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Supporting information for article:

Crystal structure of Re-substituted lanthanum tungstate La5.4W1-yReyO12-δ (0 ≤ y ≤ 0.2) studied by neutron diffraction

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Supporting information

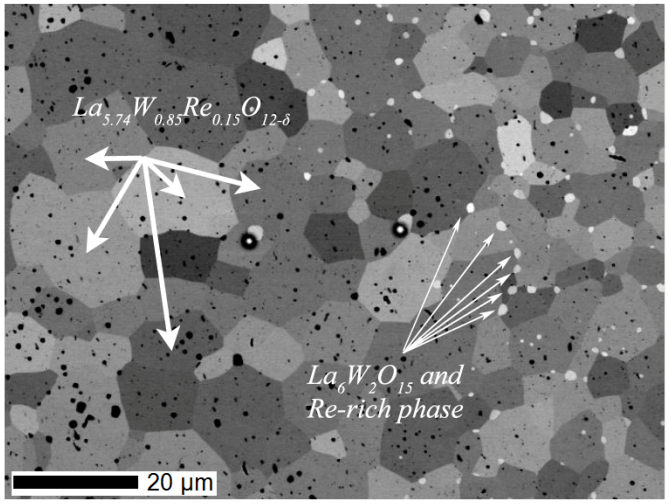

Figure S1 Electron back-scattered image of sample Re20_IMP. Different grain sizes can be identified in the figure, where larger grains (between 5 µm and 20 µm, some of them indicated by thick white arrows) correspond to the main phase $La_{5.74}W_{0.85}Re_{0.15}O_{12-\delta}$ and smaller grains (< 2 µm, some of them indicated by thin white arrows) correspond to the secondary phase $La_6W_2O_{15}$ plus an unidentified Re-rich phase (cf. text). Bright points surrounded by black rings (sputtered carbon built-up) are the electron beam marks (Ø ~ 500 nm) caused by the EPMA measurements.

The BSE image of sample Re20_IMP is shown in Figure S1. Large (diameter ~ 5 µm to ~ 20 µm) and small (< 2 µm) grains are observed. The difference in grain colour (whitish to dark grey) is due to different grain orientations and elemental contrast. According to the simulations of the beam penetration depth, the measured compositions of the biggest grains are reliable, while for the grains of the secondary phase (< 2 µm) the composition measured yields a mixture of different phase compositions. For the Re20_IMP sample, the La/(W+Re) ratio of 3.5(4) corresponds to the $La_6W_2O_{15}$ phase. However, some of a highly Re-enriched phase was also found by EPMA, which gives rise a Re/(W+Re) ratio of ~ 0.30. However, only $La_6W_2O_{15}$ has been indexed in the available XRD data base, hinting that the highly Re-enriched phase is present in small amounts and/or their crystallite size is appreciably below the coherence length of X-rays. Another possibility could be that the highly Re-enriched and the $La_6W_2O_{15}$ phases are the same phase in the form of $La_6W_{2-x}Re_xO_{15}$ and cannot be distinguished from $La_6W_2O_{15}$ by XRD. As at present neither the composition nor the amount of this highly Re-enriched phase can be estimated, only $La_6W_2O_{15}$ is mentioned in the phase diagram (Figure 1).

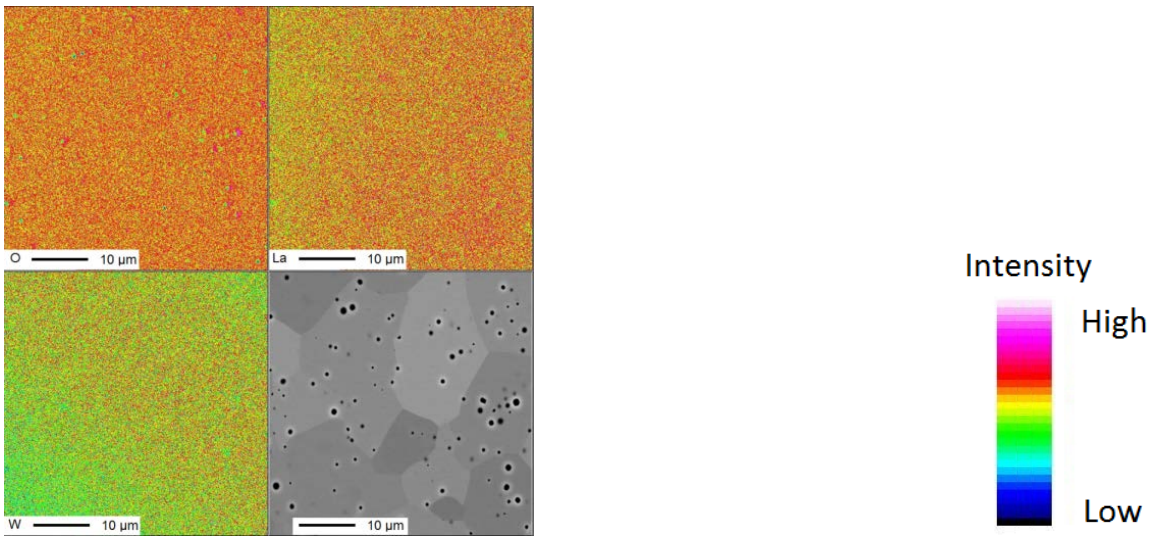

Figure S2 EPMA maps of the constituting elements of LWO_**P** ($La_{5.56(3)}WO_{12-\delta}$) along with the corresponding backscattered electron image. The relative intensity scale used by each detector is also reported.

