Determination of Phase Purity by Powder X-ray Diffraction

Phase Purity & Powder X-ray diffraction

In order to determine accurate structure-property relationships in a material, it is crucial to ensure that the material being studied is pure. Powder diffraction gives a direct representation of the bulk sample, with the observed pattern derived from all the crystalline components within the material.

Within this case study, we will look at the determination bulk purity of a porous material known as a metal-organic framework. We will compare the powder diffraction pattern to the single crystal structure using a whole pattern fitting method known as a LeBail fit.

Introduction

Metal-organic frameworks are a class of material in which metal ions or clusters are linked together with organic ligands to yield a porous crystalline polymeric array. In this example, dinuclear copper paddlewheels are joined together with the pyridyl-isophthaloc acid ligand 4-(pyridin-4-yl)biphenyl-3,5-dicarboxylic acid, yielding the material $[Cu(L^1)]$[1] (Figure 1).

Within this study, the structure was determined using single crystal X-ray diffraction, and the H_2, CO_2 and CH_4 gas adsorption isotherms were measured. In order to correlate the observed properties with the structure, the phase purity of the material was determined by powder diffraction.

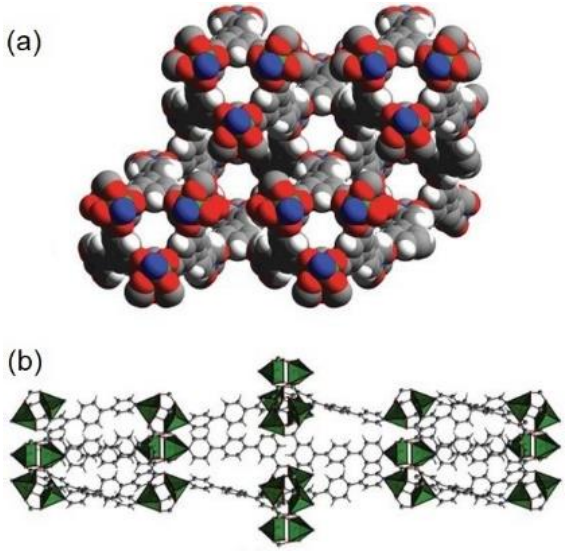

Figure 1: The porous metal-organic framework $[Cu(L^1)]$, where L^1 = 4-(pyridin-4-yl)biphenyl-3,5-dicarboxylic acid

Powder X-ray diffraction methodology

PXRD data were collected on a Panalytical X'pert diffractometer using Cu Kα radiation. The LeBail fit was completed using the software package *FULLPROF*.[2] The powder diffraction patterns were indexed using the program *CHEKCELL*,[3] using a least squares refinement on the observed unit cell parameters determined from single crystal X-ray diffraction as a starting point.

Comparing the measured diffraction pattern with one simulated from the crystal structure (solved using single crystal X-ray diffraction) shows a near perfect match (Figure 2a), however only a whole pattern fit will give a measure of phase purity. A LeBail fit is a simplification of the Rietveld analysis, allowing the accurate determination of phase purity by refining the whole pattern against the unit cell and space group parameters. This refinement can determine whether the space group

assignment is correct, or whether other phases are present. With calibration, LeBail fits can quantify relative phase distributions. Within this example, the LeBail fit was applied to determine the phase purity of the sample (Figure 2b).

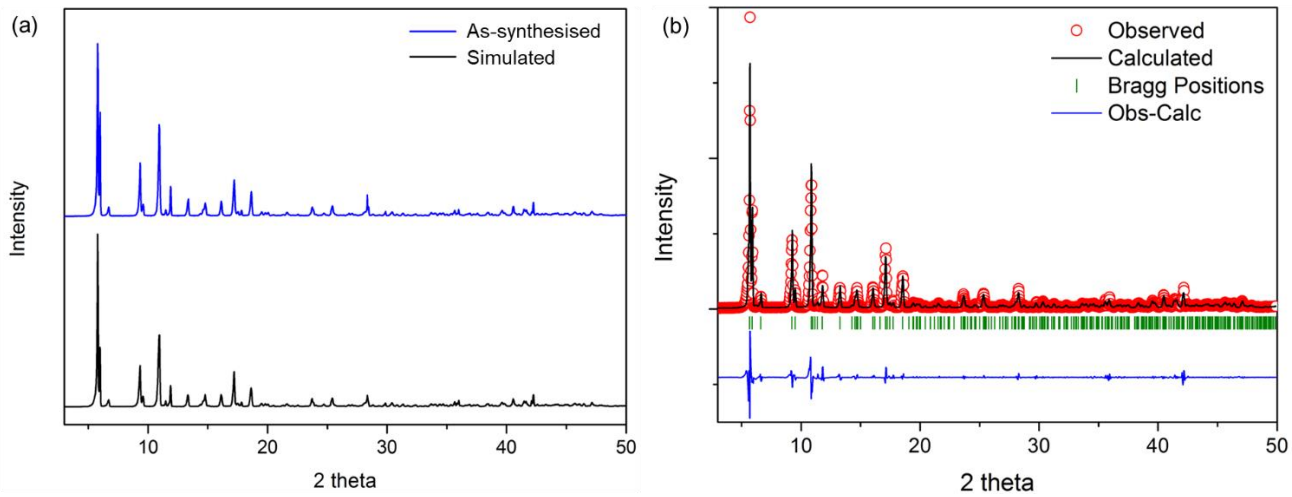

Figure 2: (a) PXRD patterns for the as-synthesised (top) [Cu(L^1)], compared to the pattern simulated from the single crystal structure. (b) Le Bail fitting for [Cu(L1)] performed using FULLPROF. Refined cell parameters (as-synthesised): a = b = 19.135(2) c = 45.007(3) Å, single crystal cell parameters (90K): a = b = 18.9144(3) c = 44.9901(9) Å.

Conclusions

The LeBail whole pattern fitting method permits the determination of phase purity of the metal-organic framework material [Cu(L^1)]. When used in conjunction with other techniques, such as elemental analysis and scanning electron microscopy (available within SAgE analytical), this allows the determination of the absolute purity of the materials. This information permitted the correlation of structure-property relationships within a family of metal-organic framework materials.[1]

References

1. J. A. Gould, H. Singh Athwal, A. J. Blake, W. Lewis, P. Hubberstey, N. R. Champness and M. Schröder, *Phil. Trans. R. Soc. A.* (2017), **375**, 20160334

2. J. Rodríguez-Carvajal, *Physica B.*, (1993), **192**, 55.

3. *Chekcell* - http://www.ccp14.ac.uk/tutorial/lmgp/achekcelld.htm.