Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
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Supplementary information

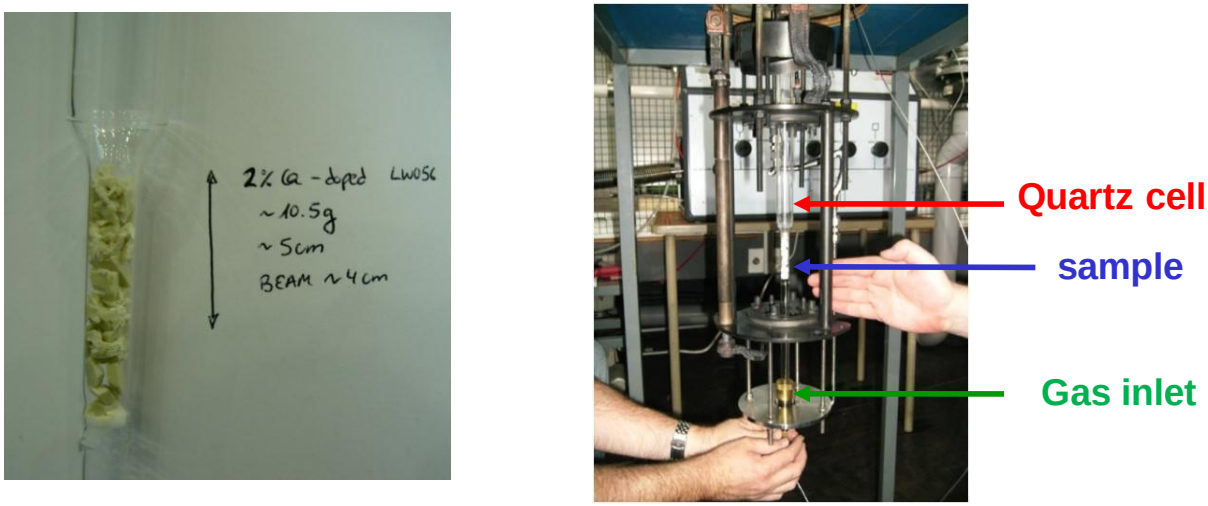

Figure S1. The setup used in POLARIS is special in this experiment, because it can control temperature (T ≈ 300-800 ºC), control pO_2 (in our case, it is Ar) and control pD_2O (by bubbling through a D_2O bath under controlled temperature, which then determines the pD_2O). In order to avoid condensation of water after the D_2O bath (leading to uncontrolled pD_2O), a heating cable surrounded the gas tubes from the D_2O bath until the cell. The image on the left shows the quartz cell with the Ca-doped LWO56.

Table S1. The microanalysis of the sintered bodies was measured by EPMA (electron probe microanalysis) using the same equipment as reference [5]. No significant deviation from the nominal cation ratio is measured:

Sample name *(internal reference)*	**LWO 30.2A**	**LWO 31.3D**	
	La/W	**La/W**	**Ca/La**
ratio average	**5.65**	**5.49**	**0.0200**
$2\sigma_{st}$ (95%)	0.07	0.08	0.0010
ratio nominal	**5.6**	**5.49**	**0.0206**

Table S2. Clarification of the nomenclature and small description of the coordination environment of each cation in the $Fm\bar{3}m$ space group and $F\bar{4}3m$ space group:

atom	Wyckoff position	surrounded by	comments and descriptions
La1	(4a)	O1	relatively symmetric LaO_8 cube
	(4a)	O1a, O1b	
La2	(24d)	O1, O2	distorted LaO_8 cube Links $(La1)O_8$ cubes with $(W1)O_8$ "cubes"
	(24g)	O1a, O1b O2a, O2b	
W1	(4b)	O2	In average (by diffraction techniques) it can be represented as WO_8 "cubes", but the local structure reveals it is octahedral WO_6, disordered in space and time, which average out as "cubes".
	(4b)	O2a, O2b	
W2	(24d)	same as La2	This is the tungsten that dissolves in La2 sites (not in La1 sites), and can be written as W_{La} or more specifically, W_{La2} or even $W2_{La2}$, to highlight where it sits.
	(24g)		

