Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Ultra-Rapid Microwave Synthesis of Triplite $LiFeSO_4F$

Rajesh Tripathi, Guerman Popov, Xiaoqi Sun, and Linda F. Nazar [*]

[a] Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, ON, N2L 3G1, Canada; E-mail: lfnazar@uwaterloo.ca

Experimental Details

To prepare tavorite $LiFeSO_4F$, LiF and $FeSO_4 \cdot H_2O$ (1.1:1) were mixed under an argon atmosphere for 2 hours in a planetary ball mill. The homogeneous reaction mixture, along with 20 ml tetraethylene glycol (TEG), was sealed in a closed Teflon™ vessel which was fitted to a rotor with pressure and temperature sensors. The rotor containing the closed Teflon™ vessels was then placed on a turntable for uniform heating in an Anton Paar microwave synthesis system (Synthos 3000). The desired exposure time and temperature were software controlled, allowing continuous monitoring and control of the internal temperature. A preset profile (desired time, temperature) was followed automatically by continuously adjusting the applied microwave power (0-1200W, 2.45 GHz). The system temperature was raised to 230°C in 5 min and maintained for 10 min. The final pressure (20 bar) remained constant for the remainder of the reaction after the temperature ramp reached its plateau. The as-synthesized samples were washed with THF in order to remove the TEG.

Powder X-ray diffraction was performed on a Bruker D8-Advance powder diffractometer equipped with a Våntec-1 detector, using Cu-Kα radiation (λ= 1.5405Å) in the range from 10° to

120° 2θ at a step size of 0.025° in Bragg-Brentano geometry. X-ray data processing was carried out using GSAS and EXPGUI[1,2] and Bruker TOPAS 4.2. For time-of-flight neutron diffraction, samples were sealed in vanadium containers inside a dry He-filled glove box and experiments were carried out at 300K on the POWGEN powder diffractometer at the Oak Ridge National Laboratory, Tennessee, USA; banks 2 and 5 were utilized providing a range from 0.3 to 6.18 Å in d-spacing. Rietveld refinements of the neutron data were performed using GSAS and EXPGUI. Absorption correction was necessary due to the presence of ^{6}Li in natural Li.

Mössbauer spectra were collected over a counting time of 20 hr in a hermetically sealed holder using a 50mCi ^{57}CoRh source mounted on a constant-acceleration spectrometer calibrated using a Fe foil at room temperature. Fitting was accomplished using standard least-squares methods. A Bruker Tensor infrared spectrometer was used to collect spectra of as-prepared materials ground with KBr and pressed into pellets. Pellets were dried overnight at 100°C in a vacuum oven. For electron microscopy imaging, powder samples were gold coated and examined in a LEO 1530 field emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray spectroscopy (EDX) attachment. Images were recorded at 15 kV with a back-scattered electron detector.

The hydrogen content in the materials was analyzed by elastic recoil detection (ERD), data were collected at Western Tandetron Accelerator Facility, Western University, London, Ontario, Canada. The microwave-prepared tavorite $LiFeSO_4F$ was heated at 300°C under vacuum for 1hr to volatilize any remaining TTEG before being pressed into a pellet and mounted into a vacuum chamber for ERD. A 1.6 MeV ^{4}He beam was used in a conventional ERD setup with an incident angle of 75°, recoil angle of 30° in IBM geometry and 6.1μm Al-coated Mylar range foil. Kapton and H-implanted Si targets were used as standards to determine the detector

solid angle. Measurements were performed at multiple spots separated by at least 1-2 mm; the spot- to-spot variation was below 5%. The software package SIMNRA[3] was used to fit the experimental ERD data in order to extract hydrogen depth profiles.

For electrochemical measurements, materials were mixed with Super-P carbon in a 80:20 mass ratio. The cell loading was 5-6 mg/cm^2. The electrochemical performance was evaluated using a lithium metal anode and an electrolyte solution comprised of 1M $LiPF_6$ in 1:1 ethylene carbonate/dimethyl carbonate. Room temperature galvanostatic cycling was performed between 2-2.5 and 4.5 V.

