

01-Instrumentation and Experimental Techniques (X-rays, Neutrons, Electrons)

PS-01.01.10 COMBINED QEXAFS-XRD, A NEW TECHNIQUE COMBINING *IN-SITU* FAST SCANNING X-RAY ABSORPTION SPECTROSCOPY AND X-RAY DIFFRACTION.

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We have recently demonstrated the value of the combined use of Energy Dispersive X-Ray Absorption Spectroscopy and X-ray Diffraction (XRD) in tracing the *in-situ* conversion of a mineral precursor, aurichalcite ($\text{Cu}_{5-x}\text{Zn}_x(\text{OH})_6(\text{CO}_3)_2$) through its various intermediate stages to an active (Cu, ZnO) catalyst using a dispersive monochromator. (Couves J W, Thomas J M, Waller D, Jones R H J, Dent A J, Derbyshire G E, Greaves G N, Nature, (1991), 89, 119). Two detectors were operated in tandem: a photodiode array to record the dispersed transmission XAFS and a curved position sensitive detector to record the angular dispersed Debye-Scherrer patterns. Time-resolved XAFS and XRD pattern were obtained within a few seconds of one another under *in-situ* conditions. We now report a separate, but related development pioneered at the Synchrotron Radiation Source at Daresbury Laboratory, whereby quick scanning XAFS (QEXAFS) technique (Frahm R, Physica B, (1989), 158, 342) has been combined with the previous method of XRD detection to collect high quality X-ray spectra at elevated temperatures in a few minutes.

The layout of the experiment is such that the sample is housed in a variable atmosphere high temperature (Linkam) furnace at the centre of a 120° (INEL) position sensitive detector. The XAFS is collected by rotating the Bragg angle of the double crystal monochromator continuously, thereby practically eliminating the deadtime associated with conventional angle-by-angle scanning. The rapid slewing rate of the monochromator is then used to collect the XRD at a wavelength away from the edge region.

We have tested the QEXAFS/XRD combination to follow the cause of production of a commercially important example: the ceramic material cordierite, idealised formula $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$. We made the chance discovery that cordierite is preparable from Mg^{2+} zeolite B when traces of ZnO are present. We will present data showing from diffraction the zeolite transitions from crystalline to amorphous, then to a transitory "stuffed quartz" phase before finally becoming cordierite. The Zn environment was followed by means of the XAFS and it will be shown that the Zn, at least in part, is incorporated into the final product.

PS-01.01.11 SYNCHROTRON RADIATION FOR MICROCRYSTAL STRUCTURE DETERMINATION AND FOR LAUE TIME RESOLVED STUDIES
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1. Monochromatic synchrotron radiation (wavelength 0.90 Å) from the SRS wiggler beamline (Daresbury) and the Enraf-Nonius FAST area detector diffractometer have allowed data collection and structure determination for a number of microcrystals of moderate complexity and different chemical types. Examples include:

a gold cluster, $\text{Au}_{10}(\text{PPh}_3)_7 \dots$, 10x10x30 μm
reference 1
 $\text{AlPO}_4\text{-CHA}$, $\text{Al}_3\text{P}_3\text{O}_{12}\text{F}\cdot\text{C}_4\text{H}_{10}\text{NO}$, 35x20x15 μm
reference 2
Aurichalcite, $(\text{Zn/Cu})_5(\text{OH})_6(\text{CO}_3)_2$, 40x100x5 μm
This is a natural mineral and catalyst precursor³; it is monoclinic, $a=13.86$, $b=6.417$, $c=5.294$ Å, $\beta=101.0^\circ$, space group $P2_1/m$, twinned on $(20\bar{1})$. 410 unique intensities were measured, each of which has two component reflections because of the twinning; the structure was solved and refined to $R1=0.07$, $wR2=0.19$ (at present), with SHELXL-92 (our thanks to George Sheldrick). The structure is similar to that of hydroxyzincite³. There are four metal sites, two are distorted octahedral (probably Cu), one tetrahedral (probably Zn) and the other trigonal bipyramidal.

2. The SR Laue method with white radiation has allowed complete structure determination for a small crystal of a new organometallic compound, $\text{AuOs}_3(\text{CO})_8\text{PPh}_3\text{dppm}\cdot\text{PF}_6$. This includes unit cell determination, and refinement (to $R=0.075$) allowing for the wavelength dependence of the atom scattering factors, and is to be described in a related poster (IM Dodd, Hao Quan, MM Harding).

3. Laue diffraction has great potential for time resolved studies. As a pilot project we have studied the transition (at ca67°C) in single crystals of $\text{P}_4\text{N}_2\text{Cl}_8$ from the metastable form containing 'boat' molecules to the stable form containing 'chair' molecules (crystals from Dr K Venkatesan, Bangalore). The experimental part of the work has been described⁴. Selected results from one series of Laue diffraction photographs show how many reflections can be recorded from each film pack and used in structure refinement:

| | | | | | | | |
|----------|-----|-----|-----|-----|-----|-----|-----|
| time/min | 0 | 5 | 7 | 9 | 12 | 22 | 32 |
| T/°C | 52 | 62 | 67 | 72 | 77 | 87 | 102 |
| n reflns | 234 | 229 | 228 | 318 | 315 | 301 | 276 |
| %boat | 79 | 76 | 55 | 43 | 38 | 24 | 12 |

Analysis of this and other series should allow the effects of time, temperature and crystal variation to be understood better.

1. GMT Cheetham, MM Harding, JL Haggitt, MP Mingos, HR Powell (1993) submitted to JCS Chem Comm.
2. MM Harding, BM Kariuki, LB McCusker, A Simmen (1992) in preparation for Zeolites.
3. JW Couves, JM Thomas, D Waller, RH Jones, AJ Dent, GE Derbyshire, GN Greaves (1991) Nature 354, 465-468.
4. S Ghose (1964) Acta Cryst 17, 1051-1057.
5. PD Carr, GMT Cheetham, MM Harding, RJ Rule (1992) Phase Transitions, 39, 33-43.

PS-01.01.12 SYNCHROTRON RADIATION DIFFRACTION FOR COMPLETE STRUCTURE DETERMINATION OF A SMALL ORGANOMETALLIC CRYSTAL,
 $\text{AuOs}_3(\text{CO})_8\text{PPh}_3\text{dppm}\cdot\text{PF}_6\cdot 0.5\text{C}_6\text{H}_5\text{Cl}$
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