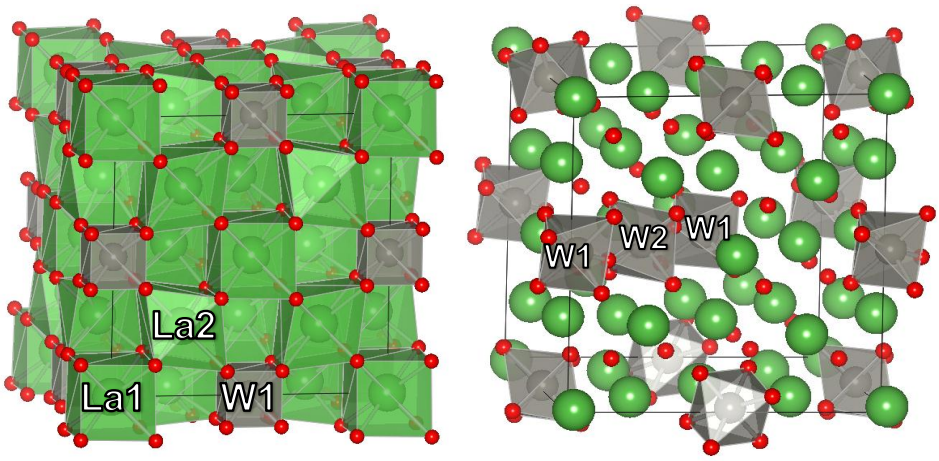

Figure S2. (a) High-symmetry averaged structural model where the different polyhedra are drawn and the cation positions are highlighted (W2 can not be detected in the average diffraction techniques, because it can sit in 24 different positions, and can not be located with confidence). **(b)** A lower symmetry structural model calculated from DFT where the local structure of one possible configuration is drawn. The tungsten polyhedra are drawn, and the different tungsten positions (W1 and W2) are represented. Lanthanum polyhedra have not been drawn, for clarity.

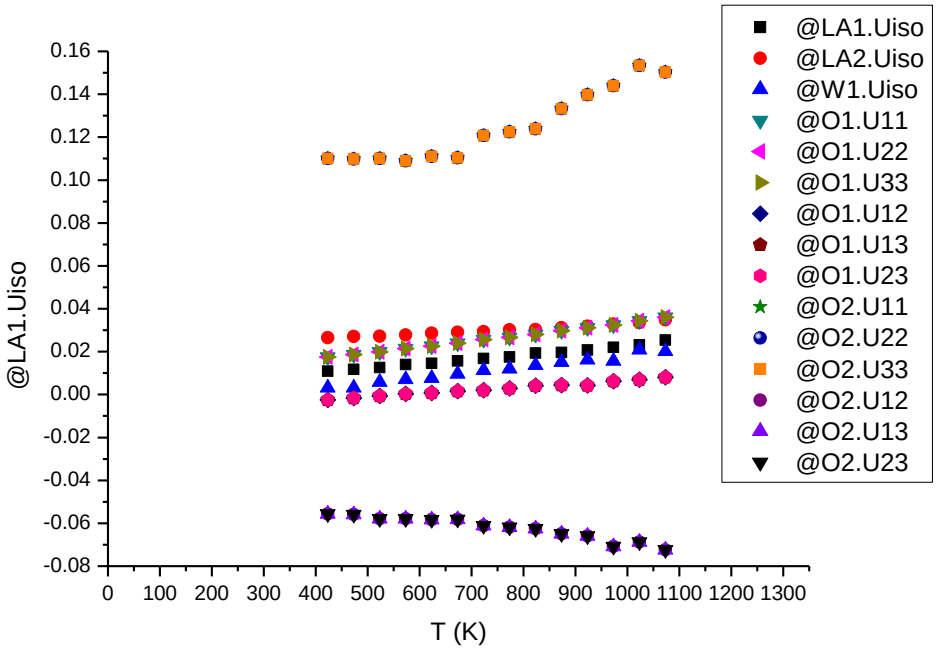

Figure S3. Evolution of displacement parameters with temperature in dry Ar using the "simple model" (O2 in *32f* position).

