

Supporting information

Soft-Chemistry of Garnet-Type $\text{Li}_{5+x}\text{Ba}_x\text{La}_{3-x}\text{Nb}_2\text{O}_{12}$ ($x = 0, 0.5, 1$): A Case Study of Reversible H^+/Li^+ Ion-Exchange Reaction and Their X-ray, ^7Li MAS NMR, IR and AC Impedance Spectroscopy Characterization

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Table S1. Indexed PXRD Data for As-Prepared $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$, Proton-Exchanged “ $\text{Li}_{0.17}\text{H}_{4.83}\text{La}_3\text{Nb}_2\text{O}_{12}$,” and Reverse Ion-Exchanged “ $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ ” from $\text{Li}_{0.56}\text{H}_{4.44}\text{La}_3\text{Nb}_2\text{O}_{12}$ using 5 M LiNO_3 at Room Temperature for 4 days.

h	k	l	as-prepared $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$			“ $\text{Li}_{0.56}\text{H}_{4.44}\text{La}_3\text{Nb}_2\text{O}_{12}$ ”			reverse ion-exchanged “ $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ ”		
			d_{obs} (Å)	$d_{\text{cal.}}$ (Å)	I_{obs} (%)	d_{obs} (Å)	$d_{\text{cal.}}$ (Å)	I_{obs} (%)	d_{obs} (Å)	$d_{\text{cal.}}$ (Å)	I_{obs} (%)
2	1	1	5.175	5.208	100	5.199	5.216	100	5.205	5.221	100
2	2	0	4.484	4.510	18	4.507	4.517	20	4.509	4.522	17
3	2	1	3.396	3.410	63	3.409	3.414	57	3.416	3.418	59
4	0	0	3.177	3.189	49	3.189	3.194	39	3.193	3.197	60
4	2	0	2.846	2.853	92	2.854	2.857	62	2.857	2.860	92
3	3	2	2.715	2.720	10	2.719	2.724	61	2.769	2.791	10
4	2	2	2.600	2.604	77	2.606	2.608	56	2.609	2.611	91
5	1	0	2.499	2.502	5	2.505	2.506	3	2.529	2.508	14
5	2	1	2.327	2.329	55	2.334	2.333	27	2.334	2.335	44
6	1	1	2.068	2.070	50	2.074	2.073	29	2.075	2.075	7
6	2	0	2.016	2.017	8	2.022	2.020	4	2.021	2.022	11
6	3	1	1.881	1.881	10	1.885	1.884	6	1.885	1.886	44

4	4	4	1.841	1.841	8	1.843	1.844	6	1.846	1.846	8
6	4	0	1.769	1.769	32	1.772	1.772	16	1.774	1.774	9
7	2	1	1.736	1.736	23	1.737	1.739	14	1.741	1.740	10
6	4	2	1.705	1.705	69	1.707	1.707	33	1.709	1.709	29
6	5	1	1.621	1.620	15	1.622	1.623	9	1.625	1.624	16
8	0	0	1.596	1.595	19	1.597	1.597	9	1.599	1.599	56
8	4	0	1.427	1.426	18	1.429	1.428	8	1.431	1.430	17
8	4	2	1.393	1.392	18	1.395	1.394	5	1.396	1.395	17
			$a = 12.757(3) \text{ \AA}$			$a = 12.775(2) \text{ \AA}$			$a = 12.789(3) \text{ \AA}$		

Table S2. Indexed PXRD Data for As-Prepared $\text{Li}_{5.5}\text{Ba}_{0.5}\text{La}_{2.5}\text{Nb}_2\text{O}_{12}$, Proton-Exchanged “ $\text{Li}_3\text{H}_{2.5}\text{Ba}_{0.5}\text{La}_{2.5}\text{Nb}_2\text{O}_{12}$,” and Reverse Ion-Exchanged “ $\text{Li}_{5.5}\text{Ba}_{0.5}\text{La}_{2.5}\text{Nb}_2\text{O}_{12}$ ” from $\text{Li}_3\text{H}_{2.5}\text{Ba}_{0.5}\text{La}_{2.5}\text{Nb}_2\text{O}_{12}$ using 5 M LiNO_3 at Room Temperature for 4 days.

