ space group from neutron total scattering data fitted at 115 K with density functional theory calculations using different functionals.

Atoms	Method	x	y	z
Pb(1)	Experimental	0.00110	0.91620	0.12330
	PBE	0.00019	0.91648	0.12498
	PBEsol	-0.00006	0.91656	0.12504
	AM05	-0.00006	0.91656	0.12504
Pb(2)	Experimental	0.99730	0.25040	0.12790
	PBE	0.99974	0.24985	0.12499
	PBEsol	-0.00008	0.24990	0.12502
	AM05	-0.00008	0.24990	0.12502
Pb(3)	Experimental	0.00520	0.58160	0.12570
	PBE	-0.00033	0.58315	0.12501
	PBEsol	0.00004	0.58322	0.12502
	AM05	0.00004	0.58322	0.12502
W(1)	Experimental	-0.00450	0.75240	0.37520
	PBE	0.00018	0.74977	0.37506
	PBEsol	0.00010	0.74986	0.37509
	AM05	0.00010	0.74986	0.37509
W(2)	Experimental	1.00100	0.08190	0.36960
	PBE	0.00004	0.08315	0.37508
	PBEsol	0.00014	0.08321	0.37502
	AM05	0.00014	0.08321	0.37502
W(3)	Experimental	0.00150	0.41410	0.37420
	PBE	0.00008	0.41649	0.37499
	PBEsol	-0.00001	0.41656	0.37505
	AM05	-0.00001	0.41656	0.37505
O(11)	Experimental	-0.24040	0.70370	0.45410
	PBE	0.76548	0.70316	0.45706
	PBEsol	0.76674	0.70085	0.45905
	AM05	0.76674	0.70085	0.45905
O(12)	Experimental	0.24030	0.79860	0.45150
	PBE	0.23485	0.79672	0.45677
	PBEsol	0.23348	0.79904	0.45885
	AM05	0.23348	0.79904	0.45885
O(13)	Experimental	-0.13830	0.82790	0.28690
	PBE	0.85971	0.82781	0.29300
	PBEsol	0.85273	0.82755	0.29109
	AM05	0.85273	0.82755	0.29109
O(14)	Experimental	0.12780	0.67260	0.29360
	PBE	0.14017	0.67137	0.29335
	PBEsol	0.14710	0.67199	0.29127
	AM05	0.14710	0.67199	0.29127

O(21)	Experimental	0.77780	0.03440	0.45710
	PBE	0.76529	0.03653	0.45708
	PBEsol	0.76662	0.03426	0.45893
	AM05	0.76662	0.03426	0.45893
O(22)	Experimental	1.24040	0.12930	0.44820
	PBE	0.23465	0.13007	0.45685
	PBEsol	0.23333	0.13240	0.45887
	AM05	0.23333	0.13240	0.45887
O(23)	Experimental	0.84790	0.15830	0.28950
	PBE	0.85964	0.16122	0.29306
	PBEsol	0.85285	0.16092	0.29103
	AM05	0.85285	0.16092	0.29103
O(24)	Experimental	1.15530	0.00570	0.28980
	PBE	0.14007	0.00478	0.29335
	PBEsol	0.14726	0.00531	0.29126
	AM05	0.14726	0.00531	0.29126
O(31)	Experimental	-0.23860	0.37030	0.45610
	PBE	0.76531	0.36985	0.45697
	PBEsol	0.76647	0.36759	0.45896
	AM05	0.76647	0.36759	0.45896
O(32)	Experimental	0.22570	0.46320	0.45950
	PBE	0.23469	0.46342	0.45677
	PBEsol	0.23331	0.46575	0.45883
	AM05	0.23331	0.46575	0.45883
O(33)	Experimental	-0.13850	0.48810	0.28550
	PBE	0.85961	0.49456	0.29295
	PBEsol	0.85264	0.49424	0.29105
	AM05	0.85264	0.49424	0.29105
O(34)	Experimental	0.14170	0.33440	0.29540
	PBE	0.14029	0.33814	0.29325
	PBEsol	0.14695	0.33867	0.29125
	AM05	0.14695	0.33867	0.29125

Table S11: Comparison of the experimentally observed neutron pair distribution function unit cell parameters and distortion of the PbO_8 polyhedra in space group $P2_1/c$ with those obtained with DFT calculations employing different exchange correlation functionals. The ground state energies of the three investigated structure with each of the functionals are also listed.

