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Keywords: lanthanides; phosphonates; singlecrystal; powder diffraction; structural characterization; rietveld

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Polytypism, Polymorphism and Compositional Faults in Layered Ternary and Quaternary Compounds. Mahmud Kyazumov^a, Lale Rustamova^a, Mahbub Kazimov^a. ^a*Institute of Physics of the National Academy of Sciences of Azerbaijan, Baku, Azerbaijan.*

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It has been determined that on depend on various growth conditions in crystals and type of their synthesis the multicomponent layered crystals have a big variety of polytypic and polymorphic modifications. Not only separate crystal's bits taken from various places of the same ampoule may distinguish by their structures but many other polytypic phases can also exist in the same crystal. It is naturally that the presence of one phase on the basis of another one is connecting with packing defects of sulphur atoms and formation of cation's base of a new phase. Deficit of sulphur atoms as a rule is leading to change the cation's valency in crystals as a result of which the ionic radii of cations are also changed and element's base of a new phase is forming. An increase of octahedral (O) position's shares due to decrease of tetrahedral (T) ones in $\text{O}^{\text{II}}\text{O}^{\text{I}}$, $\text{O}^{\text{I}}\text{O}^{\text{I}}$, $\text{O}^{\text{I}}\text{O}^{\text{I}}$, $\text{O}^{\text{I}}\text{O}^{\text{I}}\text{O}^{\text{I}}\text{O}^{\text{I}}$, O^{I} , $\text{O}^{\text{I}}\text{O}^{\text{I}}$, $\text{O}^{\text{I}}\text{O}^{\text{I}}\text{O}^{\text{I}}$ types of structural units stimulates creation of such a phases. In shares of octahedral position in common tetrahedral and octahedral share's positions are as followed: 20%, 25%, 33%, 50%, 50%, 50%, 60%. In case when cations have a permanent valences a creation of a new phase becomes impossible and for packing defects of sulphur atoms only compositional faults are coming up.

Keywords: polytypism; polymorphism; layered compounds

FA5-MS01-P10

Two-Level Genetic Algorithm for Direct-Space Structure Solution and Refinement. Yaroslav I. Yakimov^a, Eugene S. Semenko^a, Igor S. Yakimov^a. ^a*Siberian Federal University, Krasnoyarsk, Russian Federation.*

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Genetic algorithms (GA) have been used to generate crystal structure models from the knowledge of only the

unit cell and constituent elements by powder diffraction data in the direct space [1]. This work is dedicated to GA spread-out to Rietveld method including full-profile fitting and refinement of crystal structure models. A two-level genetic algorithm has been developed for this purpose. The two-level genetic algorithm is based on a combination of conventional GA similar to [2] with a new Rietveld-like derivative difference minimization (DDM) method [3]. First-level GA chromosomes comprise values of profile and structure parameters used in the Rietveld method. Since initial population is generated randomly, a priori known parameter values are not required. GA fitness function is based on the weighted profile R-factor of DDM (R_{DDM}). Second-level GA chromosomes are bit strings containing one bit per parameter of first-level parameter string, where bit values specify parameters to be refined with the DDM on a current iteration. In whole, a path of local descent on R_{DDM} - hypersurface is defined by second-level GA. Both levels are executed alternately with transferring better found parameter values to another level.

The algorithm was tested on some powder patterns of single and multi-phase samples with known crystal structures. As an example, the crystal structure of $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ which initially had been solved from powder diffraction data by the Patterson method [4] was found from X-ray powder diffraction data by applying the proposed GA method. All general atomic coordinates and thermal factors including coordinates of hydrogen atoms were searched and refined successfully in a fully automatic way (26 structural parameters in total). The GA was applied for quantitative phase analysis of three- and four-phase samples CPD1 and CPD2 from Round Robin on QPA [5] as well. All profile parameters, general atomic coordinates and thermal factors (20 profile and 9 structural parameters in total in case of CPD1 sample) were searched with the GA simultaneously and then phase concentrations were calculated as usual for QPA by Rietveld method with mean error about 0.3% mass.

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Keywords: genetic algorithm; structure solution; powder diffraction

FA5-MS01-P11

Successful Cryocooling of Protein Microcrystalline Samples for Powder Diffraction. Yves Watier^{a*}, Irene Margiolaki^a, Jonathan Wright^a, Andrew Fitch^a, Mathias Norrman^b, Gerd Schluckebier^b. ^a*European Synchrotron Radiation Facility (ESRF), Grenoble, France.* ^b*Novo Nordisk A/S, Copenhagen.*

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Modern developments of the powder diffraction technique have allowed the investigation of systems with large unit cells such as proteins [1]. Protein powder specimens consist of a large number of randomly oriented diffracting micro-crystals. These micro-crystals are usually formed rapidly by batch crystallization. Frequently, the resolution and quality of the data are limited mainly by rapid deterioration of the protein crystal structure during exposure to the intense synchrotron X-ray beam. In a typical single crystal diffraction experiment radiation damage can be minimized by collecting diffraction data under cryocooled conditions (typically 100K) which requires the addition of a cryoprotecting agent to the protein sample to prevent freezing of the mother liquor. In this study, we succeeded in obtaining various cryocooled samples of human insulin at 100K avoiding ice formation. Powder diffraction data were collected at both room temperature and under cryocooled conditions (ID31, ESRF, Grenoble, France). As expected both the cryoprotectant and the sample container have a remarkable impact on the data quality. Significant variation of the lattice parameters and peak widths with the type and concentration of cryoprotecting agent has already been observed and will be presented for the case of insulin. Preliminary data interpretation correlating these changes with the structural and microstructural characteristics of the systems under study will be shown.