			as-prepared $\text{Li}_{5.5}\text{Ba}_{0.5}\text{La}_{2.5}\text{Nb}_2\text{O}_{12}$			“ $\text{Li}_3\text{H}_{2.5}\text{Ba}_{0.5}\text{La}_{2.5}\text{Nb}_2\text{O}_{12}$ ”			reverse ion-exchanged “ $\text{Li}_{5.5}\text{Ba}_{0.5}\text{La}_{2.5}\text{Nb}_2\text{O}_{12}$ ”		
h	k	l	d_{obs} (Å)	$d_{\text{cal.}}$ (Å)	I_{obs} (%)	d_{obs} (Å)	$d_{\text{cal.}}$ (Å)	I_{obs} (%)	d_{obs} (Å)	$d_{\text{cal.}}$ (Å)	I_{obs} (%)
2	1	1	5.223	5.243	100	5.217	5.234	100	5.229	5.254	100
2	2	0	4.525	4.540	21	4.521	4.533	20	4.534	4.550	21
3	2	1	3.426	3.432	75	3.424	3.427	67	3.434	3.440	59
4	0	0	3.206	3.211	53	3.204	3.205	51	3.211	3.217	36
4	2	0	2.869	2.872	96	2.868	2.867	93	2.875	2.878	74
3	3	2	2.736	2.738	9	2.734	2.733	8	2.741	2.744	6
4	2	2	2.619	2.621	80	2.618	2.617	66	2.625	2.627	8
5	1	0	2.515	2.519	5	2.516	2.514	4	2.528	2.524	58
5	2	1	2.343	2.345	43	2.342	2.341	45	2.349	2.350	27
6	1	1	2.083	2.083	41	2.083	2.080	39	2.087	2.088	29
6	2	0	2.030	2.031	4	2.030	2.027	6	1.896	1.898	6
6	3	1	1.894	1.894	8	1.894	1.890	7	1.857	1.858	5
4	4	4	1.854	1.854	8	1.854	1.851	7	1.784	1.785	18
6	4	0	1.781	1.781	26	1.780	1.778	22	1.752	1.751	13
7	2	1	1.748	1.748	17	1.747	1.745	15	1.720	1.720	37
6	4	2	1.716	1.716	55	1.716	1.713	52	1.635	1.634	9
			$a = 12.842(3) \text{ Å}$			$a = 12.821(1) \text{ Å}$			$a = 12.869(6) \text{ Å}$		

Table S3. Indexed PXRD Data for As-Prepared $\text{Li}_6\text{BaLa}_2\text{Nb}_2\text{O}_{12}$, Proton-Exchanged “ $\text{Li}_{4.8}\text{H}_{1.2}\text{BaLaNb}_2\text{O}_{12}$,” and Reverse Ion-Exchanged “ $\text{Li}_6\text{BaLa}_2\text{Nb}_2\text{O}_{12}$ ” from $\text{Li}_{4.8}\text{H}_{1.2}\text{BaLaNb}_2\text{O}_{12}$ using 5 M LiNO_3 at Room Temperature for 4 days.

			as-prepared $\text{Li}_6\text{BaLa}_2\text{Nb}_2\text{O}_{12}$			“ $\text{Li}_{4.8}\text{H}_{1.2}\text{La}_3\text{Nb}_2\text{O}_{12}$ ”			reverse ion-exchanged “ $\text{Li}_6\text{BaLa}_2\text{Nb}_2\text{O}_{12}$ ”		
h	k	l	d_{obs} (Å)	$d_{\text{cal.}}$ (Å)	I_{obs} (%)	d_{obs} (Å)	$d_{\text{cal.}}$ (Å)	I_{obs} (%)	d_{obs} (Å)	$d_{\text{cal.}}$ (Å)	I_{obs} (%)
2	1	1	5.248	5.277	100	5.260	5.275	100	5.273	5.286	100
2	2	0	4.553	4.570	27	4.562	4.568	21	4.571	4.578	17
3	2	1	3.445	3.455	70	3.450	3.453	65	3.458	3.460	63
4	0	0	3.224	3.232	57	3.227	3.230	42	3.231	3.237	48
4	2	0	2.884	2.891	97	2.887	2.889	84	2.893	2.895	77
3	3	2	2.754	2.756	10	2.754	2.755	8	2.762	2.760	7
4	2	2	2.637	2.639	73	2.639	2.637	60	2.643	2.643	63
5	1	0	2.532	2.535	5	2.535	2.534	4	2.530	2.539	4
5	2	1	2.360	2.360	40	2.359	2.359	31	2.363	2.364	37
6	1	1	2.097	2.097	39	2.098	2.096	28	2.100	2.100	31
6	2	0	2.041	2.044	7	2.041	2.043	8	2.045	2.047	8
6	3	1	1.907	1.906	7	1.903	1.905	5	1.910	1.909	7
4	4	4	1.866	1.866	7	1.866	1.865	5	1.869	1.869	7
6	4	0	1.795	1.793	24	1.791	1.792	15	1.795	1.796	19
7	2	1	1.759	1.759	16	1.759	1.758	12	1.762	1.762	12
6	4	2	1.728	1.727	41	1.728	1.727	37	1.731	1.730	41
			$a = 12.927(3) \text{ Å}$			$a = 12.920(3) \text{ Å}$			$a = 12.947(2) \text{ Å}$		

