Supplementary Information

Thermal behaviors during lithium diffusion in $Li_{0.4}WO_3$ bronze studied by elastic and quasi-elastic neutron scattering

M. Mangir Murshed[1,4]*, Michael Fischer[2,4], Michael M. Koza[3], Th. M. Gesing[1,4]

[1]Univeristy of Bremen, Institute of Inorganic Chemistry and Crystallography, Leobener Straße 7, D-28359 Bremen, Germany

[2]University of Bremen, Crystallography, Faculty of Geosciences, Klagenfurter Straße 2-4, D-28359 Bremen, Germany

[3]Institut Laue Langevin, 38042 GRENOBLE Cedex 9, France

[4]Univeristy of Bremen, MAPEX Center for Materials and Processes, Bibliothekstraße 1, D-28359 Bremen, Germany

∗Corresponding author Tel.: +49 (0)421 218 63144, E-mail: murshed@uni-bremen.de

ORCID:

MMM: 0000-0002-9063-372X

MF: 0000-0001-5133-1537

MMK: 0000-0002-5133-8584

TMG: 0000-0002-4119-2219

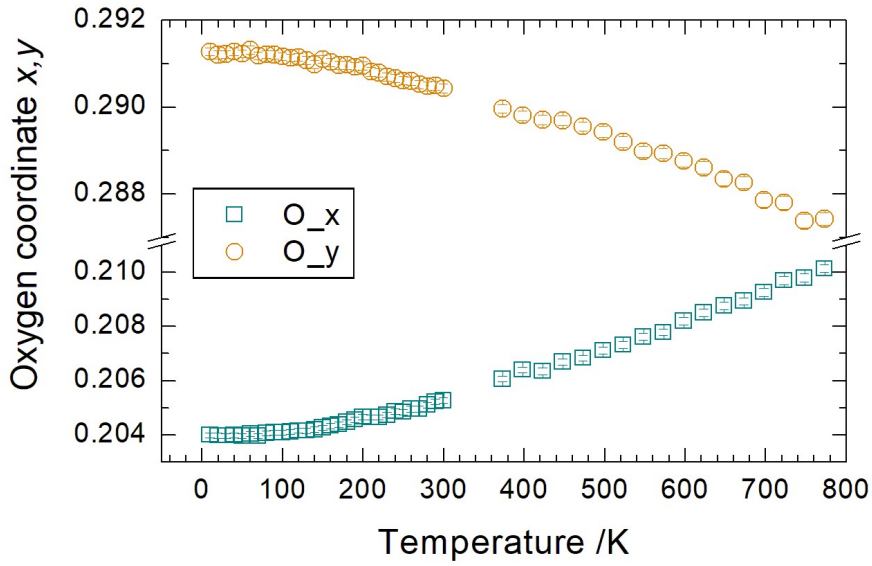

Figure S1: Changes of *x*- and *y*-coordinate of oxygen in $Li_{0.4}WO_3$ bronze **with respect** to temperature.

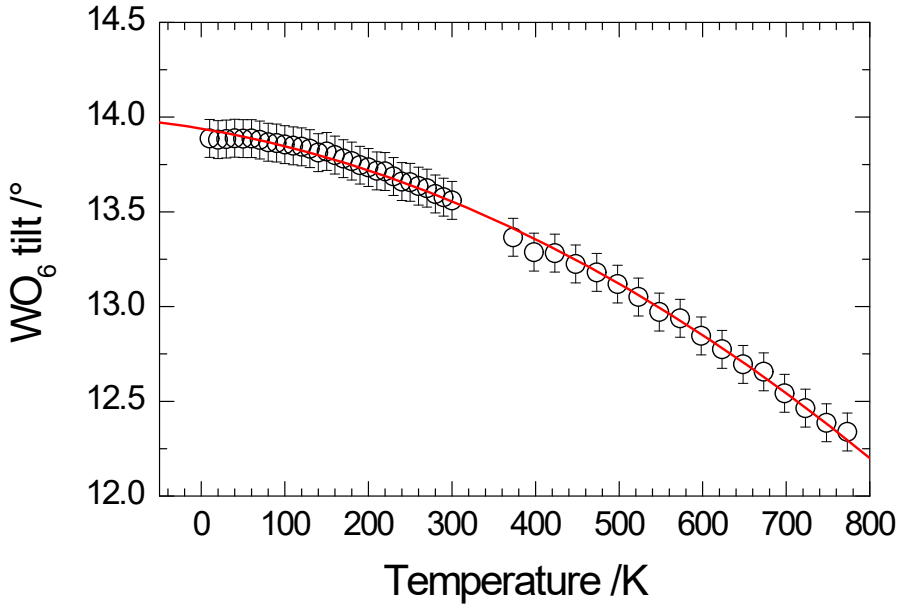

Figure S2: Temperature-dependent tilting of the WO_6 octahedra in $Li_{0.4}WO_3$ bronze.

