nanoparticle). This is the pesky problem Peter Piper picked.

In this talk I will illustrate the problem and discuss some efforts we are taking to overcome these difficulties. I will describe some developments inspired by computer science that could be brought to bear on problems like this. We are not currently able to answer the question posed in the title, but even thinking about it is proving to be a lot of fun.

Keywords: nanocrystallography, software, local structure

MS13.24.4

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Single Crystal Quality Structures from Polycrystalline Samples

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We have recently demonstrated [1,2] a method whereby single crystal quality data can be extracted from polycrystalline samples comprising up to 1000 crystals. The method works by focusing the X-ray beam on the sample such that a sufficiently small active area is illuminated such that the diffraction from the individual crystallites is sufficiently distinct that some individual spots may be extracted. With these data we simultaneously determine, via a novel algorithm [3], the orientation matrices of the crystallites which constitute the powder specimen.

Given these orientation matrices, the intensities of the contributions from the different crystallites may then be deconvoluted, scaled, and filtered/reweighted by a variety of methods. In this way we determine not only the average structure of a powder specimen, with single crystal precision, but also the distribution of structural properties within the sample.

We have now attempted to apply this technique to progressively more complicated systems; the latest results will be presented.

[1] Schmidt S., Poulsen H.F., Vaughan G.B.M., *J. Appl. Cryst.*, 2003, **36**, 326. [2] Vaughan G.B.M., Schmidt S., Poulsen H.F., *Z. Kristallogr.*, 2004, **219**, 813. [3] Lauridsen E.M., Schmidt S., Suter R.M., Poulsen. H.F., *J. Appl. Cryst.*, 2001, **34**, 744.

Keywords: structure determination methods, algorithmic methods, computer algorithm development

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'Pushing the Boundaries' of Differential Evolution in SDPD

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The development of direct space structure solution techniques is an important factor in the increasing number of crystal structures determined using PXRD [1]. Direct space methods involve assigning *R* factors to trial structures by comparison of the calculated powder profile to the experimental pattern. A global optimisation algorithm, such as Monte Carlo or evolutionary algorithms is applied to locate the correct crystal structure.

Differential Evolution (DE) is an evolutionary algorithm, which is simple to implement and offers robust searching of minima [2,3]. A population of trial structures is generated, characterised by parameters describing position, orientation of the molecule and any variable torsion angles. Associated with each parameter is a minimum and maximum boundary. The population is mated and mutated in a single step to produce successive generations until the structure with the lowest *R* factor is found.

This presentation describes a modification of the DE algorithm which enables the boundaries to be updated during a structure solution calculation, using information previously gained within the search. We examine the effect of restricting the search to regions where low *R* factor has been found on the efficiency of the DE optimisation.

[1] Tremayne M., *Phil. Trans. R. Soc. Lond. A*, 2004, **362**, 2691. [2] Price K.V. in *New Ideas in Optimization*, ed: Corne D., Dorigo M., Glover F., McGraw-Hill, London. 1999. [3] Tremayne M., Seaton C.C., Glidewell C., *Acta. Cryst.*, 2002, **B58**, 823.

Keywords: powder structure determination, structure solution methods, computer algorithms

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MS14 MODULARITY AND MODULATION IN INORGANIC AND MINERAL STRUCTURES

Chairpersons: Emil Makovicky, Stefano Merlino

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Layered Compounds: from Modular Description to Rational Design

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As a reliable *ab-initio* theory for crystal structure is still lacking, the rational design of new compounds remains a major challenge in solid state sciences. In that quest, the modular description of 2D structures could provide an interesting alternative pathway, as exemplified by the family of 2D-misfit layered chalcogenides $[(MX)_m]_{1+x}[TX_2]_n$ (M = rare earth, Sn, Pb, Sb or Bi ; T = Ti, V, Cr, Nb, or Ta ; X = S, Se) [1]. These compounds have incommensurate layered composite structures which are built from an alternated stacking of $[MX]$ module of the rock salt type and $[TX_2]$ module of the CdI_2 or NbS_2 types. Combinations of divalent or trivalent metals M and transition metals T led to the recognition of numerous new compounds with different alternated stacking sequences as defined by the m/n ratio. A careful analysis of structure databases proves that similar 2D modules (rock salt or CdI_2 types) are encountered in many structures and in many different chemical environments. This observation led to consider these modules as 2D building blocks and suggests a novel way to predict the structures and the compositions of some new inorganic compounds [2]. Starting from the modular description of misfit layered compounds this presentation aims to give an insight of the concept of 2D building blocks and to present its first application to the design of commensurate or incommensurate 2D layered compounds.

[1] *Materials Science Forum*, Trans. Tech. Publications, ed. by Meerschaut A., 1992, 100-101. [2] Cario L., Kabbour H., Meerschaut A., *Chem. Mater.*, 2005, **17**, 234.

Keywords: incommensurate modulated structures, layered materials, design

MS14.24.2

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Recurrent Modules in Modular Structures

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Modular structures are based on complex structural fragments (modules) that occur in different crystal structures. Let A and B be bidimensional and crystal-chemically different modules; A_mB_n represents a polysomatic series formed by members based on different m/n ratios. The cell parameters and chemical composition of the members linearly depend from those of the building modules.

A survey of polysomatic structures recently reported in [1] shows a large variety of recurrent modules. In oxygenated compounds, among others, the following modules recur: bafertisite, brucite, corundum, epidote, gibbsite, mica, nasonite, nolanite, palmierite, perovskite, pyrochlore, pyroxene, rutile, schafarzikite, spinel, talc, and topaz. Tetrahedral (*T*) and octahedral (*O*) modules are widespread in nature both as *TOT* and *TO* slices; slices of perovskite with various thickness and orientation are present in hundreds of synthetic inorganic materials, including superconductors, and are the basis of several series of inorganic-organic hybrids.