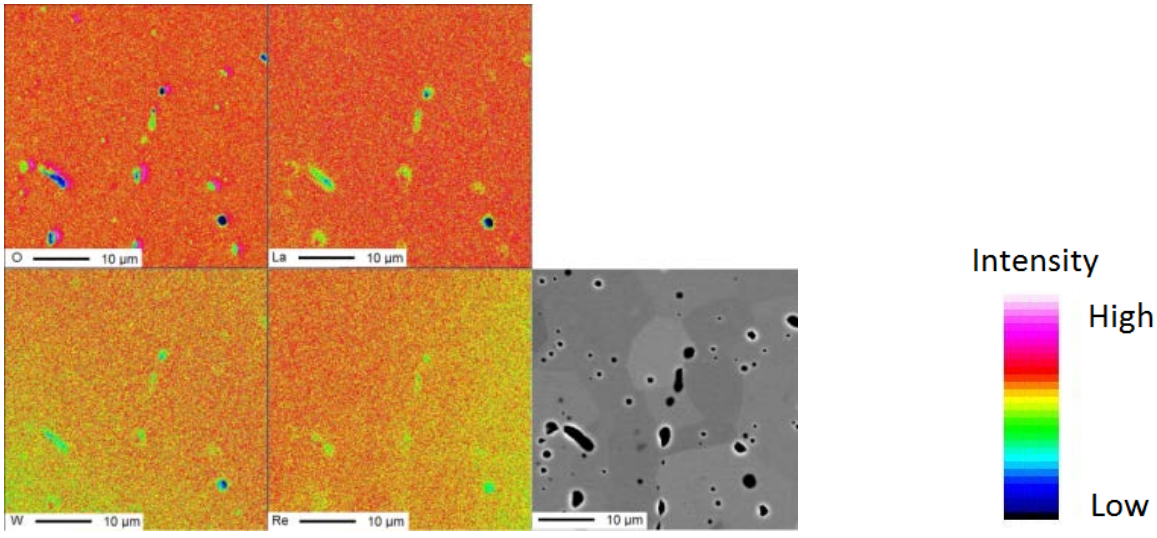

Figure S3 EPMA maps of the constituting elements of Re20 ($La_{5.86(7)}W_{0.826(7)}Re_{0.174(7)}O_{12-\delta}$) along with the corresponding backscattered electron image. The relative intensity scale used by each detector is also reported.

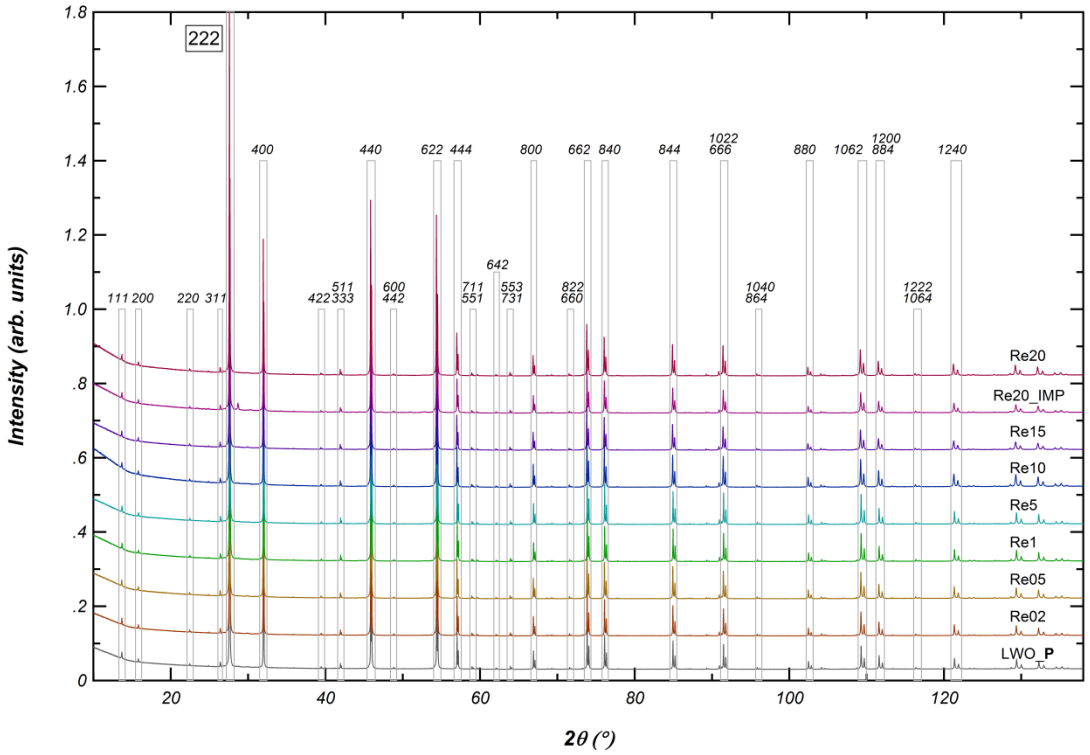

Figure S4 XRD patterns of the LW(Re)O-dry(Ar) specimens as a function of the scattering angle 2Θ ($10° \leq 2\Theta \leq 138°$). The patterns are presented from the non-substituted LWO_**P** (black pattern) to the highest nominal Re/(W+Re) ratio (Re20, in red), from bottom to top, respectively. The *hkl* indices of the main reflections below $2\Theta = 130°$ are also shown ($^{-}3F$ space group), and the patterns are normalized to the peak of highest intensity (*hkl* = 222 reflection). Peak splitting is due to CuKα_1/Kα_2 doublet.