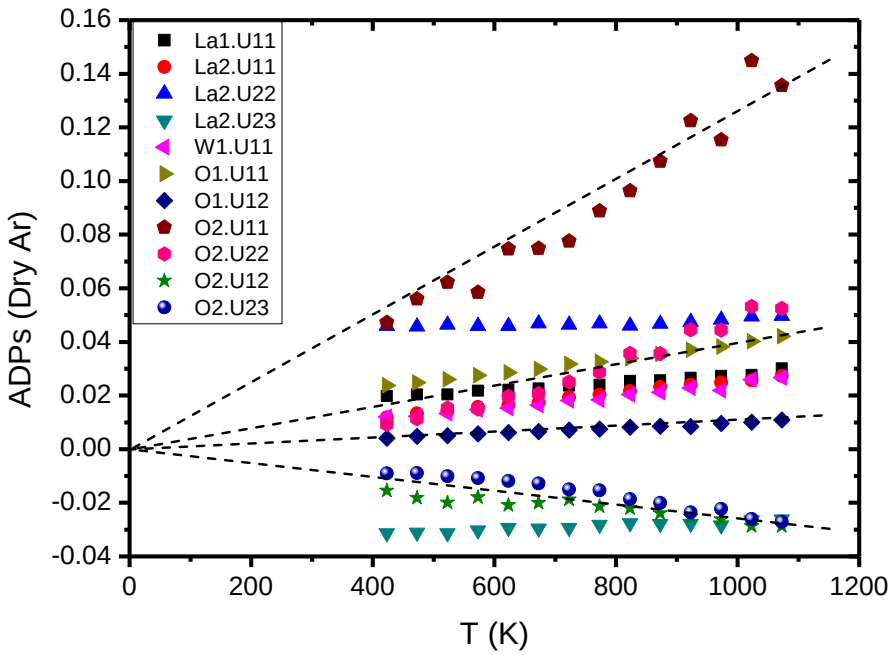

Figure S4. Evolution of Uij anisotropic displacement parameters with temperature in dry Ar using the "split model" with O2 in *96k* position. Dashed lines are guide to the eye.

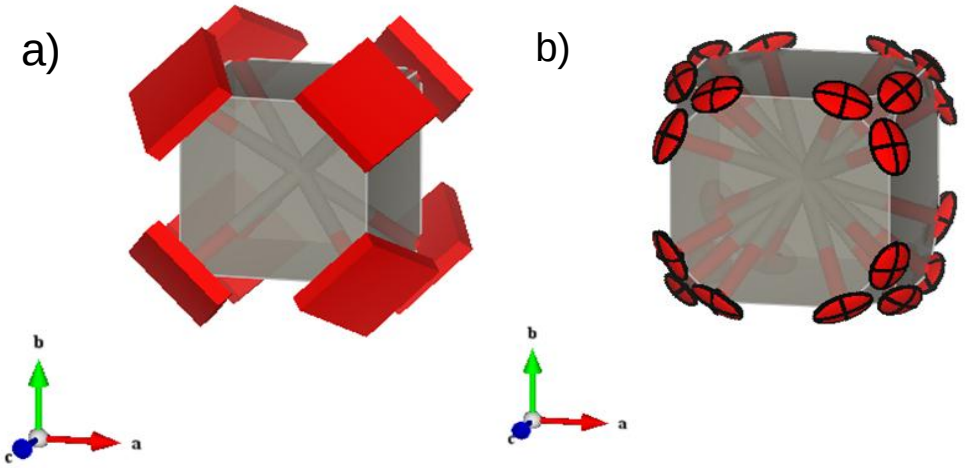

Figure S5. Representation of the refined ADPs of oxygens bonded to tungsten in **a)** the "simple model" (O in *32f*) and **b)** "split model" (O in *96k*) at room temperature. Negative mean-square displacements for oxygens in the simple (not split) model are represented by cuboids.

