Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

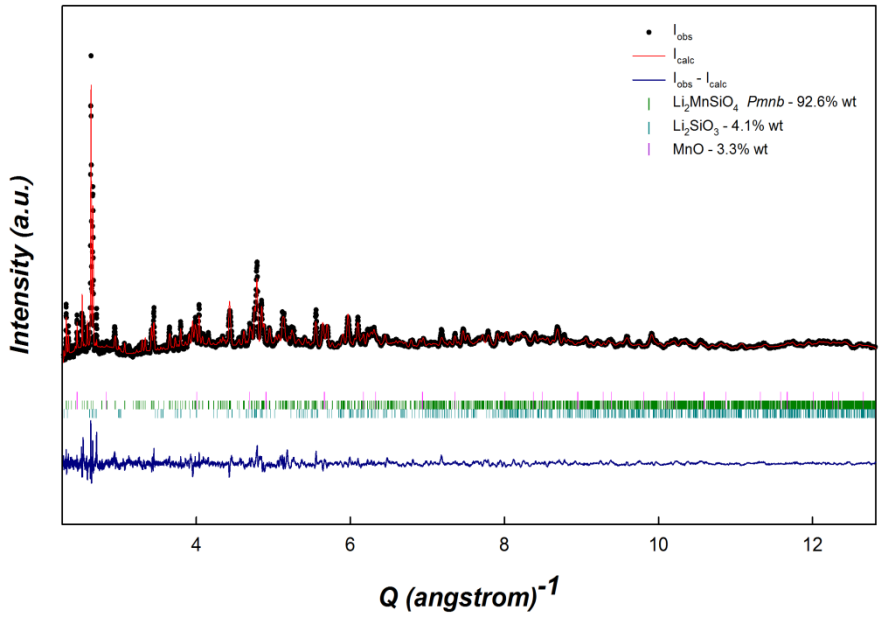

Figure 1 – Representative ND Rietveld refinement of Li_2MnSiO_4 (Pmnb phase). 1 bank shown.

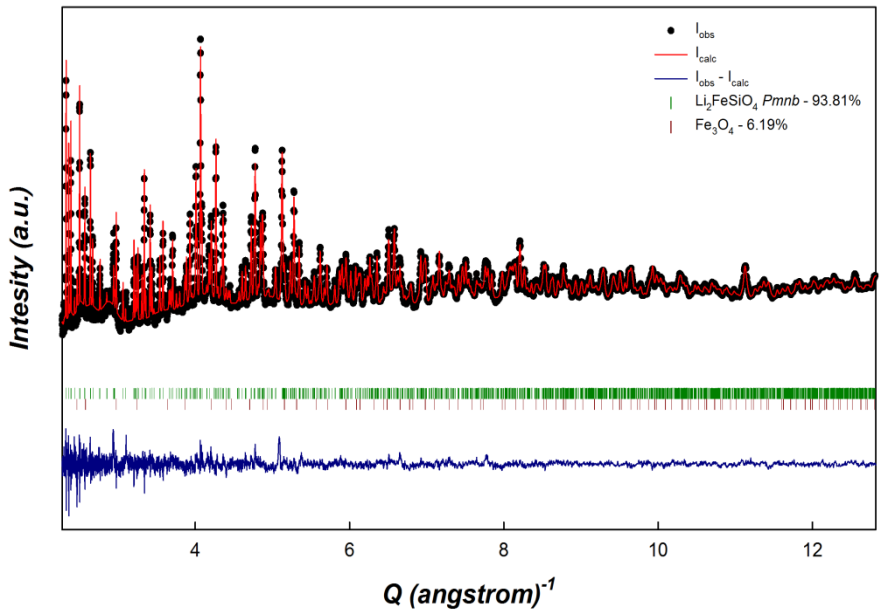

Figure 2 – Representative ND Rietveld refinement of Li_2FeSiO_4 (Pmnb phase). 1 bank shown.

Table 1 – Results of the Rietveld refinements of ND patterns for the Li_2MnSiO_4 polymorphs (average structures).

	χ^2	R_{wp} %	Impurity (wt %)
Pmnb	4.07	4.21	Li_2SiO_3 (4.1%) MnO (3.3%)
$Pmn2_1$	4.01	4.52	MnO (5.7%)
$P2_1/n$	2.01	3.16	Li_2SiO_3 (4.3%) MnO (2.9%)

Table 2 – Results of the Rietveld refinements of ND patterns for the Li_2FeSiO_4 polymorphs (average structures).