	NPD 3 K	NPDF 115 K	DFT (PBE)	DFT (PBEsol)	DFT (AM05)
Pb(1)-O(1) (Å)	2.69(2)	2.672(11)	2.66449	2.60514	2.62539
Pb(1)-O(2) (Å)	2.581(17)	2.615(11)	2.63589	2.57556	2.59410
Pb(1)-O(3) (Å)	2.557(18)	2.632(11)	2.66381	2.60554	2.62462
Pb(1)-O(4) (Å)	2.580(19)	2.641(11)	2.63455	2.57593	2.59322
Pb(1)-O(5) (Å)	2.655(18)	2.638(12)	2.63321	2.57602	2.59305
Pb(1)-O(6) (Å)	2.540(19)	2.552(11)	2.63572	2.57618	2.59443
Pb(1)-O(7) (Å)	2.58(3)	2.551(11)	2.65725	2.60238	2.61876
Pb(1)-O(8) (Å)	2.639(19)	2.610(11)	2.65878	2.60162	2.62063
Pb(2)-O(1) (Å)	2.68(3)	2.633(12)	2.66392	2.60436	2.62635
Pb(2)-O(2) (Å)	2.609(18)	2.558(10)	2.63524	2.57549	2.59374
Pb(2)-O(3) (Å)	2.59(3)	2.630(11)	2.66441	2.60534	2.62645
Pb(2)-O(4) (Å)	2.591(19)	2.681(11)	2.63601	2.57593	2.59387
Pb(2)-O(5) (Å)	2.639(18)	2.625(11)	2.63427	2.57545	2.59232
Pb(2)-O(6) (Å)	2.573(19)	2.586(11)	2.63405	2.57590	2.59298
Pb(2)-O(7) (Å)	2.60(3)	2.589(11)	2.65712	2.60246	2.61936
Pb(2)-O(8) (Å)	2.667(19)	2.553(12)	2.65706	2.60287	2.61862
Pb(3)-O(1) (Å)	2.68(2)	2.697(10)	2.66378	2.60579	2.62606
Pb(3)-O(2) (Å)	2.613(19)	2.592(10)	2.63521	2.57522	2.59410
Pb(3)-O(3) (Å)	2.64(2)	2.610(12)	2.66315	2.60515	2.62476
Pb(3)-O(4) (Å)	2.625(19)	2.585(11)	2.63519	2.57545	2.59338
Pb(3)-O(5) (Å)	2.57(2)	2.625(12)	2.63393	2.57542	2.59242
Pb(3)-O(6) (Å)	2.556(18)	2.574(10)	2.63575	2.57518	2.59417
Pb(3)-O(7) (Å)	2.635(19)	2.665(12)	2.65826	2.60253	2.61884
Pb(3)-O(8) (Å)	2.599(19)	2.723(11)	2.65800	2.60301	2.61826

Table S12: Comparison of the unit cell parameters of PbWO_4 to the monoclinic $P2_1/c$ model obtained by Rietveld refinement against NPDF data measured at 115 K with those obtained using DFT calculations.

	a (Å)	b (Å)	c (Å)	γ (°)	Volume (Å ³)	ΔV (%)
NPDF 115 K	5.458	$16.348 / 3$ $= 5.4493$	12.008	90.2	1071.5	--
DFT PBE	5.518	$16.554 / 3$ $= 5.518$	12.189	90.004	1113.6	3.92
DFT PBEsol	5.441	$16.32 / 3$ $= 5.440$	11.869	90.001	1054.1	-1.62
DFT AM05	5.46	$16.38 / 3$ $= 5.46$	11.971	90.002	1070.8	-0.06