Table S1. Refined structural parameters of triplite $LiFeSO_4F$. Combined Rietveld analysis of powder neutron and X-ray diffraction at 300K was carried out in the *C2/c* space group with all atoms in general positions.

a = 13.0375(3) Å
b = 6.3953(1) Å
c = 9.8443(2) Å
β = 119.753(1) °
V = 712.60(3) Å^3

Atom	x	y	z	Occ.	U_{iso} (Å^2)
Li1/Fe1	0.6469(2)	0.8947(4)	0.8475(3)	0.426/0.574(2)	0.0215(8)
Li2/Fe2	0.9473(3)	0.2482(5)	0.0007(4)	0.574/0.426(2)	0.027(1)
S	0.3279(2)	0.5923(4)	0.1967(3)	1	0.0271(7)
F	0.9867(3)	0.4037(6)	0.6091(4)	1	0.043(1)
O1	0.2150(3)	0.63399(4)	0.1929(3)	1	0.0239(8)
O2	0.5792(3)	0.5354(4)	0.1443(3)	1	0.0236(8)
O3	0.6928(2)	0.4155(5)	0.4138(3)	1	0.0234(8)
O4	0.6350(3)	0.7720(4)	0.3589(3)	1	0.0209(7)

χ^2 = 1.94
R_p = 1.34 %
R_{wp} = 1.95 %

Figure S1. FESEM micrograph of a) tavorite $LiFeSO_4F$ prepared by the microwave solvothermal method; b) triplite $LiFeSO_4F$ prepared by heating the microwave tavorite product; c) triplite $LiFeSO_4F$ prepared by the extended conventional solvothermal method.