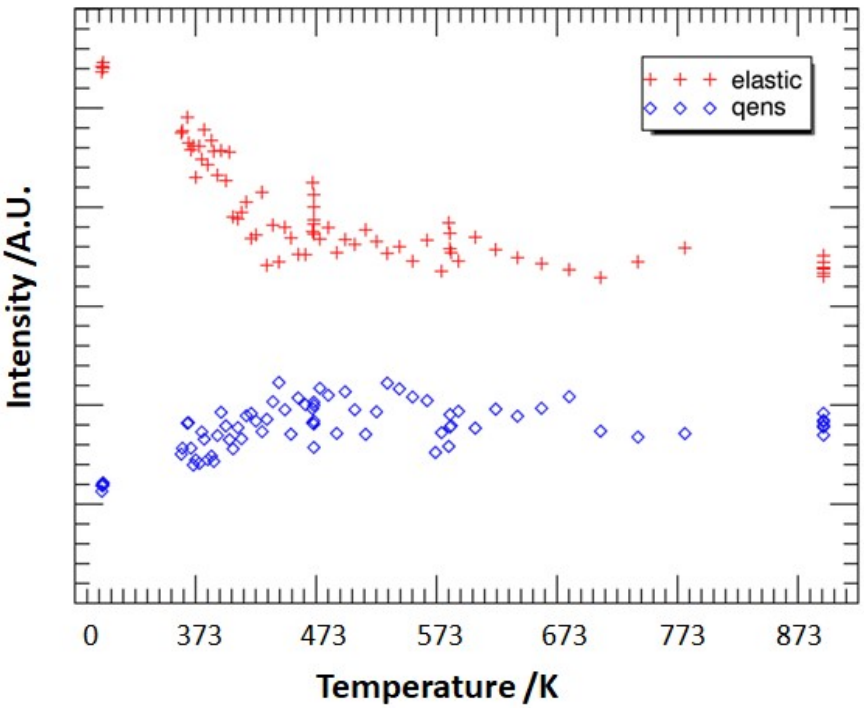

Figure S3: Temperature-dependent neutron elastic and inelastic integrated intensity over low *Q*-range. The rapid drop of the elastic intensity above 295 K is due to the onset of lithium diffusion, leading to redistribution of the scattering intensity from the elastic into the quasielastic scattering.

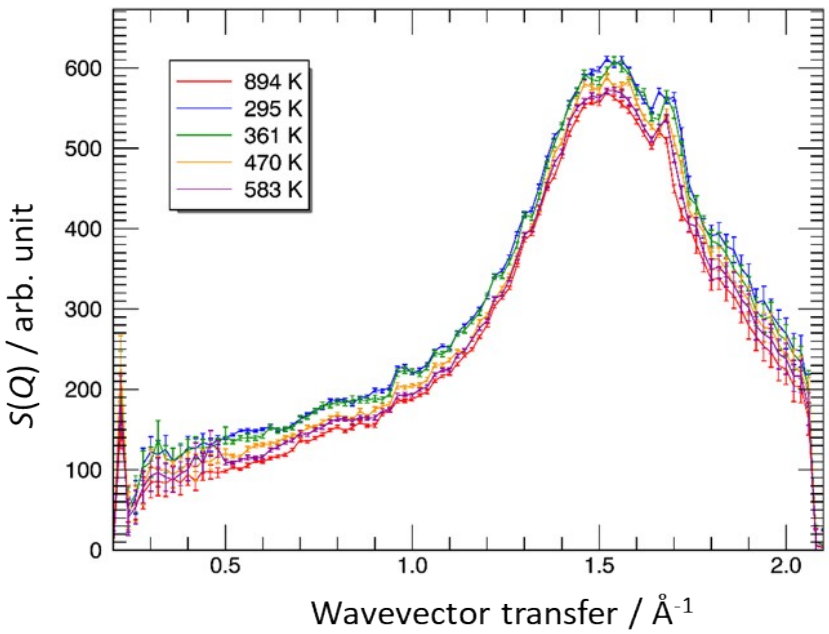

Figure S4: $S(Q)$ summed over all accessible energy of $S(Q,E)$, showing temperature-dependent Bragg peak intensity.

