SIMULTANEOUS CRYSTAL STRUCTURE REFINEMENT OF MULTIPLE PHASES IN DIFFRACTION-COINCIDENT INTERGROWTHS

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Crystal structure solution or refinement of intergrown phases is often hindered by a partial or even a full overlap of their crystal lattices. A twin refinement cannot be attempted because it is a multiphase problem involving several crystal lattices and sets of atomic parameters. A solution to this problem has recently been incorporated in the program JANA2000. Investigating sulphosalt assemblages from the scheelite deposit of Felbertal (Austria) we were able to isolate single crystals or topotactic intergrowths of all the members of the bismuthinite-aikinite series. Due to specific formation conditions they developed a very high grade of ordering and present a full range of structural variations inside this solid solution series based on combined Pb (II) and Cu (I) for Bi (III) substitution. Ordered substitutions introduce superstructure multiplicities of one of the lattice periods in the basic orthorhombic structure. While the end members of the series and the member at the 50% composition (krupkaite) are distinct 1-fold ordered structures, the other intermediate members (8 in all) are 3-fold, 4-fold, or 5-fold ordered structures. Almost all of them can be found in topotactic intergrowths with neighbors in the series and some of them exclusively in this form. Their structures could therefore be refined only by the application of the new method. The method gives satisfactory results comparable to those obtained in standard refinements of twinned crystals and could be a powerful tool for structural investigations in the large field of mineral and synthetic solid-state ex-solutions.

Keywords: MINERALS, INTERGROWTHS, CRYSTAL STRUCTURE

NEW METASTABLE Al_2SiO_5 POLYMORPHS: UNEXPECTED RESULTS OF THEORETICAL CALCULATIONS

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Ab initio simulations [1,2] and latest experiments [3] show that Al_2SiO_5 polymorphs (minerals kyanite, andalusite, sillimanite, and hypothetical dense phases with the V_3O_5-like [4] and pseudobrookite structures) at pressures above 10 GPa become thermodynamically less stable than the mixture of simple oxides $(Al_2O_3+SiO_2)$. However, at sufficiently low temperatures these polymorphs can persist as metastable phases up to much higher pressures - as long as their structures remain dynamically stable.

From *ab initio* (density functional theory) and semiclassical (ionic shell model) simulations [2] andalusite and sillimanite are predicted to become dynamically unstable and spontaneously transform to new metastable phases at ~40 GPa. According to these simulations, andalusite undergoes one- or two-dimensional pressure-induced amorphisation. Sillimanite undergoes an isosymmetric (*Pbnm*) transition into a phase where Si and half of the Al atoms are 5-fold coordinate; at very low temperatures, the high-pressure isosymmetric phase may be preceded by an incommensurately modulated form of sillimanite. I discuss geometry and nature of the 5-coordinate polyhedra and the origin of the predicted isosymmetric transition.

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Keywords: MINERALS, EXTREME CONDITIONS, PHASE TRANSITIONS

ANALYSIS OF INORGANIC STRUCTURES THROUGH THE CHARGE DISTRIBUTION METHOD: RECENT EXTENSIONS

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The Charge Distribution (CD) method is a generalization of Pauling's bond strength, based on the geometrical analysis of the coordination polyhedra in terms of the Effective Coordination Number (ECoN). We have extended CD to distorted and hetero-ligand polyhedra, by introducing a recursive formula to compute ECoN, and to hydrogen bonds, by refining a new exponent for the curve used to compute ECoN. The shortest bond distance in each coordination polyhedron is used as parameter to iteratively compute an average distance, which is then used to compute the bond weight. The more a coordination polyhedron deviates from regularity, the more the bond weight of each bond deviates from 1. The sum of the bond weights around a cation is ECoN of that cation. The distribution of the formal oxidation number (q) of the cations as a function of the bond weight gives the contribution of each bond to the atomic "charge", and the summation gives the anionic "charge" (Q). Then, by distributing the ratio q/Q for the anions, the "charges" of the cations are obtained. The deviation of q/Q from 1 for the anions (OUB or Over-Under-Bonding effect) permits to analyze the structural effects of environmental parameters like temperature and pressure. The q/Q ratio for the cations is not influenced by the OUB effect; when it deviates from 1, either the structure should be questioned or it falls outside the applicability of the CD method.

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Keywords: BOND STRENGHT, BOND VALENCE, CHARGE DISTRIBUTION

MODELING STRUCTURES BY MODULAR CRYSTALLOGRAPHY: THE LAYER TITANOSILICATES

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To make up for the lack of molecules, the description of inorganic and mineral structures is traditionally based on modules; these can consist both of single coordination polyhedra and larger fragments of the structure. Different structures sharing one or more modules form series; the same modules may be shared by different series. Systematization of structures, which share modules, is a purpose of the modular crystallography; this type of information can be useful in the process of modeling unknown structures. Titanosilicates form a growing family of minerals, which are used as model structures for the synthesis of technologically important materials. Several layer titanosilicates (heterophyllosilicates) form series based on HOH layers: H (for hetero) is a mixed tetrahedral-octahedral sheet that formally may be derived from the tetrahedral sheet of the layer silicates; O is an octahedral sheet close to those occurring in layer silicates. Bafertisite-, astrophyllite- and nafertisite-like HOH layers are known where, in the order, the ratio tetrahedra/ octahedra in the sheet H increases. The typical periodicity and Ti/Si ratio of each type of HOH layer are useful information to identify unknown heterophyllosilicates and attempt their structure modeling. Models of the structures of astrophyllite-like (yuksporite and eveslogite) and bafertisite-like (bornemanite and a pair of unnamed new minerals) minerals have been obtained by the authors and tested against electron and X-ray powder diffraction data.

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Keywords: LAYER TITANOSILICATES, STRUCTURE MODELLING, MODULAR CRYSTALLOGRAPHY