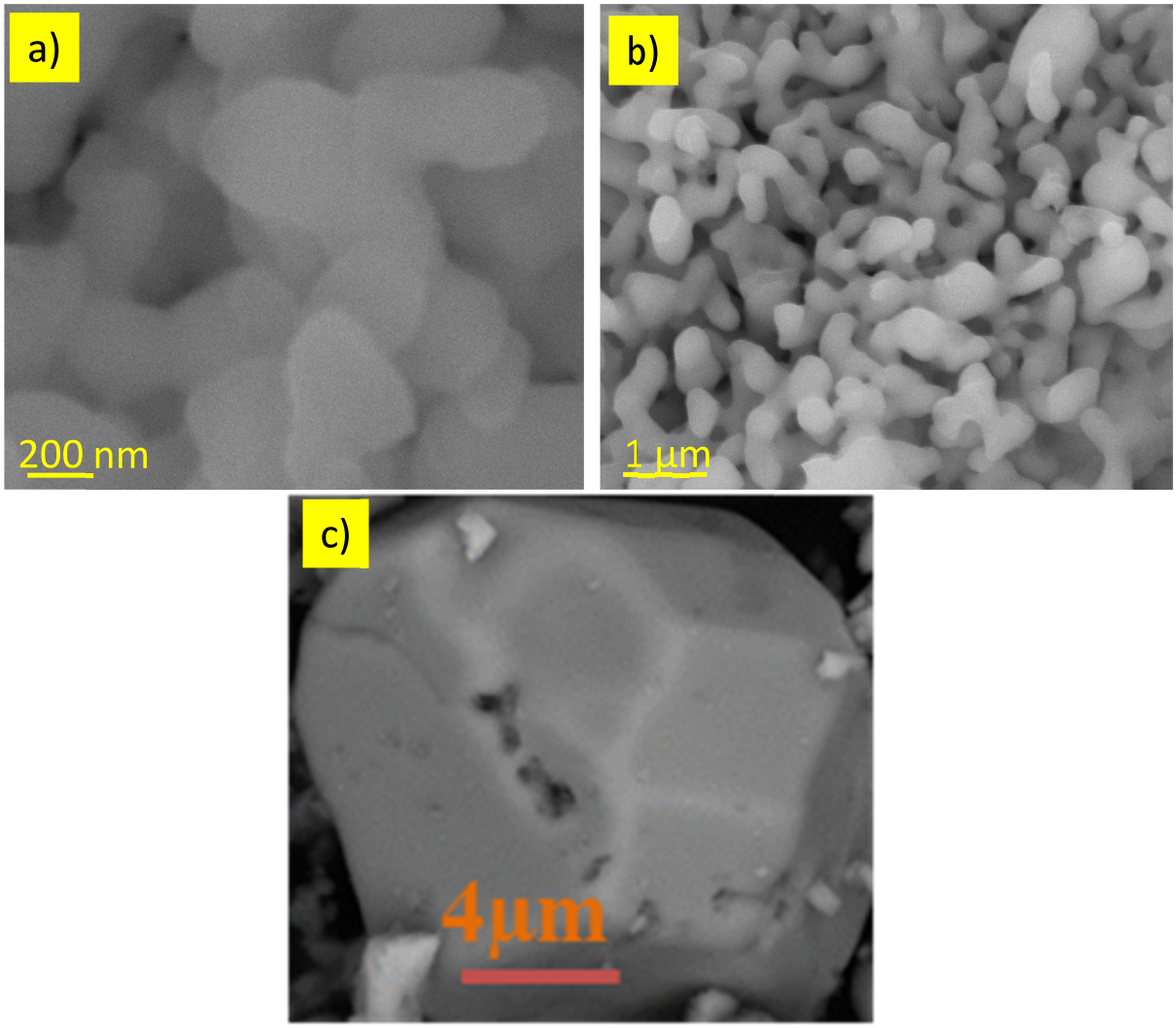
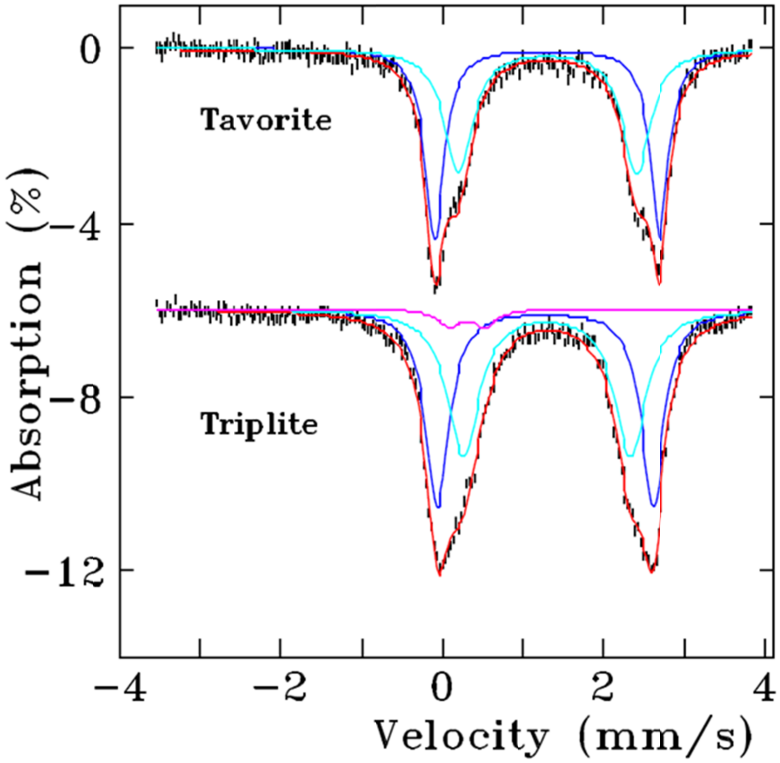
