

POWDER CRYSTALLOGRAPHY WITH A MICROFOCUS X-RAY SOURCE

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The concept that a microfocus X-ray source could be used for crystallography originated from experiments in laboratories associated with the field of protein crystallography[1,2]. The small sizes of protein crystals made them well suited to a microfocus source producing a focused beam diameter of 200 to 500 microns. More recently a commercially available source has been adopted by some major manufacturers for single crystal diffraction work as well as protein crystallography. In contrast with protein and single crystal work, in powder diffraction there is often large amounts of sample, allowing larger X-ray beams to be used. In this case the gains from using a microfocus source and consequent small beam have been considered to be not so evident. However, recent developments in optics and beam conditioning have necessitated a re-evaluation of this assumption.

In this presentation we will discuss the application of a microfocus X-ray source – the Microsource® X-ray Generator – to a variety of powder diffraction situations. These applications range from “high end” structure solving and refinement of complex organic molecules, where most stringent requirements are for low beam divergence and high monochromaticity, to real time studies of evolving structures, where maximal X-ray intensity is required. The advantages and disadvantages of using a microfocus source for powder work will be discussed and where available comparative data between a microfocus source and conventional laboratory powder system presented.

References

1. U. W. Arndt, et al (1998). J. Appl. Cryst. 31, 936-944.
2. M. Gubarev et al (2000). J. Appl. Cryst. 33, 882-887.

Keywords: MICROFOCUS SOURCE, X-RAY OPTICS, POWDER DIFFRACTION

NOVEL NANOPOROUS TRANSITION METAL SILICATES

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Hydrothermal syntheses under conditions similar to those for zeolites have led to a series of novel transition metal silicates that have nanoporous structures with channel diameters up to 0.7 nm. The channels are filled by removable alkali metal cations and water molecules. More than ten different vanadosilicate framework types have been identified from single crystal X-ray structure determinations, all of which are based on bridging single silicate layers with vanadium oxygen square pyramids. In six of the seven observed layer types, each silicate tetrahedron shares three oxygen atoms with other tetrahedra and the fourth oxygen atom is terminal. The bridging pyramids each share four basal oxygen atoms with the silicate tetrahedra. Both single and double bridging pyramidal groups are observed, which require the silicate layers to have terminal oxygen atoms pointing up and down in groups of two and three, respectively. Generalization of these structure-building principles to other transition metal bridging groups has been proved effective. Several novel open-framework uranium silicates and copper silicates have been synthesized. Their structures determined from single crystal X-ray diffraction are based on bridging silicate layers with distorted uranium oxygen octahedra and copper oxygen squares, respectively.

All these novel compounds have transition metal centers that are an integral part of the frameworks and are accessible to molecular species via the pore systems. Their good thermal stability, adsorption and ion exchange properties suggest their potential for technological applications as molecular sieves or in catalysis.

Keywords: SILICATES OPEN-FRAMEWORK MICROPOROUS

MULTI-STEP REFINEMENT YBCO WITH OVERLAPPING BRAGG REFLECTIONS

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The software complex CSD was used for development of a new iterative procedure of refinement diffraction profile parameters when diffraction pattern is very complex. This technique is similar to one that we operated earlier at step-to-step refinement in A 15 non-stoichiometric compounds. The approbation was carried out on samples in system Y-Ba-Cu-O. As a result, we achieve to increase almost two times the number of individual peaks in line profile analysis and to construct a detailed angle dependence of FWHM for different crystallographic directions.

The time-dependencies of diffraction pattern change composition is described as undamped auto-oscillation process, formation of complex, organized superstructures from individual building blocks by exploiting forces and processes that are intrinsic to the system and interaction with environmental variation. These are in agreements with hypothesis (MRS Spring Meeting, 1994; VINITI, Nature, 1995) about the role of nonlinear phase transitions include self-organizations of the all of micro- and macro-structural parameters in this multi-components system. As in biological systems, it has been achieved through long evolutionary optimization processes and is often the result of a complex interplay between a large number of constituents and interactions. Proposed iterative procedure can used for the analysis of x-ray diffraction profiles of other samples with low symmetry and overlapped peaks (among them rhombic manganates composites, solid solutions of titanium aluminides, cementitious materials and other key engineering materials.

Keywords: SELF-ORGANIZATION LINE BROADENING OVERLAPPING PEAKS

STRUCTURAL STUDIES OF ULTRAFINE-GRAINED COPPER PREPARED BY HIGH-PRESSURE TORSION DEFORMATION

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Samples of ultrafine-grained (UFG) copper and copper with Al₂O₃ were subjected to high-pressure (6 GPa) severe plastic torsion deformation. The evolution of real structure of thin foil samples with annealing temperature was studied by powder diffraction (PXRD) using different diffraction geometries, diffuse scattering in transmitted wave and positron life-time spectroscopy (PL). The powder diffraction line profile analysis shown that dislocations of the density of about 1.10¹⁵m⁻² are the main source of line broadening. A new method of crystallite size determination based on the measurement of small-angle diffuse scattering in the transmitted wave has been applied. Both methods indicated bimodal crystallite size distribution after sample annealing when only a few grains start to grow quickly while the others remain the same (~ 100 nm).

The decrease of the mean dislocation density (determined by PXRD and PL) related to the reduction of volume fraction of distorted regions was shifted to higher temperatures of about 400°C after addition of 0.5% wt. Al₂O₃ to pure Cu for which primary recrystallization occurs above 160°C. Significantly higher number of microvoids of about 5-8 monovacancies for the former case was detected by PL too. Defect density remarkably decreases with the depth and there is also in-plane inhomogeneity in the subsurface layer. As concluded from the comparison of PXRD and PL, the depth gradient may be caused both by the reduction of dislocation density and decrease of number of microvoids while the change of defect density with the distance from the specimen center in the subsurface layer is related mainly to the microvoids.

Keywords: POWDER DIFFRACTION POSITRON ANNIHILATION SPECTROSCOPY DIFFUSE SCATTERING