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A Fully Ordered Triplite, LiCuSO₄F

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Batteries are a major technological challenge in this new century as they stand as a key way to make a more efficient use of energy. Rechargeable Li-ion batteries, by having the highest energy density of any such device, have emerged as the technology of choice for powering electric vehicles and show great promises for grid applications. For such promises to fully materialize, the quest for new positive electrode materials showing safety, sustainability and cost advantages must continue. Progresses have been recently achieved with the arrival of polyanionic compounds. Among them LiFePO₄ is the most attractive, although its energy density is penalized by the low redox voltage (3.45 V vs. Li⁺/Li⁰) of the Fe³⁺/Fe²⁺ redox couple.

A path to increase this redox voltage, as described earlier by Goodenough et al.¹, relies on the feasibility to tune the redox potential of polyanionic compounds via the inductive effect. Pursuing chemical substitutions on the anionic sites, a new *triplite* LiFeSO₄F phase showing a redox voltage of 3.9 V vs. Li⁺/Li⁰ was recently synthesized.² Another way to modify the redox potential of polyanionic compounds consists in changing the nature of the 3d-metal. Recent DFT calculations have indicated that potentials as high as 5.1 V should be achievable for *tavorite* LiCuSO₄F.³ This, combined with our recent finding of a 4.7 V redox activity in Li₂CuO(SO₄)₂⁴, was an impetus to further explore the Cu-based fluorosulfate chemistry which so far counts a sole member, the electrochemically inactive *tavorite* NaCuSO₄F phase⁵.

Herein we report the synthesis and physical properties of a newly synthesized LiCuSO₄F phase. Interestingly, we show that this new compound crystallizes in a fully-ordered *triplite* structure with M₁ being fully occupied with Cu and M₂ with Li. This is, to the best of our knowledge, the first experimental realization of *triplite* without any site mixing. This ordered *triplite* phase, whose stability was confirmed by DFT calculations, was characterized for its electrochemical and transport properties.

Anhydrous CuSO₄ (Sigma Aldrich, 99%) and LiF (Sigma Aldrich, 300 mesh) were used as Cu and Li-based precursors

for the targeted phase. Stoichiometric amounts of powders were thoroughly ball milled, pressed into a pellet and annealed at 400°C - 415°C in an alumina boat for 8h under argon flow. The recovered pellet, once scrapped to remove a thin greenish film of previously reported Li₂Cu₂O(SO₄)₂, was grounded for XRD and SEM characterizations. The XRD powder pattern shows sharp reflections reminiscent of a new phase. In agreement to the nominal composition, Cu to S and Cu to F atomic ratios of 1 were confirmed by energy dispersive X-ray analysis and absorption analysis (Supporting Information, Note 1 and Figure S1).

The structure of LiCuSO₄F was solved from X-ray powder diffraction coupled with neutron powder diffraction. The finely ground yellowish powder was loaded in a 0.7 mm diameter capillary and the sample was measured in transmission mode ($\lambda=0.41374$ Å) on the 11-BM beamline at Argonne National Lab. The XRD pattern of the as-prepared powder shows the presence of many sharp peaks coexisting with tiny peaks attributed to CuSO₄ and Li₂Cu₂O(SO₄)₂ which were treated with the Rietveld method; all remaining peaks were attributed to LiCuSO₄F. These could be indexed using the Dcivol program⁶ in a C-centered monoclinic unit cell, with lattice parameters $a=12.83164(12)$ Å, $b=6.13124(6)$ Å, $c=10.01640(11)$ Å and $\beta=117.3549(7)^\circ$, ie structural characteristics of *triplite*. Systematic extinctions are consistent with the C₂/c space group, which was further confirmed by electron diffraction (Supporting Information, Figure S2). The corresponding volume ($V=699.918(12)$ Å³) is suitable to accommodate eight formulae per unit cell. The structure was then refined from Rietveld refinement against high resolution neutron powder diffraction data recorded on the same powder at HRPT, SINQ (PSI, Switzerland) with a wavelength of 1.495 Å (Figure 1), starting from structural models derived from the *triplite* crystal structure.