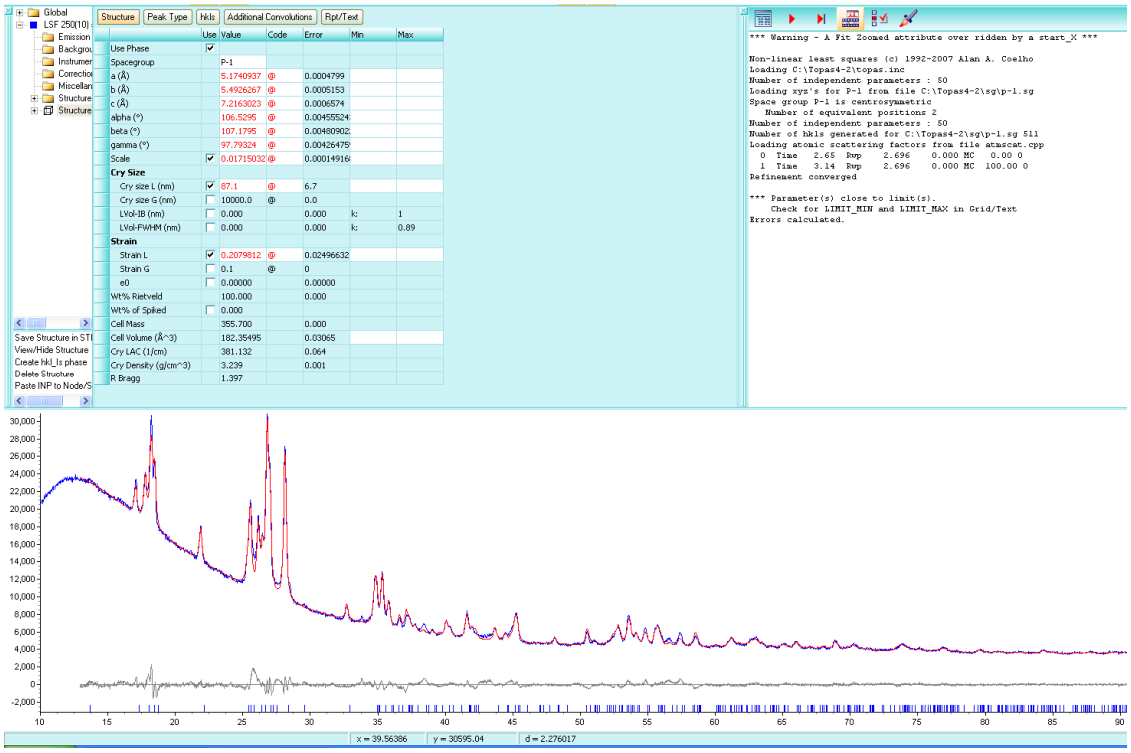


