Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Structural properties and energetics of Li_2FeSiO_4 polymorphs and their delithiated products from first-principles

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Table S1. Crystal-structure Description of Li_xFeSiO_4 (x = 2, 1, 0), Space Group *Pmn2₁*

	Li_2FeSiO_4			Li_1FeSiO_4			$FeSiO_4$		
site	x	y	z	x	y	z	x	y	z
Li1	0.2498	0.3307	0.9423						
Li2	0.2501	0.6693	0.4423	0.2498	0.6648	0.4444			
Li3	0.7498	0.6693	0.4423	0.7498	0.3351	0.9444			
Li4	0.7501	0.3307	0.9423						
Fe1	0.5000	0.8261	0.9360	0.5020	0.8388	0.9453	0.5000	0.8133	0.9779
Fe2	0.0000	0.1738	0.4360	0.0020	0.1612	0.4453	0.0000	0.1866	0.4779
Si1	0.0000	0.8297	0.9512	0.9987	0.8343	0.9492	0.0000	0.8646	0.9762
Si2	0.5000	0.1702	0.4512	0.4987	0.1656	0.4492	0.5000	0.1353	0.4762
O1	0.2145	0.6849	0.8413	0.2270	0.7089	0.8349	0.2210	0.7061	0.9279
O2	0.2854	0.3150	0.3413	0.2761	0.3230	0.3848	0.2789	0.2938	0.4279
O3	0.7145	0.3150	0.3413	0.7270	0.2910	0.3349	0.7210	0.2938	0.4279
O4	0.7854	0.6849	0.8413	0.7761	0.6769	0.8848	0.7789	0.7061	0.9279
O5	0.0000	0.1231	0.8518	0.9771	0.1009	0.8139	0.0000	0.0975	0.8055
O6	0.5000	0.8768	0.3518	0.4771	0.8990	0.3139	0.5000	0.9024	0.3055
O7	0.5000	0.1794	0.7817	0.5192	0.1354	0.7733	0.5000	0.0603	0.7722
O8	0.0000	0.8205	0.2817	0.0192	0.8645	0.2733	0.0000	0.9397	0.2722
	a = 6.3219			a = 6.0813			a = 6.0847		
	b = 5.3935			b = 5.6351			b = 5.7922		
	c = 4.9937			c = 5.0421			c = 5.3621		
	β = 90º			β = 89.243º			β = 90º		

Table S2. Crystal-structure Description of Li_xFeSiO_4 (x = 2, 1, 0), Space Group $P2_1/n$