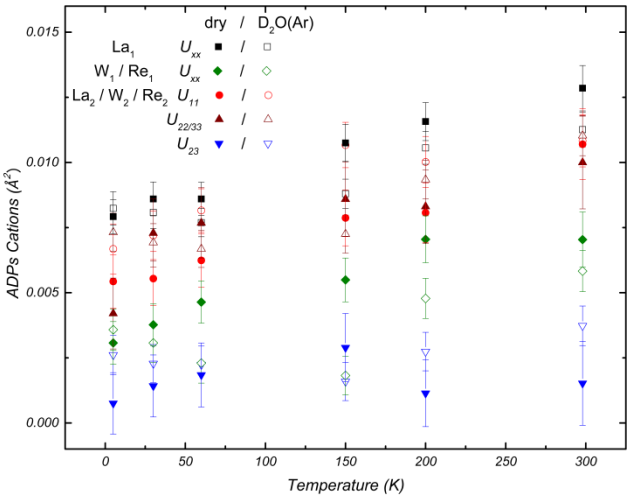

Figure S5 Anisotropic displacement parameters (ADPs) as a function of temperature for cations of Re20-dry(Ar) (full symbols) and Re20-D_2O(Ar) (open symbols), obtained from ND data measured at D2B (ILL).

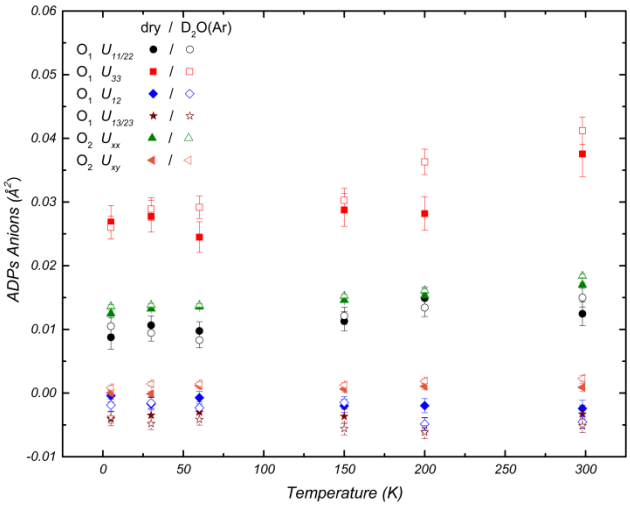

Figure S6 Anisotropic displacement parameters (ADPs) as a function of temperature for anions of Re20-dry(Ar) (full symbols) and Re20-D_2O(Ar) (open symbols), obtained from ND data measured at D2B (ILL).

Anharmonic vibration study on LWO

The W_1, O_1 and O_2 equivalent displacement parameter values (B_{eq}) for LWO are taken from Figure 4, including the two datasets of the present work (LWO_**P**-dry(Ar) specimen) and of Magraso et al. (2013). B_{eq} data were interpolated with the harmonic approximation according to the Willis and Pryor (1975) model (Eq. (10)) and the quasi-harmonic approximation used in Erich and Ma (1998)

$$B_{eq}^{An}(k) = B_{eq}^{static}(k) + B_{eq}^{thermal}(k)(1 + AT) \quad \text{(S1)}$$

where $B_{eq}(k)$ is the atomic equivalent thermal vibration B_{eq} of atom k and the quasi-harmonic correction A is a constant dependent on the atom potential force constants, the Grüneisen parameter and the volume coefficient of thermal expansion (see Erich and Ma (1998) for details). Notice that Eq. (S1) reduces to the harmonic approximation of Willis and Pryor (1975), applied to a single atom, when $A = 0$. The B_{eq} parameters of O_1, O_2 and W_1 atoms obtained from LWO_**P** data ($T \leq 298$ K, present work) and from the LWO data reported in literature ($T \geq 298$ K, Magraso *et al.* (2013)) are depicted in Figure S7, along with the interpolations performed according to Eq. (S1) with $A = 0$ (harmonic approximation) and $A \neq 0$ (quasi-harmonic approximation).