Figure S2. Mössbauer spectra and corresponding fits for $LiFeSO_4F$ in the tavorite (upper) and triplite (lower) phases. Table with fitting parameters.



Compound ($LiFeSO_4F$)		δ (mm/s)	Δ (mm/s)	Γ (mm/s)	%
Tavorite	Inner doublet	1.297(3)	2.20(1)	0.211(10)	49
	Outer doublet	1.295(2)	2.787(5)	0.141(4)	51
Triplite	Inner doublet	1.269(2)	2.670(9)	0.236(14)	47.8
	Outer doublet	1.287(3)	2.06(2)	0.174(5)	48.0

Figure S3. Screenshot of the TOPAS program showing the Rietveld fit and relevant parameters of the ST tavorite (upper) and MW tavorite (lower).



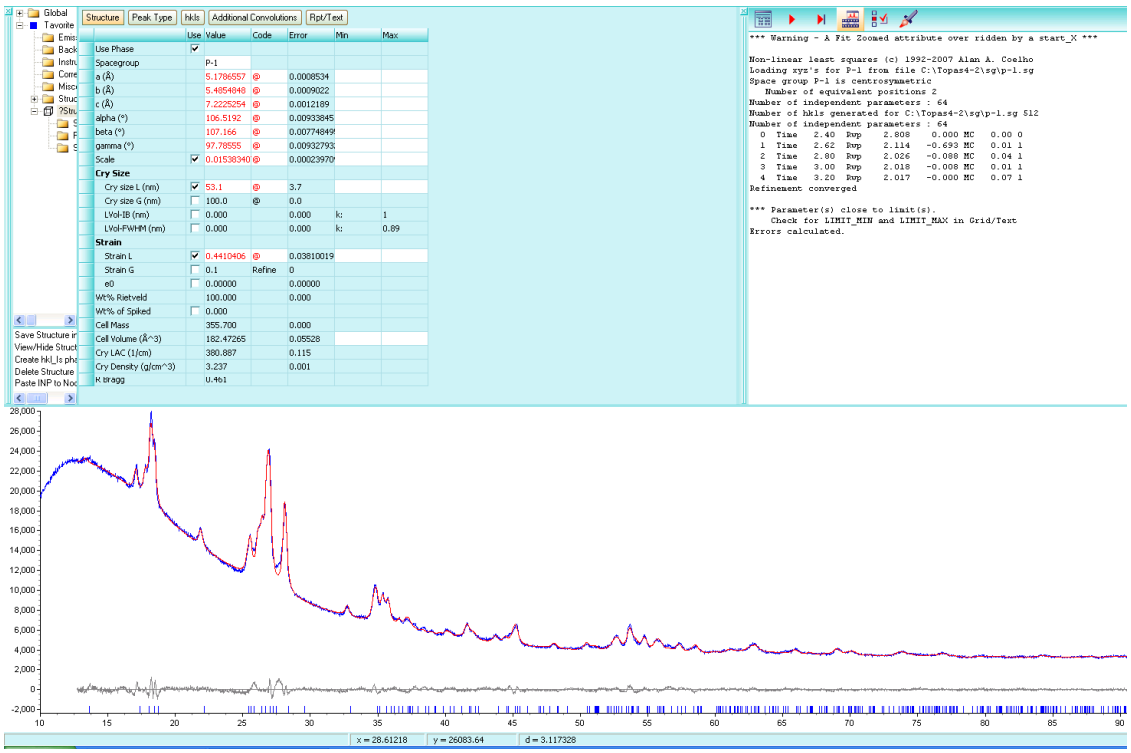


Figure S4. X-ray diffraction patterns (Cu-Kα) of triplite $LiFeSO_4F$, prepared by the conventional solvothermal route followed by heat treatment for at 350°C for 12h. Asterisks show the reflections of impurity phases (Fe_2O_3; $Fe_{1-x}S$) generated by this process.

