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STRUCTURE REFINEMENT AND POWDER X-RAY DIFFRACTION DATA FOR $LiLa_2TaO_6$

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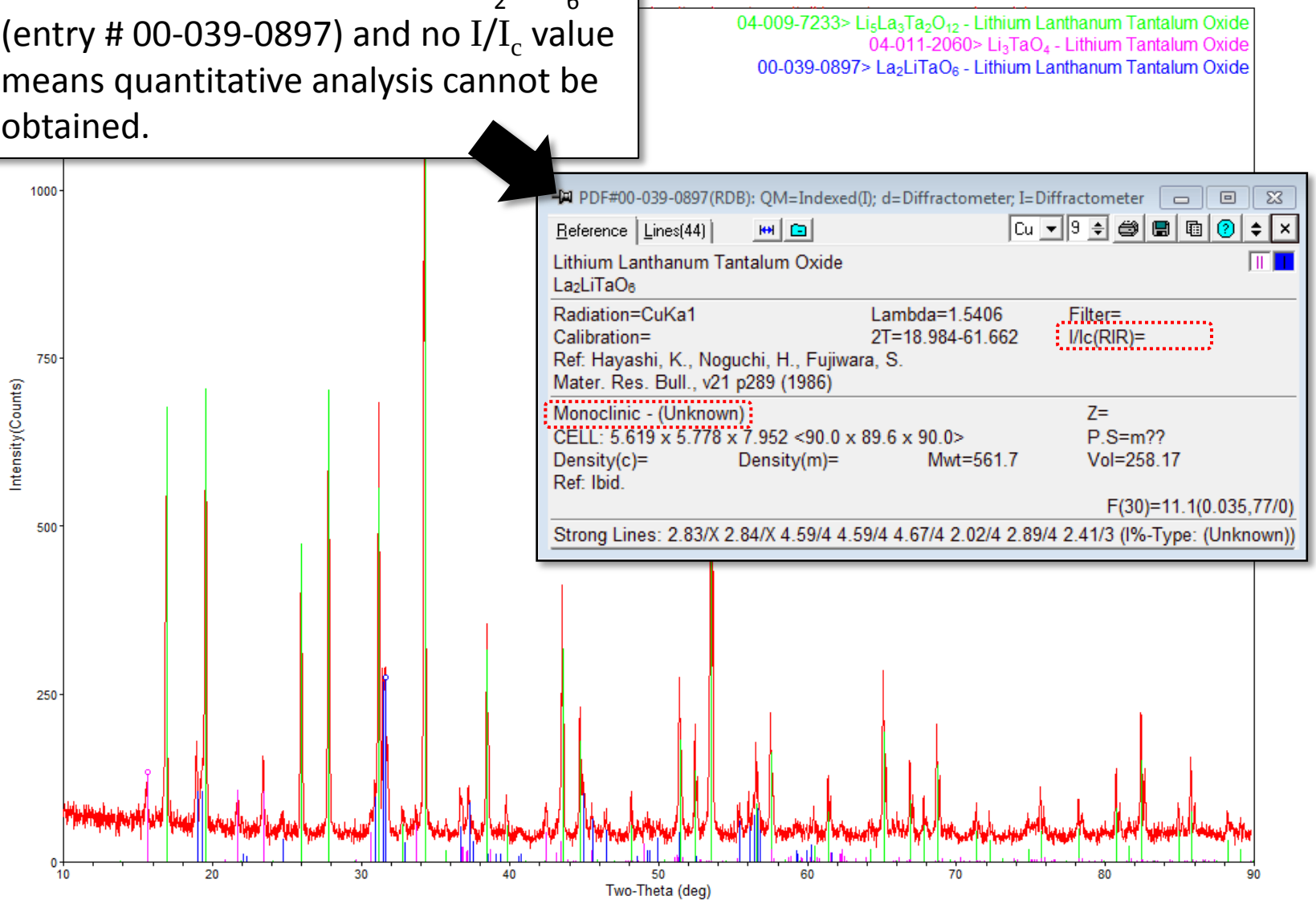
Motivation

- $Li_5La_3Ta_2O_{12}$ is being investigated as a fast Li-ion conductor with applications as a separator material in Li-ion batteries.
- We observed a $LiLa_2TaO_6$ as an impurity in our synthesis of $Li_5La_3Ta_2O_{12}$ garnet powders.
- We desired to quantify the weight fraction of this impurity phase via Rietveld refinement to help direct our materials processing.
- $LiLa_2TaO_6$ is documented in the PDF database, but the full structure has not been elucidated. This makes quantitative analysis difficult.
- We have isolated the $LiLa_2TaO_6$ phase and refined its structure for documentation in the PDF database.

A lack of structural data for $LiLa_2TaO_6$ (entry # 00-039-0897) and no I/I_c value means quantitative analysis cannot be obtained.