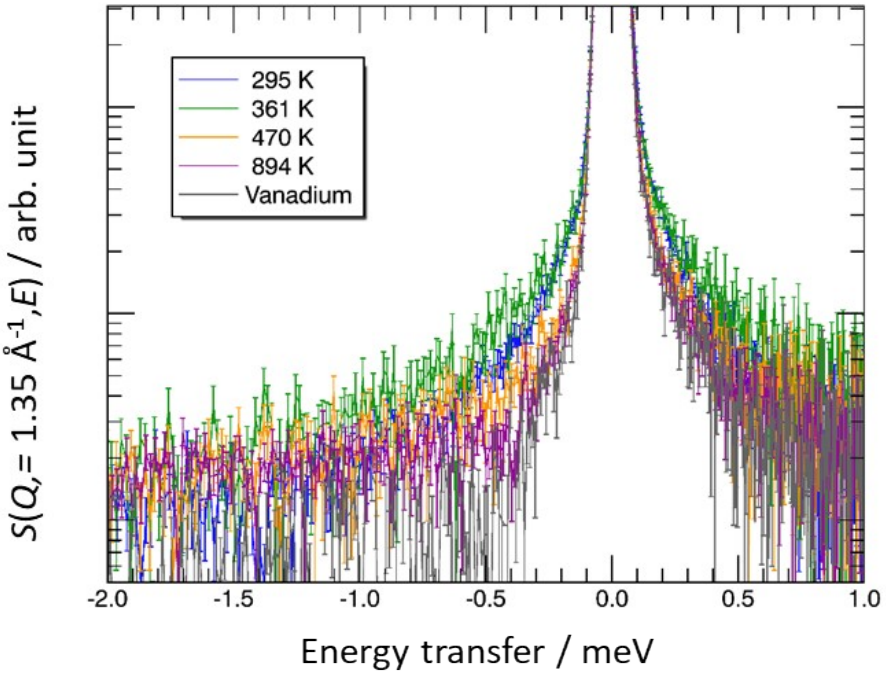

Figure S5: Temperature-dependent $S(Q,E)$ at 1.35 A^{-1}, showing Lorentzian broadening.

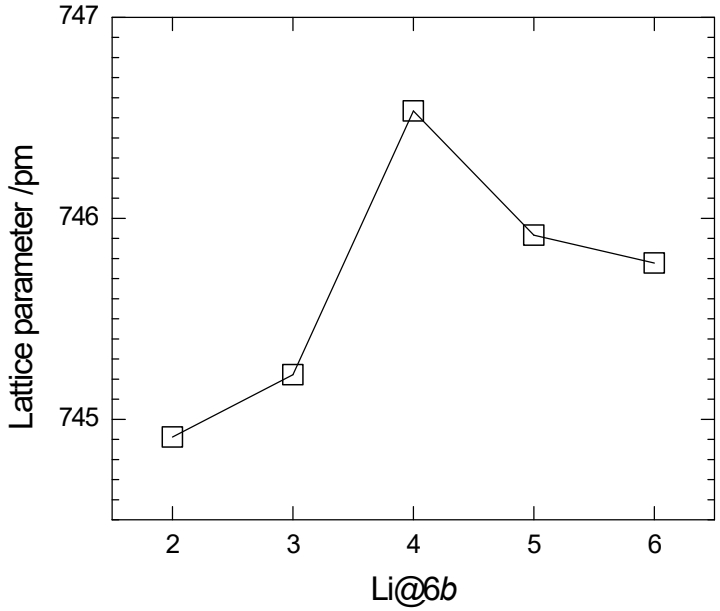

Figure S6: DFT calculated lattice parameter as function of lithium content only at the 6*b* site of $Li_xO_8O_{24}$.

