Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unveiling the electrochemical mechanisms of the $Li_2Fe(SO_4)_2$ polymorphs by neutron diffraction and density functional theory calculations

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Supplementary Information

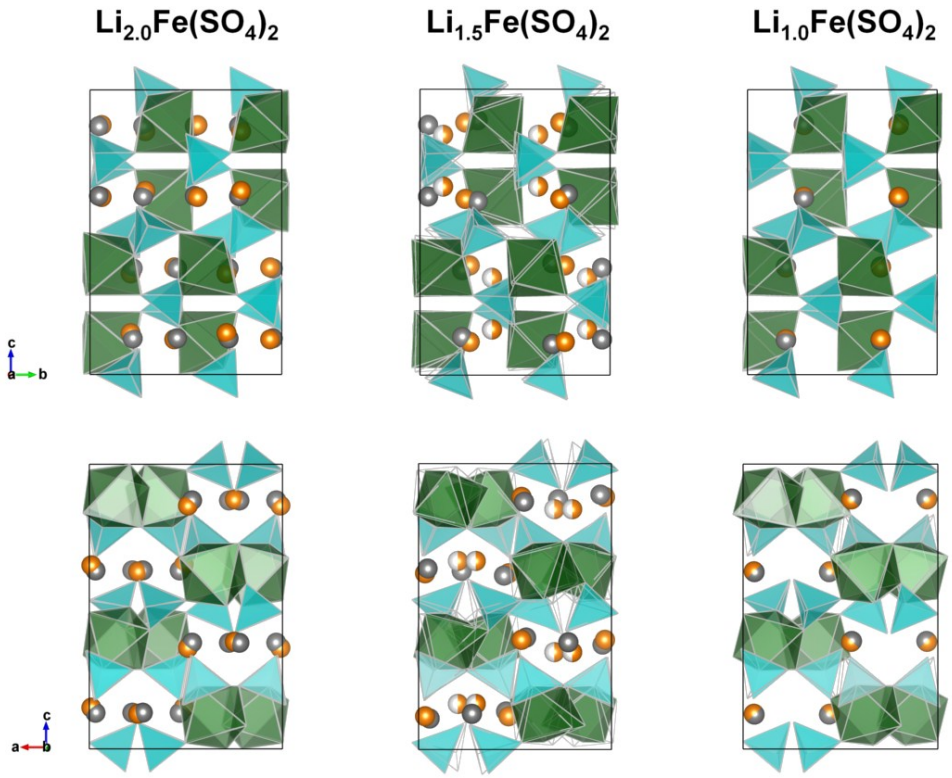

Figure SI 1: Comparison of the structures of the orthorhombic phases $Li_xFe(SO_4)_2$ (x = 2.0, 1.5, 1.0) determined from neutron powder diffraction data (colored) and from DFT calculations (gray lines and balls). Note that for the sake of the comparison the DFT-calculated structure has been here described with the experimental unit cell.

Table SI 1: Structural parameters for orthorhombic $Li_2Fe(SO_4)_2$ calculated by DFT. a_x, a_y, a_z etc. are the cartesian components of the respective lattice vector.