	Li_2FeSiO_4			Li_1FeSiO_4			$FeSiO_4$		
site	x	y	z	x	y	z	x	y	z
Li1	0.6658	0.7909	0.6715						
Li2	0.3342	0.2090	0.3284						
Li3	0.8342	0.2909	0.8284						
Li4	0.1658	0.7090	0.1715						
Li5	0.5854	0.1928	0.0850	0.6491	0.1631	0.0106			
Li6	0.4145	0.8071	0.9149	0.3508	0.8369	0.9893			
Li7	0.9145	0.6928	0.4149	0.8508	0.6631	0.4893			
Li8	0.0854	0.3071	0.5850	0.1491	0.3369	0.5106			
Fe1	0.2928	0.8018	0.5427	0.3322	0.8344	0.5031	0.2587	0.8158	0.5494
Fe2	0.7071	0.1981	0.4572	0.6677	0.1655	0.4968	0.7413	0.1841	0.4506
Fe3	0.2071	0.3018	0.9572	0.1677	0.3344	0.9968	0.2413	0.3158	0.9506
Fe4	0.7928	0.6981	0.0427	0.8322	0.6655	0.0031	0.7587	0.6841	0.0494
Si1	0.0411	0.8079	0.7905	0.0779	0.8379	0.7563	0.0350	0.8102	0.8223
Si2	0.9588	0.1920	0.2094	0.9220	0.1620	0.2436	0.9650	0.1898	0.1776
Si3	0.4588	0.3079	0.7094	0.4220	0.3379	0.7436	0.4650	0.3102	0.6776
Si4	0.5411	0.6920	0.2905	0.5779	0.6620	0.2563	0.5350	0.6898	0.3223
O1	0.8620	0.6915	0.8217	0.9207	0.7485	0.7567	0.8230	0.7344	0.8654
O2	0.1380	0.3084	0.1782	0.0792	0.2514	0.2432	0.1769	0.2655	0.1345
O3	0.6380	0.1915	0.6782	0.5792	0.2485	0.7432	0.6769	0.2344	0.6345
O4	0.3620	0.8084	0.3217	0.4207	0.7514	0.2567	0.3230	0.7655	0.3654
O5	0.4197	0.2000	0.8873	0.3492	0.2349	0.9545	0.4504	0.2670	0.8520
O6	0.5802	0.7999	0.1126	0.6507	0.7650	0.0454	0.5495	0.7329	0.1479
O7	0.0802	0.7000	0.6126	0.1507	0.7349	0.5454	0.0495	0.7670	0.6479
O8	0.9197	0.2999	0.3873	0.8492	0.2650	0.4545	0.9504	0.2329	0.3520
O9	0.6877	0.7876	0.4372	0.6563	0.7961	0.4484	0.6906	0.8544	0.4156
O10	0.3122	0.2123	0.5627	0.3436	0.2038	0.5515	0.3093	0.1455	0.5843
O11	0.8122	0.2876	0.0627	0.8436	0.2961	0.0515	0.8093	0.3544	0.0843
O12	0.1877	0.7123	0.9372	0.1563	0.7038	0.9484	0.1906	0.6455	0.9156
O13	0.9655	0.8673	0.2152	0.9081	0.8372	0.2265	0.9242	0.8925	0.1429
O14	0.0344	0.1326	0.7847	0.0918	0.1627	0.7734	0.0757	0.1074	0.8570
O15	0.5344	0.3673	0.2847	0.5918	0.3372	0.2734	0.5757	0.3925	0.3570
O16	0.4655	0.6326	0.7152	0.4081	0.6627	0.7265	0.4242	0.6074	0.6429
	a = 8.2865			a = 10.0975			a = 7.1936		
	b = 5.0879			b = 5.0347			b = 5.3401		
	c = 8.3177			c = 6.6521			c = 9.3155		
	β = 98.932°			β = 89.085°			β = 93.355°		

Table S3. Crystal-structure Description of Li_xFeSiO_4 (x = 2, 1, 0), Space Group *Pmnb*

