integrated intensities extracted from a powder pattern and random starting phases) with a specialized framework search specific to zeolite structures, which can be described as 3-dimensional 4-connected topologies. The capabilities of FOCUS have been tested with six examples of medium to high complexity (zeolite topologies DOH, LEV, RSN, AFR, LTA, EMT), and the method was then applied to three novel zeolite structures - the two zincosilicates VPI-9 and VPI-10, and the beryllosilicate B2 - and a promising model was obtained in all cases. The structure of VPI-9 has since been confirmed with a full Rietveld refinement, and the code VNI has been assigned to that topology. Refinements for VPI-10 and B2 are in progress.

Experience shows that the approach of using chemical and geometrical knowledge can compensate for some of the information that is lost as a result of the overlap problem. At the same time, there is an intrinsic disadvantage: any method based on assumptions of certain structural properties is also limited to materials which conform to these assumptions. Examples which show the consequences of relaxing the structural assumptions were investigated, and it was found that the computing time requirements of FOCUS grow very rapidly with the number of different possible connectivity types. Suggestions for further developments to overcome this problem are outlined.

MS02.05.04 POWDER STRUCTURES FROM LIMITED DATA SETS.

Damodara M. Poojary, Abraham Clearfield, Department of Chemistry, Texas A & M University, College Station, TX 7783

Structures of compounds which can be obtained only in the polycrystalline form depend mainly on the use of their powder diffraction data. Substantial progress has been made in instrumentation and computational aspects during the last decade for the application of powder diffraction techniques to solve unknown structures. One of the crucial steps involved in this process is to acquire the best possible diffraction data. Synchrotron sources, with their high brightness, excellent collimation and wavelength tunability provide optimum conditions for extracting individual intensities in the powder pattern. In most cases we have been able to arrive at the solution using data from a rotating X-ray source. However, synchrotron data was required to complete the structures in some cases.

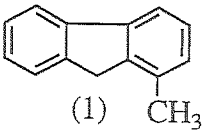
This talk focuses mainly on the structure determination of metal phosphonates and phosphates. These compounds are difficult to obtain in single crystalline form and in most cases even their powder samples are poorly crystalline. The compounds yield only weak diffraction peaks whose intensities fall off very rapidly at higher scattering angles. Despite these difficulties, we have been able to solve the structures of a large number of compounds. Generally, the structures of these compounds are layered, where the metal-phosphate inorganic framework forms a two-dimensional layers which are separated by the organic groups on either side. In some cases metal phosphonate interactions led to unusual linear or porous structures. General methods used in solving the structures will be discussed using some representative examples.

In many cases the structures were solved by the use of 30-70 low angle(CuKα; $2\theta<60°$) reflections by a combination of direct methods and heavy atom methods. The success comes from experience both in the structural aspects of these materials as well as the systematic application of efficient methods. It is equally important to use the results from other methods like spectroscopy, thermogravimetry, electron diffraction, etc. to arrive at the solution when only a limited number of powder diffraction data are available.

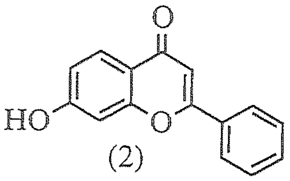
MS02.05.05 DETERMINATION OF MOLECULAR CRYSTAL STRUCTURES FROM X-RAY POWDER DIFFRACTION BY MONTE CARLO METHODS.

MaryJane Tremayne, Department of Chemistry, UCL, London, WC1H 0AJ, U.K; Benson M. Kariuki, and Kenneth D. M. Harris, School of Chemistry, University of Birmingham, Birmingham, B15 2TT, U.K.