Orthorhombic $Li_2Fe(SO_4)_2$

Space group: *P*1

a = 9.3738 Å *b* = 9.3078 Å *c* = 13.8328 Å

$a = 9.3738\ a_x + 0.0000\ a_y + 0.0000\ a_z$

$b = 0.0000\ b_x + 9.3078\ b_y + 0.0000\ b_z$

$c = 0.0000\ c_x + 0.0000\ c_y + 13.8328\ c_z$

Atom	Occupancy	*x*/*a*	*y*/*b*	*z*/*c*
Li	1.0	0.46791	0.72258	0.37325
Li	1.0	0.53209	0.27742	0.62675
Li	1.0	0.03209	0.27742	0.87325
Li	1.0	0.96791	0.72258	0.12675
Li	1.0	0.53209	0.22258	0.12675
Li	1.0	0.46791	0.77742	0.87325
Li	1.0	0.96791	0.77742	0.62675
Li	1.0	0.03209	0.22258	0.37325
Li	1.0	0.72295	0.54645	0.62722
Li	1.0	0.27705	0.45355	0.37278
Li	1.0	0.77705	0.45355	0.12722
Li	1.0	0.22295	0.54645	0.87278
Li	1.0	0.27705	0.04645	0.87278
Li	1.0	0.72295	0.95355	0.12722
Li	1.0	0.22295	0.95355	0.37278
Li	1.0	0.77705	0.04645	0.62722
Fe	1.0	0.85938	0.60197	0.37690
Fe	1.0	0.14062	0.39803	0.62310
Fe	1.0	0.64062	0.39803	0.87690
Fe	1.0	0.35938	0.60197	0.12310
Fe	1.0	0.14062	0.10197	0.12310
Fe	1.0	0.85938	0.89803	0.87690
Fe	1.0	0.35938	0.89803	0.62310
Fe	1.0	0.64062	0.10197	0.37690
S	1.0	0.66192	0.81199	0.50981
S	1.0	0.33808	0.18801	0.49019
S	1.0	0.83808	0.18801	0.00981
S	1.0	0.16192	0.81199	0.99019
S	1.0	0.33808	0.31199	0.99019
S	1.0	0.66192	0.68801	0.00981
S	1.0	0.16192	0.68801	0.49019
S	1.0	0.83808	0.31199	0.50981
S	1.0	0.57257	0.43082	0.27245
S	1.0	0.42743	0.56918	0.72755
S	1.0	0.92743	0.56918	0.77245
S	1.0	0.07257	0.43082	0.22755
S	1.0	0.42743	0.93082	0.22755
S	1.0	0.57257	0.06918	0.77245
S	1.0	0.07257	0.06918	0.72755
S	1.0	0.92743	0.93082	0.27245
O	1.0	0.50487	0.80219	0.52477

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O	1.0	0.49513	0.19781	0.47523
O	1.0	0.99513	0.19781	0.02477
O	1.0	0.00487	0.80219	0.97523
O	1.0	0.49513	0.30219	0.97523
O	1.0	0.50487	0.69781	0.02477
O	1.0	0.00487	0.69781	0.47523
O	1.0	0.99513	0.30219	0.52477
O	1.0	0.70861	0.96458	0.49761
O	1.0	0.29139	0.03542	0.50239
O	1.0	0.79139	0.03542	0.99761
O	1.0	0.20861	0.96458	0.00239
O	1.0	0.29139	0.46458	0.00239
O	1.0	0.70861	0.53542	0.99761
O	1.0	0.20861	0.53542	0.50239
O	1.0	0.79139	0.46458	0.49761
O	1.0	0.68651	0.73141	0.41792
O	1.0	0.31349	0.26859	0.58208
O	1.0	0.81349	0.26859	0.91792
O	1.0	0.18651	0.73141	0.08208
O	1.0	0.31349	0.23141	0.08208
O	1.0	0.68651	0.76859	0.91792
O	1.0	0.18651	0.76859	0.58208
O	1.0	0.81349	0.23141	0.41792
O	1.0	0.74319	0.75192	0.59250
O	1.0	0.25681	0.24808	0.40750
O	1.0	0.75681	0.24808	0.09250
O	1.0	0.24319	0.75192	0.90750
O	1.0	0.25681	0.25192	0.90750
O	1.0	0.74319	0.74808	0.09250
O	1.0	0.24319	0.74808	0.40750
O	1.0	0.75681	0.25192	0.59250
O	1.0	0.47979	0.50115	0.34480
O	1.0	0.52021	0.49885	0.65520
O	1.0	0.02021	0.49885	0.84480
O	1.0	0.97979	0.50115	0.15520
O	1.0	0.52021	0.00115	0.15520
O	1.0	0.47979	0.99885	0.84480
O	1.0	0.97979	0.99885	0.65520
O	1.0	0.02021	0.00115	0.34480
O	1.0	0.52457	0.46054	0.17053
O	1.0	0.47543	0.53946	0.82947
O	1.0	0.97543	0.53946	0.67053
O	1.0	0.02457	0.46054	0.32947
O	1.0	0.47543	0.96054	0.32947
O	1.0	0.52457	0.03946	0.67053
O	1.0	0.02457	0.03946	0.82947
O	1.0	0.97543	0.96054	0.17053
O	1.0	0.56969	0.27086	0.28027
O	1.0	0.43031	0.72914	0.71973
O	1.0	0.93031	0.72914	0.78027
O	1.0	0.06969	0.27086	0.21973
O	1.0	0.43031	0.77086	0.21973
O	1.0	0.56969	0.22914	0.78027