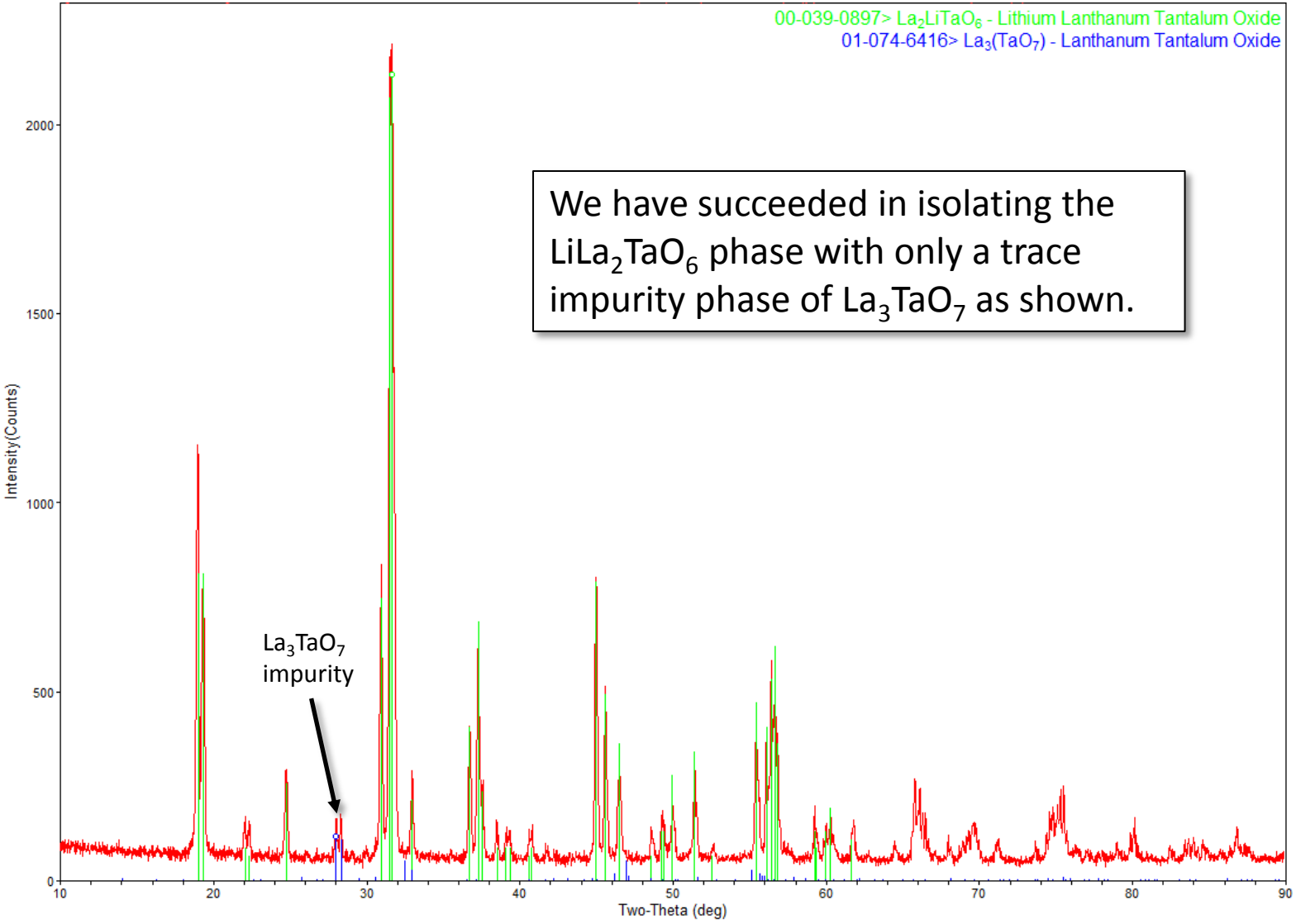


XRD shows mixed phases during processing of $Li_5La_3Ta_2O_{12}$

Synthesis

- The $LiLa_2TaO_6$ phase was prepared by solid-state synthesis using, Li_2CO_3, La_2O_3, and Ta_2O_5. Samples were batched with 1 wt% excess Li (i.e. Li-rich) and ball-milled 12 hrs in ethanol prior to calcination.
- The sample was calcined in air at 1000°C for 12 hrs using a 5°C/min heating rate. $LiLa_2TaO_6$ material was ball-milled after calcining to reduce particle size.
- Initial XRD analysis suggested a near phase pure sample of $LiLa_2TiO_6$ with a small fraction of impurity phase ($LaTa_3O_7$).

