Supplementary Information

Li^+ conductivity of tungsten bronze $Li_xSr_{1-0.5x}Ta_2O_6$ studied by neutron diffraction analysis

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Neutron Rietveld refinement

The crystal structure of β-$SrTa_2O_6$ includes 16 atomic sites in an orthorhombic unit cell, which can be fully described by using 3 lattice parameters, 37 positional parameters, 16 temperature factors, and 3 occupancy parameters. Several of the above parameters can be reasonably constrained, and a previous study could refine the structure of β-$SrTa_2O_6$ using the powder diffraction patterns [1]. However, the solid solution $Li_xSr_{1-0.5x}Ta_2O_6$ (x = 0.08, 0.17. and 0.25) presents even more challenging situations: extra degrees of freedom arise because Sr, Li, and vacancy can be distributed over three different sites; the random distribution of Sr/Li affects the crystallinity and hence the overall quality of the diffraction pattern.

In this context, the neutron Rietveld refinement of $Li_xSr_{1-0.5x}Ta_2O_6$ was conducted in a semi-constrained manner, where the constraints were imposed on the occupancy factors (occ) and isotropic temperature factors (U_{iso}), as follows.

First, atomic sites for oxygen were grouped into four types taking into account the coordination environment. The sites in each group were constrained to have the same U_{iso}, and all the occupancies were fixed to 1. Second, the three Ta sites were constrained to have the same U_{iso}, and again, their occupancies were fixed to 1. Finally, the three Sr/Li sites were distinguished by the coordination environment: Sr1 corresponds to the 12-coordinate A1 site; Sr2 and Sr3 correspond to the 15-coordinate A2 site. Therefore Sr2 and Sr3 sites were set to have the same U_{iso} and occ. In addition, the occupancies of Sr1, Sr2, and Sr3 were constrained to add up to the chemical composition of each phase.

Following the common practice, the refinement was gradually extended by sequentially including the variables: scale factor, background, lattice constants, zero-point error, atomic positions, profile parameters, U_{iso}, and occ. In general, the refinements proceeded without a serious failure. However, in the later stage of the refinement, the U_{iso} values of all the cation sites (Sr1, Sr2/3, Ta1/2/3) converged to negative values. Such a tendency was observed similarly from all the three phases (x = 0.08, 0.17, and 0.25). As the U_{iso} and occ parameters are heavily correlated with each other, we could not pass over the above results. After examining the (negative) refined U_{iso} values of Sr and Ta sites in the three different $Li_xSr_{1-0.5x}Ta_2O_6$ phases, we opted to fix the U_{iso} values uniformly: 0.001 Å^2 for Sr1, 0.015 Å^2 for Sr2/3, 0.0015 Å^2 for Ta1/2/3. By using the above fixed U_{iso} values, the occ parameters for Sr1 slightly increased and those for Sr2/3 sites slightly decreased. However, it can be mentioned that the fixation of the above U_{iso} values did not alter the main conclusion of the Rietveld refinement, that is, the Sr1 site is mainly involved in the Li/Sr exchange.

A combined Rietveld refinement of synchrotron X-ray and neutron diffraction patterns (collected from the same batch of the sample) was also examined, but not successful. We suspect that there were incompatibilities between those diffraction experiments but could not identify the cause clearly.

[1] E. Lee, C.H. Park, D.P. Shoemaker, M. Avdeev, Y.I. Kim, Crystal structure analysis of tungsten bronzes β-$SrTa_2O_6$ and β′-$SrTa_2O_6$ by synchrotron X-ray and neutron powder diffraction, J. Solid State Chem. 191 (2012) 232–238.

Table S1. Summary of neutron Rietveld refinement of $Li_xSr_{1-0.5x}Ta_2O_6$ (x = 0.08, 0.17, 0.25).

	$Li_{0.08}Sr_{0.96}Ta_2O_6$	$Li_{0.17}Sr_{0.92}Ta_2O_6$	$Li_{0.25}Sr_{0.88}Ta_2O_6$
λ (Å)	2.4395	2.4395	2.4395
2θ range	10–163.95	10–163.95	10–163.95
N_{data}	3079	3079	3079
N_{obs}	379	380	379
R_{wp} (%)	5.94	11.26	11.37
R_p (%)	4.72	8.57	8.93
χ^2	1.25	3.98	3.82
space group	*Pnam*	*Pnam*	*Pnam*
a (Å)	12.3604(3)	12.3752(6)	12.3733(6)
b (Å)	12.4137(4)	12.3694(8)	12.3648(9)
c (Å)	7.7207(2)	7.7225(2)	7.7227(3)
V (Å^3)	1184.65(5)	1182.11(8)	1181.52(9)
Z	10	10	10