Many important crystalline solids cannot be prepared in the form of single crystals of sufficient size and quality for single-crystal X-ray diffraction studies, and in such cases it is essential that structural information can be extracted from powder diffraction data. We have developed and applied a method employing a Monte Carlo algorithm for crystal structure determination from powder diffraction data. In this method, a series of structural models is generated by random movement of a collection of atoms within the unit cell, and each trial structure is accepted or rejected on the basis of the agreement between the experimental powder diffraction pattern and the powder diffraction pattern calculated for the structural model. This technique differs considerably from the normal approach for structure determination from powder diffraction data, in that intensity information is not directly extracted from the diffraction pattern, and hence the problems of assigning intensities to overlapping reflections are avoided. The success of this method for *ab initio* crystal structure determination from X-ray powder diffraction data has been demonstrated by its application to the solution of several crystal structures including *p*-$BrC_6H_4CH_2CO_2H$ [K. D. M. Harris, M. Tremayne, P. Lightfoot, P. O. Bruce, *J. Am. Chem. Soc. (1994)*, **116**, 3543] and the γ-phase of 3-$ClC_6H_4CHCHCO_2H$ [B. M. Kariuki, D. M. S. Zin, M. Tremayne and K. D. M. Harris, *Chem. Mat.* (1996), in press]. In the work presented here, we have extended the Monte Carlo method to structure solution by a) simultaneous translation and rotation of a rigid structural fragment within the unit cell - illustrated by the structure determination of 1-methylfluorene (1) - and b) simultaneous translation and rotation with additional rotation about intramolecular bonds - illustrated by the structure determination of 7-hydroxyflavone (2).



(1)



(2)

MS02.05.06 CRYSTAL CHEMISTRY FROM POWDER DATA.

Ian E. Grey CSIRO Division of Minerals, PO Box 124, Port Melbourne, Australia

A strength of structure analyses using powder data is the relatively short time required to obtain high quality data sets. This makes powder diffraction analysis particularly suitable for systematic structural studies on series of related compounds such as solid solutions in minerals and their synthetic equivalents. The high precision obtained when collecting and processing powder data sets under identical conditions allows the detailed study of subtle crystal chemistry correlations, for example variations in cation site occupancies, anion vacancies and bonding interactions.

The use of variable counting time (VCT) data collections (Madsen and Hill, 1994) enhances the capability to analyse subtle structure variations using X-ray data collected using a conventional laboratory configuration. In particular it yields more consistent thermal parameters, more accurate site occupancies and more stable refinement of light atoms.

Examples will be presented of the application of Rietveld analysis of VCT powder X-ray data to investigate chemical and structure variations in synthetic mineral systems. These include studies on cation substitutions in synthetic loveringite, $(Ca, Ti^{3+}, Ti^{4+}, Mn)_{22}O_{38}$ prepared under reducing conditions, studies on anion vacancy and Fe^{3+}/Fe^{4+} variations in the solid solution of hexagonal $BaTiO_3$ with $Ba_2Fe_2O_5$, and crystal chemistry systematics of sulphate and oxysulphate phases formed during sulphuric acid digestion of ilmenite.

ref. I.C. Madsen and R.J.Hill, *J.Appl. Cryst.* (1994). **27**, 385-392

MS02.05.07 INFORMATION ON SYMMETRY IN POWDER DIFFRACTION DATA.

M. Ohmasa[1], K. Ohsumi[2] and H. Toraya[3]. [1]Department of Life Science, Himeji Institute of Technology, Japan; [2]Photon Factory, National Laboratory for High Energy Physics, Japan; [3]Ceramics Research Laboratory, Nagoya Institute of Technology, Japan.