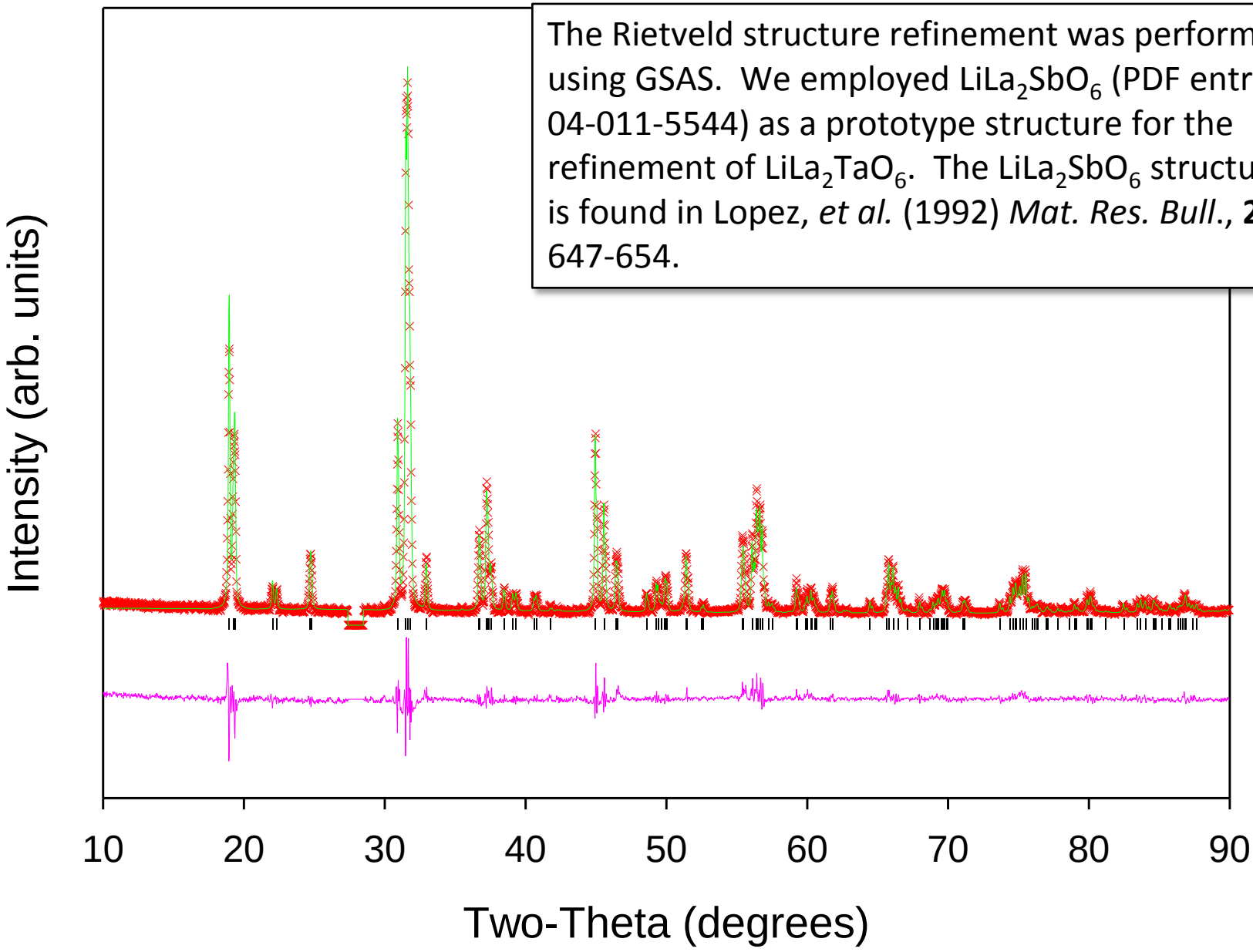
Isolation of $LiLa_2TaO_6$



We have succeeded in isolating the $LiLa_2TaO_6$ phase with only a trace impurity phase of La_3TaO_7 as shown.

Structure refinement of $LiLa_2TaO_6$

The Rietveld structure refinement was performed using GSAS. We employed $LiLa_2SbO_6$ (PDF entry 04-011-5544) as a prototype structure for the refinement of $LiLa_2TaO_6$. The $LiLa_2SbO_6$ structure is found in Lopez, *et al.* (1992) *Mat. Res. Bull.*, **27**, 647-654.