[1] Margiolaki, I. & Wight, J. P. *Acta Cryst.*, **2008**. A64, 169-180

Keywords: proteins; powder diffraction; cryocooling

FA5-MS01-P12

Two Quinoline Zirconium Phosphate Structures Solved Using Powder Charge Flipping. Dubravka Sisak^a, Christian Baerlocher^a, Lynne McCusker^a, Lei Liu^b, Jinxiang Dong^b. ^a*ETH Zurich, Laboratory of crystallography, Zurich, Switzerland.* ^b*Taiyuan University of Technology, Taiyuan, Shanxi, China.*
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Two novel zirconium phosphate compounds with the chemical formulae $[(C_9H_8N)_4(H_2O)_4][Zr_8P_{12}O_{40}(OH)_8F_8]$ (ZrPOF-Q1) and $[(C_9H_8N)_2][Zr_2P_2O_4(OH)_2F_4]$ (ZrPOF-Q2) were synthesized hydrothermally in the HF-ZrO₂-P₂O₅-quinoline-H₂O system. Because they could only be obtained in polycrystalline form, their structures had to be analyzed using powder diffraction techniques. Both diffraction patterns (ZrPOF-Q1 : synchrotron, SNBL at ESRF; ZrPOF-Q2 : laboratory, Stoe) could be indexed with triclinic unit cells, but the dimensions and volumes are significantly different (ZrPOF-Q1: ; $a = 10.7567\text{\AA}$, $b = 13.8503\text{\AA}$, $c = 14.8994\text{\AA}$, $\alpha = 109.6^\circ$, $\beta = 101.1^\circ$, $\gamma = 100.5^\circ$; $V = 1979\text{\AA}^3$, and ZrPOF-Q2: ; $a = 7.7058\text{\AA}$, $b = 12.3546\text{\AA}$, $c = 6.5851\text{\AA}$, $\alpha = 97.0^\circ$, $\beta = 89.7^\circ$, $\gamma = 101.9^\circ$; $V = 610\text{\AA}^3$). In both cases, reflection intensities were extracted from the powder diffraction pattern using the Le Bail method and then used as input to the powder charge-flipping (pCF) algorithm [1] in the program Superflip [2]. In this implementation, the original single-crystal charge-flipping algorithm of Oszlányi and Sütő [3,4] has been modified to include a second type

of perturbation of the electron density map. This is based on a histogram matching algorithm and is performed prior to a repartitioning of the intensities of reflections that overlap in the powder pattern. The histogram used simply reflects the chemical composition per unit cell. The electron density maps obtained from Superflip showed localized electron densities in the form of tetrahedra and octahedra, which were interpreted as PO₄ and Zr(O,F)₆ groups. Some residual, less well-localized electron density, assumed to be due to the quinoline species, was also observed, but was not used in constructing the initial model for Rietveld refinement. Instead, the positions of the quinoline C and N atoms were derived from a series of difference Fourier maps. The structure of ZrPOF-Q1 (60 non-H atoms, 3909 of 4522 reflections overlapping, $R_F = 0.053$, $R_{wp} = 0.144$) consists of zirconium phosphate layers with quinolinium ions and water molecules in between. The layers are unusual in that they have isolated ZrO₂F₄ octahedra anchored on their surfaces that protrude into the interlayer space. The ZrPOF-Q2 structure (19 non-H atoms, 928 of 1265 reflections overlapping, $R_F = 0.059$, $R_{wp} = 0.162$) consists of zirconium phosphate chains with an unusual Zr:P ratio of 1.0, interspersed with quinolinium ions. The charge-flipping algorithm allowed a straightforward structure solution in both cases, although the degree of reflection overlap is considerable. The effect of the various charge-flipping parameters on the structure solution will be presented.

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Keywords: charge flipping; structure determination; X-ray powder diffraction

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High Throughput Phase Diagram Mapping of Urate Oxidase via Powder Diffraction. Ines Collings^a, Sotonye Dagogo^a, Yves Watier^a, Irene Margiolaki^a, Andrew N. Fitch^a, Jonathan P. Wright^a, Marion Giffard^b, Françoise Bonnetet^b, Richard Kahn^c. ^a*European Synchrotron Radiation Facility, Grenoble, France.* ^b*Centre Interdisciplinaire de Nanoscience de Marseille, France.* ^c*Institut de Biologie Structurale, Grenoble, France.*
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Modern developments of the powder diffraction technique have allowed the investigation of systems with large unit cells such as proteins [1]. Polycrystalline protein precipitates are frequently obtained under a variety of crystallization conditions and thus powder methods can be employed for structural characterization of small proteins when single crystals are unavailable. The recombinant urate oxidase from *Aspergillus flavus* (Uox) is a protein used to reduce toxic uric acid accumulation and also for the treatment of hyperuricaemia which occurs during chemotherapy. In this study, we investigate the effects of pH, salt and polyethylene