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O	1.0	0.06969	0.22914	0.71973
O	1.0	0.93031	0.77086	0.28027
O	1.0	0.72196	0.48583	0.27884
O	1.0	0.27804	0.51417	0.72116
O	1.0	0.77804	0.51417	0.77884
O	1.0	0.22196	0.48583	0.22116
O	1.0	0.27804	0.98583	0.22116
O	1.0	0.72196	0.01417	0.77884
O	1.0	0.22196	0.01417	0.72116
O	1.0	0.77804	0.98583	0.27884

Table SI 2: Structural parameters for orthorhombic $Li_{1.5}Fe(SO_4)_2$ calculated by DFT. a_x, a_y, a_z etc. are the cartesian components of the respective lattice vector.

Orthorhombic $Li_{1.5}Fe(SO_4)_2$

Space group: *P*1

a = 9.3651 Å *b* = 9.1963 Å *c* = 13.8307 Å

$a = 9.36425\ a_x - 0.12609\ a_y + 0.0000\ a_z$

$b = -0.11786\ b_x + 9.19557\ b_y + 0.0000\ b_z$

$c = 0.0000\ c_x + 0.0000\ c_y + 13.83073 c_z$

Atom	Occupancy	*x*/*a*	*y*/*b*	*z*/*c*
Li	1.0	0.27650	0.04236	0.87526
Li	1.0	0.72350	0.95764	0.12474
Li	1.0	0.22350	0.95764	0.37526
Li	1.0	0.77650	0.04236	0.62474
Li	1.0	0.44275	0.69657	0.39159
Li	1.0	0.55725	0.30343	0.60841
Li	1.0	0.05725	0.30343	0.89159
Li	1.0	0.94275	0.69657	0.10841
Li	1.0	0.54635	0.22204	0.13299
Li	1.0	0.45365	0.77796	0.86701
Li	1.0	0.95365	0.77796	0.63299
Li	1.0	0.04635	0.22204	0.36701
Fe	1.0	0.85965	0.60532	0.37389
Fe	1.0	0.14035	0.39468	0.62611
Fe	1.0	0.64035	0.39468	0.87389
Fe	1.0	0.35965	0.60532	0.12611
Fe	1.0	0.13789	0.11126	0.12657
Fe	1.0	0.86211	0.88874	0.87343
Fe	1.0	0.36211	0.88874	0.62657
Fe	1.0	0.63789	0.11126	0.37343
S	1.0	0.66559	0.81692	0.51119
S	1.0	0.33441	0.18308	0.48881
S	1.0	0.83441	0.18308	0.01119
S	1.0	0.16559	0.81692	0.98881
S	1.0	0.34731	0.31331	0.99654
S	1.0	0.65269	0.68669	0.00346
S	1.0	0.15269	0.68669	0.49654
S	1.0	0.84731	0.31331	0.50346
S	1.0	0.57559	0.44461	0.27608
S	1.0	0.42441	0.55539	0.72392
S	1.0	0.92441	0.55539	0.77608
S	1.0	0.07559	0.44461	0.22392
S	1.0	0.42251	0.92830	0.22880
S	1.0	0.57749	0.07170	0.77120
S	1.0	0.07749	0.07170	0.72880
S	1.0	0.92251	0.92830	0.27120
O	1.0	0.50933	0.78788	0.52348
O	1.0	0.49067	0.21212	0.47652
O	1.0	0.99067	0.21212	0.02348
O	1.0	0.00933	0.78788	0.97652
O	1.0	0.50377	0.30464	0.97451
O	1.0	0.49623	0.69536	0.02549
O	1.0	0.99623	0.69536	0.47451