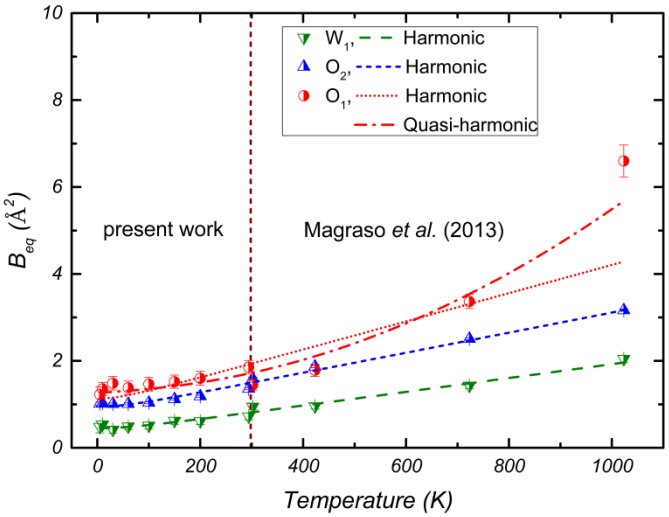

Figure S7 Equivalent displacement parameter B_{eq} for O_1, O_2 and W_1 atoms in LWO as a function of the temperature. The data from the present work and the data of Magraso et al. (2013) are shown in the temperature regions $T \leq 298$ K and $T \geq 298$ K, respectively, as in Figure 4, where the wine dashed line is drawn at $T = 298$ K. The data point at $T = 298$ K from the present work is shifted to $T = 294$ K, while the data point at $T = 298$ K taken from Magraso et al. (2013) is shifted to $T = 302$ K, for better visualization. Fits with the harmonic approximation (Eq. (S1), $A = 0$) were performed for O_1 (red dotted line), O_2 (blue short dashed line) and W_1 (green dashed line) atoms. For the O_1 atom, the fit using the quasi-harmonic approximation (Eq. (S1), $A \neq 0$) is also reported in red dash-dotted line.

For the W_1 and O_2 atoms, the harmonic approximation yields good residuals, with $R^2 = 0.99$ and $R^2 = 0.97$, respectively. For the O_1 atom, instead, the residual obtained is poor ($R^2 = 0.72$, cf. red short-dotted line in Figure S7). When the quasi-harmonic approximation is used, the improvement of the fit is substantial, with a residual $R^2 = 0.93$. Applying Eq. (S1) to W_1, O_1 and O_2 allows for estimating a Debye temperature for each of these atoms. Such Debye temperatures for the individual ions do not have great physical significance: in order to obtain physically relevant values, Eq. (S1) should, instead, be applied to the cell-weighted displacement parameter, B_M^{An}, in the same fashion as shown in

Figure 9 for low temperatures. Lack of precise data at high temperature, however, did not allow this procedure. The harmonic (Eq. (S1), $A = 0$) and anharmonic (Eq. (S1), $A \neq 0$) interpolations give two values of T_D for the O_1 atom, where $T_D(O_1)$ = 233(21) K and $T_D{}^{An}(O_1)$= 841(37) K, respectively. From these estimations, it follows that an implementation of an anharmonic correction in O_1 would increase substantially the $T_D{}^{An}(O_1)$ weighted contribution to the T_D (LWO_**P**) established by the Willis and Pryor (1975) approach. To conclude, there is indeed a non-negligible anharmonic vibration of the anions occupying the 96*k* Wyckoff sites, which is not present for the O_2 and W_1 atoms. In general, anharmonic vibrations are not likely to exist for heavy cations, as discussed for the YSZ system in Erich and Ma (1998). At present, it is not clear whether the discrepancy between the two estimates of T_D reported in Table 5 is mainly due to anharmonic parameters not included in Eq. (10) or due to the lack of high-temperature data. In addition, the non-modelling of the O_1 libration around W_1 could also contribute to an apparent anion anharmonicity. However, it is reasonable to conclude that the three terms may have contributed to the underestimation of the Debye temperature determined with the harmonic approach of Willis and Pryor (1975). Therefore, it is assumed that the Debye temperatures in the present case are better estimated through the thermal expansion coefficients, resulting in Debye temperatures of T_D = 580(33) K and T_D = 571(45) K for LWO_**P** and Re20 specimens, respectively. However, in order to understand how much the anionic/cationic vibrations in the LWO system deviate from the harmonic oscillator approximation, and consequently to determine the Debye temperatures of LWO based systems within independent approaches such as that of Willis and Pryor (1975), further insights are needed. For instance, an improved structural model that allows for anharmonic vibrations should be tested for diffraction patterns and more data should be collected in the $T > T_D$ region, where the anharmonic displacement terms become more relevant (Erich & Ma, 1998; Willis & Pryor, 1975).

Table S1 LWO_**P**-dry(Ar) T = 5 K ILL 'Scherb model'

Lattice constants are

a = 11.15354(6) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1387.518(12) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.68(11)	M3M	4	LA	1	1.000(16)
La2	0.000000	0.23601(28)	0.23601(28)	0.69*	MM2(011)	48	LA	2	0.484(7)
W1	0.000000	0.000000	0.000000	0.61(17)	M3M	4	W	3	1.021(28)
O1	0.11201(22)	0.11201(22)	0.06539(34)	1.55*	M(+-0)	96	O	4	0.237(4)
O2	0.36615(12)	0.36615(12)	0.36615(12)	1.29*	3M(111)	32	O	5	0.938(6)
W2	0.000000	0.23601(28)	0.23601(28)	0.69*	MM2(011)	48	W	6	0.016(7)