	χ^2	R_{wp} %	Impurity (wt %)
Pmnb	2.20	3.02	Fe_3O_4 (6.2%)
$Pmn2_1$	4.37	4.87	Li_2SiO_3 (2.6%) Fe_3O_4 (2.8%)
$P2_1$	3.66	4.69	Li_2SiO_3 (2.1%) Fe_3O_4 (7.8%)

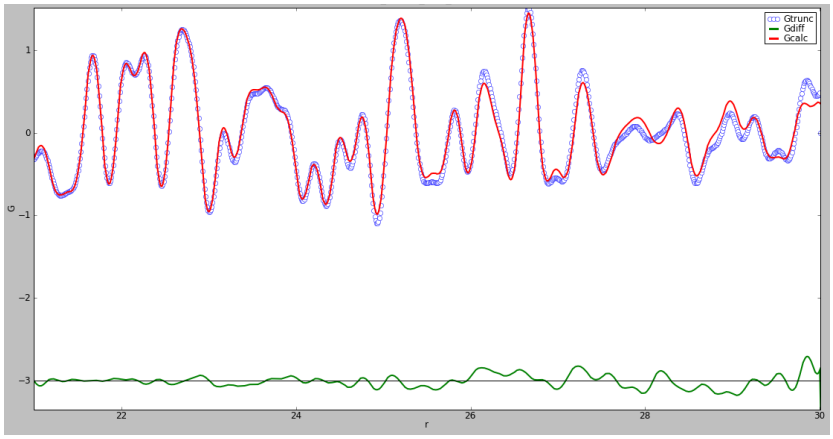

Figure 3 – Fit of the neutron PDF in the 21-30 Å for the Li_2MnSiO_4 ($Pmn2_1$ phase) with the $Pmn2_1$ s.g. Fit results: a=6.2492(1), b=5.3333(1), c=5.0167(3), R_{wp}=0.156.

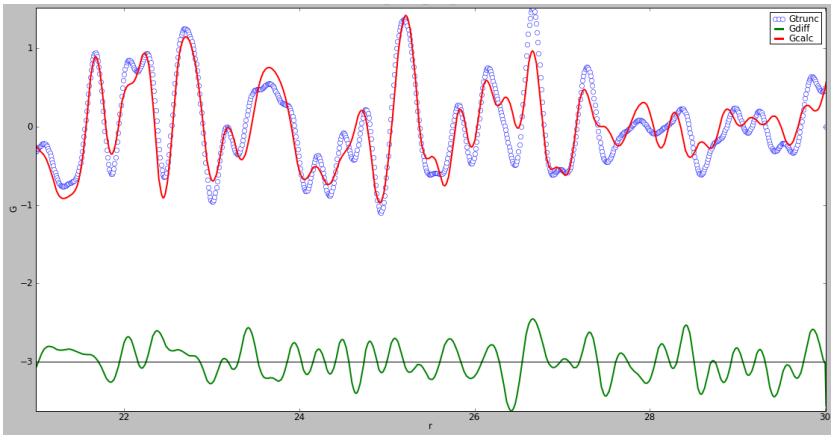

Figure 4 – Fit of the neutron PDF in the 21-30 Å for the Li_2MnSiO_4 ($Pmn2_1$ phase) with the $P2_1$ s.g. Fit results: a=8.2192(2), b=5.0031(3), c=8.2568(3), β=99.52(1) R_{wp}=0.365.

