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Supporting information for article:

Crystal structure of Mo-substituted lanthanum tungstate $La_{5.4}W_{1-y}Mo_yO_{12-\delta}$ ($0 \leq y \leq 0.2$) studied by X-ray and neutron diffraction

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S1. Average X-ray scattering power

Table S1 Refined site occupancy factors, SOF, of the cation sites 4a and 48h of the non-substituted LWO_**P** and the single-phase LW(Mo)O-D_2O(SA) specimens obtained through the average X-ray scattering power approach. Also, the corresponding La/(W+Mo) ratio determined by EPMA, the amount of anti-site disorder, W_2 + Mo_2 on La_2 (at. % and e^-/atom), and the contributions of W_2 and Mo_2 on La_2 (e^-/atom) according to EPMA, are depicted.

Samples in D_2O(SA) state, temperature	SOF_{4a}^{W}	$SOF_{48h}^{La_2}$	La/(W+Mo) EPMA	W_2 + Mo_2 on La_2 (EPMA) at. %	W_2 + Mo_2 on La_2 (EPMA) e^-/atom	W_2, Mo_2 on La_2 (EPMA) e^-/atom
LWO_P (295 K)	1.044(2)	0.5076(6)	5.56(3)	3.66(7)	2.46	2.46, 0
Mo1 (100 K)	1.027(2)	0.5053(7)	5.62(3)	3.43(7)	2.293	2.29, 0.003
Mo5 (100 K)	1.003(2)	0.5037(6)	5.64(3)	3.42(8)	2.28	2.23, 0.05
Mo20(1) (100 K)	0.927(4)	0.5030(13)	5.64(3)	3.40(9)	2.06	1.85, 0.21
Mo20(2) (295 K)	0.923(2)	0.5028(6)	5.64(5)	3.42(17)	2.06	1.85, 0.21

The occupancy of the 48*h* position is delicate in a sense that it depends on the La/(W+Mo) ratio and is also correlated to the other occupancies, especially to SOF_{4b}^{La1}. To reduce this correlation, La_1, O_1 and O_2 occupancies for all the specimens were fixed to SOF_{4b}^{La1} = 1, SOF_{96k}^{O1} = 0.25 and SOF_{32f}^{O2} = 0.95, respectively. The minor differences in the oxygen content for all specimens have been assumed invisible with X-rays such as the vacancy concentration difference on the O_2 position. The amount of anti-site disorder calculated (W_2 + Mo_2 on La_2, Table 4) shows that for each LW(Mo)O specimen about 3.5 at. % of the 48*h* site is available to locate W (W_2) and/or Mo (Mo_2), and the remaining 96.5 at. % locates La (La_2). If W and Mo statistically occupy the available 3.5 at. % of anti-site disorder, a difference of only about 0.4 e^-/atom between LWO_**P** and the Mo20 specimens is obtained (see last two columns in Table 4). Moreover, the reported values of electron per atom in the last column of Table 4 have to be divided by a factor of two to account for the 48*h* site half-occupancy. Such small contributions to the scattering by a mixture of W (67.3 e^-) and Mo (31.4 e^-) are expected to be difficult to separate from the main scatterer of the 48*h* site, La_2 (96.5 at. %, 53.5 e^-, see Table 1) even with synchrotron X-ray diffraction.

S2. Temperature dependence of LW(Mo)O with neutron diffraction

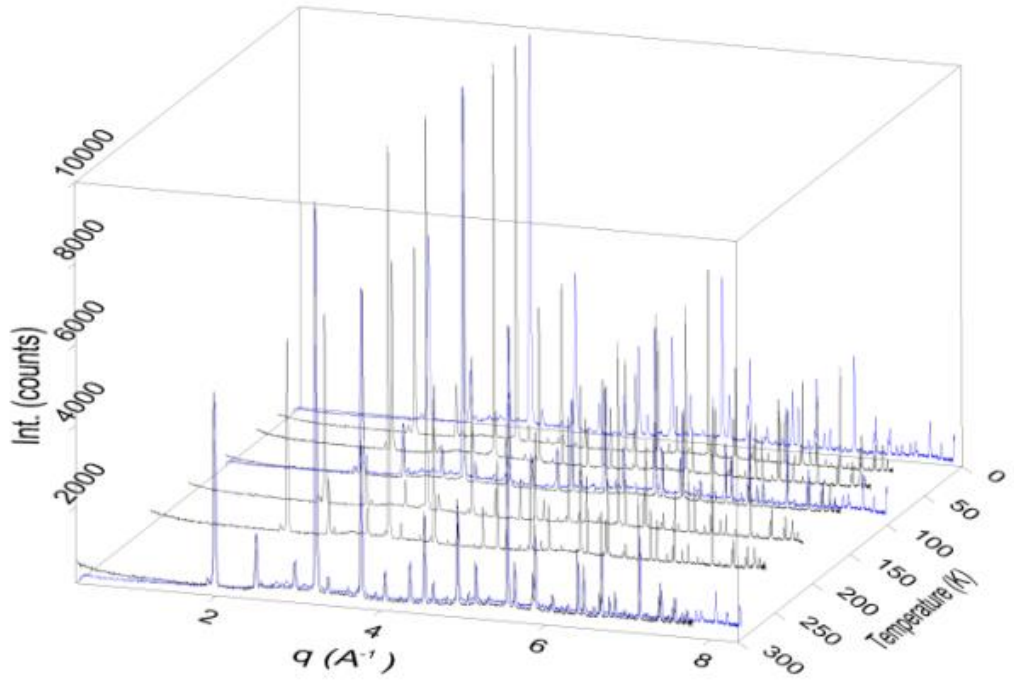

Figure S1 Neutron diffraction intensity as a function of q of sample Mo20(2)-dry(Ar) for various temperatures between T = 10 K and T = 298 K. The black and blue lines represent the diffraction patterns taken at D2B (T = 30 K, 60 K, 100 K, 150 K, 200 K, 298 K) and at HRPT (T = 10 K, 100 K, 295 K), respectively. The patterns are normalized to 10000 counts. The representation in q is required due to the different wavelengths used at D2B (λ^{D2B}=1.594 Å, black patterns) and at HRPT (λ^{HRPT}=1.494 Å, blue patterns).