The refined structural parameters for LiCuSO₄F are gathered in Supporting Information, Table S1, and the structure of LiCuSO₄F is shown in Figure 2. Cu is coordinated to O₁, O₂, O₃, F at distances ranging between 1.88 and 1.98 Å (Figure 2c,d), which gives an almost square

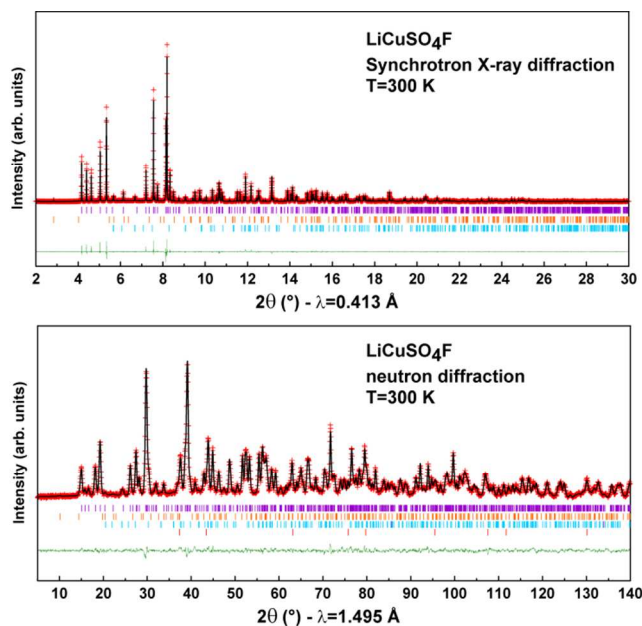


Figure 1. Rietveld refinement of synchrotron and neutron diffraction patterns of LiCuSO_4F ($T=300\text{ K}$). The red crosses, black continuous line and bottom green line represent the observed, calculated, and difference patterns, respectively. Vertical tick bars mark the Bragg reflections (from top to bottom): purple: LiCuSO_4F (95%); orange: $\text{Li}_2\text{Cu}_2\text{O}(\text{SO}_4)_2$ (1%); blue: CuSO_4 (3%); red: LiF (1%, seen from neutron diffraction only).

planar coordination as commonly observed for this Jahn-Teller $3d^9$ cation. When larger distances are considered, we notice a fifth fluorine ligand at 2.34 \AA (Figures 2b,c) and an oxygen atom at 2.62 \AA , reminiscent of highly elongated octahedra linked by alternate F-F and O-O edges (Figure 2e). Therefore, if we consider metal-ligands at distances below 2.5 \AA , Cu is coordinated by three oxygen and two fluorine atoms to form CuO_3F_2 square-based pyramid which are linked via F-F edges, leading to $\text{Cu}_2\text{O}_6\text{F}_2$ dimers (Figure 2a). These $\text{Cu}_2\text{O}_6\text{F}_2$ entities are connected through SO_4 tetrahedra so as to form layers stacked along $[001]^*$ (Figure 2b). The lithium environment is easier to describe unambiguously as it adopts a similar coordination with distorted LiO_4F_2 octahedra sharing alternatively F-F and O-O bonds (Figure 2f). Therefore, one-dimensional pathways for Li conduction may occur along $[010]$ in LiCuSO_4F . It is worth noting that the structure of LiCuSO_4F is very close to the one observed for $\text{Cu}_2\text{PO}_4\text{F}$,⁷ in particular for the copper environment (Supporting Information, Figure S3).

This LiCuSO_4F *triplite* structure differs from those reported for LiFeSO_4F ,^{2a} LiMnSO_4F ,^{2b} and *triplite* minerals (Mn, Fe, Mg, Ca),^{2c} PO_4F ⁸ that all present a statistical cationic distribution over the two M_1 and M_2 crystallographic sites (Figure 3b); in the present case, M_1 is fully occupied with Cu and M_2 with Li, making LiCuSO_4F the first experimental realization of a fully ordered *triplite* (Figure 3a).

The competitive formation of disordered or ordered triplite phase was evaluated through Density functional