$LiLa_2TaO_6$ structure

Crystal Data

Symmetry: Monoclinic

Space group: $P2_1/n$

a (Å) = 5.621(1)

b (Å) = 5.775(1)

c (Å) = 7.954(1)

β (^{o}) = 89.660(2)^o

Cell Vol (Å^3) : 258.26(1)

MW (g/mol) : 1123.39

ρ_x (g/cm^3) = 7.22

B_{iso} (Å^2)= 0.3(1)

R_p (%) = 8.91

R_{wp} (%) = 11.41

Reduced χ^2 = 1.313

Refined fractional coordinates for $LiLa_2TaO_6$

Atom	Site	X	Y	Z	occupancy
Li	2c	0	½	0	1
La	4e	0.5102(5)	0.5510(3)	0.2521(3)	1
Ta	2d	½	0	0	1
O1	4e	0.211(3)	0.206(3)	-0.042(3)	1
O2	4e	0.299(3)	0.710(3)	-0.046(3)	1
O3	4e	0.413	0.978	0.239	1

New Powder XRD Data for $LiLa_2TaO_6$

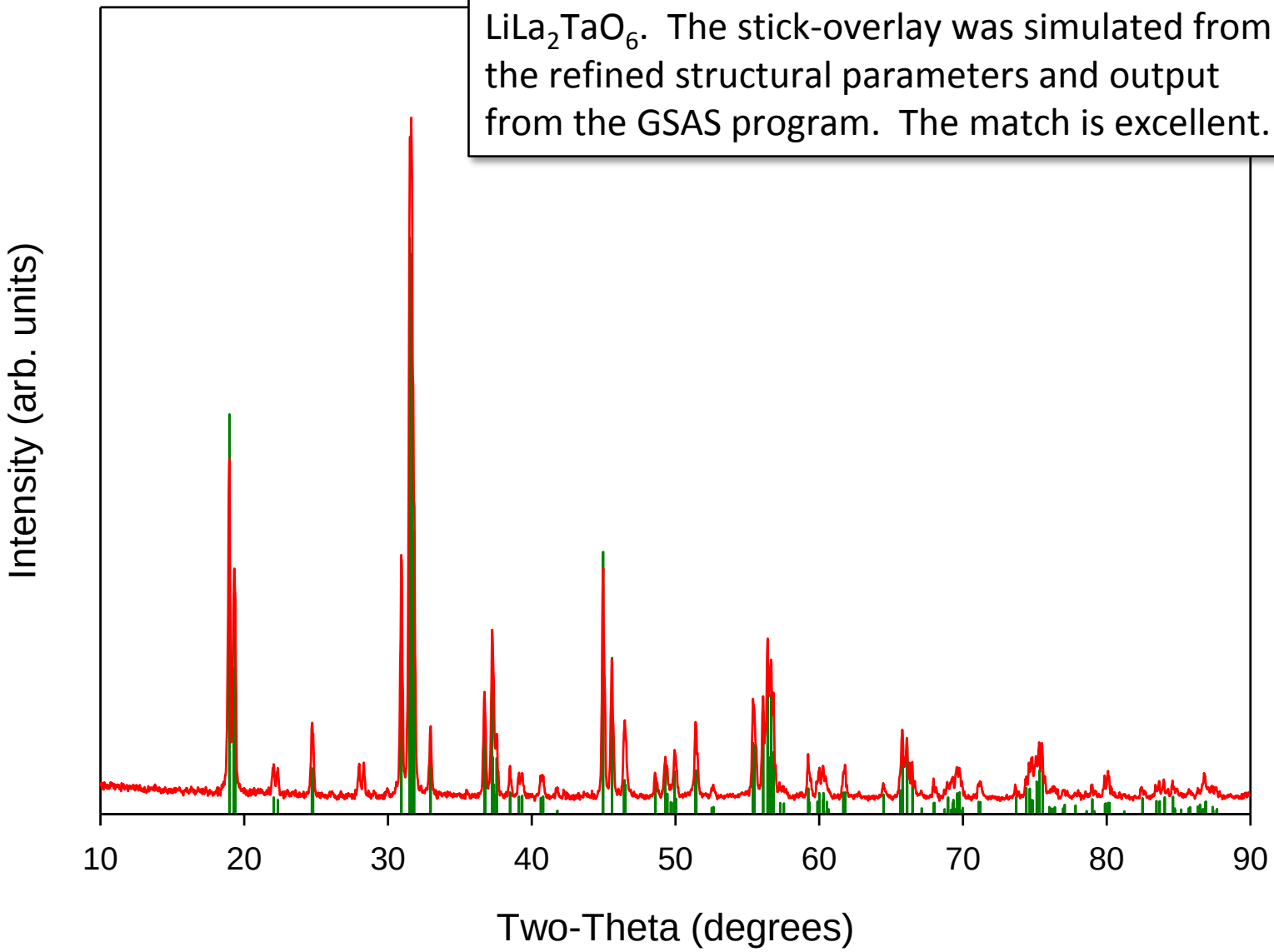
2θ (°)	d (Å)	I_{rel}	(hkl)
18.973	4.6737	69.4	0 1 1
19.266	4.6032	25.3	1 0 1
19.375	4.5776	37.4	-1 0 1
22.048	4.0283	2.9	1 1 0
22.337	3.9769	2.4	0 0 2
24.711	3.5999	7.9	1 1 1
24.798	3.5875	7.7	-1 1 1
30.939	2.8880	44.1	0 2 0
31.519	2.8361	100.0	1 1 2
31.657	2.8241	97.2	-1 1 2
31.815	2.8105	49.0	2 0 0
32.970	2.7146	10.6	0 2 1
36.706	2.4464	14.5	1 2 1
36.766	2.4425	9.6	-1 2 1
37.245	2.4122	22.4	2 1 1
37.288	2.4096	9.8	0 1 3
37.364	2.4048	5.1	-2 1 1
37.386	2.4034	3.5	1 0 3
37.564	2.3925	9.7	-1 0 3
38.493	2.3368	3.8	0 2 2
39.106	2.3016	3.0	2 0 2
39.334	2.2888	3.2	-2 0 2
40.625	2.2190	2.8	1 1 3
40.791	2.2103	3.0	-1 1 3
41.776	2.1605	0.6	1 2 2
44.970	2.0142	45.5	2 2 0
45.584	1.9885	27.1	0 0 4
46.422	1.9545	5.0	2 2 1
46.458	1.9531	5.9	0 2 3
46.521	1.9505	5.1	-2 2 1
48.616	1.8713	5.6	0 3 1
49.287	1.8474	7.7	1 2 3
49.429	1.8424	3.5	-1 2 3
49.665	1.8342	2.1	2 1 3
49.899	1.8261	2.0	3 0 1
49.949	1.8244	7.4	-2 1 3
50.036	1.8214	0.8	1 3 0
50.040	1.8213	2.6	-3 0 1
51.402	1.7762	7.6	1 3 1
51.448	1.7747	7.5	-1 3 1