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O	1.0	0.00377	0.30464	0.52549
O	1.0	0.69524	0.97443	0.48971
O	1.0	0.30476	0.02557	0.51029
O	1.0	0.80476	0.02557	0.98971
O	1.0	0.19524	0.97443	0.01029
O	1.0	0.30585	0.46570	0.01529
O	1.0	0.69415	0.53430	0.98471
O	1.0	0.19415	0.53430	0.51529
O	1.0	0.80585	0.46570	0.48471
O	1.0	0.70380	0.72934	0.42313
O	1.0	0.29620	0.27066	0.57687
O	1.0	0.79620	0.27066	0.92313
O	1.0	0.20380	0.72934	0.07687
O	1.0	0.32915	0.22666	0.08716
O	1.0	0.67085	0.77334	0.91284
O	1.0	0.17085	0.77334	0.58716
O	1.0	0.82915	0.22666	0.41284
O	1.0	0.74888	0.78157	0.59711
O	1.0	0.25112	0.21843	0.40289
O	1.0	0.75112	0.21843	0.09711
O	1.0	0.24888	0.78157	0.90289
O	1.0	0.26108	0.25430	0.91587
O	1.0	0.73892	0.74570	0.08413
O	1.0	0.23892	0.74570	0.41587
O	1.0	0.76108	0.25430	0.58413
O	1.0	0.48718	0.50075	0.35307
O	1.0	0.51282	0.49925	0.64693
O	1.0	0.01282	0.49925	0.85307
O	1.0	0.98718	0.50075	0.14693
O	1.0	0.51766	0.99533	0.15547
O	1.0	0.48234	0.00467	0.84453
O	1.0	0.98234	0.00467	0.65547
O	1.0	0.01766	0.99533	0.34453
O	1.0	0.51795	0.47960	0.17667
O	1.0	0.48205	0.52040	0.82333
O	1.0	0.98205	0.52040	0.67667
O	1.0	0.01795	0.47960	0.32333
O	1.0	0.47166	0.96025	0.32980
O	1.0	0.52834	0.03975	0.67020
O	1.0	0.02834	0.03975	0.82980
O	1.0	0.97166	0.96025	0.17020
O	1.0	0.58167	0.28172	0.27617
O	1.0	0.41833	0.71828	0.72383
O	1.0	0.91833	0.71828	0.77617
O	1.0	0.08167	0.28172	0.22383
O	1.0	0.42180	0.76430	0.22209
O	1.0	0.57820	0.23570	0.77791
O	1.0	0.07820	0.23570	0.72209
O	1.0	0.92180	0.76430	0.27791
O	1.0	0.72466	0.50782	0.28033
O	1.0	0.27534	0.49218	0.71967
O	1.0	0.77534	0.49218	0.78033
O	1.0	0.22466	0.50782	0.21967
O	1.0	0.27405	0.98048	0.22175
O	1.0	0.72595	0.01952	0.77825
O	1.0	0.22595	0.01952	0.72175
O	1.0	0.77405	0.98048	0.27825

Table SI 3: Structural parameters for orthorhombic $Li_{1.0}Fe(SO_4)_2$ calculated by DFT. a_x, a_y, a_z etc. are the cartesian components of the respective lattice vector.

