Supporting information

Neutron and X-ray diffraction

Samples were sealed in vanadium containers inside a dry He-filled glove box for neutron diffraction studies at the time-of-flight POWGEN powder diffractometer at the Oak Ridge National Laboratory. Neutron diffraction experiments were carried out at 300 K. Neutron diffraction data was also collected at 80K (to more accurately pin down atomic displacement parameters) for $LiFe_{0.8}Mn_{0.2}SO_4F$ and $LiFe_{0.5}Mn_{0.5}SO_4F$, although the data is not reported here since the results are very similar to the 300K data. For X-ray diffraction, the crystalline powders were placed on a zero-background anaerobically-maintained holder to prevent any possible reaction with atmospheric moisture, with measures taken to prevent preferred orientation. Neutron data were fitted using the GSAS refinement platform using profile function 3, and absorption function 0, with absorption constrained to the same value for both banks owing to the specifics of the 3rd generation POWGEN diffractometer. Absorption correction was necessary due to the presence of ^{6}Li in natural Li. The same GSAS platform was used for X-ray data and, obviously, for the combined neutron/X-ray refinements.

When refining the occupancies of three elements on two sites a common method of splitting one element into two parts (in our case – Li) was used. The total occupancy of Li is reported. Fractional coordinates of all elements on the same site were constrained to be the same. Appropriate constraints were applied to the occupancies of Li, Fe and Mn in order to maintain the proper sample stoichiometry and a total occupancy of each metal site of 1, and the separate occupancies were then refined. Table S1 (below) summarizes the refinement results.

With reference to specific asterisked points in Table S1 (see below):

* Li U_{iso}'s were constrained to the same value for sites 1 and 2. Both Fe and Mn U_{iso}'s were constrained to the same value for sites 1 and 2.

Table S1. Refined structural parameters of $LiMnSO_4F$, $LiFe_{0.5}Mn_{0.5}SO_4F$, $LiFe_{0.8}Mn_{0.2}SO_4F$, $LiFe_{0.9}Mn_{0.1}SO_4F$ and $LiFeSO_4F$. Rietveld analyses of powder neutron and X-ray diffraction data were carried out in the *C2/c* space group with all atoms in general positions.

		$LiMnSO_4F$ 300K XRD	$LiFe_{0.5}Mn_{0.5}SO_4F$ 300K XRD + neutron combined	$LiFe_{0.8}Mn_{0.2}SO_4F$ 300K XRD + neutron combined	$LiFe_{0.9}Mn_{0.1}SO_4F$ 300K XRD+ neutron combined	$LiFeSO_4F$ 300K XRD
a (Å)		13.2406(2)	3.1490(3)	13.0713(2)	13.0540(2)	13.0300(7)
b (Å)		6.4082(1)	6.4005(1)	6.3958(1)	6.3958(1)	6.3924(3)
c (Å)		10.0229(2)	9.9394(2)	9.8735(2)	9.8589(2)	9.8391(7)
β (deg)		120.499(1)	120.163(1)	119.891(1)	119.819(1)	119.750(2)
V (Å^3)		732.76(3)	723.24(4)	715.63(3)	714.15(2)	711.51(8)
Li1/ Fe1/Mn1	frac	**0.484(3)/ 0/0.516(3)**	**0.465(5)/ 0.313(3)/0.222(5)**	**0.430(3)/ 0.475(3)/0.095(3)**	**0.408(3)/ 0.529(3)/0.063(3)**	**0.35(1)/ 0.65(1)/0**
	x	0.6474(3)	0.6462(4)	0.6462(2)	0.6461(3)	0.6455(8)
	y	0.8942(5)	0.8980(8)	0.8934(5)	0.8945(5)	0.898(1)
	z	0.8449(3)	0.8425(5)	0.8473(3)	0.8473(3)	0.8446(9)
	U_{iso} (Å^2) Li/(Fe,Mn)	0.029(1)	0.047(2)	0.026(1)	0.016(1)	0.050(3)
Li2/ Fe2/Mn2	frac	**0.516(3)/ 0/0.484(3)**	**0.535(5)/ 0.187(3)/0.278(5)**	**0.570(3)/ 0.325(3)/0.105(3)**	**0.592(3)/ 0.371(3)/0.037(3)**	**0.65(1)/ 0.35(1)/0**
	x	0.9481(2)	0.9522(4)	0.9475(3)	0.9464(4)	0.950(1)
	y	0.2526(5)	0.2539(9)	0.2516(7)	0.2492(8)	0.249(2)
	z	0.0068(3)	0.0063(6)	0.0025(5)	0.0035(5)	0.011(1)
	U_{iso} (Å^2) Li/(Fe,Mn)	0.022(1)	0.065(3)	0.031(1)	0.016(2)	0.028(5)
S	*x*	0.3271(3)	0.3263(3)	0.3276(3)	0.3265(3)	0.3295(8)
	y	0.5912(4)	0.5909(5)	0.5936(5)	0.5944(6)	0.592(1)
	z	0.1976(3)	0.1951(4)	0.1966(3)	0.1960(4)	0.1956(9)
	U_{iso} (Å^2)	0.0280(6)	0.032(1)	0.0307(9)	0.0205(9)	0.028(2)
F	*x*	0.9849(4)	0.9850(2)	0.9864(3)	0.9851(3)	0.987(1)
	y	0.4001(8)	0.4052(5)	0.4042(5)	0.4034(5)	0.412(2)
	z	0.6079(4)	0.6074(3)	0.6089(3)	0.6086(4)	0.617(1)
	U_{iso} (Å^2)	0.024(1)	0.031(1)	0.040(1)	0.029(1)	0.020
O1	*x*	0.2132(4)	0.2165(3)	0.2157(3)	0.2161(3)	0.224(1)
	y	0.6426(8)	0.6416(4)	0.6406(4)	0.6412(4)	0.655(2)
	z	0.1857(5)	0.1922(3)	0.1918(3)	0.1928(3)	0.177(1)
	U_{iso} (Å^2)	0.023(2)	0.0200(9)	0.0261(8)	0.0148(7)	0.020
O2	*x*	0.5811(5)	0.5826(2)	0.5808(2)	0.5813(3)	0.586(2)
	y	0.5363(8)	0.5342(4)	0.5358(4)	0.5343(4)	0.516(2)
	z	0.1451(6)	0.1450(4)	0.1448(3)	0.1452(3)	0.147(2)
	U_{iso} (Å^2)	0.020(2)	0.0163(7)	0.0264(8)	0.0138(7)	0.020
O3	*x*	0.6949(4)	0.6931(2)	0.6921(2)	0.6927(2)	0.704(1)
	y	0.4189(8)	0.4176(5)	0.4162(5)	0.4166(5)	0.413(3)
	z	0.4152(5)	0.4129(3)	0.4127(3)	0.4132(3)	0.419(1)
	U_{iso} (Å^2)	0.022(2)	0.0176(8)	0.0280(9)	0.0132(7)	0.020
O4	*x*	0.6338(4)	0.6348(2)	0.6352(2)	0.6350(2)	0.643(2)
	y	0.7765(8)	0.7743(4)	0.7744(4)	0.7738(4)	0.778(2)
	z	0.3545(5)	0.3561(3)	0.3576(3)	0.3587(3)	0.364(2)
	U_{iso} (Å^2)	0.019(2)	0.0165(8)	0.0242(8)	0.0106(6)	0.020
χ^2		2.31	2.65	5.90	4.26	7.25
R_p (%)		1.50	1.30	1.56	1.76	1.78
R_{wp} (%)		1.97	2.14	2.33	2.81	2.65