2θ (°)	d (Å)	I_{rel}	(hkl)
55.484	1.6548	12.0	-1 3 2
56.111	1.6378	17.8	0 2 4
56.411	1.6298	21.5	3 1 2
56.486	1.6278	9.9	2 0 4
56.670	1.6230	20.6	-3 1 2
56.831	1.6187	10.7	-2 0 4
57.280	1.6071	1.9	2 2 3
57.537	1.6006	1.8	-2 2 3
59.237	1.5586	4.4	2 3 1
59.267	1.5579	2.5	0 3 3
59.321	1.5566	2.0	-2 3 1
59.877	1.5435	2.2	3 2 1
60.002	1.5405	3.6	-3 2 1
60.267	1.5344	2.5	3 0 3
60.299	1.5337	3.6	0 1 5
60.326	1.5330	0.6	1 0 5
60.534	1.5283	2.1	-1 0 5
60.640	1.5259	0.8	-3 0 3
61.678	1.5026	3.7	1 3 3
61.801	1.5000	3.8	-1 3 3
64.477	1.4440	3.4	0 4 0
65.663	1.4208	4.1	0 4 1
65.804	1.4181	11.5	2 2 4
66.120	1.4121	11.8	-2 2 4
66.483	1.4052	6.4	4 0 0
67.123	1.3934	1.0	0 2 5
67.984	1.3778	1.9	1 4 1
68.023	1.3771	1.9	-1 4 1
68.735	1.3646	0.8	2 3 3
68.967	1.3605	2.9	-2 3 3
69.155	1.3573	0.7	0 4 2
69.288	1.3550	1.9	3 2 3
69.343	1.3541	2.4	1 2 5
69.536	1.3508	1.0	-1 2 5
69.612	1.3495	3.6	2 1 5
69.634	1.3491	2.0	-3 2 3
69.760	1.3470	3.7	4 1 1
69.914	1.3444	0.6	-4 1 1
69.996	1.3430	1.1	-2 1 5
71.095	1.3250	2.1	3 3 1

