XRD analysis of freeze-cast, compressed, LFA'd MXene films - PANalytical X'Pert Pro

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Tags: XRD XRD5 LFA Freeze-cast Calendering Aerogel 11/10/2021Synth Nanoplexus 200 2021 Punch
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Goal : Characterise phase change of a Ti_3C_2 MXene film as a result of conducting laser flash analysis using Rietveld refinement

Procedure :

Sample preparation

Two freeze-cast, lyophilised, calendared and punched $Ti_3C_2T_z$ aerogels (∅ = 12 mm, thickness either 0.65 or 1.3 mm), produced in Experiment - Punch pressing of freeze-cast, lyophilized and calendered MXene aerogels and subject to laser flash analysis in Experiment - Laser flash analysis of uniaxially freeze-cast and compressed MXene aerogel, are placed in back-loading sample holders with the phase exposed to the laser facing upward (i.e. being measured) where the sample surface is made flush with the holder surface.

Instrument set-up

Geometry	Bragg-Brentano
Spinner	PW3064
Detector	1D X'Celerator (2.122 ° active length)
X-ray source	Copper line focus
Radiation	$K_{\alpha1}$= 0.1540598 nm, $K_{\alpha2}$= 0.1544426 nm, K_{α} ratio 0.5, $K_{\alpha\ av}$ = 0.1541874 nm
K_{β} absorber	0.02 mm Ni
Incident beam optics	0.04 rad Soller, 2 ° fixed anti-scatter, 10 mm incident beam mask, 0.03125° fixed divergence slit for ≤ 5 mm irradiated length
Diffracted beam optics	0.04 rad Soller
2θ start:finish:step / °	3:100:0.017
Dwell time / s	0.66
Stage oscillation (φ)	Yes

Data analysis

The methodology is much similar to that followed in [Experiment] Quantitative Phase Analysis (QPA) of MXene synthesis product PXRD patterns, such that:

- A structure is defined to represent Ti_3C_2 MXene, based on a model of 10wt% HF direct-etched Ti_3C_2 (https://pubs.acs.org/doi/abs/10.1021/acs.chemmater.5b04250)
- Other present phases are identified using the HighScore software and a priori knowledge of sample oxidation. The additional identified phases are all titania, including the polymorphs anatase and rutile TiO_2 and Ti_2O_3 for which the .pdf and .str files are generated by PDF-4+ software.
- The instrument and emission line profiles are carried forward from the Rietveld refinement to the LaB_6 calibrant in [Experiment] Quantitative Phase Analysis (QPA) of MXene synthesis product PXRD patterns, using a jEdit script which interfaces with TOPAS v5
- In the absence of other phases (no internal standard), the XRD pattern has its fit optimised within physically jusitfiable limits to minimize errors using a .inp jEdit script named BGIndividualScan.inp. Absent phases are commented out where necessary. A fifth order Cheybshev polynomial is fit to the background, minimum and maxium 2θ values (2theta_min and 2theta_max, respectively) are selected and the order of spherical harmonics is varied to improve the fit to account for crystallographic texture.

Results :

Sample	**Filename**
0.65 mm thick freeze-cast, lyophilised, calendared and punched $Ti_3C_2T_z$ aerogel	LLFAd_Ti3C2Pellet_0.65mmThickness_20211214 `pt65mm'
1.3 mm thick freeze-cast, lyophilised, calendared and punched $Ti_3C_2T_z$ aerogel	LLFAd_Ti3C2Pellet_1.30mmThickness_20211214 `1pt3mm'

.xy files are xy data of 2θ vs intensity, .xrdml files are raw outputs from diffractometer, .raw files are the TOPAS-legible direct conversion of the .xrdml files (converted with PowDLL Convertor), .inp is the jEdit input script for Rietveld refinement in TOPAS v5, .out files are the outputs of the same script, .txt files contain data of the fit phase hklm values, d-spacings, 2θ spacings and scaled intensities (suffixed hklm_d_Th2_IScaled.txt), columnar data of observed intensities, calculated fit intensities and the difference between these (suffixed Yobs_Ycalc_and_Difference.txt) and .png files are images of the plotted data, created using a Python script available on Github (XRD_TOPASfits_allphasehkl.py).

The goodness of fit parameters R-weighted pattern (R_{wp}) of the whole diffraction pattern and R_{Bragg} for each phase, along with weight percentages, the order of spherical harmonics used and the 2θ limits are detailed in the table below.