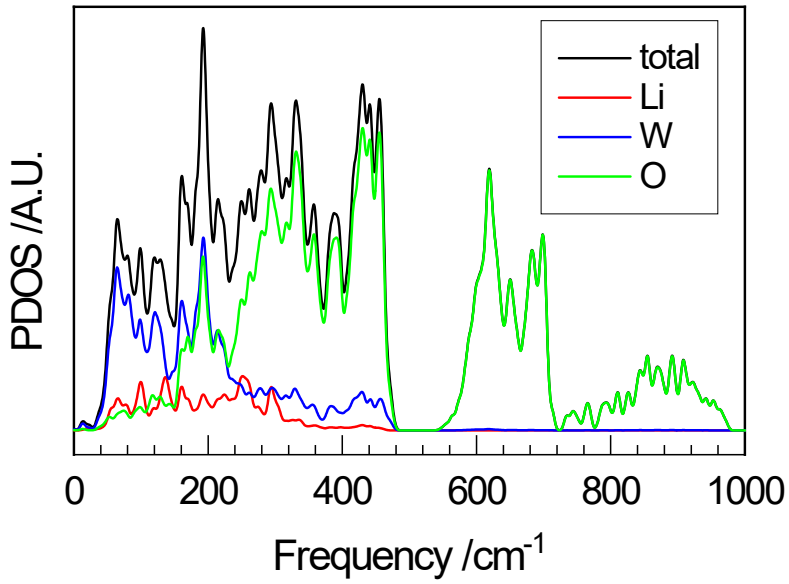

Figure S7: DFT calculated phonon density of states (PDOS) of $Li_3W_8O_{24}$, where all there lithium atoms are located only at 6*b* of the space group *Pm*-3.

Table S1: DFT calculated total energy (E) along with the lattice parameter for the distribution of lithium at two crystallographic sites for different unit cell compositions of $Li_xW_8O_{24}$. ΔE refers to energy difference with respect to the lowest-energy model for a given composition.

Composition	Li @6b	Li@2a	Symmetry	E/ eV	ΔE/ kJ mol^{-1}	*a* / pm
$Li_2W_8O_{24}$	2	0	*Immm*	**-84997.36**	5.54	745.82
	2	0	*Pmmm*	**-84997.42**	0.00	744.91
	2	0	*Pmmm*	**-84997.41**	0.93	744.86
	1	1	*Pmmm*	**-84997.38**	3.35	749.53
	1	1	*Pmmm*	**-84997.40**	2.11	749.10
	0	2	*Im*-3	**-84996.74**	65.64	763.56
$Li_3W_8O_{24}$	3	0	*Pm*-3	**-85201.15**	3.30	745.11
	3	0	*Pmmm*	**-85201.11**	7.00	745.42
	3	0	*Pmmm*	**-85201.18**	0.00	745.22
	3	0	*Pmmm*	**-85201.12**	6.25	745.46
	2	1	*Pmmm*	**-85200.62**	54.31	746.68
	2	1	*Pmmm*	**-85200.73**	43.62	746.46
	2	1	*Pmmm*	**-85201.11**	7.42	746.86
	2	1	*Pmmm*	**-85200.69**	48.07	746.55
	2	1	*Pmmm*	**-85200.68**	48.14	747.46
	1	2	*Pmmm*	**-85201.04**	14.08	751.98

$Li_4W_8O_{24}$	4	0	*Immm*	**-85404.03**	7.17	746.75
	4	0	*Pmmm*	**-85404.10**	0.00	746.53
	4	0	*Pmmm*	**-85404.08**	1.83	746.01
	3	1	*Pm*-3	**-85403.52**	56.07	747.20
	3	1	*Pm*-3	**-85403.70**	39.28	747.29
	3	1	*Pmmm*	**-85403.58**	50.91	747.43
	3	1	*Pmmm*	**-85403.61**	47.09	747.64
	3	1	*Pmmm*	**-85403.54**	54.10	747.45
	3	1	*Pmmm*	**-85403.61**	47.55	747.46
	3	1	*Pmmm*	**-85403.61**	47.85	747.15
	3	1	*Pmmm*	**-85403.66**	42.42	747.21
	2	2	*Immm*	**-85404.01**	9.35	748.66
	2	2	*Pmmm*	**-85404.03**	6.68	749.56
	2	2	*Pmmm*	**-85404.07**	2.72	748.64
$Li_5W_8O_{24}$	5	0	*Pmmm*	**-85606.94**	0.00	745.92
	3	2	*Pm*-3	**-85605.98**	92.30	749.32
	3	2	*Pmmm*	**-85606.89**	5.12	749.55
	3	2	*Pmmm*	**-85605.94**	96.37	749.53
	3	2	*Pmmm*	**-85605.99**	91.22	749.22
$Li_6W_8O_{24}$	6	0	*Im-3*	**-85809.72**	0.00	745.78
	4	2	*Immm*	**-85809.64**	7.52	750.67
	4	2	*Pmmm*	**-85808.73**	95.91	749.43
	4	2	*Pmmm*	**-85808.74**	94.77	749.63
$Li_7W_8O_{24}$	6	1	*Pm*-3	**-86011.90**	0.00	747.63
	5	2	*Pmmm*	**-86011.40**	48.04	749.68
$Li_8W_8O_{24}$	6	2	*Im*-3	**-86214.08**	0	749.39