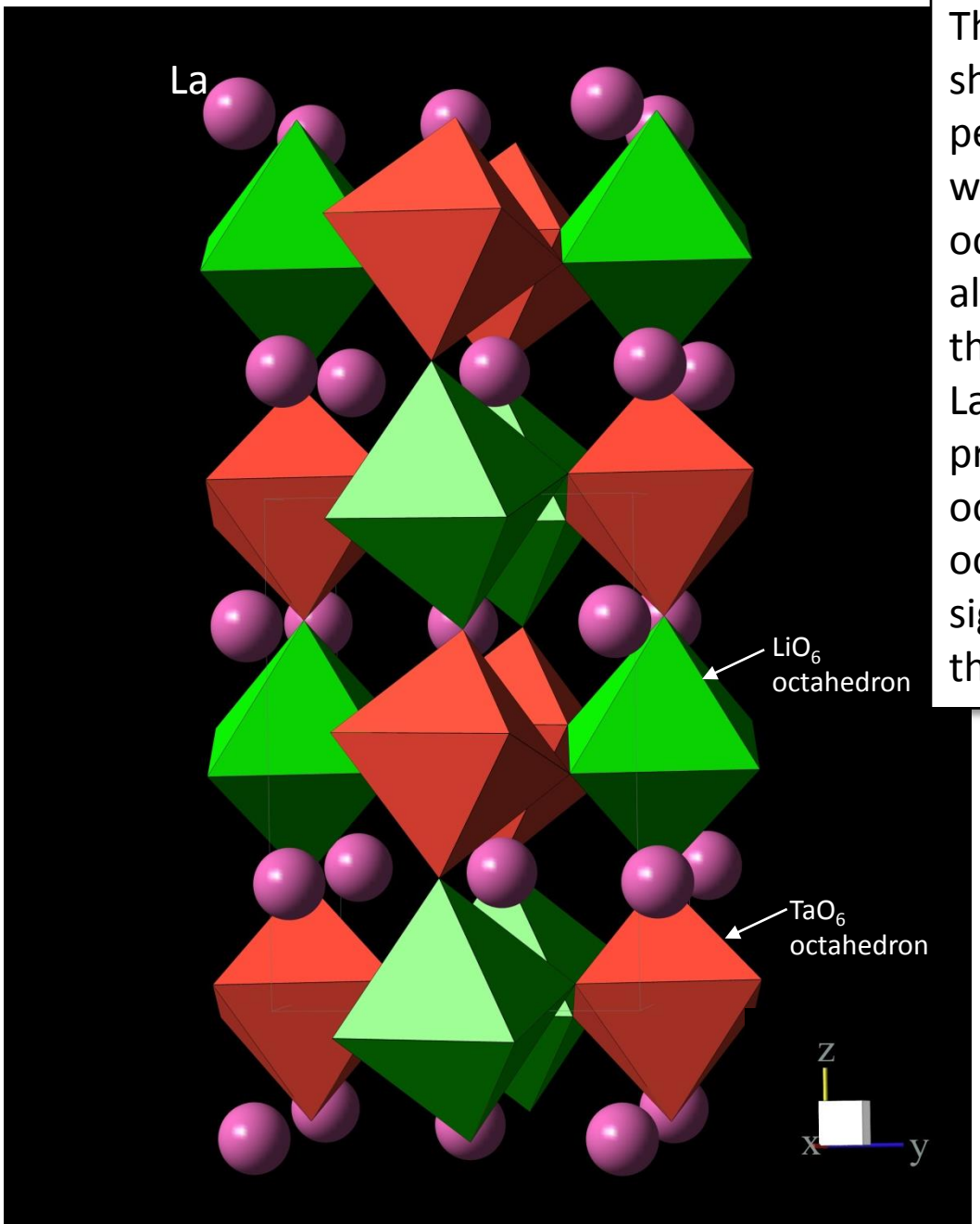
2θ (°)	d (Å)	I_{rel}	(hkl)
74.640	1.2706	4.4	-3 3 2
74.782	1.2685	2.4	2 4 1
74.809	1.2681	1.9	0 4 3
74.857	1.2674	2.3	-2 4 1
75.123	1.2636	5.6	4 2 0
75.318	1.2608	7.5	1 1 6
75.541	1.2576	7.3	-1 1 6
76.015	1.2510	1.2	2 2 5
76.158	1.2490	1.0	4 2 1
76.307	1.2469	0.9	-4 2 1
76.387	1.2458	1.2	-2 2 5
76.972	1.2378	1.0	1 4 3
77.083	1.2363	1.6	-1 4 3
77.825	1.2263	1.5	0 3 5
78.596	1.2162	0.5	3 0 5
78.998	1.2110	2.5	-4 1 3
79.148	1.2091	0.5	-3 0 5
79.873	1.2000	1.8	3 3 3
79.926	1.1993	1.8	1 3 5
80.109	1.1970	1.9	-1 3 5
80.203	1.1959	1.9	-3 3 3
81.217	1.1835	0.5	-3 1 5
82.488	1.1684	2.8	0 4 4
83.472	1.1571	2.3	2 4 3
83.690	1.1547	2.2	-2 4 3
84.034	1.1508	2.9	4 0 4
84.615	1.1444	3.0	-4 0 4
84.723	1.1432	1.0	0 5 1
84.739	1.1430	0.8	4 2 3
85.174	1.1383	0.8	-4 2 3
85.699	1.1327	1.0	3 4 1
85.804	1.1316	1.2	1 5 0
85.807	1.1315	0.8	-3 4 1
86.341	1.1259	1.3	2 3 5
86.480	1.1244	1.6	4 3 1
86.703	1.1221	0.9	-2 3 5
86.863	1.1205	2.1	1 5 1
86.899	1.1201	2.1	-1 5 1
87.364	1.1153	1.2	-3 2 5
87.405	1.1149	0.6	0 1 7

Simulated and to Observed Powder XRD Data for $LiLa_2TaO_6$

Here we show the original raw data XRD pattern along with the newly generated stick pattern for $LiLa_2TaO_6$. The stick-overlay was simulated from the refined structural parameters and output from the GSAS program. The match is excellent.

