Supplementary information for the article:

Milović, M.D., Vasić Anićijević, D.D., Jugović, D., Anićijević, V.J., Veselinović, L., Mitrić, M., Uskoković, D., 2019. On the presence of antisite defect in monoclinic Li2FeSiO4 – A combined X-Ray diffraction and DFT study. Solid State Sciences 87, 81–86. https://doi.org/10.1016/j.solidstatesciences.2018.11.008

Supplementary

Table S1. Lattice and structural parameters of the prepared Li_2FeSiO_4 (s.g. #14, $P2_1/c$).

Lattice parameters: a = 8.2295 Å, b = 5.0170 Å, c = 10.6808 Å, β = 130.436 ° Cell volume: 335.65 Å^3						
Atomic position	Wyckoff symbol	Fractional coordinates			B (Å^2)	Occ.
		x	y	z		
Li1	4e	0.101	0.854	0.355	2.8	1.0
Li2	4e	0.484	0.199	0.406	1.66	0.940
Fe1	4e	0.254	0.7995	0.7110	1.66	0.940
Li3	4e	= Fe1	= Fe1	= Fe1	1.66	0.060
Fe2	4e	= Li2	= Li2	= Li2	1.66	0.060
Si	4e	0.760	0.817	0.961	1.46	1.0
O1	4e	0.927	0.737	0.116	2.09	1.0
O2	4e	0.497	0.218	0.599	2.09	1.0
O3	4e	0.759	0.761	0.321	2.09	1.0
O4	4e	0.248	0.878	0.036	2.09	1.0

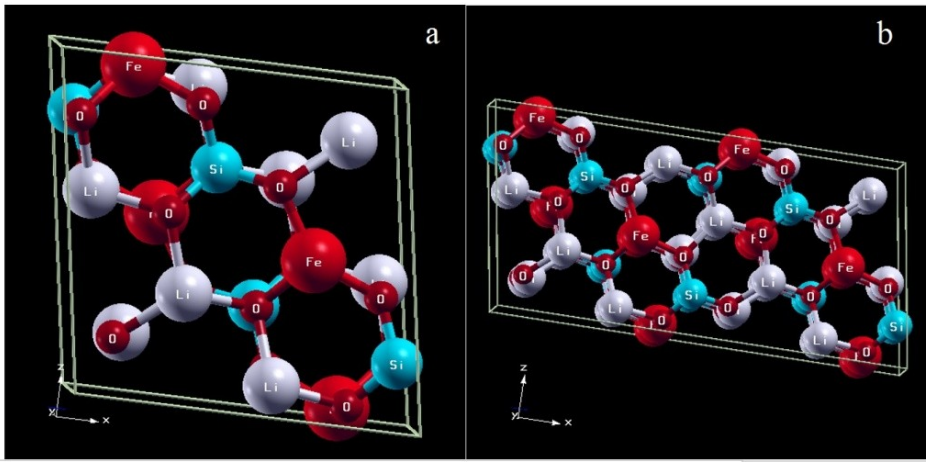

Figure S1. Periodic cells used in DFT calculations: a) 32-atom cell, b) 128-atom cell.

Estimation of configuration entropy arising from antisite

Boltzmann's equation:

$$S = k_b \ln W \qquad (1)$$

Entropy change due to antisite defect formation:

$$\Delta S = S_{(antisite)} - S_{(pristine)} = S_{(antisite)} \qquad (2)$$

since $S_{(pristine)} = 0$. (There is only one possible arrangement W=1, where all atoms are placed on its own positions).

If Fe- Li2 antisite interchange occurs, the number of possible arrangements, due to the mixing of Li and Fe atoms, is given by

$$W = N_{Li2}!/(N_{Li2/Li}!N_{Li2/Fe}!) \quad x \quad N_{Fe}!/(N_{Fe/Fe}!N_{Fe/Li}!) \qquad (3)$$

Where $N_{Li2}!/(N_{Li2/Li}!N_{Li2/Fe}!)$ is the number of arrangements arising from the mixing of lithium and iron on Li2 sites; N_{Li2} is the number of Li2 positions, $N_{Li2/Li}$ is the number of Li2 positions occupied by lithium and $N_{Li2/Fe}$ is the number of Li2 positions occupied by iron ($N_{Li2} = N_{Li2/Li} + N_{Li2/Fe}$). And $N_{Fe}!/(N_{Fe/Fe}!N_{Fe/Li}!)$ is the the number of arrangements arising from the mixing of lithium and iron on Fe sites.

For every arrangement of atoms on Li2 sites there is $N_{Fe}!/(N_{Fe/Fe}!N_{Fe/Li}!)$ number of arrangements on Fe sites, and since $N_{Li2} = N_{Fe}$, $N_{Li2/Li} = N_{Fe/Fe}$, $N_{Li2/Fe} = N_{Fe/Li}$, the number of all possible arrangements is given by the equation (3) or by

$$W = (N_{Li2}!/(N_{Li2/Li}!N_{Li2/Fe}!))^2 \qquad (4)$$

If antisite interchange occurs in the amount of 25% (32-atom cell, $N_{Li2} = N_{Fe}= 4$) there is 4!/(3!1!) number of arrangements on Li2 sites and the same number of arrangements on Fe sites, while the total number of arrangements is

W = 16.

Similarly, if antisite interchange occurs in the amount of 6.75% (128-atom supercell, $N_{Li2} = N_{Fe}= 16$) there is 16!/(15!1!) number of arrangements on Li2 sites and the total number of arrangements is

W = 256.

The configuration entropy change due to 6.75% antisite (in 128-atom supercell) therefore is

$$\Delta S = k_b \ln(N_{Li2}!/(N_{Li2/Li}!N_{Li2/Fe}!))^2 \approx 47.8 \times 10^{-5} \text{ eV/K}$$

and per elementary cell, $\Delta S \approx 11.95 \times 10^{-5}$ eV/K.