Figures

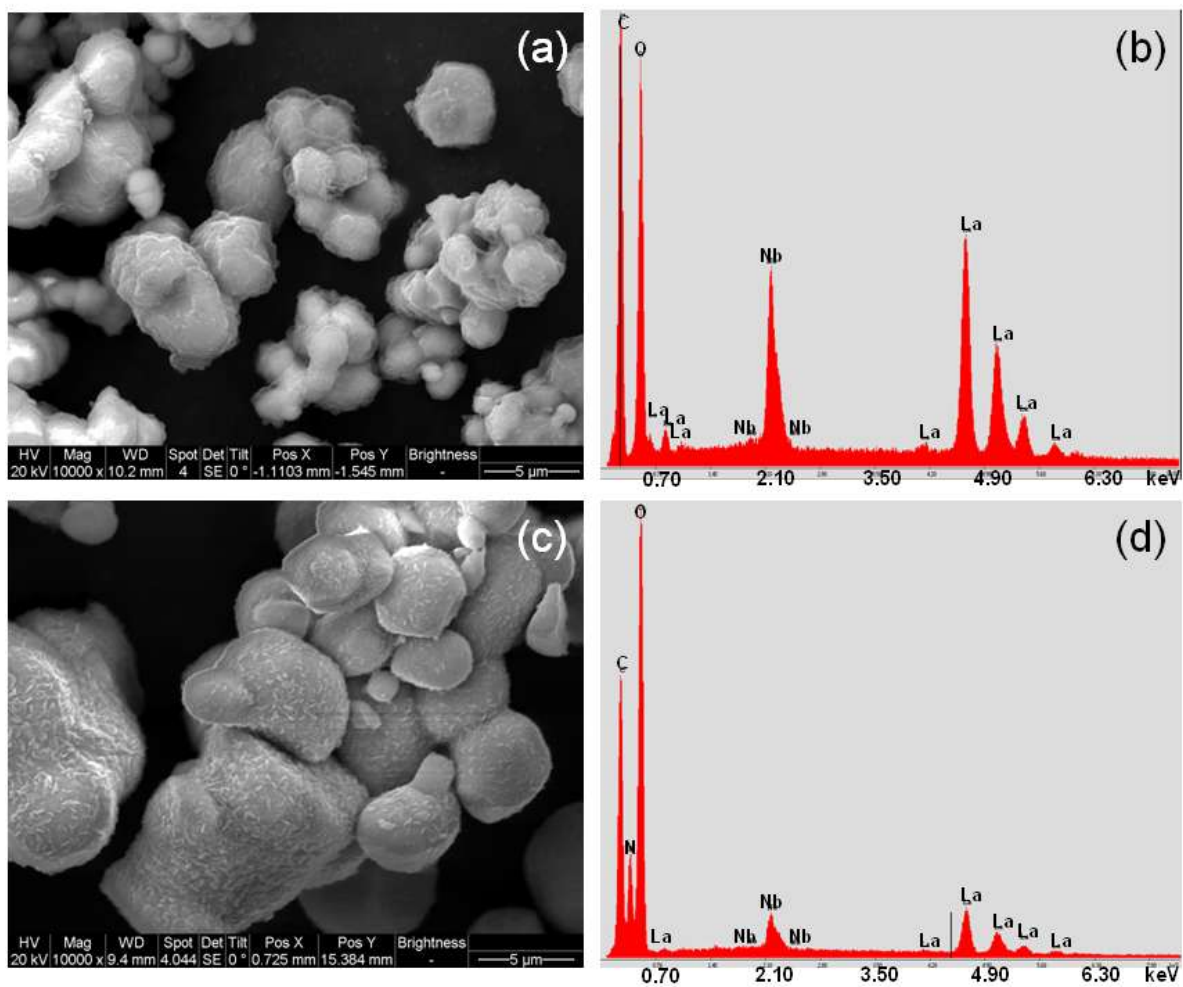


Figure S1. Typical SEM images (5 μm) for (a) $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ as-prepared with its corresponding EDX spectrum in (b), and for (c) sample “a” treated with H_2O with its corresponding EDX spectrum in d).