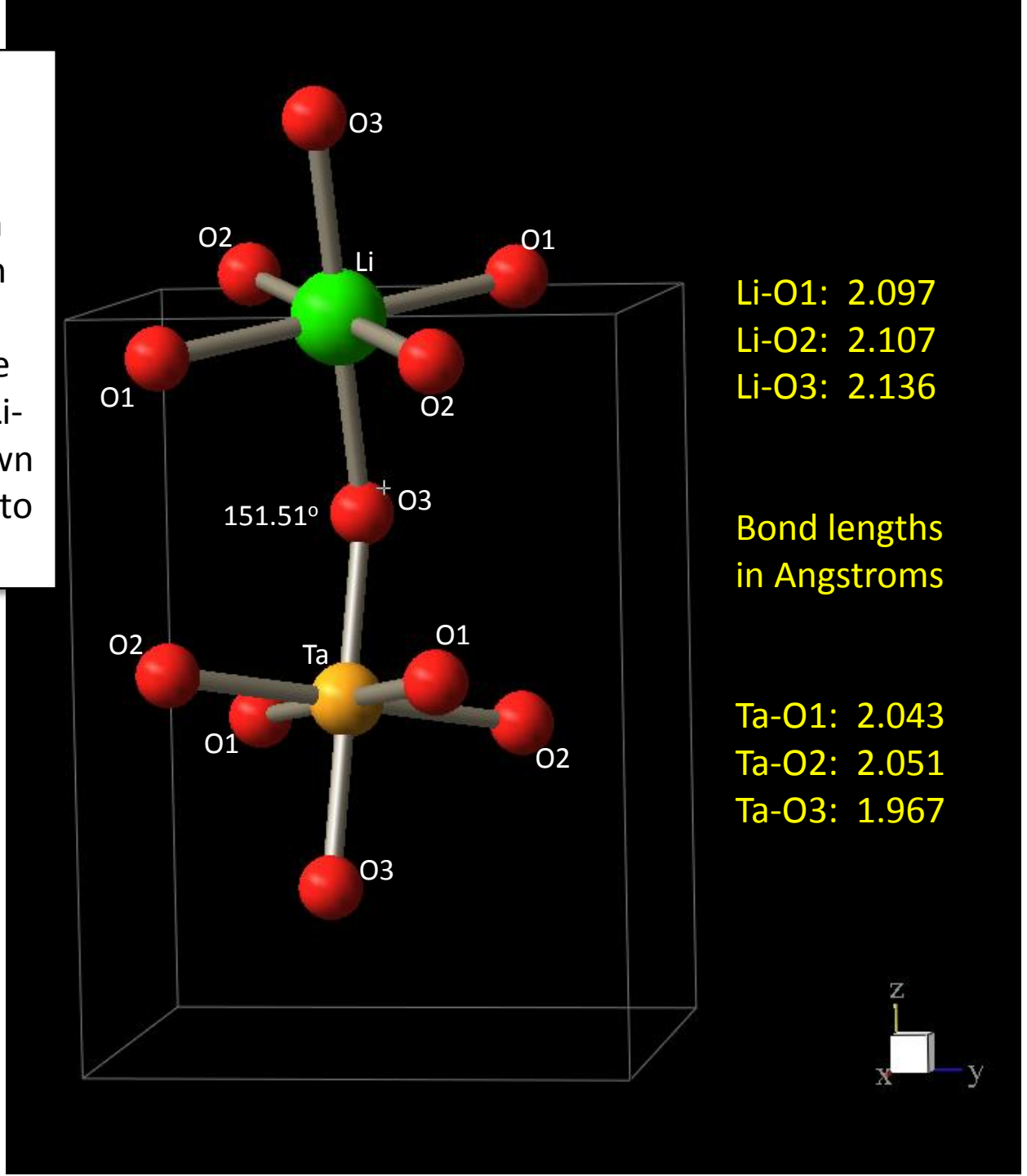


Polyhedral representation of $LiLa_2TaO_6$



The $LiLa_2TaO_6$ phase shows an ordered perovskite structure with LiO_6 and TaO_6 octahedra alternating along the c-axis to form the expanded unit cell. La atoms fill the cavities provided by the tilted octahedra. These tilted octahedra give rise to significant variability in the La-O bond lengths.