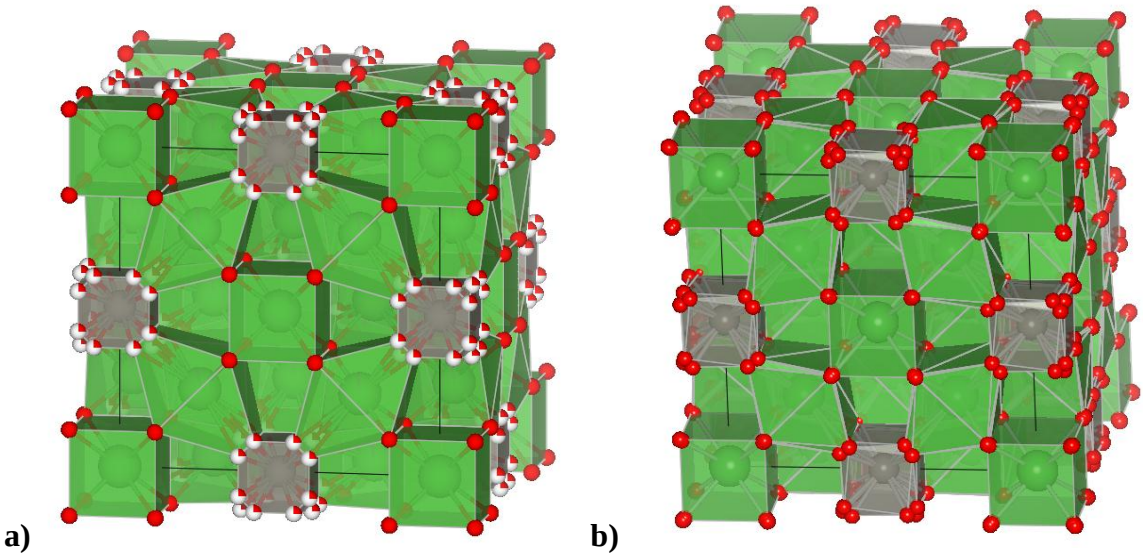

Figure S6. (a) This is the crystal structural model of $La_{28-x}W_{4+x}O_{54+3x/2}$ used in the final Rietveld refinements. This is comparable to the model obtained independently from the averaged DFT model **(b)** with relaxed oxygen positions, which generates 3 equivalent O positions around each cube corner.

Table S3. La–O distances in dry and wet argon atmosphere at selected temperatures.

Dry Ar

T (°C)	La1—O1(×8)	La2—O1(×4)	La2—O2(×4)	La2—O2(×8)
150	2.5926 (16)	2.3696 (4)	2.313 (3)	2.890 (3)
450	2.6059 (17)	2.3754 (4)	2.329 (3)	2.907 (3)
750	2.6182 (19)	2.3832 (5)	2.369 (6)	2.917 (4)

Wet Ar

T (°C)	La1—O1(×8)	La2—O1(×4)	La2—O2(×4)	La2—O2(×8)
150	2.5939 (17)	2.3723 (4)	2.310 (3)	2.895 (3)
450	2.6060 (18)	2.3788 (5)	2.325 (3)	2.912 (3)
750	2.619 (2)	2.3848 (5)	2.360 (5)	2.929 (4)

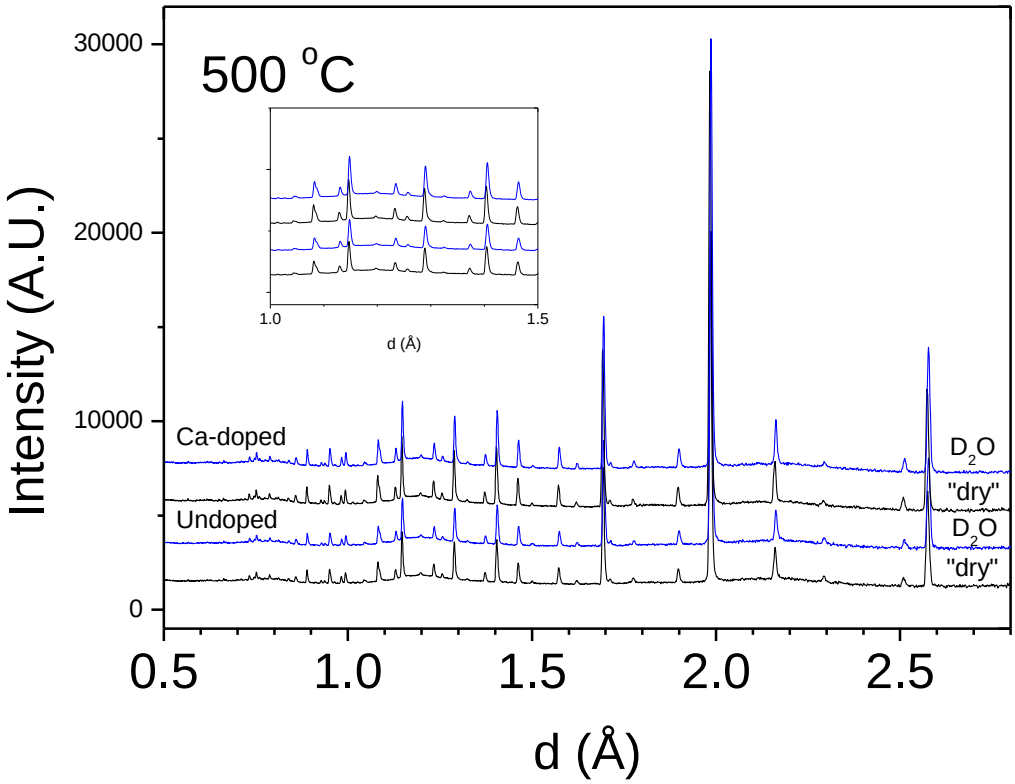

Figure S7. Representative ND diffractograms recorded under wet (bubbling through D_2O) and "dry" (no bubbling through D_2O) at 500 °C for both Ca-doped and undoped LWO56. It shows that there is essentially no difference between the different conditions and doping levels.