Table S2. Atomic parameters of $Li_{0.17}Sr_{0.92}Ta_2O_6$ obtained from neutron Rietveld refinement.

atom		*x*	*y*	*z*	U_{iso} (Å^2)	occ
Sr1	4*c*	0.002(3)	0.006(4)	0.25	0.001	0.50(1)
Sr2	4*c*	0.328(2)	0.158(2)	0.25	0.015	0.843(7)
Sr3	4*c*	0.316(2)	0.160(2)	0.75	0.015	0.843(7)
Ta1	4*b*	0	0.5	0.5	0.0015	
Ta2	8*d*	0.0714(9)	0.2129(9)	0.501(2)	0.0015	
Ta3	8*d*	0.2879(8)	0.4273(9)	0.502(2)	0.0015	
O1	4*c*	0.975(2)	0.486(2)	0.25	0.032(2)	
O2	4*c*	0.066(2)	0.206(3)	0.25	0.032(2)	
O3	4*c*	0.059(2)	0.210(3)	0.75	0.032(2)	
O4	4*c*	0.322(2)	0.390(2)	0.25	0.032(2)	
O5	4*c*	0.287(2)	0.397(2)	0.75	0.032(2)	
O6	8*d*	0.2230(9)	0.273(1)	0.484(2)	0.011(3)	
O7	8*d*	–0.004(1)	0.350(2)	0.534(2)	0.031(2)	
O8	8*d*	0.339(1)	0.005(2)	0.532(2)	0.031(2)	
O9	8*d*	0.134(1)	0.064(2)	0.475(2)	0.047(3)	
O10	8*d*	0.434(1)	0.359(2)	0.492(3)	0.047(3)	

Table S3. Atomic parameters of $Li_{0.25}Sr_{0.88}Ta_2O_6$ obtained from neutron Rietveld refinement.

atom		*x*	*y*	*z*	U_{iso} (Å^2)	occ
Sr1	4*c*	0.002(3)	0.004(5)	0.25	0.001	0.43(1)
Sr2	4*c*	0.331(2)	0.164(3)	0.25	0.015	0.799(7)
Sr3	4*c*	0.318(2)	0.160(2)	0.75	0.015	0.799(7)
Ta1	4*b*	0	0.5	0.5	0.0015	
Ta2	8*d*	0.0718(9)	0.2134(9)	0.501(2)	0.0015	
Ta3	8*d*	0.2873(8)	0.4299(9)	0.503(2)	0.0015	
O1	4*c*	0.973(2)	0.488(2)	0.25	0.030(3)	
O2	4*c*	0.068(2)	0.207(3)	0.25	0.030(3)	
O3	4*c*	0.062(2)	0.211(3)	0.75	0.030(3)	
O4	4*c*	0.323(2)	0.394(2)	0.25	0.030(3)	
O5	4*c*	0.284(2)	0.398(2)	0.75	0.030(3)	
O6	8*d*	0.2229(9)	0.274(1)	0.481(2)	0.011(3)	
O7	8*d*	–0.004(1)	0.352(2)	0.538(2)	0.032(3)	
O8	8*d*	0.337(1)	0.006(2)	0.534(2)	0.032(3)	
O9	8*d*	0.134(1)	0.062(2)	0.485(3)	0.054(3)	
O10	8*d*	0.433(1)	0.358(2)	0.494(3)	0.054(3)	

