

P02.11.38*Acta Cryst.* (2008). A64, C212**Powder structure analysis of oxotitanium phthalocyanine as charge generation materials**Yuko Kojima

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Oxotitanium phthalocyanine (TiOPc) has been developed as a high sensitive charge generation material for organic photoconductors. It is known that TiOPc has four polymorphs (form I, II, C and Y) and the photosensitivity as charge generation materials depends on the crystal structures (sensitivity: form Y > I >> II >> C). The crystal structures of more stable polymorphs (form I and II) have been reported [1]. TiOPc form Y that has highest photosensitivity in the four polymorphs have never grown in large enough crystals for single crystal analysis. The crystal structure of form Y was determined by X-ray powder structure analysis using synchrotron radiation (Photon Factory BL4B2). TiOPc form Y crystal includes water solvents and MEM analysis using RIETAN-FP and VESTA[2] reveals the site of Oxygen atom of H₂O in the crystal. This result suggests that TiOPc form Y crystal has hydrogen bonds between the oxygen atoms of water solvents and Ti atoms of TiOPc.

[1] W. Hiller et al., *Z.Krist.*, 159, 173 (1982)[2] F. Izumi and K. Momma, *Proc. XX Conf. Appl. Cryst., Solid State Phenom.*, 130, 15 (2007)

Keywords: powder structure determination, polymorphs, organic photoconductors

P02.11.39*Acta Cryst.* (2008). A64, C212**Single crystal analysis of magnetically prepared pseudo-single crystal of sucrose**Masataka Maeyama¹, Fumiko Kimura², Katsunari Sasaki¹, Tsune-hisa Kimura²

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The single crystal analysis with the x-ray diffraction is best suited for determining the three-dimensional structure of new compounds. However, preparing a single crystal that is large enough for the x-ray analysis is getting more and more difficult recently because the crystal growth is difficult for many compounds with complicated structures demanded in recent advanced materials sciences. Instead of the method of single crystal analysis, the ab-initio or direct space method is now available for the powder diffraction analyses and a number of crystal structures have been determined using this method. Unfortunately, the use of this method is limited to specialists who can correctly determine the cell constants and structure only from the two-dimensional information. Recently, a magnetic technique of 3-dimensional alignment of powder crystallites has been developed. This technique enables to convert a powder to a pseudo-single crystal. In the present work, we demonstrate a single crystal analysis of a pseudo-single crystal of sucrose. We were able to index and solve the structure from this pseudo-single crystal using only a conventional method of single crystal analysis. The presentation includes the process of measurement, the solution of structure and the comparison of experimental data with simulation.

Keywords: pseudo-single crystal, magnetic technique, *ab-initio* structure determination

P02.12.40*Acta Cryst.* (2008). A64, C212**Crystal structure model assembly program using Monte Carlo simulation**Hiroyuki Miura

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A crystal structure model assembly program (SMAP) which designs starting models of Rietveld refinement was developed. This program requires XRD data, cell constants, space group, chemical formula and Z-number. On the basis of atomic positions selected by the Monte Carlo simulation, this program calculates the R-factor of the model from theoretical and observed XRD data. Hundreds of models of low-R-factor are selected and stored. Then, they gradually converge to a true structure. Using this program, the crystal structure of sibirskite (CaHBO₃) was solved and confirmed by the Rietveld refinement. The mineral sibirskite is monoclinic with space group *P2₁/a*. The calcium atom is surrounded by six oxygen atoms in an octahedral coordination, and a symmetrical pair of edge-shared CaO₆ octahedra forming a double chain elongates the crystallographic c axis. The BO₃ triangles are linked to three CaO₆ double chains to form the sibirskite structure. Sibirskite is isostructural with nahcolite (NaHCO₃), which consists of NaO₆ double chains and CO₃ triangles.

Keywords: Monte Carlo treatment, X-ray powder diffraction software, Rietveld method

P02.12.41*Acta Cryst.* (2008). A64, C212-213**Application of the S-FFT phasing method to the solution of inorganic structures from powder data**Carlos Miravittles, Jordi Rius

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Since its discovery, the direct methods origin-free modulus sum function *S* [Rius (1993) *Acta Cryst.* A49, 406-409] has been used for solving some relatively complex inorganic crystal structures from powder X-ray diffraction data. This function was implemented in program XLENS [Rius (1999) *Powder Diffraction* 14, 267-273]. In this program phase values were estimated by maximising *S* with a modified tangent formula applied in sequential form. However, further progress in the powder diffraction field was hampered by the complexity of combining the tangent formula refinement (that makes explicit use of triple-phase sums) with the introduction of constraints in real space necessary to counterbalance the information loss produced by peak overlap. Recently, a considerably simpler and completely general phasing procedure (S-FFT) has been developed that maximises *S* by means of the FFT algorithm so that the triple-phase sums are considered implicitly [Rius, Crespi, Torrelles (2007) *Acta Cryst.* A63, 131-134]. This algorithm has been adapted now to powder diffraction data and implemented in a new XLENS Windows version that can be retrieved from the toolbar of the FULLPROF-suite of programs (<http://www.ill.fr/sites/fullprof/php/downloads.html>) (Rodríguez-Carvajal, 2008). The effectiveness of the program

to treat powder data is illustrated on a series of inorganic structures of variable complexity.