Table S4. Atomic coordinates and displacement parameters at **150°C, dry Ar**. Lattice parameter: a = 11.183(1) Å

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	*x*	*y*	*z*	*U*eq	Occ.(<1)
La1	0.0	0.0	0.0	0.02016	
La2	0.0	0.25	0.25	0.0348	0.95
W1	0.5	0.5	0.5	0.01206	
O1	0.13385(8)	0.13385(8)	0.13385(8)	0.02372	
O2	0.4374(3)	0.38938(15)	0.38938(15)	0.02259	0.193(5)
W2	0.0	0.25	0.25	0.15794	0.05

Atomic displacement parameters (Å^2)

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
La1	0.0202(6)	0.0202(6)	0.0202(6)	0.0	0.0	0.0
La2	0.0124(10)	0.0460(7)	0.0460(7)	0.0	0.0	−0.0316(8)
W1	0.0121(8)	0.0121(8)	0.0121(8)	0.0	0.0	0.0
O1	0.0237(4)	0.0237(4)	0.0237(4)	0.0042(4)	0.0042(4)	0.0042(4)
O2	0.049(3)	0.0094(12)	0.0094(12)	−0.0158(10)	−0.0158(10)	−0.0087(9)
W2	−0.0436(18)	0.26(8)	0.26(8)	0.0	0.0	−0.25(8)

χ^2 = 5.108, *R*p = 0.022, *R*wp = 0.014, *R*exp = 0.006 for 56 parameters

Table S5: Atomic coordinates and displacement parameters at **450 °C, dry Ar**. Lattice parameter: a = 11.217(1) Å

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	*x*	*y*	*z*	*U*eq	Occ.(<1)
La1	0.0	0.0	0.0	0.02372	
La2	0.0	0.25	0.25	0.03739	0.95
W1	0.5	0.5	0.5	0.01814	
O1	0.13412(9)	0.13412(9)	0.13412(9)	0.03176	
O2	0.4383(4)	0.39018(17)	0.39018(17)	0.04255	0.213(5)
W2	0.0	0.25	0.25	0.06371	0.05

Atomic displacement parameters (Å^2)

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
La1	0.0237(6)	0.0237(6)	0.0237(6)	0.0	0.0	0.0
La2	0.0194(10)	0.0464(7)	0.0464(7)	0.0	0.0	−0.0294(9)
W1	0.0181(9)	0.0181(9)	0.0181(9)	0.0	0.0	0.0
O1	0.03176(28)	0.03176(28)	0.03176(28)	0.0071(4)	0.0071(4)	0.0071(4)
O2	0.078(3)	0.0250(16)	0.0250(16)	−0.0188(13)	−0.0188(13)	−0.0150(11)
W2	−0.0419(16)	0.12(4)	0.12(4)	0.0	0.0	−0.10(4)

χ^2 = 1.716, *R*p = 0.022, *R*wp = 0.011, *R*exp = 0.008 for 56 parameters

Table S6. Atomic coordinates and displacement parameters at **750°C, dry Ar**. Lattice parameter: a = 11.258(1) Å

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	*x*	*y*	*z*	*U*eq	Occ.(<1)
La1	0.0	0.0	0.0	0.0277	
La2	0.0	0.25	0.25	0.04148	0.95
W1	0.5	0.5	0.5	0.02594	
O1	0.13427(10)	0.13427(10)	0.13427(10)	0.04014	
O2	0.4378(6)	0.3922(3)	0.3922(3)	0.08367	0.250(6)
W2	0.0	0.25	0.25	0.05837	0.05

Atomic displacement parameters (Å^2)

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
La1	0.0277(6)	0.0277(6)	0.0277(6)	0.0	0.0	0.0
La2	0.0256(11)	0.0494(9)	0.0494(9)	0.0	0.0	−0.0266(10)
W1	0.0259(11)	0.0259(11)	0.0259(11)	0.0	0.0	0.0
O1	0.04014(31)	0.04014(31)	0.04014(31)	0.0100(5)	0.0100(5)	0.0100(5)
O2	0.145(8)	0.053(3)	0.053(3)	−0.029(3)	−0.029(3)	−0.0261(15)
W2	−0.037(3)	0.11(4)	0.11(4)	0.0	0.0	−0.10(4)