		R_{Bragg}				Concentrations								Range		Spherical harmonics (sh) order			
Sample thickness / mm	R_{wp}	Rutile TiO_2	Anatase TiO_2	Ti_2O_3	MXene	[Rutile] / wt%	err	[Anatase] / wt%	err	[Ti_2O_3] / wt%	err	[MXene] / wt%	err	2theta_min / deg	2theta_max / deg	Rutile sh / #	Anatase sh / #	Ti_2O_3 sh / #	MXene sh /#
0.65	16.68	4.85	7.21	3.81	3.65	29.394	1.939	5.060	0.553	14.443	1.983	51.103	2.112	3	100	4	2	4	6
1.3	16.68	8.05	3.90	n/a	n/a	93.672	0.4	6.328	0.4	n/a	n/a	n/a	n/a	5	100	8	8	n/a	n/a

The elemental composition can hence be broken down, for comparison again other quantitative compositional analyses, in the table given below:

Sample thickness / mm	[Ti] / wt%	err	[O] / wt%	err	[C] / wt%	err	[F] / wt%	err
0.65	66.36	0.19	19.67	0.74	6.04	0.25	7.93	0.33
1.3	59.93	0	40.07	0	n/a	n/a	n/a	n/a

Conclusions:

Heating both samples to 700°C during laser flash analysis resulted in varying amounts of oxidation, with a correlation to the sample thickness. The fit to both diffraction patterns is good - the only notable issue is the unit cell definition used for the Ti_3C_2 MXene aerogel which doesn't match perfectly to the obseved diffraction pattern. Namely, the presumed (004) reflection of the MXene is offset. As previously, it is likely that the restacking of the two-dimensional nanomaterials leads to the $P6_3$/m m c space group no longer providing a suitable definition of the structure, hence the offset peak locations when the structure is constrained to that of perfectly stacked particles.

Attached files

LLFAd_Ti3C2Pellet_0.65mmThickness_20211214.xrdml
sha256: 50398a32fa2ce4017ff357d9ffb51adb598b6a905476a433da60a164f0aa8040

LLFAd_Ti3C2Pellet_0.65mmThickness_20211214.raw
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sha256: 228d038d4ff7b10f4a13061081766e1ac5d6255bcd6351df88c687622bde2def

pt65mm_rutile_hklm_d_Th2_IScaled.txt
sha256: c2bbe71ab193cc30b08b37922b842840691ef1d965d8b45b3a3f5820029bf28a

pt65mm_Ti2O3_hklm_d_Th2_IScaled.txt
sha256: aaca8a6244fb908c1c71a725b76b0fdf4680db3df70981a4ae2627dfdef1b834

pt65mm_Yobs_Ycalc_and_Difference.txt
sha256: 20466e1c115b8d263de41d8ada2d85886aacb7e8f3599ad1b17fd8af2e054ae8

BGIndividualScan.INP
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LLFAd_Ti3C2Pellet_0.65mmThickness_20211214.out
sha256: 7f8c7bd3cf93d04084b4d04ed377e5e09628a6c4aa11e496789907bc4dbf2b55

pt65mm_anatase_hklm_d_Th2_IScaled.txt
sha256: 2ecc6dd2cc0e8b59a7876a9b8dc15dd97df6290111585fa239fd53c7d882aed8

pt65mm_MXene_hklm_d_Th2_IScaled.txt
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pt65mm_plot.png
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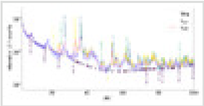

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1pt3mm_plot.png
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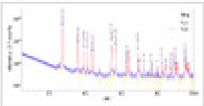

1pt3mm_Yobs_Ycalc_and_Difference.txt
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LLFAd_Ti3C2Pellet_1.30mmThickness_20211214.out
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1pt3mm_anatase_hklm_d_Th2_IScaled.txt
sha256: 7b6a50aadaeab8569e75ff71d4b167951e39d254a3a1ff743e46578aadd59285

LLFAd_Ti3C2Pellet_1.30mmThickness_20211214.xy
sha256: 553e8cbf122f7d3d693fdf7bcc07dbbbd56907d81c007292874aea33d0bff0a8

LLFAd_Ti3C2Pellet_1.30mmThickness_20211214.xrdml
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LLFAd_Ti3C2Pellet_1.30mmThickness_20211214.raw
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Unique eLabID: 20230707-acd3a7ea79d0691ddc1502a00eb5a0a7623bea3d
Link: https://frankel-elab.manchester.ac.uk/experiments.php?mode=view&id=130