Orthorhombic $Li_{1.0}Fe(SO_4)_2$

Space group *P*1

a = 9.2941 Å *b* = 9.0511 Å *c* = 13.7374 Å

$a = 0.0000\ a_x + 9.0511\ a_y + 0.0000\ a_z$

$b = 9.2941\ b_x + 0.0000\ b_y + 0.0000\ b_z$

$c = 0.0000\ c_x + 0.0000\ c_y - 13.7374\ c_z$

Atom	Occupancy	*x*/*a*	*y*/*b*	*z*/*c*
Li	1.0	0.70275	0.44174	0.62134
Li	1.0	0.29725	0.55826	0.37866
Li	1.0	0.29725	0.05826	0.12134
Li	1.0	0.70275	0.94174	0.87866
Li	1.0	0.20275	0.55826	0.87866
Li	1.0	0.79725	0.44174	0.12134
Li	1.0	0.79725	0.94174	0.37866
Li	1.0	0.20275	0.05826	0.62134
Fe	1.0	0.61041	0.86010	0.62657
Fe	1.0	0.38959	0.13990	0.37343
Fe	1.0	0.38959	0.63990	0.12657
Fe	1.0	0.61041	0.36010	0.87343
Fe	1.0	0.11041	0.13990	0.87343
Fe	1.0	0.88959	0.86010	0.12657
Fe	1.0	0.88959	0.36010	0.37343
Fe	1.0	0.11041	0.63990	0.62657
S	1.0	0.81650	0.65667	0.49103
S	1.0	0.18350	0.34333	0.50897
S	1.0	0.18350	0.84333	0.99103
S	1.0	0.81650	0.15667	0.00897
S	1.0	0.31650	0.34333	0.00897
S	1.0	0.68350	0.65667	0.99103
S	1.0	0.68350	0.15667	0.50897
S	1.0	0.31650	0.84333	0.49103
S	1.0	0.44128	0.57976	0.72462
S	1.0	0.55872	0.42024	0.27538
S	1.0	0.55872	0.92024	0.22462
S	1.0	0.44128	0.07976	0.77538
S	1.0	0.94128	0.42024	0.77538
S	1.0	0.05872	0.57976	0.22462
S	1.0	0.05872	0.07976	0.27538
S	1.0	0.94128	0.92024	0.72462
O	1.0	0.79208	0.49836	0.47425
O	1.0	0.20792	0.50164	0.52575
O	1.0	0.20792	0.00164	0.97425
O	1.0	0.79208	0.99836	0.02575
O	1.0	0.29208	0.50164	0.02575
O	1.0	0.70792	0.49836	0.97425
O	1.0	0.70792	0.99836	0.52575
O	1.0	0.29208	0.00164	0.47425
O	1.0	0.97439	0.68405	0.51563
O	1.0	0.02561	0.31595	0.48437
O	1.0	0.02561	0.81595	0.01563