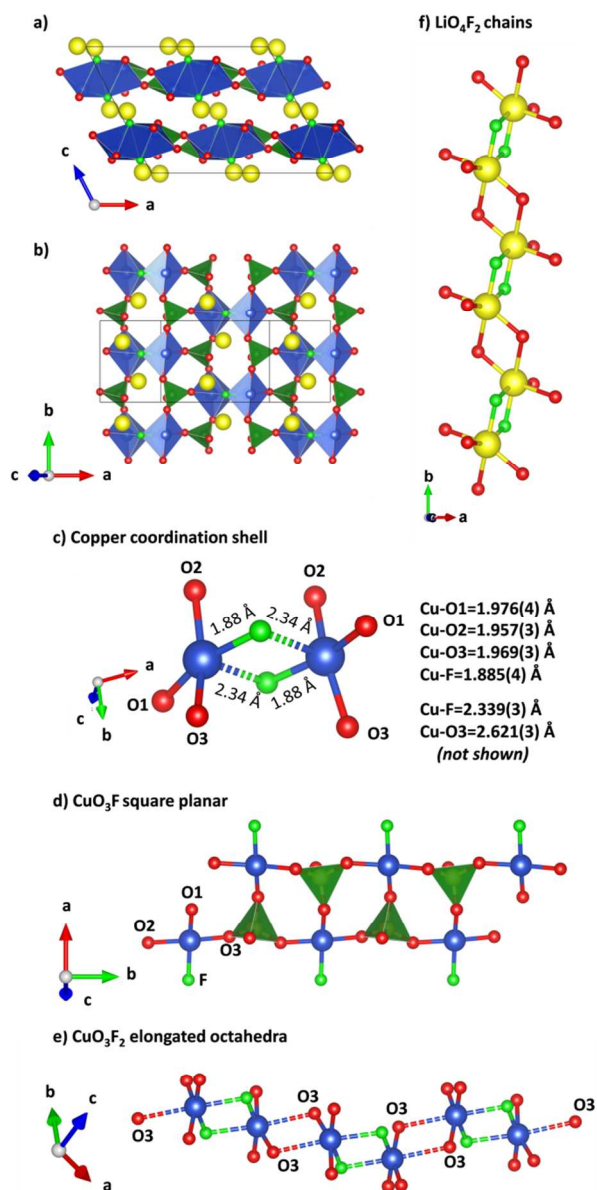


Figure 2. (a) Structure of LiCuSO_4F along the $[010]$ direction. (b) View of one layer made of $\text{Cu}_2\text{O}_6\text{F}_2$ dimers and SO_4 tetrahedra. (c) Cu coordination in $\text{Cu}_2\text{O}_6\text{F}_2$. (d) CuO_3F_2 square planar (e) CuO_3F_2 elongated octahedra (f) Chains of edge-sharing LiO_4F_2 octahedra. Cu is blue, O is red, F is light green, Li is yellow, SO_4 are dark green,

theory calculations (DFT). Two perfectly ordered Li-Cu distributions were first considered in which Cu ions exclusively lies on the M_1 sites (noted Cu_{M_1} as experimentally found) and on the M_2 sites (Cu_{M_2} , hypothetical structure). Then, 9 different partially disordered Li-Cu orders (noted $\text{Cu}_{M_1M_2}$) were investigated, following the methodology described in ref. [4] (Supporting Information, Figure S4). After full structural relaxations, the perfectly ordered distributions Cu_{M_1} and Cu_{M_2} are found as two different polymorphs with equivalent energies, the latter being only 10 meV/FU higher than the former. This is rationalized in terms of local Cu environments which are

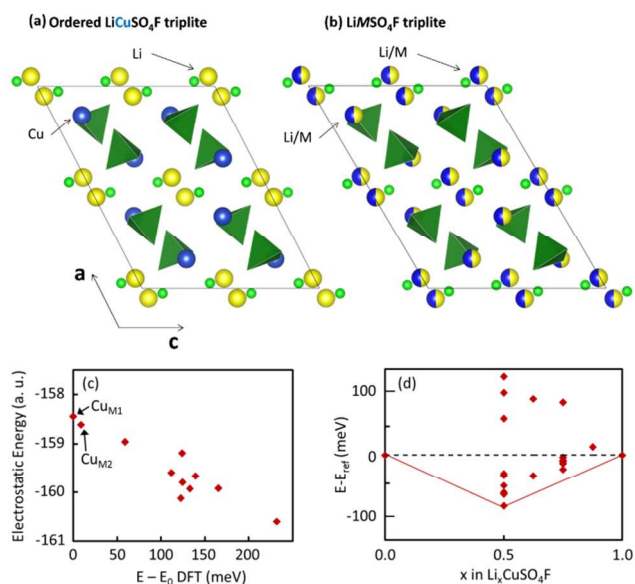


Figure 3. (a) Structure of LiCuSO_4F compared to (b) *triplite* structure reported for LiFeSO_4F , LiMnSO_4F and $(\text{Mn, Fe, Mg, Ca})_2\text{PO}_4\text{F}$ minerals. M is blue, Li is yellow, F is light green, and SO_4 tetrahedra are dark green. (c) Electrostatic energy of the different Li-Cu order test-cases considered for the *triplite* structure (d) T=0K phase stability diagram of $\text{Li}_x\text{CuSO}_4\text{F}$ as a function of x from DFT + U calculations (details see Supporting information).