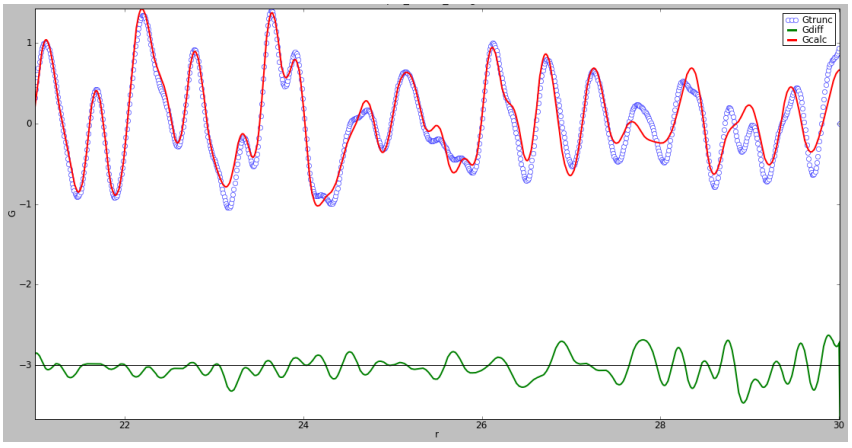

Figure 5 – Fit of the neutron PDF in the 21-30 Å for the Li_2MnSiO_4 (Pmnb phase) with the Pmnb s.g. Fit results: a=6.2691(1), b=10.6545(1), c=5.0353(3), R_{wp}=0.229

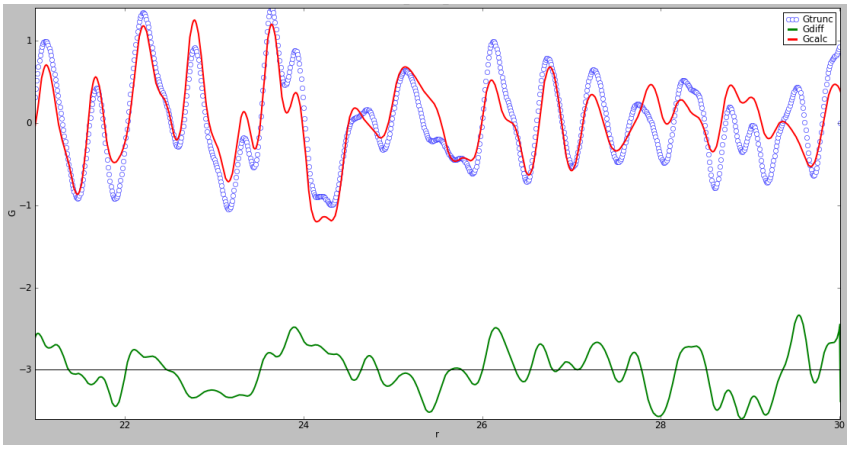

Figure 5 – Fit of the neutron PDF in the 21-30 Å for the Li_2MnSiO_4 (Pmnb phase) with the $P2_1$ s.g. Fit results: a=8.259(3), b=5.002(5), c=8.168(1), β=98.67(1) R_{wp}=0.502.

Table 3 – Bond lengths derived from the 1-6 Å PDF fits for the Li_2MnSiO_4 $Pmn2_1$ polymorph with the $Pmn2_1$ s.g. and the $P2_1/n$ s.g.

	Pmnb	***$P2_1/n$***
Li1-O	*1.778(2)*	*1.777(2)*
Li1-O	*1.949(1)*	*1.894(2)*
Li1-O	*1.973(2)*	*1.976(2)*
Li1-0	*2.056(2)*	*2.089(2)*
Li2-O		*2.051(2)*
Li2-O		*2.162(2)*
Li2-O		*2.350(2)*
Li2-O		*2.372(1)*

	Pmnb	***$P2_1/n$***
Mn-O	*1.805(1)*	*1.687(2)*
Mn-O	*2.056(1)*	*1.920(1)*
Mn-O	*2.184(1)*	*2.060(1)*
Mn-O		*2.222(1)*
Si-O	*1.610(1)*	*1.566(1)*
Si-O	*1.781(1)*	*1.602(1)*
Si-O	*2.025(1)*	*1.673(1)*
Si-O		*1.777(1)*

Table 4 – Bond lengths derived from the 1-6 Å PDF fits for the Li_2MnSiO_4 Pmnb polymorph with the Pmnb s.g. and the $P2_1/n$ s.g.

	Pmn2₁	***P2₁/n***
Li1-O	*1.775(2)*	*1.694(2)*
Li1-O	*1.933(1)*	*2.001(1)*
Li1-O	*1.985(2)*	*2.022(1)*
Li1-0	*2.075(2)*	*2.091(2)*
Li2-O		*1.982(1)*
Li2-O		*2.004(2)*
Li2-O		*2.016(2)*
Li2-O		*2.151(2)*

	Pmn2₁	***P2₁/n***
Mn-O	*1.979(1)*	*1.848(2)*
Mn-O	*2.023(2)*	*1.945(1)*
Mn-O	*2.113(1)*	*2.103(1)*
Mn-O		*2.117(1)*
Si-O	*1.622(1)*	*1.612(1)*
Si-O	*1.675(1)*	*1.652(1)*
Si-O	*2.333(1)*	*1.655(1)*
Si-O		*1.656(2)*