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.68(11)	0.68	0.68	0.00	0.00	0.00
La2	0.64(11)	0.72(18)	0.72(18)	0.00	0.00	0.28(16)
W1	0.61(17)	0.61	0.61	0.00	0.00	0.00
O1	0.63(18)	0.63(18)	3.40(30)	-0.14(10)	-0.69(11)	-0.69(11)
O2	1.29(5)	1.29(5)	1.29(5)	-0.03(4)	-0.03(4)	-0.03(4)
W2	0.64(11)	0.72(18)	0.72(18)	0.00	0.00	0.28(16)

Table S2 LWO_**P**-dry(Ar) T = 5 K ILL 'Magraso model'

Lattice constants are

a = 11.15354(6) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1387.518(12) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.66(11)	M3M	4	LA	1	0.982(16)
La2	0.000000	0.250000	0.250000	2.84*	MMM(100)	24	LA	2	0.967(14)
W1	0.000000	0.000000	0.000000	0.64(18)	M3M	4	W	3	1.001(28)
O1	0.11148(19)	0.11148(19)	0.06567(34)	---	M(+-0)	96	O	4	0.226(4)
O2	0.36586(10)	0.36586(10)	0.36586(10)	1.21*	3M(111)	32	O	5	0.915(6)
W2	0.000000	0.250000	0.250000	2.84*	MMM(100)	24	W	6	0.034(14)

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.66(11)	0.66	0.66	0.00	0.00	0.00
La2	0.66(10)	3.93(7)	3.93(7)	0.00	0.00	3.21(8)
W1	0.64(18)	0.64	0.64	0.00	0.00	0.00
O1	0.10(16)	0.10(16)	3.61(32)	-0.41(9)	-0.51(10)	-0.51(10)
O2	1.21(4)	1.21(4)	1.21(4)	-0.04(4)	-0.04(4)	-0.04(4)
W2	0.66(10)	3.93(7)	3.93(7)	0.00	0.00	3.21(8)

Table S3 LWO_**P**-dry(Ar) T = 10 K ILL 'Scherb model'

Lattice constants are

a = 11.153450(32) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1387.483(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.78(6)	M3M	4	LA	1	1.0005
La2	0.000000	0.23627(28)	0.23627(28)	0.77*	MM2(011)	48	LA	2	0.4838
W1	0.000000	0.000000	0.000000	0.68(10)	M3M	4	W	3	1.0215
O1	0.11226(22)	0.11226(22)	0.06557(32)	1.71*	M(+-0)	96	O	4	0.2373
O2	0.36617(11)	0.36617(11)	0.36617(11)	1.30*	3M(111)		32	O	5 0.9379
W2	0.000000	0.23627(28)	0.23627(28)	0.77*	MM2(011)	48	W	6	0.0162

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.78(6)	0.78	0.78	0.00	0.00	0.00
La2	0.64(10)	0.83(17)	0.83(17)	0.00	0.00	0.32(15)
W1	0.68(10)	0.68	0.68	0.00	0.00	0.00
O1	0.874(148)	0.874(148)	3.395(284)	-0.14(10)	-0.75(12)	-0.75(12)
O2	1.304(28)	1.304(28)	1.304(28)	0.03(5)	0.03(5)	0.03(5)
W2	0.64(10)	0.83(17)	0.83(17)	0.00	0.00	0.32(15)

Table S4 LWO_**P**-dry(Ar) T = 10 K ILL 'Magraso model'

Lattice constants are

a = 11.153457(32) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1387.485(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.76(6)	M3M	4	LA	1	0.9823
La2	0.000000	0.250000	0.250000	2.82*	MMM(100)	24	LA	2	0.9666
W1	0.000000	0.000000	0.000000	0.69(10)	M3M	4	W	3	1.0008
O1	0.11175(20)	0.11175(20)	0.06584(32)	---	M(+-0)	96	O	4	0.2257
O2	0.36588(10)	0.36588(10)	0.36588(10)	1.23*	3M(111)	32	O	5	0.9146
W2	0.000000	0.250000	0.250000	2.82*	MMM(100)	24	W	6	0.0345

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.76(6)	0.76	0.76	0.00	0.00	0.00
La2	0.67(10)	3.90(7)	3.90(7)	0.00	0.00	3.14(8)
W1	0.69(10)	0.69	0.69	0.00	0.00	0.00
O1	0.364(128)	0.364(128)	3.599(292)	-0.39(10)	-0.59(11)	-0.59(11)
O2	1.228(28)	1.228(28)	1.228(28)	0.02(5)	0.02(5)	0.02(5)
W2	0.67(10)	3.90(7)	3.90(7)	0.00	0.00	3.14(8)

Table S5 LWO_**P**-dry(Ar) T = 30 K ILL 'Scherb model'

Lattice constants are

a = 11.153437(31) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1387.478(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.76(6)	M3M	4	LA	1	1.0005
La2	0.000000	0.23641(30)	0.23641(30)	0.87*	MM2(011)	48	LA	2	0.4838
W1	0.000000	0.000000	0.000000	0.53(10)	M3M	4	W	3	1.0215
O1	0.11202(23)	0.11202(23)	0.06521(32)	1.88*	M(+-0)	96	O	4	0.2373
O2	0.36617(11)	0.36617(11)	0.36617(11)	1.28*	3M(111)	32	O	5	0.9379
W2	0.000000	0.23641(30)	0.23641(30)	0.87*	MM2(011)	48	W	6	0.0162