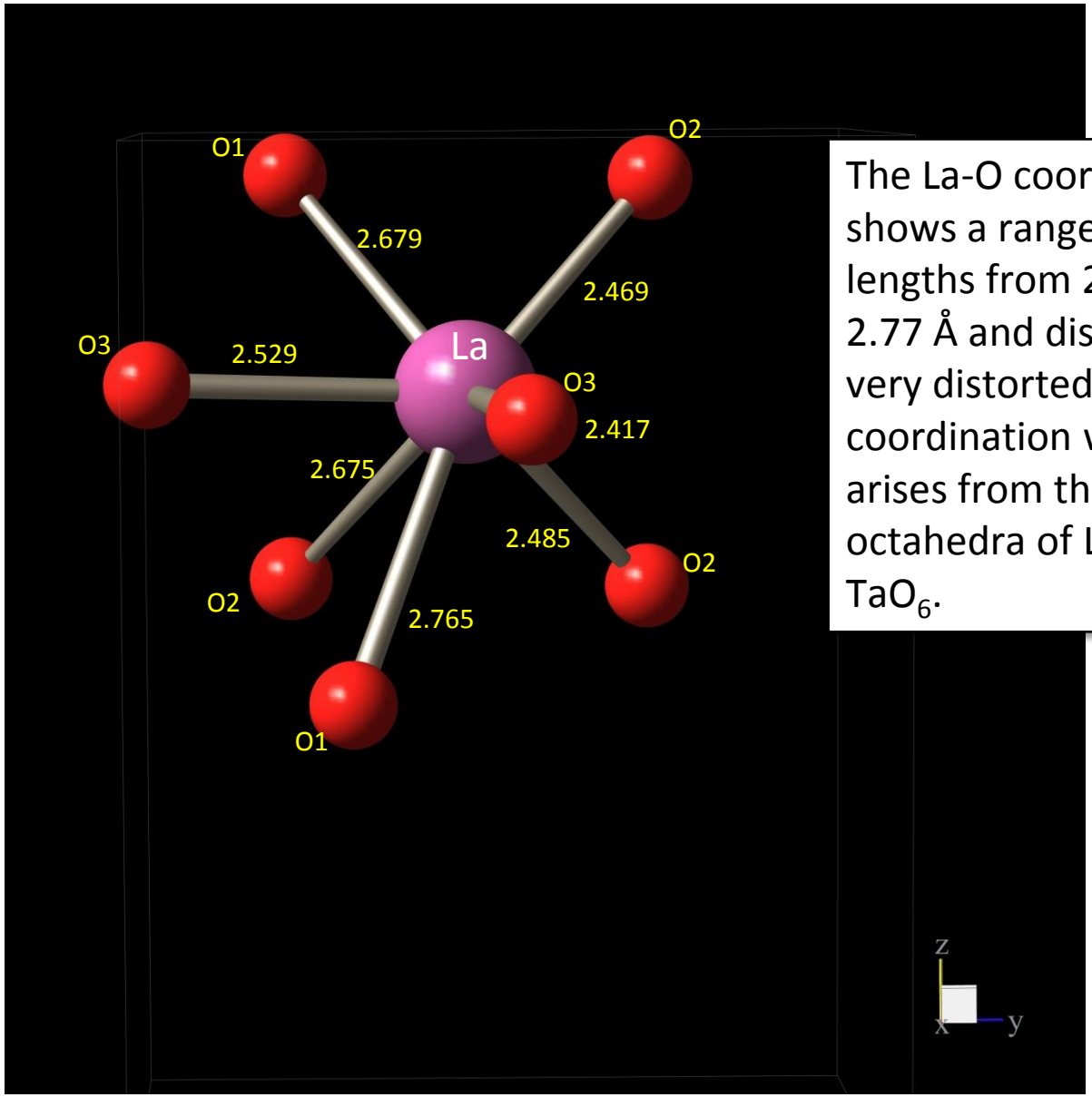
Bond lengths for LiO_6 and TaO_6 octahedra show relatively uniform M-O bonds within their respective coordination. The tilt angle for the Li-O-Ta bond is shown as 151.5°, similar to other structures.



Li-O1: 2.097
Li-O2: 2.107
Li-O3: 2.136

Bond lengths in Angstroms

Ta-O1: 2.043
Ta-O2: 2.051
Ta-O3: 1.967



The La-O coordination shows a range of bond lengths from 2.42 to 2.77 Å and displays a very distorted 8-fold coordination which arises from the tilted octahedra of LiO_6 and TaO_6.

Summary

- The $LiLa_2TaO_6$ phase has been isolated and refined.
- The structure is a monoclinic ordered-perovskite.
- TaO_6 and LiO_6 octahedra are relatively rigid, but display a Li-O-Ta tilt angle of ~151^o between alternating octahedra.
- The La atom displays a variety of La-O bond lengths as a result of the octahedral tilting of Li and Ta.
- Powder XRD data have been generated for $LiLa_2TaO_6$.
- We can now perform quantitative analysis of the $LiLa_2TaO_6$ impurity phase present in our $Li_5La_3Ta_2O_{12}$ synthesis.