	Li_2FeSiO_4			Li_1FeSiO_4			$FeSiO_4$		
site	x	y	z	x	y	z	x	y	z
Li1	0.0050	0.3314	0.2090	0.0150	0.3313	0.1913			
Li2	0.9949	0.6685	0.7910						
Li3	0.9949	0.1685	0.7090						
Li4	0.0050	0.8314	0.2910	0.0150	0.8313	0.3086			
Li5	0.5050	0.6685	0.7910	0.5150	0.6686	0.8086			
Li6	0.4949	0.3314	0.2090						
Li7	0.4949	0.8314	0.2910						
Li8	0.5050	0.1685	0.7090	0.5150	0.1686	0.6913	0.2517	0.5907	0.1900
Fe1	0.2500	0.5811	0.2006	0.2418	0.5759	0.1857	0.7517	0.4092	0.8099
Fe2	0.7500	0.4188	0.7993	0.7418	0.4240	0.8143	0.7517	0.9092	0.6900
Fe3	0.7500	0.9188	0.7006	0.7418	0.9240	0.6857	0.2517	0.0907	0.3099
Fe4	0.2500	0.0811	0.2993	0.2418	0.0759	0.3143	0.2519	0.4327	0.6947
Si1	0.2500	0.4158	0.6951	0.2498	0.4146	0.6863	0.7519	0.5672	0.3052
Si2	0.7500	0.5841	0.3049	0.7498	0.5854	0.3136	0.7519	0.0672	0.1947
Si3	0.7500	0.0841	0.1951	0.7498	0.0854	0.1863	0.2519	0.9327	0.8052
Si4	0.2500	0.9158	0.8049	0.2498	0.9146	0.8136	0.2516	0.4654	0.3964
O1	0.2500	0.4093	0.3708	0.2253	0.4359	0.3778	0.7516	0.5345	0.6035
O2	0.7500	0.5906	0.6291	0.7253	0.5641	0.6221	0.7516	0.0345	0.8964
O3	0.7500	0.0906	0.8708	0.7253	0.0641	0.8778	0.2516	0.9654	0.1035
O4	0.2500	0.9093	0.1291	0.2253	0.9359	0.1221	0.2516	0.5513	0.8595
O5	0.2500	0.5629	0.7857	0.2729	0.5425	0.8347	0.7516	0.4486	0.1404
O6	0.7500	0.4370	0.2142	0.7729	0.4575	0.1652	0.7516	0.9486	0.3595
O7	0.7500	0.9370	0.2857	0.7729	0.9575	0.3347	0.2516	0.0513	0.6404
O8	0.2500	0.0629	0.7142	0.2729	0.0425	0.6652	0.0310	0.3534	0.7558
O9	0.0380	0.3431	0.8068	0.0231	0.3464	0.7892	0.9724	0.6467	0.2437
O10	0.9619	0.6568	0.1931	0.9766	0.6647	0.2534	0.9724	0.1467	0.2562
O11	0.9619	0.1568	0.3068	0.9766	0.1647	0.2465	0.0310	0.8534	0.7441
O12	0.0380	0.8431	0.6931	0.0231	0.8464	0.7107	0.5310	0.6465	0.2441
O13	0.5380	0.6568	0.1931	0.5231	0.6535	0.2107	0.4724	0.3532	0.7562
O14	0.4619	0.3431	0.8068	0.4766	0.3352	0.7465	0.4724	0.8532	0.7437
O15	0.4619	0.8431	0.6931	0.4766	0.8352	0.7534	0.5310	0.1465	0.2558
O16	0.5380	0.1568	0.3068	0.5231	0.1535	0.2892			
	a = 6.3400			a = 5.9577			a = 6.0202		
	b = 10.7635			b = 11.3231			b = 11.5492		
	c = 5.1010			c = 5.2627			c = 5.3673		
	β = 90º			β = 90º			β = 90º		

Table S4. Selected bond lengths of Li_xFeSiO_4 polymorphs with space group (a) *Pmn2₁*, (b) *P2₁/n*, and (c) *Pmnb*.

(a) *Pmn2₁*

Li_2FeSiO_4	Bond length (Å)			
LiO_4	1.9884	2.0072	1.9518	1.9879
SiO_4	1.6586	1.6586	1.6584	1.6512
FeO_4	2.0152	2.0152	2.0555	2.0940
$LiFeSiO_4$				
LiO_4	1.9557	1.9875	2.0151	2.0023
SiO_4	1.6543	1.6560	1.6543	1.6495
FeO_4	1.9149	1.8936	1.9208	1.8854
$FeSiO_4$				
SiO_4	1.6488	1.6302	1.6460	1.6488
FeO_4	1.8273	1.8309	1.8064	1.8273

(b) *P2₁/n*

Li_2FeSiO_4	Bond lenghth (Å)			
$LiO_4(1)$	1.9719	2.0137	1.9767	1.9865
$LiO_4(2)$	1.9290	1.9853	2.0531	1.9571
SiO_4	1.6560	1.6563	1.6554	1.6535
FeO_4	2.0086	2.0075	2.0991	2.0513
$LiFeSiO_4$				
LiO_4	2.0971	2.0177	2.0317	1.9715
SiO_4	1.6494	1.6568	1.6577	1.6453
FeO_4	1.9159	1.9014	1.8911	1.8920
$FeSiO_4$				
SiO_4	1.6496	1.6503	1.6332	1.6430
FeO_4	1.8208	1.8268	1.8234	1.8152

(c) *Pmnb*

Li_2FeSiO_4	Bond length (Å)			
LiO_4	1.9766	1.9636	1.9485	2.0657
SiO_4	1.6556	1.6495	1.6562	1.6562
FeO_4	2.0003	2.0426	2.1251	2.0003
$LiFeSiO_4$				
LiO_4	2.0345	1.9221	1.9833	2.1236
SiO_4	1.6468	1.6534	1.6510	1.6481
FeO_4	1.9064	1.8836	1.8946	1.8964
$FeSiO_4$				
SiO_4	1.6479	1.6473	1.6449	1.6305
FeO_4	1.8245	1.8225	1.8314	1.8234