Table 5 – Bond lengths derived from the 1-6 Å PDF fit for the Li_2MnSiO_4 $P2_1/n$ polymorph

	P2₁/n		
Li1-O	*1.899(1)*	***Mn-O***	*1.972(1)*
Li1-O	*1.950(2)*	***Mn-O***	*2.003(1)*
Li1-O	*2.068(1)*	***Mn-O***	*2.060(1)*
Li1-0	*2.087(1)*	***Mn-O***	*2.103(1)*
Li2-O	*1.983(1)*	***Si-O***	*1.614(1)*
Li2-O	*2.087(1)*	***Si-O***	*1.631(1)*
Li2-O	*2.140(1)*	***Si-O***	*1.641(1)*
Li2-O	*2.156(2)*	***Si-O***	*1.661(1)*

Table 6 – Bond lengths derived from the 1-6 Å PDF fits for the Li_2FeSiO_4 Pmnb polymorph with the Pmnb s.g. and the $P2_1$ s.g.

	Pmnb		***$P2_1$***		***Pmnb***	***$P2_1$***
Li1-O	*1.765(3)*	***Li1-O***	*1.713(1)*	***Fe-O***	*1.977(1)*	*1.916(1)*
Li1-O	*1.851(3)*	***Li1-O***	*1.843(1)*	***Fe-O***	*2.045(2)*	*1.944(1)*
Li1-O	*2.103(3)*	***Li2-O***	*1.834(1)*	***Fe-O***	*2.125(2)*	*2.059(1)*
Li1-0	*2.217(3)*	***Li2-O***	*1.929(1)*	***Fe-O***		*2.179(1)*
		Li3-O	*1.635(1)*	***Si-O***	*1.977(1)*	*1.622(1)*
		Li3-O	*1.855(1)*	***Si-O***	*2.045(2)*	*1.686(1)*
		Li4-O	*1.830(1)*	***Si-O***	*2.125(2)*	*1.691(1)*
		Li-4O	*1.854(1)*	***Si-O***		*1.710(1)*

Table 7 – Bond lengths derived from the 1-6 Å PDF fits for the Li_2FeSiO_4 $Pmn2_1$ polymorph with the $Pmn2_1$ s.g. and the $P2_1$ s.g.

	$Pmn2_1$		***$P2_1$***		***$Pmn2_1$***	***$P2_1$***
Li1-O	1.763(1)	***Li1-O***	*1.800(1)*	***Fe-O***	*1.607(1)*	*1.942(1)*
Li1-O	1.772(2)	***Li1-O***	*2.234(1)*	***Fe-O***	*2.021(2)*	*1.985(1)*
Li1-O	1.981(1)	***Li-O***	*1.806(1)*	***Fe-O***	*2.025(1)*	*1.992(1)*
Li1-O	2.270(1)	***Li2-O***	*1.830(1)*	***Fe-O***		*2.092(1)*
		Li3-O	*1.596(1)*	***Si-O***	*1.490(1)*	*1.629(1)*
		Li3-O	*1.783(1)*	***Si-O***	*1.657(1)*	*1.641(1)*
		Li4-O	*1.814(1)*	***Si-O***	*1.664(1)*	*1.642(1)*
		Li4-O	*1.940(1)*	***Si-O***		*1.661(1)*

Table 8 – Bond lengths derived from the 1-6 Å PDF fits for the Li_2FeSiO_4 $P2_1$ polymorph with the the $P2_1$ s.g.

	$P2_1$		***$P2_1$***
Li1-O	*1.860(1)*	***Fe-O***	*1.948(1)*
Li1-O	*1.953(1)*	***Fe-O***	*2.013(1)*
Li1-O	*1.744(1)*	***Fe-O***	*2.031(1)*
Li1-0	*1.809(1)*	***Fe-O***	*2.045(1)*
Li2-O	*1.834(1)*	***Si-O***	*1.628(1)*
Li2-O	*1.847(1)*	***Si-O***	*1.669(1)*
Li2-O	*1.819(1)*	***Si-O***	*1.730(1)*
Li2-O	*1.982(1)*	***Si-O***	*1.789(1)*