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.76(6)	0.76	0.76	0.00	0.00	0.00
La2	0.74(10)	0.93(18)	0.93(18)	0.00	0.00	0.51(16)
W1	0.53(10)	0.53	0.53	0.00	0.00	0.00
O1	1.119(156)	1.119(156)	3.406(282)	-0.17(11)	-0.88(12)	-0.88(12)
O2	1.279(28)	1.279(28)	1.279(28)	0.05(4)	0.05(4)	0.05(4)
W2	0.74(10)	0.93(18)	0.93(18)	0.00	0.00	0.51(16)

Table S6 LWO_**P**-dry(Ar) T = 30 K ILL 'Magraso model'

Lattice constants are

a = 11.153450(31) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1387.483(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.75(6)	M3M	4	LA	1	0.9823
La2	0.000000	0.250000	0.250000	2.86*	MMM(100)	24	LA	2	0.9666
W1	0.000000	0.000000	0.000000	0.55(9)	M3M	4	W	3	1.0008
O1	0.11156(21)	0.11156(21)	0.06547(32)	---	M(+-0)	96	O	4	0.2257
O2	0.36591(10)	0.36591(10)	0.36591(10)	1.20*	3M(111)	32	O	5	0.9146
W2	0.000000	0.250000	0.250000	2.86*	MMM(100)	24	W	6	0.0345

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.75(6)	0.75	0.75	0.00	0.00	0.00
La2	0.74(10)	3.92(7)	3.92(7)	0.00	0.00	3.27(8)
W1	0.55(9)	0.55	0.55	0.00	0.00	0.00
O1	0.615(136)	0.615(136)	3.556(290)	-0.39(10)	-0.71(11)	-0.71(11)
O2	1.202(27)	1.202(27)	1.202(27)	0.05(4)	0.05(4)	0.05(4)
W2	0.74(10)	3.92(7)	3.92(7)	0.00	0.00	3.27(8)

Table S7 LWO_P-dry(Ar) T = 60 K ILL 'Scherb model'

Lattice constants are

a = 11.153840(32) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1387.629(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.78*	M3M	4	LA	1	1.0005
La2	0.000000	0.23617(27)	0.23617(27)	0.74*	MM2(011)	48	LA	2	0.4838
W1	0.000000	0.000000	0.000000	0.63*	M3M	4	W	3	1.0215
O1	0.11201(22)	0.11201(22)	0.06569(32)	1.75*	M(+-0)	96	O	4	0.2373
O2	0.36615(12)	0.36615(12)	0.36615(12)	1.29*	3M(111)	32	O	5	0.9379
W2	0.000000	0.23617(27)	0.23617(27)	0.74*	MM2(011)	48	W	6	0.0162

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.78(6)	0.78(6)	0.78(6)	0.00	0.00	0.00
La2	0.77(10)	0.73(16)	0.73(16)	0.00	0.00	0.31(15)
W1	0.63(10)	0.63(10)	0.63(10)	0.00	0.00	0.00
O1	0.869(151)	0.869(151)	3.503(292)	-0.13(10)	-0.77(12)	-0.77(12)
O2	1.290(28)	1.290(28)	1.290(28)	0.09(5)	0.09(5)	0.09(5)
W2	0.77(10)	0.73(16)	0.73(16)	0.00	0.00	0.31(15)

Table S8 LWO_P-dry(Ar) T = 60 K ILL 'Magraso model'

Lattice constants are

a = 11.153853(32) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1387.634(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.76(6)	M3M	4	LA	1	0.9823
La2	0.000000	0.250000	0.250000	2.82*	MMM(100)	24	LA	2	0.9666
W1	0.000000	0.000000	0.000000	0.65(10)	M3M	4	W	3	1.0008
O1	0.11150(20)	0.11150(20)	0.06600(33)	---	M(+-0)	96	O	4	0.2257
O2	0.36584(10)	0.36584(10)	0.36584(10)	1.20*	3M(111)	32	O	5	0.9146
W2	0.000000	0.250000	0.250000	2.82*	MMM(100)	24	W	6	0.0365

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.76(6)	0.76	0.76	0.00	0.00	0.00
La2	0.75(10)	3.85(7)	3.85(7)	0.00	0.00	3.18(8)
W1	0.65(10)	0.65	0.65	0.00	0.00	0.00
O1	0.333(129)	0.333(129)	3.769(300)	-0.40(10)	-0.60(11)	-0.60(11)
O2	1.200(28)	1.200(28)	1.200(28)	0.07(4)	0.07(4)	0.07(4)
W2	0.75(10)	3.85(7)	3.85(7)	0.00	0.00	3.18(8)

Table S9 LWO_P-dry(Ar) T = 100 K ILL 'Scherb model'

Lattice constants are

a = 11.155488(32) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1388.244(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.83(7)	M3M	4	LA	1	1.0005
La2	0.000000	0.23644(31)	0.23644(31)	0.91*	MM2(011)	48	LA	2	0.4838
W1	0.000000	0.000000	0.000000	0.64(10)	M3M	4	W	3	1.0215
O1	0.11230(23)	0.11230(23)	0.06537(32)	1.85*	M(+-0)	96	O	4	0.2373
O2	0.36619(12)	0.36619(12)	0.36619(12)	1.31*	3M(111)	32	O	5	0.9379
W2	0.000000	0.23644(31)	0.23644(31)	0.91*	MM2(011)	48	W	6	0.0162

