MS41-P5 Advanced materials analysis with the powder diffraction file™

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Ten years ago the ICDD launched a new family of database products PDF-4. The purpose of these new databases were to provide researchers with an array of solid state analysis tools based on the powerful combination of single crystal and powder reference data, housed in a relational database format that could provide flexibility and powerful data mining. The ICDD has developed reference data and editorial procedures for experimental nanomaterials as well as amorphous materials. PDF-4 products now contain both amorphous and nanomaterial references. The use of digital patterns for both the material being analyzed and reference materials allows us to study crystallite size [1], molecular orientation and various instrumental and specimen contributions to the coherent and incoherent scatter, allowing for the analysis of crystallinity. Digital simulation tools are used to make the analyses radiation independent so that we can use experimental x-ray, neutron[2], electron [3] or synchrotron diffraction data for the analyses. We continue to work with our global membership to develop new methods and procedures. Most recently we have reviewed and published the largest collection of modulated structures, properly described by superspace groups, with up to 6-dimensional indexing and modulation vectors [4]. For improved quantitative analyses we have added massive numbers of atomic coordinates, digitized all patterns and calculated I/Ic scaling factors for both X-rays and neutron analyses.

References

[1] Scardi, P., Leoni, M. and Faber J., **2006**, "*Diffraction Line Profile from a Disperse System: A Simple Alternative to Voightian Profiles*", Powder Diffraction, Vol. 21, No. 4, p 270

[2] Faber, J., Crowder, C.E., Blanton, J., Kabekkodu, S, Gourdon, O., Blanton, T, Fawcett, T. G, "*New Neutron Diffraction Data Capability in the PDF-4, 2014 Relational Database*", **2015**, accepted for publication in Adv. In X-ray Anal. Vol. 58

[3] Reid, J., Crane, D., Blanton, J., Crowder, C., Kabekkodu, S., and Fawcett, T., **2011**, "*Tools for Electron Diffraction Pattern Simulation for the Powder Diffraction File*", Microscopy Today, January, 38-42.

[4] http://www.icdd.com/products/2014/modulatedstructures.htm and https://www.youtube.com/user/TheICDD

Keywords: powder diffraction file, database, diffraction

MS41-P6 What pushes some molecular materials beyond the edge of crystallinity : an experimental study based on machine-learning predictive models

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Many molecular systems, perhaps a substantial minority, exist near the 'edge of crystallinity'. Often, despite repeated crystallisation attempts, these materials, at best, form polycrystalline solids and frequently exhibit substantial defects in crystal growth. Why is long-range order facile in some organic materials while others exhibit significant build-ups of defects and lattice strain?[1]

We have recently established predictive models, developed using machine learning algorithms,[2] that provide a set of chemical and geometrical reasons why some materials crystallise more straightforwardly than others. Here, we present our initial experimental results from a set of 200 materials with unknown crystal structure that we predict using our machine learning algorithms to span the boundary between poorly crystallising materials and those which form single crystals.

Using the high resolution MAC detectors on ESRF beamline ID22, we have measured the powder diffraction patterns of all 200 structures. The materials are constituted into thirteen families, each containing a set of chemically similar derivatives. A substantial number of potential pharmaceutical materials are included in the study. While some structures are amorphous, most of the data are of sufficient quality to determine not only the crystal structure but also the extent and nature of microstructural imperfections such as lattice strain and stacking defects which are common and clearly visible.

Here, we will present an overview of the results, which includes analysis of *hkl*-dependent anisotropic and asymmetrical line broadening as well as particle-size distributions. With 200 organic materials, in thirteen chemical families, we have a substantial body of information that allows us to rationalise the difference in behaviour across families as functional group derivatives vary, and enables us to correlate the propensity for crystallisation with the degree of microstructural imperfection.

1. Hursthouse, M. B., Huth, L. S. & Threlfall, T. L. Why Do Organic Compounds Crystallise Well or Badly or Ever so Slowly ? Why Is Crystallisation Nevertheless Such a Good Purification Technique ? *Org. Process Res. Dev.* **13,** 1231–1240 (2009).

