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Refinement of Partially Disordered OD Structures

Jiří Hybler^a, Slavomil Durovič^b, ^a*Institute of Physics, Academy of Sciences of the Czech Republic, Prague.* ^b*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava.* E-mail: hybler@fzu.cz

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.

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Incommensurately Modulated Structure in Natural Melilites

Luca Bindi, Paola Bonazzi, *Dipartimento di Scienze della Terra, Università di Firenze, Firenze, Italy.* E-mail: lbindi@geo.unifi.it

Melilite-type compounds have general formula $X_2T_1(T_2)_2O_7$ ($X = Ca, Sr, Pb, Ba, Na, REE$; $T_1 = Be, Mg, Mn^{2+}, Fe^{2+}, Co, Cu, Zn, Al, Fe^{3+}, Si$; $T_2 = Si, Ge, Al, Fe^{3+}, B, Be$). Natural members mainly consist of solid-solution between gehlenite, $Ca_2Al_2SiO_7$, and åkermanite, $Ca_2MgSi_2O_7$. The structure, space group $P4_21m$, 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.

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Modular Approach Applied to Tailoring of Bismuth-Containing Layered Perovskites

Dmitri O. Charkin^a, Igor V. Kul'bakin^a, Dmitri N. Moskvina^b, ^a*Department of Materials Sciences.* ^b*Department of Chemistry, Moscow State University.* E-mail: charkin@inorg.chem.msu.ru

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, ferroelectric and related materials