

EXPOL: DATA ANALYSIS SOFTWARE FOR EXTRACTING MORE SINGLE-CRYSTAL-LIKE INTENSITIES FROM DATA COLLECTED ON A TEXTURED SAMPLE

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By exploiting the preferred orientation of the crystallites in a textured polycrystalline sample, the individual intensities of reflections that overlap in 2θ can be estimated more reliably and more single-crystal-like data obtained for structure solution. The viability of this approach has been demonstrated for data collected in reflection mode, but 3 days of synchrotron beamtime are required per sample. In an attempt to reduce the data collection time, to reduce the size of the sample and to obtain more complete data, experiments in transmission mode using a 2-dimensional detector have been performed. Typically 36 image plate frames, each corresponding to a 5° rotation of the sample, are measured. Each of these frames is subsequently divided into 72 radial wedges (5° sample tilt) using the program Fit2d. Thus the dataset consists of $36 \times 72 = 2592$ powder diffraction patterns, each corresponding to a different sample orientation. To analyze this large amount of data, the program Expol has been reorganized and expanded. In the first step of data analysis, an automatic intensity extraction procedure based on the Pawley algorithm is used to obtain pole figure data (intensity change as a function of sample orientation) for non-overlapping reflections. These data are then used to determine the orientation of the crystallites for the subsequent extraction of a single set of reflection intensities from the full dataset.

Keywords: STRUCTURE SOLUTION TEXTURE COMPUTER PROGRAM

BULK SOLVENT AND ITS ROLE IN MACROMOLECULAR PHASING

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Disordered solvent occupies about a half of macromolecular crystals and the information about its structure is very helpful for phasing. For molecular replacement when a similarity of the search model with the molecule under study can be relatively poor at the atomic level but is much better at low resolution where the influences of the bulk solvent is strong. Therefore, the search criterion can be drastically improved when it includes low resolution data corrected by the flat solvent model [1]. We have developed a fast and efficient procedure which allows such correction even when the position of the model is unknown, differently from the original method. A key moment of our approach is the use of the standard bulk solvent parameters $ksol=0.35 \text{ e/\AA}^3$ and $Bsol=50 \text{ \AA}^2$. These values, whose physical meaning has been also clarified, correspond to the centroid of their distribution for the PDB models. The bulk solvent plays also the key role in the direct phasing at low resolution. The connectivity-based phasing method [2] has been tested for the same crystal of the AspRS complex for which the neutron diffraction data have been measured for different solvent contrast masking different components of the crystal [3]. The tests showed a perfect correlation of the results with the solvent level.

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STRUCTURE SOLUTION AND REFINEMENT OF VARIOUS MINERALS BY AB INITIO POWDER DIFFRACTION METHODS

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The structure solution of a number of minerals has, in the past eluded crystallographers by virtue of their occurrence only as microcrystalline masses, which make them unsuitable for study by single crystal methods. In such cases, when the symmetry is high, it has often been possible, to establish the crystal structure from the powder diffraction pattern. There remains, however, a group of microcrystalline minerals of monoclinic and triclinic symmetry, for which crystal structure determination has proven to be intractable. The recent development of methods to fit powder diffraction profiles obtained using synchrotron x-ray sources together with the development of new software to accurately extract intensity data from these patterns has made possible the *ab initio* determination of the structure of microcrystalline compounds. We report here the crystal structures of two such minerals, kingite and priceite. Kingite, $\text{Al}_3(\text{PO}_4)_2(\text{OH},\text{F})_{3,9}\text{H}_2\text{O}$ from the Fairview phosphate working near Robertstown, South Australia was first described in 1957. The structure solution showed a layer structure consisting of strips of three-corner-linked AlO_6 octahedra which are inter-linked by PO_4 tetrahedra. Priceite, $\text{Ca}_4\text{B}_{10}\text{O}_{19,7}\text{H}_2\text{O}$, was described in 1873. We obtained a monoclinic cell $a = 12.356(1)$, $b = 6.980(1)$, $c = 11.627(1) \text{ \AA}$, and $\beta = 110.677(2)^\circ$. The structure solution from direct methods showed chains of Ca polyhedra linked by oxygen bridges, further investigation revealed that the Ca polyhedra are also linked via BO_3 and BO_4 groups.

Keywords: AB INITIO POWDER DIFFRACTION MINERALS

HYDROGEN MIGRATION MECHANISM IN CHIRAL LACTAM FORMATION BY X-RAY AND NEUTRON DIFFRACTIONS

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The achiral α , β -unsaturated thioamide has been found to give optically active β -thiolactam in high optical and chemical yields on exposure to UV light in the solid state. When a crystal of N,N-dibenzyl-1-cyclohexenecarbothioamide was irradiated with UV light at -10° , the cell dimensions gradually changed with retention of the single crystal form. After 330 hours exposure the structure was analyzed by X-rays. The thioamide molecule was converted by 65 % to the thiolactam molecule. The chirality of the produced thiolactam is well explained from the topochemical point of view. Although the reaction process was fully explained, it is still obscure which of the hydrogen atoms is extracted and transferred to the other carbon atom at the transition state. To solve the problem, the four hydrogen atoms of the thioamide were replaced with deuterium atoms and the crystal after irradiation was analyzed by neutron diffraction to examine the hydrogen migration. A crystal of $1.0 \times 1.5 \times 4.5 \text{ mm}^3$ was used. A part of the crystal analyzed by X-ray analysis indicated that more than 30 % of the thioamide molecules converted to thiolactam. The intensity data were collected on a 4-circle diffractometer, FONDER, set up at the Japan Atomic Energy Research Institute. The analyzed structure indicated that the photoreaction did not occur although the deuterium atoms were successfully exchanged. This may indicate that the crystal is too large for UV light to penetrate into the crystal and only the surface molecules are converted to the thiolactam. Further experiment is in progress.

Keywords: NEUTRON DIFFRACTION CRYSTALLINE STATE REACTION PHOTOCYCLIZATION