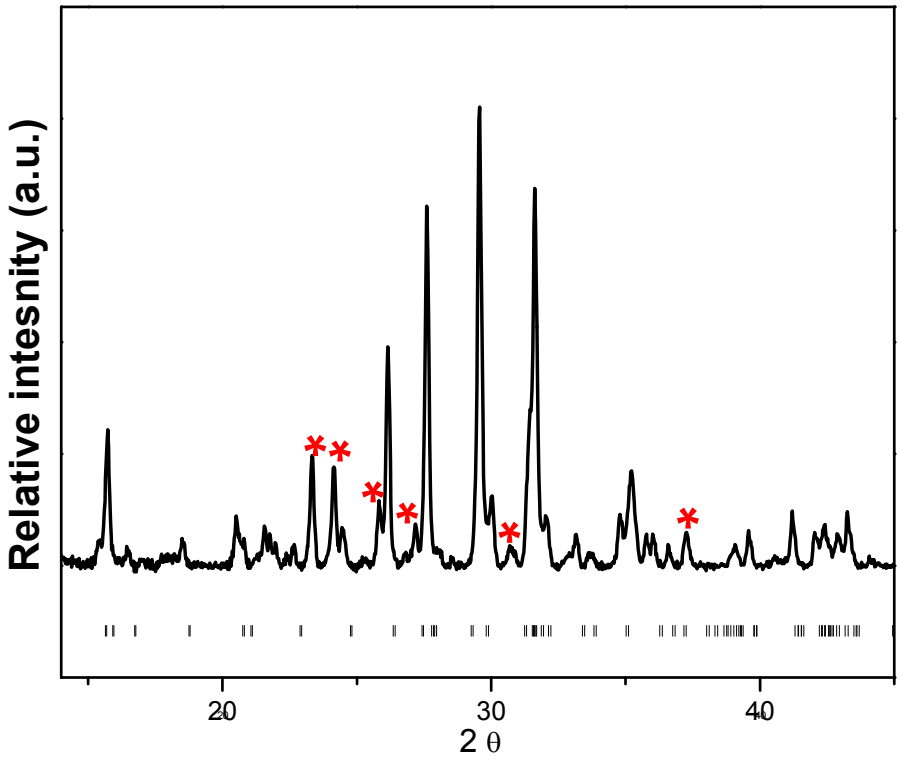


Figure S5. FTIR spectra (as KBr pellets) collected for a) tavorite prepared by the conventional solvothermal route; b) tavorite prepared by the microwave solvothermal route; and c) triplite prepared by heating the microwave-prepared tavorite sample.