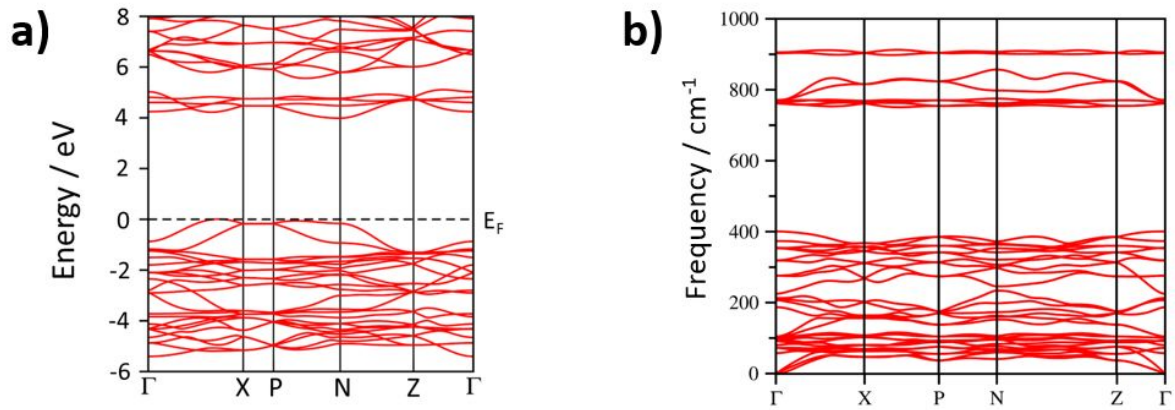


Figure S24: (a) Band structure of PbWO_4 in the monoclinic $P2_1/c$ space group calculated using the TB-mBJ functional. The valence band maximum is found in the Γ -X and P-N directions, whereas the conduction band has a minimum in the N direction, suggesting PbWO_4 to be an indirect band gap material. (b) Phonon dispersions for a $2 \times 2 \times 2$ supercell of PbWO_4 in the monoclinic $P2_1/c$ space group. No imaginary phonons are observed, confirming the dynamic stability of the calculations.

Calculations Relating to CaWO₄

Table S13: Comparison of the ground state energy calculation of the CaWO₄ structures using different functionals. Irrespective of the functional used the tetragonal $I4_1/a$ structure is more stable.

Ground State Energy (eV)	$I4_1/a$	$I2/b$
PBE	-202.31092588	-202.31068574
PBEsol	-210.81594231	-210.81582238
AM05	-206.25348721	-206.25275001

Table S14: Comparison of the unit cell parameters of CaWO₄ to the tetragonal $I4_1/a$ model obtained by Rietveld refinement against NPD data measured at 3 K or NPDF data measured at 100 K with those obtained using DFT calculations.

	a (Å)	c (Å)	Volume (Å ³)	ΔV (%)
NPD 3 K	5.2357	11.3506	311.14	-0.090
NPDF 115 K	5.2353	11.3620	311.42	--
DFT PBE	5.2563	11.3292	313.02	+0.51
DFT PBEsol	5.3104	11.5164	324.78	+4.29
DFT AM05	5.2337	11.2326	307.69	-1.19

Table S15: Comparison of the atomic coordinates of CaWO₄ fitted to the tetragonal $I4_1/a$ space group from neutron total scattering data fitted at 100 K with density functional theory calculations using different functionals.

Atoms	Method	x	y	z
Ca	Experimental	= 0	= 1/4	= 5/8
	PBE	= 0	= 1/4	= 5/8
	PBEsol	= 0	= 1/4	= 5/8
	AM05	= 0	= 1/4	= 5/8
W	Experimental	= 0	= 1/4	= 1/8
	PBE	= 0	= 1/4	= 1/8
	PBEsol	= 0	= 1/4	= 1/8
	AM05	= 0	= 1/4	= 1/8
O	Experimental	0.7581	0.4024	0.0391
	PBE	0.7573	0.4008	0.0394
	PBEsol	0.7585	0.4072	0.0372
	AM05	0.7582	0.4037	0.0382

Table S16: Comparison of the unit cell parameters of CaWO₄ to the monoclinic *I2/b* model obtained by Rietveld refinement against NPD data measured at 3 K or NPDF data measured at 115 K with those obtained using DFT calculations.

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	γ (°)	Volume (Å ³)	ΔV (%)
NPD 3 K	5.2353	5.2364	11.35103	90.001	311.18	-0.077
NPDF 115 K	5.2351	5.2351	11.3620	89.98	311.39	--
DFT PBE	5.2478	5.2635	11.3267	89.75	312.87	+0.47
DFT PBEsol	5.3083	5.3127	11.5193	89.93	324.86	+4.32
DFT AM05	5.2224	5.2413	11.2412	89.79	307.69	-1.18

Table S17: Comparison of the atomic coordinates of CaWO₄ fitted to the monoclinic *I2/b* space group from neutron total scattering data fitted at 100 K with density functional theory calculations using different functionals.