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.83(7)	0.83	0.83	0.00	0.00	0.00
La2	0.71(10)	1.01(18)	1.01(18)	0.00	0.00	0.41(16)
W1	0.64(10)	0.64	0.64	0.00	0.00	0.00
O1	1.108(156)	1.108(156)	3.346(287)	-0.08(11)	-0.72(12)	-0.72(12)
O2	1.314(28)	1.314(28)	1.314(28)	0.05(5)	0.05(5)	0.05(5)
W2	0.71(10)	1.01(18)	1.01(18)	0.00	0.00	0.41(16)

Table S10 LWO_P-dry(Ar) T = 100 K ILL 'Magraso model'

Lattice constants are

a = 11.155488(32) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1388.244(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.82(6)	M3M	4	LA	1	0.9823
La2	0.000000	0.250000	0.250000	2.90*	MMM(100)	24	LA	2	0.9666
W1	0.000000	0.000000	0.000000	0.65(10)	M3M	4	W	3	1.0008
O1	0.11185(21)	0.11185(21)	0.06565(33)	---	M(+-0)	96	O	4	0.2257
O2	0.36593(11)	0.36593(11)	0.36593(11)	1.23*	3M(111)	32	O	5	0.9146
W2	0.000000	0.250000	0.250000	2.90*	MMM(100)	24	W	6	0.0365

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.82(6)	0.82	0.82	0.00	0.00	0.00
La2	0.73(10)	3.98(7)	3.98(7)	0.00	0.00	3.15(8)
W1	0.65(10)	0.65	0.65	0.00	0.00	0.00
O1	0.618(137)	0.618(137)	3.499(295)	-0.31(10)	-0.58(11)	-0.58(11)
O2	1.235(28)	1.235(28)	1.235(28)	0.05(5)	0.05(5)	0.05(5)
W2	0.73(10)	3.98(7)	3.98(7)	0.00	0.00	3.15(8)

Table S11 LWO_P-dry(Ar) T = 150 K ILL 'Scherb model'

Lattice constants are

a = 11.158355(32) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1389.314(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.89(7)	M3M	4	LA	1	1.0005
La2	0.000000	0.23639(31)	0.23639(31)	0.95*	MM2(011)	48	LA	2	0.4838
W1	0.000000	0.000000	0.000000	0.79(10)	M3M	4	W	3	1.0215
O1	0.11220(22)	0.11220(22)	0.06533(32)	1.93*	M(+-0)	96	O	4	0.2373
O2	0.36601(11)	0.36601(11)	0.36601(11)	1.42*	3M(111)	32	O	5	0.9379
W2	0.000000	0.23639(31)	0.23639(31)	0.95*	MM2(011)	48	W	6	0.0162

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.89(7)	0.89	0.89	0.00	0.00	0.00
La2	0.74(10)	1.05(18)	1.05(18)	0.00	0.00	0.47(16)
W1	0.79(10)	0.79	0.79	0.00	0.00	0.00
O1	0.961(147)	0.961(147)	3.859(290)	-0.28(10)	-0.71(12)	-0.71(12)
O2	1.420(29)	1.420(29)	1.420(29)	0.00(5)	0.00(5)	0.00(5)
W2	0.74(10)	1.05(18)	1.05(18)	0.00	0.00	0.47(16)

Table S12 LWO_P-dry(Ar) T = 150 K ILL 'Magraso model'

Lattice constants are

a = 11.158355(32) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1389.314(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.87(6)	M3M	4	LA	1	0.9823
La2	0.000000	0.250000	0.250000	2.95*	MMM(100)	24	LA	2	0.9666
W1	0.000000	0.000000	0.000000	0.80(10)	M3M	4	W	3	1.0008
O1	0.11175(20)	0.11175(20)	0.06562(33)	---	M(+-0)	96	O	4	0.2257
O2	0.36576(10)	0.36576(10)	0.36576(10)	1.34*	3M(111)	32	O	5	0.9146
W2	0.000000	0.250000	0.250000	2.95*	MMM(100)	24	W	6	0.0365

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.87(6)	0.87	0.87	0.00	0.00	0.00
La2	0.76(10)	4.05(7)	4.05(7)	0.00	0.00	3.21(8)
W1	0.80(10)	0.80	0.80	0.00	0.00	0.00
O1	0.474(128)	0.474(128)	4.065(298)	-0.50(10)	-0.59(11)	-0.59(11)
O2	1.340(28)	1.340(28)	1.340(28)	-0.01(5)	-0.01(5)	-0.01(5)
W2	0.76(10)	4.05(7)	4.05(7)	0.00	0.00	3.21(8)

Table S13 LWO_P-dry(Ar) T = 200 K ILL 'Scherb model'

Lattice constants are

a = 11.162082(33) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1390.707(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	1.00(7)	M3M	4	LA	1	1.0005
La2	0.000000	0.23645(32)	0.23645(32)	1.08*	MM2(011)	48	LA	2	0.4838
W1	0.000000	0.000000	0.000000	0.78(10)	M3M	4	W	3	1.0215
O1	0.11221(23)	0.11221(23)	0.06488(33)	2.03*	M(+-0)	96	O	4	0.2373
O2	0.36622(12)	0.36622(12)	0.36622(12)	1.50*	3M(111)	32	O	5	0.9379
W2	0.000000	0.23645(32)	0.23645(32)	1.08*	MM2(011)	48	W	6	0.0162

