

CALCULATION OF THE B-O TRIANGLE TO B-O TETRAHEDRON RATIO IN BORATES

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The ratio of the numbers of BO_3 triangles and BO_4 tetrahedra which make up an anion complex is frequently used for the identification of the so-called fundamental building blocks. Assuming the following bonding model this ratio can be calculated in advance from the borate composition. A covalently bound anion complex extends weak ionic bonds towards the cations. To complete its octet each O forms two covalent bonds either with 2B or 1B+1H. The B atoms, which have no preference for triangular or tetrahedral O coordination, adopt a mixing ratio, expressed by (1), where all O atoms can have the proper number of B-O-B and/or B-O-H bonds.

$$\% \Delta = 4 - A/C' \cdot (2 - \% \text{OH}) \quad (1)$$

$\% \Delta$ is the ratio of the number of triangularly coordinated B atoms to the total number of B atoms. A/C' is the ratio of the number of anions (O and/or OH) of the anion complex to the number of central atoms (B). $\% \text{OH}$ is the ratio of the number of OH groups bound to a central atom to the total number of O atoms bound to a central atom. Eq. (1) is valid in a restricted composition range where lie one quarter of all borates. 222 of these borates had been tested with eq. (1) and an agreement was found for 85% of them. A detailed account is in print with Z. Kristallogr.

Keywords: BORATES, TRIANGLE TO TETRAHEDRON RATIO, BO_3 TO BO_4 RATIO

MONOCLINIC SUPERSTRUCTURE OF SrMgF_4 WITH PEROVSKITE-TYPE SLABS

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Crystals of Ce-doped SrMgF_4 have been found to have a monoclinic $\text{P}112_1$ structure with doubled a and tripled c lengths with respect to the orthorhombic Cmcm structure previously reported in the literature. The perovskite-type slabs, composed of corner-sharing MgF_6 octahedra and Sr atoms, are stacked along the b axis. The six crystallographically independent MgF_6 octahedra are rotated so as to provide long periodicities along a and c. The coordination numbers and bond distances around six crystallographically independent Sr atoms are slightly different in each case. Although there are no constraints among the positional parameters of the six independent Sr atoms in $\text{P}112_1$, they align almost on a plane perpendicular to a. The $\text{Mg}1\text{F}_6$ and $\text{Mg}4\text{F}_6$, $\text{Mg}2\text{F}_6$ and $\text{Mg}5\text{F}_6$, and $\text{Mg}3\text{F}_6$ and $\text{Mg}6\text{F}_6$ octahedra are pairwise related by these pseudo-mirror planes defined by the Sr atoms. These local mirror planes are thought to originate at the high temperature phase transition from the Cmcm archetype.

Keywords: INORGANIC FERROELECTRIC STRUCTURE

CRYSTAL STRUCTURES OF PHASES IN THE SYSTEM $\text{CaO-K}_2\text{O-P}_2\text{O}_5$

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There are a number of elements constituting the condensed phases formed during combustion and gasification of biomass fuels. In addition to the traditionally studied major ash forming elements (Ca, K, Na, Si), a significant amount of P is contained in many biomass fuels and sludges. However, reliable identification tools such in terms of powder X-ray diffraction (XRD) patterns for many ash species containing P are lacking. To remedy this situation structural investigations for a number of phases in the system $\text{CaO-K}_2\text{O-P}_2\text{O}_5$ has been initiated. The situation is complicated by the fact that many ternary compounds in the system shows several structurally close-related phase modifications. A combination of single-crystal high-temperature structures, high-temperature powder diffraction and Rietveld techniques are used to clarify the intricate phase relations.

The crystal structures of $\text{CaK}_2\text{P}_2\text{O}_7$ and $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$, formed from high-temperature melts, have been determined using single-crystal X-ray diffractometry. $\text{CaK}_2\text{P}_2\text{O}_7$ crystallizes in a monoclinic space-group $\text{P}21/n$ with the cell parameters: $a=9.8170(2)$ Å, $b=5.6750(1)$ Å, $c=13.0030(3)$ Å and $\beta=104.218(1)^\circ$. $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ crystallizes in the trigonal space-group $\text{R}3c$ with the cell parameters (hexagonal axes): $a=10.4636(1)$ Å and $c=37.2493(1)$ Å. Calculated and experimental powder XRD pattern for the different phase modifications of the structures will be presented.

Keywords: PHOSPHATE, HIGH-TEMPERATURE STRUCTURE, XRD PATTERN

A COMPARATIVE TOPOLOGICAL ANALYSIS OF CRYSTAL STRUCTURES OF ANHYDROUS SIMPLE BORATES, CARBONATES AND NITRATES

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Using the program package for multipurpose crystal-chemical analysis TOPOS the topological comparative analysis was performed for crystal structures of anhydrous inorganic salts containing triangular oxo-anions L (borates, carbonates and nitrates). The cases of topological similarity between these classes of substances and binary compounds (comprising A and X atoms) were revealed and discussed within the following scheme: $\text{M} \leftrightarrow \text{A}$ (or X); $\text{L} \leftrightarrow \text{X}$ (or A). This scheme describes the representation of a salt as a quasi-binary compound composed by M cations and L anions considering as a whole. Thus the crystal structures of anhydrous salts topologically often correspond to widespread structure types based on ionic close packings: NaCl, fluorite, NiAs, α -alumina. The analysis performed showed that in majority of compounds one can select ionic substructures to be built with close packing or b.c.c. motifs. The most valid crystal structure representation (both in the view of crystal structure as a net of interatomic bonds, and in respect to its representation as an ionic packing) is the selection of M cations and L anions as the main structure-forming components. Increase of ion charge promotes increase of its structure-forming role. Thus, it is the borate ions with the maximum charge that tend to be arranged on b.c.c. lattice with the maximum uniformity among all three-dimensional frameworks. Increase of ion size also increases its structure-forming role, as a rule. This phenomenon is the most clear in the case of aragonite topological type where large metal cations form the most uniform lattice with the b.c.c. topology.

Keywords: TOPOLOGY, PACKINGS, CLASSIFICATION