Atoms	Method	<i>x</i>	<i>y</i>	<i>z</i>
Ca	Experimental	= 0	= 1/4	0.6252
	PBE	= 0	= 1/4	0.6248
	PBEsol	= 0	= 1/4	0.6247
	AM05	= 0	= 1/4	0.6247
W	Experimental	= 0	= 1/4	0.1251
	PBE	= 0	= 1/4	0.1253
	PBEsol	= 0	= 1/4	0.1260
	AM05	= 0	= 1/4	0.2122
O(1)	Experimental	0.1548	0.4877	0.2127
	PBE	0.1504	0.4927	0.2108
	PBEsol	0.1584	0.4916	0.2129
	AM05	0.1548	0.4916	0.2122
O(2)	Experimental	0.2533	0.4001	0.4588
	PBE	0.2571	0.4002	0.4064
	PBEsol	0.2584	0.4064	0.4621
	AM05	0.2583	0.4030	0.4612

Table S18: Comparison of the unit cell parameters and *A*-site polyhedra of PbWO₄ and CaWO₄ from density functional theory calculations using the Armiento-Mattsson 2005 exchange-correlation functionals.

	PbWO₄		CaWO₄	
	Tetragonal <i>I</i>4₁/<i>a</i>	Monoclinic <i>I</i>2/<i>b</i>	Tetragonal <i>I</i>4₁/<i>a</i>	Monoclinic <i>I</i>2/<i>b</i>
<i>a</i> (Å)	5.45978	5.46114	5.25633	5.24789
<i>b</i> (Å)	= <i>a</i>	5.46021	= <i>a</i>	5.26352
<i>c</i> (Å)	11.96014	11.97134	11.32923	11.32679
<i>γ</i> (°)	= 90	90.00477	= 90	89.75952
<i>A</i> -O (Å)	2.59182	2.59350	2.43268	2.43093
<i>A</i> -O (Å)	--	2.59391	--	2.43448
<i>A</i> -O (Å)	2.6216	2.62233	2.47393	2.47008
<i>A</i> -O (Å)	--	2.62242	--	2.47632
<i>D</i> (AO ₈) (×10 ⁻³)	5.71	5.50	8.41	8.26