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	1.00(7)	1.00	1.00	0.00	0.00	0.00
La2	0.91(11)	1.16(19)	1.16(19)	0.00	0.00	0.47(17)
W1	0.78(10)	0.78	0.78	0.00	0.00	0.00
O1	1.137(156)	1.137(156)	3.812(293)	-0.22(11)	-0.81(12)	-0.81(12)
O2	1.503(29)	1.503(29)	1.503(29)	0.07(5)	0.07(5)	0.07(5)
W2	0.91(11)	1.16(19)	1.16(19)	0.00	0.00	0.47(17)

Table S14 LWO_P-dry(Ar) T = 200 K ILL 'Magraso model'

Lattice constants are

a = 11.162082(33) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1390.707(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	0.98(7)	M3M	4	LA	1	0.9823
La2	0.000000	0.250000	0.250000	3.06*	MMM(100)	24	LA	2	0.9666
W1	0.000000	0.000000	0.000000	0.90(10)	M3M	4	W	3	1.0215
O1	0.11178(21)	0.11178(21)	0.06511(33)	---	M(+-0)	96	O	4	0.2257
O2	0.36597(11)	0.36597(11)	0.36597(11)	1.42*	3M(111)	32	O	5	0.9146
W2	0.000000	0.250000	0.250000	3.06*	MMM(100)	24	W	6	0.0365

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	0.98(7)	0.98	0.98	0.00	0.00	0.00
La2	0.92(10)	4.13(7)	4.13(7)	0.00	0.00	3.22(8)
W1	0.90(10)	0.90	0.90	0.00	0.00	0.00
O1	0.654(137)	0.654(137)	4.004(302)	-0.45(10)	-0.69(11)	-0.69(11)
O2	1.417(29)	1.417(29)	1.417(29)	0.07(5)	0.07(5)	0.07(5)
W2	0.92(10)	4.13(7)	4.13(7)	0.00	0.00	3.22(8)

Table S15 LWO_P-dry(Ar) T = 298 K ILL 'Scherb model'

Lattice constants are

a = 11.171657(31) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1394.289(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	1.17(6)	M3M	4	LA	1	1.0005
La2	0.000000	0.23634(27)	0.23634(27)	1.10*	MM2(011)	48	LA	2	0.4838
W1	0.000000	0.000000	0.000000	0.92(10)	M3M	4	W	3	1.0215
O1	0.11181(22)	0.11181(22)	0.06529(32)	2.36*	M(+-0)	96	O	4	0.2373
O2	0.36608(11)	0.36608(11)	0.36608(11)	1.72*	3M(111)	32	O	5	0.9379
W2	0.000000	0.23634(27)	0.23634(27)	1.10*	MM2(011)	48	W	6	0.0162

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	1.17(6)	1.17	1.17	0.00	0.00	0.00
La2	0.83(9)	1.23(16)	1.23(16)	0.00	0.00	0.46(15)
W1	0.92(10)	0.92	0.92	0.00	0.00	0.00
O1	1.349(153)	1.349(153)	4.370(271)	-0.54(10)	-0.77(12)	-0.77(12)
O2	1.722(28)	1.722(28)	1.722(28)	0.18(4)	0.18(4)	0.18(4)
W2	0.83(9)	1.23(16)	1.23(16)	0.00	0.00	0.46(15)

Table S16 LWO_P-dry(Ar) T = 298 K ILL 'Magraso model'

Lattice constants are

a = 11.171657(32) Å, b = a, c = a

Alpha = 90° Beta = 90° Gamma = 90°

Cell volume = 1394.289(7) Å^3

Name	*X*	*Y*	*Z*	*Ui/Ue*100*	*Site sym*	*Mult*	*Type*	*Seq*	*Fractn*
La1	0.500000	0.500000	0.500000	1.16(6)	M3M	4	LA	1	0.9823
La2	0.000000	0.250000	0.250000	3.13*	MMM(100)	24	LA	2	0.9666
W1	0.000000	0.000000	0.000000	0.88(9)	M3M	4	W	3	1.0008
O1	0.11143(20)	0.11143(20)	0.06544(31)	---	M(+-0)	96	O	4	0.2257
O2	0.36590(10)	0.36590(10)	0.36590(10)	1.64*	3M(111)	32	O	5	0.9146
W2	0.000000	0.250000	0.250000	3.13*	MMM(100)	24	W	6	0.0345

Thermal parameters multiplied by 100.0 are

Name	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
La1	1.16(6)	1.16	1.16	0.00	0.00	0.00
La2	0.87(9)	4.26(6)	4.26(6)	0.00	0.00	3.30(8)
W1	0.88(9)	0.88	0.88	0.00	0.00	0.00
O1	0.871(134)	0.871(134)	4.206(273)	-0.71(9)	-0.59(11)	-0.59(11)
O2	1.636(28)	1.636(28)	1.636(28)	0.22(4)	0.22(4)	0.22(4)
W2	0.87(9)	4.26(6)	4.26(6)	0.00	0.00	3.30(8)

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