Keywords: direct methods, powder data, inorganic crystals

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Combining X-ray powder diffraction and electron microscopy to solve complex structures

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When a complex structure of a polycrystalline material cannot be solved from X-ray powder diffraction (XPD) or electron microscopy data alone, combining the two techniques might succeed. Phase information derived from high-resolution transmission electron microscopy (HRTEM) images can be combined with XPD intensities to facilitate structure solution. Alternatively, the single-crystal intensities from electron diffraction (ED) data can be used to improve the estimate of the relative intensities of reflections that overlap in the XPD pattern. The first approach has already proven to be a powerful one, but it requires HRTEM images, which are not always easy to obtain. The second is the subject here. Tests show that intensities from conventional selected area electron diffraction patterns are not very reliable because of multiple scattering effects, so they cannot be used directly to repartition the intensities of overlapping reflections. However, the precession electron diffraction (PED) technique reduces these effects. The PED intensities are still distorted, so we took a very conservative approach, using them simply to identify the weak reflections. These reflections were then eliminated from the XPD intensity extraction. Initial tests of the feasibility of this approach were performed on the zeolite ZSM-5 using the powder charge flipping (pCF) program and simulated ED patterns along 3 zone axes. Then real PED data were used. In both cases, the final pCF electron density maps revealed the positions of all 12 Si and 26 O atoms in the framework structure. This is not the case when the original XPD data without weak reflection elimination are used. It appears that even this simple modification of the dataset has a significant impact on structure solution.

Keywords: electron crystallography, powder diffraction, structure determination

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Powder diffraction, electron microscopy, focus, charge flipping and zeolites

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As a result of impressive methodological advances in recent years, the determination of a crystal structure from powder diffraction data is no longer a rarity. However, some zeolite structures remain intractable. To address such problems, the powder diffraction data can be supplemented with information from other sources. Both the zeolite-specific structure-solution program Focus and the more generally applicable powder charge-flipping (pCF) algorithm have been adapted to accommodate such data combinations, and this has

allowed the complex structures of TNU-9 (24 Si atoms), IM-5 (24 Si atoms) and SSZ-74 (23 Si atoms) to be solved. The key in all cases was the combination of high-resolution powder diffraction data with information derived from high-resolution transmission electron microscopy (HRTEM) images. For TNU-9, Focus was used to combine the reflection intensities extracted from the powder diffraction pattern with phases and a structure envelope derived from HRTEM images. For the other two, the pCF algorithm implemented in Superflip was used to effect the combination. Both algorithms work in both direct and reciprocal space, so they are particularly well-suited for bringing data from different sources together, whether the data be in diffraction or real space. Adding even a very limited amount of phase information to the initial (usually random) phases in either algorithm, can make the difference between solving and not solving a structure, and this proved to be the case for TNU-9, IM-5 and SSZ-74. With 23-24 Si atoms in the asymmetric unit, these are by far the most complex zeolite framework structures known. The approach used to elucidate their structures is not only generally applicable, but many extensions to include other types of data can be envisioned.

Keywords: powder diffraction, electron microscopy, charge flipping

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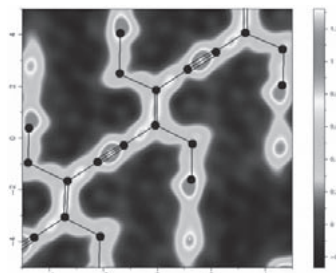
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First success in direct evaluation of electron density distribution of polymer by X-N method

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Bonded electron density distribution along the skeletal chains of polydiacetylene single crystal has been successfully and quantitatively evaluated for the first time on the basis of the organizedly combined X-ray diffraction and neutron diffraction data (X-N method). The application of X-X method, where only the X-ray diffraction data were used in an approximation, resulted in the abnormal distribution of electrons on the triple bond. This comes from ambiguity of atomic positions and an overestimation of temperature factors in the X-ray method since the atomic positions and thermal parameters were approximated from the information on the center of gravity of electron density clouds. Contrarily the neutron method gave us the exact positions and thermal parameters of atomic nuclei themselves. The X-N method was applied also to the low-molecular-weight model compounds to get the reasonable bonded electron density distributions. The thus evaluated electron density distributions were compared with those calculated by density functional theory.



Keywords: electron density distribution, polymer, X-N method