The concept of modularity is a powerful tool increasingly used to handle various crystal-chemical aspects of the structures: (i) modelling the unknown structure of new members of a series; (ii) interpreting topotactic reactions and defects in real structures; (iii) tuning the properties of synthetic materials; (iv) inspiring the synthesis of mesoporous (e.g., pillared clays) and intercalation materials.

[1] Ferraris G., Makovicky E., Merlino S., *Crystallography of Modular Materials*, 2004.

Keywords: modular materials, structure modelling, polysomatism

MS14.24.3

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Refinement of Partially Disordered OD Structures

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In the diffraction pattern of OD structures two kinds of reflections can be distinguished: (i) Family reflections represent the Fourier transform of the so called family structure: a fictitious structure comprising all possible positions of OD layers superimposed with equal probability. They are always sharp, even for totally disordered crystals, and common for all polytypes of the family. (ii) Non-family, or polytype reflections, characteristic for a given polytype . These are sharp only for ordered (3D periodic) polytypes, otherwise they are more or less smeared out into diffuse streaks [1]. For partially disordered crystals, the intensities of the non-family reflections are underestimated due to their diffusivity and the moduli of their structure factors are reduced by a common factor.

If both kinds of reflections are constrained on the same scale in the refinement process, spurious ”ghost” peaks can appear on the Fourier map [2]. These peaks are in fact residuals of the family structure. The structure can be in most cases successfully refined if separate scale factors are assigned to either of the two kinds of reflections [3]. Several artificial and real examples are presented in order to demonstrate how various degree of disorder affects diffraction pattern, Fourier maps, and structure refinements.

[1] Ďurovič S., *International Tables for Crystallography*, 1999, **C**, 752-765. [2] Nespolo M., Ferraris G., *Eur. J. Miner.*, 2001, **13**, 1035-1045. [3] Ďurovič S., Hybler J., Kogure T., *Clays Clay Min.*,2004, **50**, 613-621.

Keywords: OD structures, polytypism, fourier methods

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Incommensurately Modulated Structure in Natural Melilites

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Melilite-type compounds have general formula $X_2T1(T2)_2O_7$ (X = Ca, Sr, Pb, Ba, Na, REE; T1 = Be, Mg, Mn^{2+}, Fe^{2+}, Co, Cu, Zn, Al, Fe^{3+}, Si; T2 = Si, Ge, Al, Fe^{3+}, B, Be). Natural members mainly consist of solid-solution between gehlenite, $Ca_2Al_2SiO_7$, and åkermanite, $Ca_2MgSi_2O_7$. The structure, space group $P\bar{4}2_1m$, consists of a linkage of tetrahedral layers connected to each other by eight-coordinated X cations. As with peculiar chemical compositions, at room temperature, synthetic melilite-type compounds exhibit weak satellite reflections indicating a two-dimensional incommensurately (IC) modulated structure. To date, the presence of IC reflections in natural samples was only observed in both hardystonite [1] and åkermanite [2]. TEM-EDX investigations proved hardystonite to be chemically slightly inhomogeneous, with detectable IC satellites in the regions where composition approaches the $Ca_2ZnSi_2O_7$ end-member. Stronger and sharper IC satellites were observed in åkermanite. Therefore, a five-dimensional refinement and *in situ* low- and high-temperature (100 - 773 K) studies were carried out using single-crystals of åkermanite. As already observed for synthetic $Ca_2MgSi_2O_7$ [3], the displacive modulation of the atoms is mainly related to a variation of the X cation coordination. On the other hand, with respect to the temperature dependence of the **q** value, strong differences were found between the natural and the synthetic compound.

[1] Bindi L., Czank M., Röthlisberger F., Bonazzi P., *Am. Mineral.*, 2001, **86**, 747. [2] Bindi L., Bonazzi P., Dusek M., Petricek V., Chapuis G., *Acta Cryst.*, 2001, B**57**, 739. [3] Kusaka K., Hagiya K., Ohmasa M., Okano Y., Mukai M., Iishi K., Haga N., *Phys. Chem. Miner.*, 2001, **28**, 150.

Keywords: incommensurate structures, silicate mineralogy, XRD

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Modular Approach Applied to Tailoring of Bismuth-Containing Layered Perovskites

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Layered bismuth-containing perovskites and related oxyhalides are promising superconductors, ferroelectrics, ion conductors oxidation catalysts, *etc*. Most properties are very sensitive to chemical composition, but doping of different sites is restricted. Only recently it was understood that the problem could be overcome via more complicated mixed-layer structures involving additional new non-stoichiometric structural moduli (2D building blocks). To keep the charge balance, perovskitic layers must change their composition.

The general algorithm is suggested which consists of i) finding, by *a priori* modeling or otherwise, new 2D blocks, ii) elucidating their compositional range, both in chemistry and non-stoichiometry; iii) estimating the most reliable compositions of target mixed-layer structures, and iv) exploring full compositional range of the formed complex structures and establishing the structure - property relationship. Step ii) resulted in discovery of new unexpected structures involving novel building blocks.

The approach has been applied to structural modification of Aurivillius-type ferroelectrics and resulted in synthesis of over 200 new compounds contributing to more than 20 novel structure types. Complication of a simple structure of Bi_2WO_6 with non-stoichiometric metal-halide layers permitted to partially substitute W^{VI} by more than 20 cations, the resulting Curie points ranging from 700°C to below r.t.

Keywords: bismuth compounds, perovskite layered compounds, ferrolelectric and related materials