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O	1.0	0.97439	0.18405	0.98437
O	1.0	0.47439	0.31595	0.98437
O	1.0	0.52561	0.68405	0.01563
O	1.0	0.52561	0.18405	0.48437
O	1.0	0.47439	0.81595	0.51563
O	1.0	0.72740	0.68724	0.58185
O	1.0	0.27260	0.31276	0.41815
O	1.0	0.27260	0.81276	0.08185
O	1.0	0.72740	0.18724	0.91815
O	1.0	0.22740	0.31276	0.91815
O	1.0	0.77260	0.68724	0.08185
O	1.0	0.77260	0.18724	0.41815
O	1.0	0.22740	0.81276	0.58185
O	1.0	0.77250	0.74203	0.40819
O	1.0	0.22750	0.25797	0.59181
O	1.0	0.22750	0.75797	0.90819
O	1.0	0.77250	0.24203	0.09181
O	1.0	0.27250	0.25797	0.09181
O	1.0	0.72750	0.74203	0.90819
O	1.0	0.72750	0.24203	0.59181
O	1.0	0.27250	0.75797	0.40819
O	1.0	0.49627	0.48938	0.64662
O	1.0	0.50373	0.51062	0.35338
O	1.0	0.50373	0.01062	0.14662
O	1.0	0.49627	0.98938	0.85338
O	1.0	0.99627	0.51062	0.85338
O	1.0	0.00373	0.48938	0.14662
O	1.0	0.00373	0.98938	0.35338
O	1.0	0.99627	0.01062	0.64662
O	1.0	0.47881	0.52115	0.82391
O	1.0	0.52119	0.47885	0.17609
O	1.0	0.52119	0.97885	0.32391
O	1.0	0.47881	0.02115	0.67609
O	1.0	0.97881	0.47885	0.67609
O	1.0	0.02119	0.52115	0.32391
O	1.0	0.02119	0.02115	0.17609
O	1.0	0.97881	0.97885	0.82391
O	1.0	0.27405	0.58769	0.72567
O	1.0	0.72595	0.41231	0.27433
O	1.0	0.72595	0.91231	0.22567
O	1.0	0.27405	0.08769	0.77433
O	1.0	0.77405	0.41231	0.77433
O	1.0	0.22595	0.58769	0.22567
O	1.0	0.22595	0.08769	0.27433
O	1.0	0.77405	0.91231	0.72567
O	1.0	0.50161	0.72917	0.71960
O	1.0	0.49839	0.27083	0.28040
O	1.0	0.49839	0.77083	0.21960
O	1.0	0.50161	0.22917	0.78040
O	1.0	0.00161	0.27083	0.78040
O	1.0	0.99839	0.72917	0.21960
O	1.0	0.99839	0.22917	0.28040
O	1.0	0.00161	0.77083	0.71960