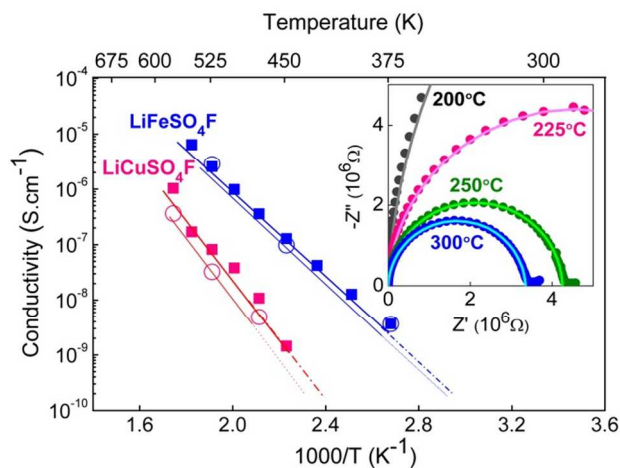


Figure 4. Transport properties of LiFeSO_4F (blue) and LiCuSO_4F (pink), the filled squares and open circles refer to a.c. and d.c. measurements, respectively; the inset shows impedance spectra (filled circles) and the fit of each spectra (continuous line) of LiCuSO_4F in argon at various temperatures.

very similar in both phases with evidence of the Jahn-Teller distortion expected. Worthwhile mentioning is that we are deviating from the classical square planar distortion owing to the presence of F atoms (CuO_3F). Given the quite unusual local Cu environment, the dynamical stability of the Cu_{M_1} polymorph has been checked with phonon band structure calculations (SI, Figure S5). Interestingly, the 9 $\text{Cu}_{\text{M}_1\text{M}_2}$ partially disordered phases, having a lower

degree of Jahn-Teller distortion (Supporting Information, Figure S6), lie 60 meV to 200 meV/FU higher in energy than the perfectly ordered Cu_{M_1} and Cu_{M_2} distributions. The fact that the energy difference between all these structures is far above the room temperature thermal energy (~ 25 meV) clearly indicates that configurational entropy associated to cation intermixing is not sufficient to stabilize the disordered polymorphs, suggesting that enthalpy governs the phase stability. Figure 3c displays, for each Cu-Li order, the electrostatic energy computed with a point charge model (using the DFT Bader charges) versus DFT energies. Surprisingly, the higher the electrostatic energy, the lower the corresponding DFT energy is, indicating that the Cu local environment overrules the cation-cation electrostatic energy. For sake of completion, we have also tested the stability of *tavorite* LiCuSO_4F using the *tavorite* LiFeSO_4F structure as the starting structure and substitute Fe for Cu, and found that the *tavorite* polymorph is 76 meV higher versus experimental ordered *triplite*.

This new phase was tested for its electrochemical activity towards Li by assembling, in an argon dry box, $\text{LiCuSO}_4\text{F}/\text{Li}$ Swagelok-type cells using a 1M LiPF_6 solution in 1:1:3 EC : PC : DMC electrolyte. The cells were charged to either 4.9 V or 5.2 V at different rates via a VMP system, but no sign of redox activity could be detected in the voltage composition curves (Supporting Information, Figure S7). This means that no Li can be removed from this structure till 5.2V, the voltage at which we found the electrolyte copiously decomposes.

Mindful the crystal structure of LiCuSO_4F and its electrochemical inactivity, we decided to measure its transport properties. Conductivities (a.c. and d.c.) were measured on a sintered LiCuSO_4F pellet (synthesized directly at 415°C, \varnothing 10 mm, compactness 89%) between ionically blocking gold electrodes. The measurement was done under argon at various stabilized temperatures ranging from 100 to 300°C using a Bio-Logic MTZ-35 Impedance Analyzer, in a frequency range of 30 MHz to 0.1 Hz and with an excitation voltage of 100 mV. Figure 4 shows the evolution of the a.c. conductivity of LiCuSO_4F . An activation energy of 1.11 eV was obtained by fitting the a.c. data with an Arrhenius law and a room temperature a.c. conductivity of $1.5 \times 10^{-15} \text{ S cm}^{-1}$ was extrapolated. The low frequency tail of the impedance spectra suggests an ionic component to the overall conductivity. To further shed some light on this issue d.c. conductivity measurements were done by applying polarization voltages. An activation energy of $E_a = 0.9$ eV was found with conductivities values slightly higher than the a.c. ones which cumulate both electronic and ionic contribution, hence indicating that the electronic conductivity is dominating. Interestingly, a similar behavior had been found for LiFePO_4 which was explained via a polaronic model (e.g. hopping of localized electrons) and was confirmed by ab-initio calculations.⁹ Lastly, For meaningful comparison we measured the conductivity of *triplite* LiFeSO_4F (sintered