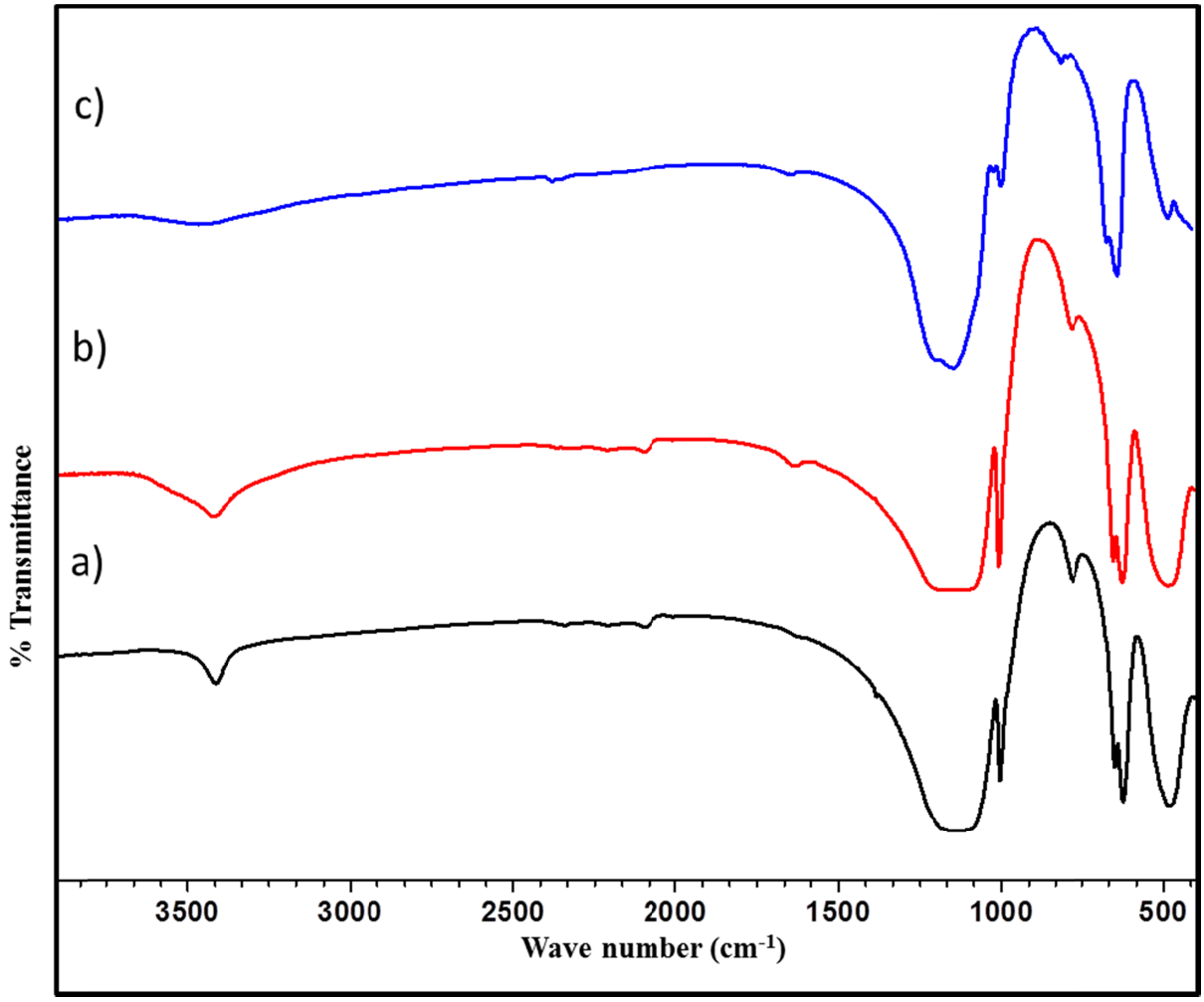
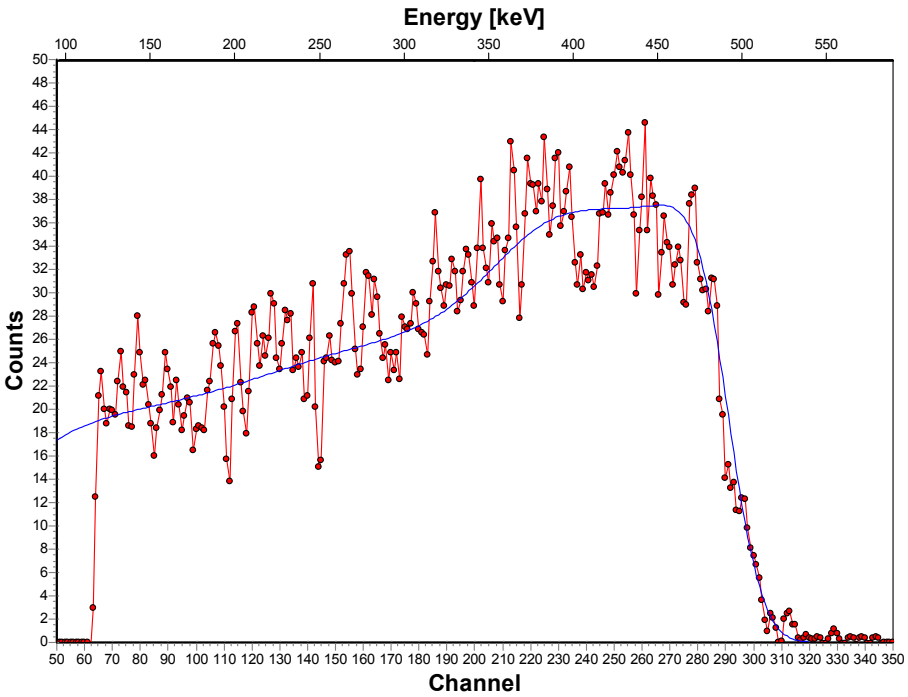


Figure S6. Elastic recoil detection (ERD) analysis of hydrogen in the MW tavorite. The fit (blue smooth curve) to the experimental data (red) supports the model with between 3.5% atomic % and 2.5 at% hydrogen (with slightly more on the surface). Note that this sample was annealed at 300°C in argon to remove any remaining TEG. The non-heat-treated sample showed 6.5 at% hydrogen.



1. A. C. Larson and R. B. Von Dreele, *Los Alamos National Laboratory Report,* **2004**, LAUR 86-748.

2. B. H. Toby, *J. Appl. Cryst.*, 2001, **34**, 210-213.

3. M. Mayer, 1997 SIMNRA user's guide IPP 9/113 Max-Planck-Institut für Plasmaphysik, Garching, Germany.