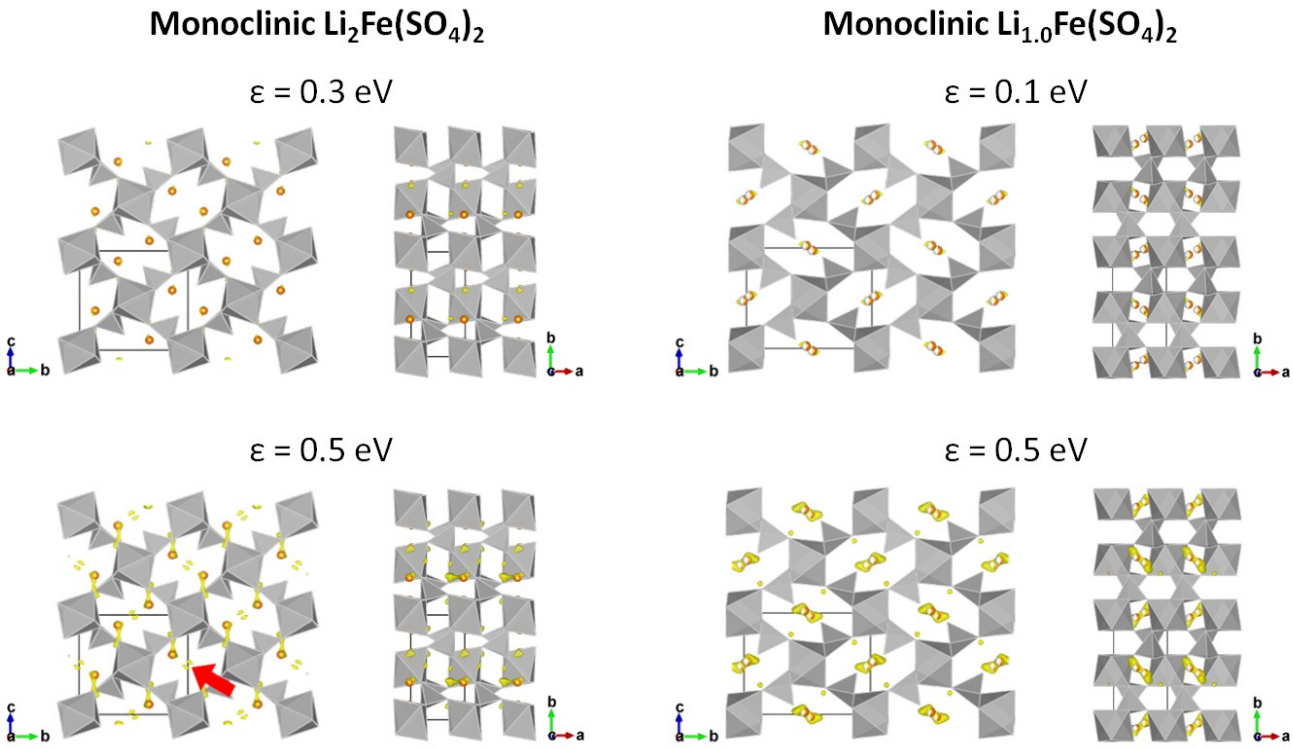

Figure SI 2: BVEL maps of monoclinic $Li_2Fe(SO_4)_2$ for chosen low energy cut-off values ε (indicated in the figure) showing the appearance of a local minimum (indicated by the red arrows) at (½ 0 ½). Grey polyhedra represent the SO_4 tetrahedra and FeO_6 octahedra of the main frameworks of the structures, orange balls indicate the position of the Li atoms as found experimentally, yellow volumes represent the volume of stability of a Li atom for the given energy cut-off ε.

Table SI 4: Band gap energies E_g for both $Li_2M(SO_4)_2$ polymorphs obtained from UV/Vis spectroscopy with the Kubelka-Munk formalism.

Band Gap E_g	$Li_2Mn(SO_4)_2$	$Li_2Fe(SO_4)_2$	$Li_2Co(SO_4)_2$	$Li_2Ni(SO_4)_2$	$Li_2Zn(SO_4)_2$
Monoclinic	5.3(1) eV	5.5(3) eV	5.3(3) eV	–	5.3(2) eV
Orthorhombic	–	5.2(5) eV	5.4(1) eV	5.5(1) eV	5.3(2) eV

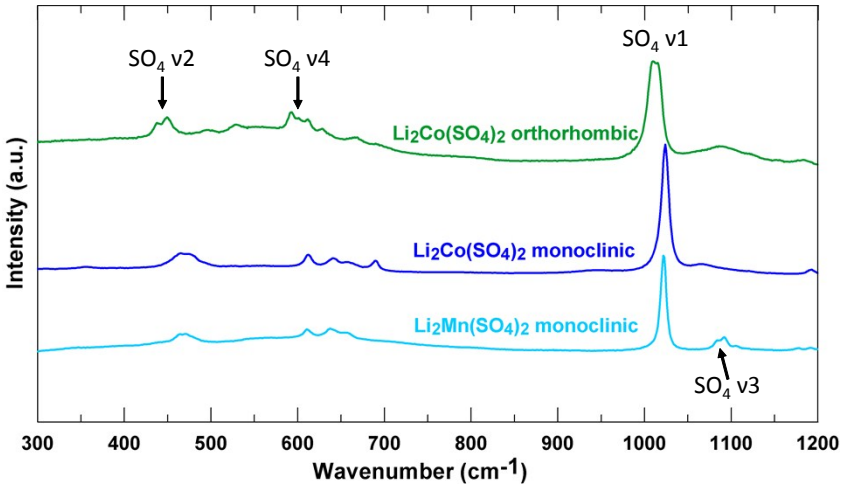

Figure SI 3: Raman spectra of orthorhombic and monoclinic $Li_2Co(SO_4)_2$ and monoclinic $Li_2Mn(SO_4)_2$. The different Raman active modes of the SO_4 groups as described in the main manuscript are indicated. The spectra were recorded outside of the DAC.