Since each crystal family except triclinic, monoclinic and orthorhombic ones doesn't correspond to a Laue class uniquely (: holohedral and hemihedral Laue classes) and no method to identify Laue classes of those families had been presented for powder specimens, their space groups had been assigned only with crystal family and reflection conditions. Because summed intensities are measured by powder diffraction methods and they are not separable to individual intensities. Recently Ohmasa & Ohsumi (1995) indicated that weighted reciprocal lattices named composite reciprocal lattices are constructed from powder diffraction data in such a way that summed intensities are distributed to reciprocal lattice points to hold holohedral symmetry and indicated that information on Laue classes can be obtained from concentrations of interatomic vectors in Patterson functions evaluated with intensities at the composite reciprocal lattice points (composite Patterson functions). For hemihedral Laue classes, a composite reciprocal lattices is regarded as a superposed record of weighted reciprocal-lattice points of a single crystal. In this case the superposition yields new symmetry generators (extra generators) which are not intrinsic to the Laue class of the single crystal. The same generators as the extra ones are included in holohedral symmetry and the distribution of the points and their relative weights in the composite Patterson function coincide with those in the Patterson function of the real structure. The same generators as the extra ones are not included in the symmetry generators of the real structure with hemihedral Laue symmetry but the apparent symmetry of the composite Patterson functions is enhanced to holohedral one by the extra generators. However the distribution of the peaks and their relative weights in the composite Patterson functions are not perturbed by the extra generators and the feature of the concentration of the peaks related to interatomic vectors in the real structure is retained. Consequently, distinction of space groups should in principle be possible by interpretation of composite Patterson functions. Composite Patterson functions of some materials will be indicated as examples.

Ohmasa, M. and Ohsumi, K. (1995). Acta Cryst. A51, 87-91.

MS02.05.08 THE TANGENT FORMULA DERIVED FROM PATTERSON FUNCTION ARGUMENTS: A USEFUL TOOL FOR SOLVING ZEOLITE STRUCTURES FROM X-RAY POWDER DATA.

J. Rius & C. Miravitlles, Institut de Ciencia de Materials de Barcelona (CSIC), Campus de la UAB, 08193-Cerdanyola, Catalunya (Spain).

The viability of solving the structure type of zeolitic and layered materials applying multisolution direct methods to low resolution (≅2.2 Angstroms) powder diffraction data is shown. The phases are refined with the tangent formula derived from Patterson function arguments [Rius (1993). Acta Cryst. A49, 406-409] implemented in the XLENS program and the correct phase sets are discriminated with the conventional figures of merit.

The two test examples presented are (a) the already known tetragonal zeolite ZSM-11 (space group I-4m2) at 2.3 Angstroms resolution and (b) the hitherto unknown layer silicate RUB-15 (Ibam) at 2.2 Angstroms resolution. In both cases, the tetrahedral Si units appear as resolved peaks in the Fourier maps computed with the phases of the highest-ranked direct methods solutions.

MS02.05.09 DIRECT PHASING FROM POWDER DATA: THE EXTRA OPTIMIZED PROCEDURE

C. Giacovazzo(+), A. Altomare(+), G. Cascarano(+), A. Guagliardi(+), A.G.G. Moliterni(+), M.C. Burla(*) & G. Polidori(*) (+) Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche - CNR c/o Dipartimento Geomineralogico - Campus Universitario Via E. Orabona, 4 - 70125 Bari - Italy. (*) Dipartimento di Scienze della Terra, Universita, 06100 Perugia, Italy.

Present difficulties in solving crystal structures from powder data are not to be found in the lack of efficiency of direct methods, but in the inaccuracy of the process which extracts structure factor amplitudes from a powder pattern. EXTRA [A. Altomare, M. C. Burla, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni & G. Polidori (1995), J. Appl. Cryst. **28**,842-846] has been an efficient answer to this problem: friendly to use, the program is able to automatically decompose, via the Le Bail algorithm, quite complicated experimental patterns.

EXTRA is now incorporating new important features. It is able to take advantage from: a) the Patterson map; b) the pseudo-translational symmetry; c) the preferred orientation; d) the statistical estimates of the diffraction amplitudes via direct methods; e) a molecular fragment.

All the above sources of information are able to dramatically improve the accuracy of the pattern decomposition process so enlarging the size of crystal structures solvable by powder data. We are merging EXTRA with SIRPOW.92 [A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi. M.C. Burla, G. Polidori, & M. Camalli, (1994), J. Appl. Cryst. **27**, 435-436], our direct methods program for powder data, to provide a unique program, transparent to the user, which should be able to solve a structure directly the diffraction pattern.