at 250°C for 1h Ø10 mm, compactness 70%) under similar experimental protocols and found E_a for a.c. and d.c. of LiFeSO_4F are 0.79 eV and 0.78 eV respectively. The strong electronic contribution to the overall conductivity displayed by these insulating-like polyanionic compounds calls for further investigations of their transport properties.

To further determine whether the observed electrochemical inactivity of *triplite* LiCuSO_4F is nested in its poor ionic conductivity or in our limitation to experimentally reach high potentials due to electrolyte instability, we performed DFT calculations. The $T=0\text{K}$ DFT phase stability diagram of the $\text{Li}_x\text{CuSO}_4\text{F}$ polymorph (Cu_{M_1}) in the range $x=0$ to 1 shows the feasibility to stabilize an intermediate ordered $\text{Li}_{0.5}\text{CuSO}_4\text{F}$ phase (Figure 3d). The electrochemical potentials computed for the two consecutive delithiation processes: $\text{LiCuSO}_4\text{F} - 0.5\text{Li} \rightarrow \text{Li}_{0.5}\text{CuSO}_4\text{F}$ and $\text{Li}_{0.5}\text{CuSO}_4\text{F} - 0.5\text{Li} \rightarrow \text{CuSO}_4\text{F}$ are 5.15 V and 5.40 V, respectively. The atom-projected density of states of the LiCuSO_4F structure (Supporting Information, Figure S8) shows a dominant contribution of the oxygen electronic levels at the Fermi level, suggesting an oxidation process mostly driven by the oxygen and negligible modification of the Cu^{2+} environment upon Li-removal. Combining the electrochemical test and DFT calculations, the removal of 0.5 Li^+ from the LiCuSO_4F phase should be achievable and reversible at 5.15 V provided that electrolytes, stable against oxidation up to such high voltages, could be developed in the future.

In summary, we have reported the synthesis of a new LiCuSO_4F phase through a low temperature solid state process which crystallizes in a fully ordered *triplite* structure, instead of a *tavorite* structure as previously predicted from high-throughput calculations.³ From DFT calculations, we could demonstrate that both ordered Cu_{M_1} and Cu_{M_2} *triplite* LiCuSO_4F polymorphs are thermodynamically equivalent, and more stable than either “*tavorite*” or “disordered *triplite*” polymorphs. The Li/Cu intermixing over the M_1 and M_2 sites was shown to minimize the Jahn-Teller distortion around the Cu^{2+} cations, which prevents Cu-orbital stabilization and leads to less stable distributions despite more favorable electrostatic energies. This indicates that enthalpy governs the formation of an ordered LiCuSO_4F *triplite* and contrasts with the entropy-driven formation of LiFeSO_4F disordered *triplite* in which all Fe-Li distributions are energetically equivalent (so as the local Fe environment).¹⁰ At this stage a remaining question deals with the inability of DFT calculations to distinguish, thermodynamically-wise, which of the two Cu_{M_1} and Cu_{M_2} polymorphs should experimentally form, indicating the importance of kinetics issues (e.g. temperature) that cannot yet be taken into account. Along the same line, we must recall that this *triplite* LiCuSO_4F polymorph was not spotted from high throughput approaches.⁵ This highlights the difficulties of periodic approaches to address polymorphism and therefore to identify potentially attractive materials.

DFT calculations have predicted a reversible electrochemical activity of *triplite* LiCuSO_4F towards Li^+/Li^0 at 5.15 V which could not be confirmed experimentally owing most likely to the lack of suitable electrolytes although we cannot eliminate kinetic issues associated to the poor Li ionic conductivity in LiCuSO_4F . Thus, the attractiveness of this new phase is limited application-wise. Nevertheless bearing in mind the richness of sulfate-/phosphate-based polyanionic electrodes adopting either the *tavorite* or disordered *triplite* structures, we believe that such a finding will contribute further in the understanding of these technologically important compounds.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the website at <http://pubs.acs.org>. Experimental details, CIF file of LiCuSO_4F , Crystallographic table, EDX analysis, ED patterns, DFT calculations and electrochemical curves.

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Notes

The authors declare no competing financial interest.

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