χ^2 = 1.103, *R*p = 0.018, *R*wp = 0.009, *R*exp = 0.008 for 56 parameters

Table S7. Atomic coordinates and displacement parameters at **150°C, wet Ar**. Lattice parameter: a = 11.194(1) Å

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	*x*	*y*	*z*	*U*eq	Occ.(<1)
La1	0.0	0.0	0.0	0.01993	
La2	0.0	0.25	0.25	0.03633	0.95
W1	0.5	0.5	0.5	0.01134	
O1	0.13378(9)	0.13378(9)	0.13378(9)	0.02346	
O2	0.4377(3)	0.38912(16)	0.38912(16)	0.02247	0.188(5)
W2	0.0	0.25	0.25	0.20251	0.05

Atomic displacement parameters (Å^2)

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
La1	0.0199(7)	0.0199(7)	0.0199(7)	0.0	0.0	0.0
La2	0.0124(11)	0.0483(8)	0.0483(8)	0.0	0.0	−0.0340(9)
W1	0.0113(8)	0.0113(8)	0.0113(8)	0.0	0.0	0.0
O1	0.0235(4)	0.0235(4)	0.0235(4)	0.0047(4)	0.0047(4)	0.0047(4)
O2	0.050(3)	0.0089(13)	0.0089(13)	−0.0178(11)	−0.0178(11)	−0.0101(9)
W2	−0.0449(19)	0.33(10)	0.33(10)	0.0	0.0	−0.31(10)

χ^2 = 3.610, *R*p = 0.023, *R*wp = 0.014, *R*exp = 0.008 for 56 parameters

Table S8. Atomic coordinates and displacement parameters at **450°C, wet Ar**. Lattice parameter: a = 11.230(1) Å

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	*x*	*y*	*z*	*U*eq	Occ.(<1)
La1	0.0	0.0	0.0	0.0248	
La2	0.0	0.25	0.25	0.04099	0.95
W1	0.5	0.5	0.5	0.01765	
O1	0.13398(9)	0.13398(9)	0.13398(9)	0.03218	
O2	0.4386(4)	0.38983(17)	0.38983(17)	0.04054	0.205(5)
W2	0.0	0.25	0.25	0.04761	0.05

Atomic displacement parameters (Å^2)

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
La1	0.0248(6)	0.0248(6)	0.0248(6)	0.0	0.0	0.0
La2	0.0217(11)	0.0506(9)	0.0506(9)	0.0	0.0	−0.0328(11)
W1	0.0176(9)	0.0176(9)	0.0176(9)	0.0	0.0	0.0
O1	0.03218(30)	0.03218(30)	0.03218(30)	0.0077(4)	0.0077(4)	0.0077(4)
O2	0.077(4)	0.0222(17)	0.0222(17)	−0.0198(13)	−0.0198(13)	−0.0157(11)
W2	−0.039(2)	0.09(4)	0.09(4)	0.0	0.0	−0.08(4)

χ^2 = 1.716, *R*p = 0.022, *R*wp = 0.011, *R*exp = 0.008 for 56 parameters

Table S9. Atomic coordinates and displacement parameters at **750°C, wet Ar**. Lattice parameter: a = 11.230(1) Å

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	*x*	*y*	*z*	*U*eq	Occ.(<1)
La1	0.0	0.0	0.0	0.02873	
La2	0.0	0.25	0.25	0.04222	0.95
W1	0.5	0.5	0.5	0.02641	
O1	0.13423(10)	0.13423(10)	0.13423(10)	0.03985	
O2	0.4392(5)	0.3918(3)	0.3918(3)	0.08536	0.270(6)
W2	0.0	0.25	0.25	0.04907	0.05

Atomic displacement parameters (Å^2)

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
La1	0.0287(7)	0.0287(7)	0.0287(7)	0.0	0.0	0.0
La2	0.0270(12)	0.0498(10)	0.0498(10)	0.0	0.0	−0.0274(10)
W1	0.0264(12)	0.0264(12)	0.0264(12)	0.0	0.0	0.0
O1	0.03985(33)	0.03985(33)	0.03985(33)	0.0093(5)	0.0093(5)	0.0093(5)
O2	0.150(8)	0.053(3)	0.053(3)	−0.024(3)	−0.024(3)	−0.0286(15)
W2	−0.037(3)	0.09(4)	0.09(4)	0.0	0.0	−0.09(4)

χ^2 = 1.188, *R*p = 0.019, *R*wp = 0.009, *R*exp = 0.008 for 56 parameters