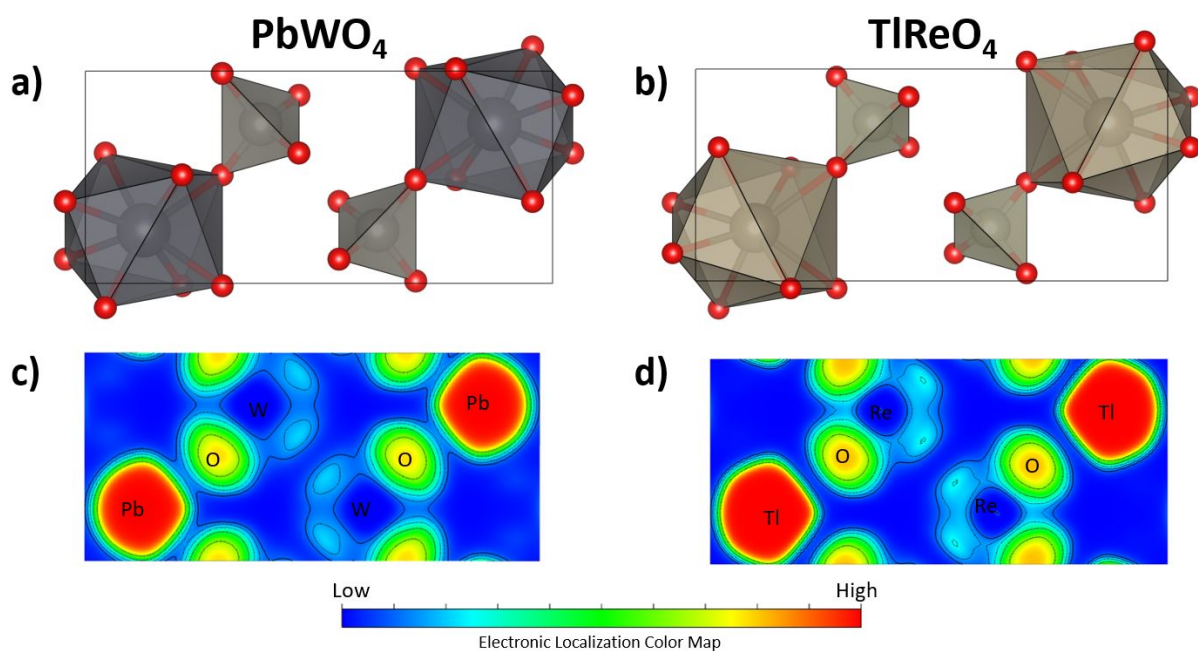


Figure S25: Visualization of the electron localization function of (a,c) PbWO_4 and (b,d) TlReO_4 in the tetragonal $I4_1/a$ model, with the electron localization of atoms in the $\langle 100 \rangle$ plane illustrated. (a,b) Drawn with the polyhedra, and (c,d) drawn with the electron localization function.

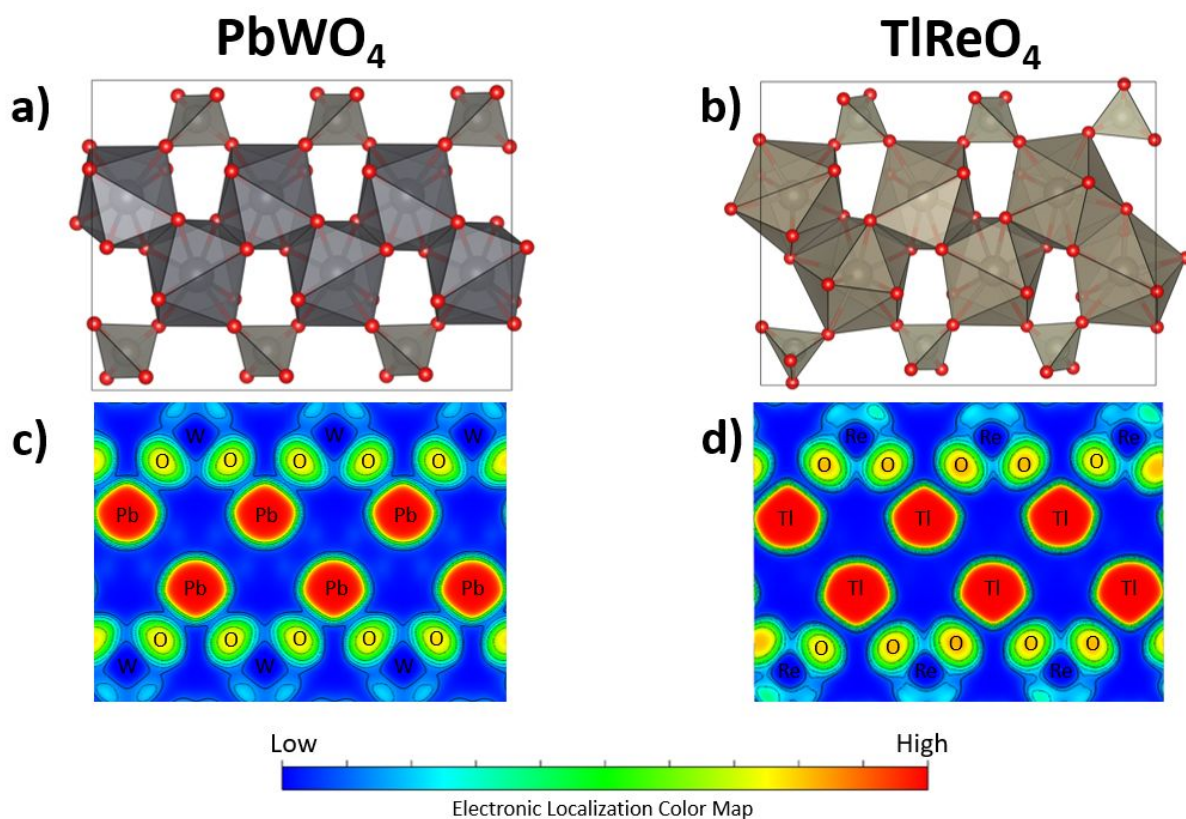


Figure S26: Visualization of the electron localization function of (a,c) PbWO_4 and (b,d) TlReO_4 in the monoclinic $P2_1/c$ model, with the electron localization of atoms in the $\langle 001 \rangle$ plane illustrated. (a,b) Drawn with the polyhedra, and (c,d) drawn with the electron localization function.

(iv) References

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