2. Wicker, J. & Cooper, R. Will it crystallise? Predicting crystallinity of molecular materials. *CrystEngComm* **17,** 1927–1934 (2014).

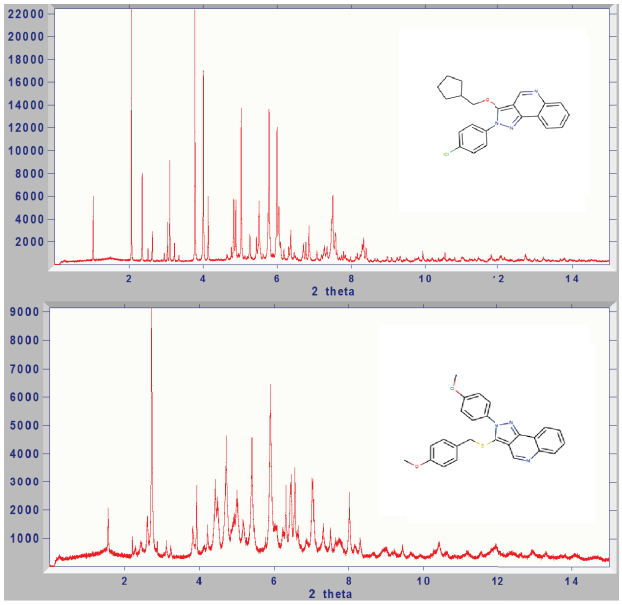

Figure 1. High resolution powder diffraction data of (a) crystalline and (b) poorly crystalline organic materials collected using ESRF beamline ID22.

Keywords: crystallization, prediction, powder diffraction, microstructure, machine learning

MS41-P7 Structural characterization of Re-substituted lanthanum tungstates $La_{5.4}W_{1-x}Re_xO_{12-\delta}$ ($0 \le x \le 0.2$) with Neutron and X-Ray Diffraction

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The presented work on proton conducting materials will show new results on the structural characterization of a substituted lanthanum tungstate: $La_{5.4}W_{1-x}Re_xO_{12-\delta}$ with $0 \le x \le 0.2$ in two different conditions (dry-Ar, wet-D2O). Among the eight specimens measured, the one without substitution ($La_{5.4}WO_{12-\delta}$) and the other with highest Re-substitution level ($x=0.2$) will be in the focus of the presentation and compared throughout the whole talk.

Their comparison will be achieved considering Neutron Diffraction results, due to the insufficient contrast between W (Z=74, b=4.86fm) and Re (Z=75, b=9.2fm) against X-Rays. The structural model of the undoped system $La_{5.4}WO_{12-\delta}$, as suggested recently by a coauthor [1] will be independently confirmed and taken as starting point to determine the position of Re-atoms in the crystal structure.

Neutron Diffraction data was obtained from D2B (ILL, Grenoble) and HRPT (SINQ, Villigen). At D2B, High-Resolution mode was employed for the two above-mentioned samples, measuring many temperature steps with a Displex-device (5K – 200 K range). At SINQ, 1.5K was reached in High-Intensity mode, using their peculiar orange cryostat ORI4.

Three models will be finally presented for the Re-substituted system within the Fm-3m space group: Re substituting W on the main W position (Wyckoff site 4a), Re substituting W on the shared La/W position (Wyckoff site 48h) and Re substituting W statistically on both sites. As low temperature minimizes thermal vibrations, structural modeling may exclude positional disorder contribution. Substitution amount in the shared sites is reached refining occupancies in a single-atom-per-site approach (average neutron scattering length). Results match with composition obtained from Electron-Micro-Probe-Analysis.

Due to the low Re amount (~1 atom per unit cell out of 32 cations and 55 oxygen anions) and the close neutron scattering length of Re to the main element La (Z=57, b=8.24fm) it is hard to determine unambiguously the very details of the structure. Finally, special importance is given to the refined oxygen occupancies in wet and dry condition and compared to thermo-gravimetric results.

[1] T. Scherb, PhD Thesis. Technische Universität Berlin, 2011, doi: http://dx.doi.org/10.5442/d0014.

Keywords: Proton Conductors, Lanthanum Tungstates, Neutron Diffraction