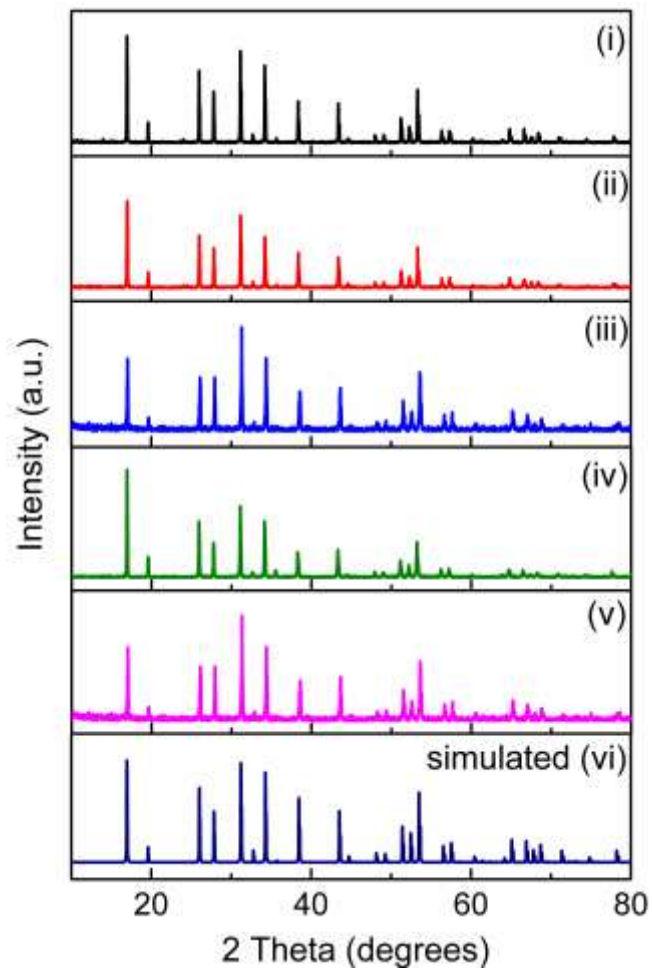


Figure S2. Powder X-ray diffraction (PXRD) patterns of (i) as-prepared $\text{Li}_{5.5}\text{Ba}_{0.5}\text{La}_{2.5}\text{Nb}_2\text{O}_{12}$, (ii) sample “i” treated with pure water, (iii) sample “ii” heated at 700 °C for 2 h in air, (iv) sample “ii” treated with 5M LiNO_3 at room temperature, (v) sample “iv” heated at 700 °C for 2 h in air, and (vi) simulated PXRD of garnet-type $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ using PowderCell software.

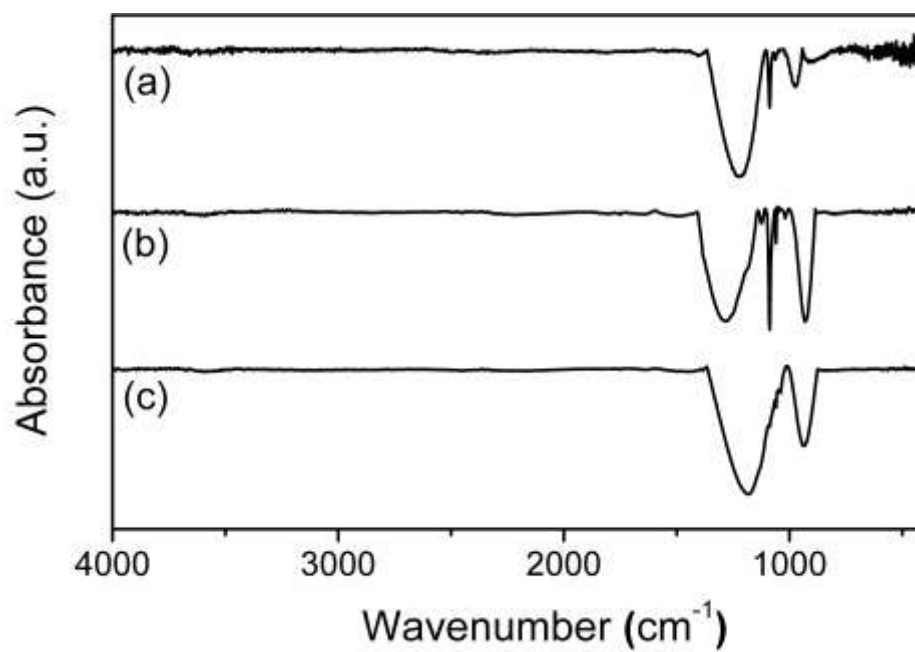


Figure S3. The FTIR spectra of (a) Li₅La₃Nb₂O₁₂ as-prepared, (b) Li_{5.5}Ba_{0.5}La_{2.5}Nb₂O₁₂ as-prepared, (c) Li₆BaLa₂Nb₂O₁₂ as-prepared.