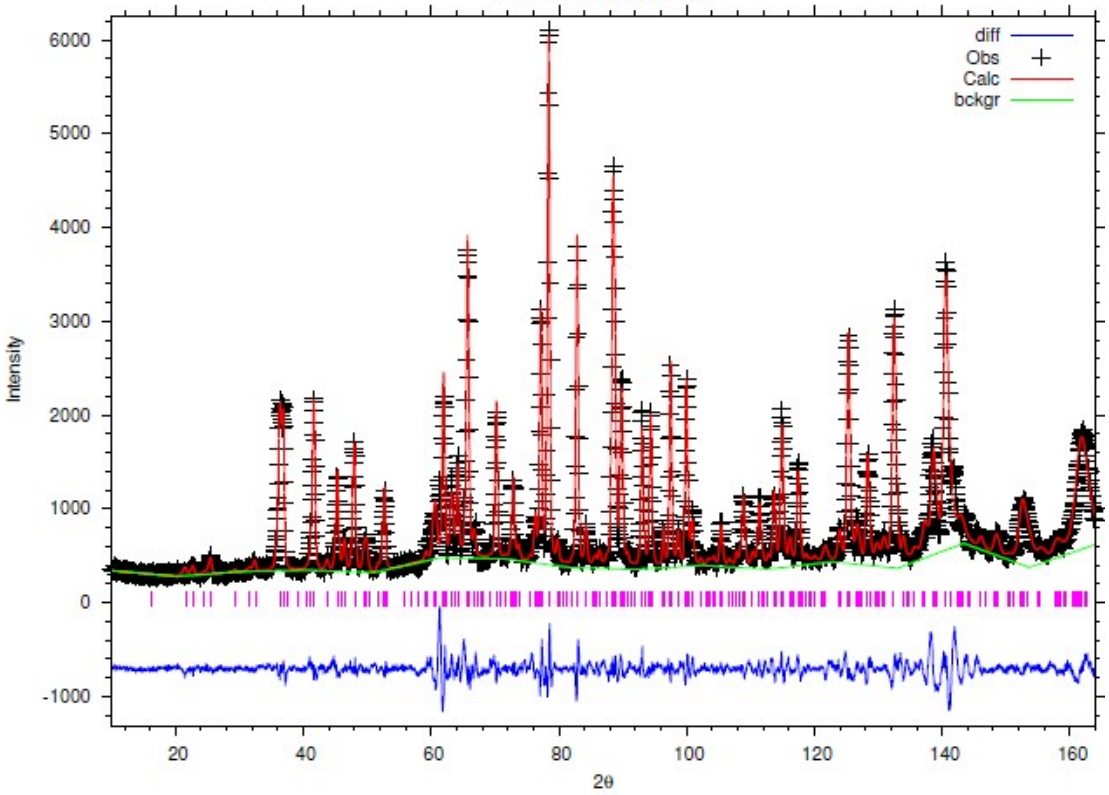

Fig. S1. Neutron Rietveld refinement of $Li_{0.17}Sr_{0.92}Ta_2O_6$.

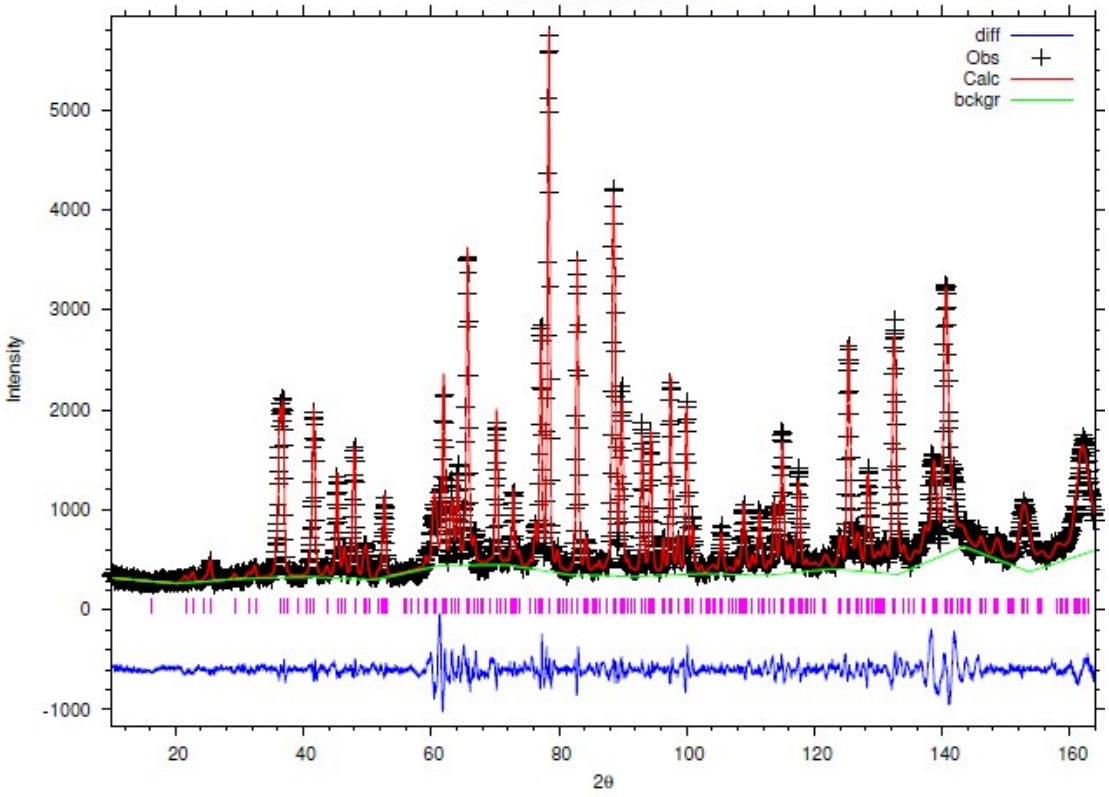

Fig. S2. Neutron Rietveld refinement of $Li_{0.25}Sr_{0.88}Ta_2O_6$.