

MS08.00.05 NEW MEASURES OF SIMILARITY FOR CRYSTAL STRUCTURES. E. Makovicky, Geological Institute, University of Copenhagen, T. Balic-Zunic, HALDOR TOPSOE A/S, Lyngby, Denmark

Modular description of complex crystal structures requires (a) definition of categories that are more general than those of isotypes, homeotypes, polytypes and homologues (polysomes), (b) definition of a measure of similarity of the (more or less distorted) derivative slabs/blocks to their archetype/aristotype.

Proposed classification categories higher than homologous series are the series of plesiotypes in which iso-/homeotypic or homologous structure portions combine with structural elements that differ from one member to another (they are called series of merotypes if these new elements are distinct types of interlayers).

Distortion of crystal structures can be quantified using the CN-dependent concept of "centroid" of the coordination polyhedron and the derived measures of cation excentricity and polyhedron sphericity (Balic-Zunic & Makovicky 1996). In addition, we shall define a parameter-free measure of distortion of the coordination polyhedron away from its ideal shape. This measure involves calculation of the ratio of the volume of (least-squares) circumscribed sphere to the volume of the coordination polyhedron under study and the comparison of this ratio to a similar ratio for the ideal polyhedron. This measure works unambiguously for tetrahedra, octahedra and all other cases for which the number of polyhedral faces is constant. Distortion measures for the studied structure (fragment) are then compared those observed for the archetype/aristotype. Balic-Zunic, T. & Makovicky, E. (1996): Acta Cryst. B52, 78-81.

MS08.00.06 MODULAR FEATURES IN THE SYSTEMATICS OF CRYSTAL STRUCTURES. B. B. Zvyagin (Inst. of Ore Mineralogy RAS, Moscow, Russia), S. Merlino (University of Pisa, Italy), G. Ferraris (Univ. of Torino, Italy)

Modular features are extremely useful for any rational and natural approach to the systematics of crystal structures. In fact several wide structural families may be clearly and neatly described as characterized by the occurrence of few distinct modules, the various members of each family differing in relative amounts, sequence and stacking order of the constituting modules. Two modular systems displaying these features will be presented. One is formed by the modules of pyroxenes and spinel and includes mixed-modules sapphirines, ferrites and surinamites, single-module spinelloids, condensed-module biopyriboles, and some additional modular sets of structures not yet found in nature. This system is outstanding not only for its various polysomatic features but also for the distinct OD and polytypic features displayed by several members of this family.

The other is formed by two distinct kinds of silicate layers alternating with octahedral layers. Different layer combinations characterize the structures of reyerite, gyrolite, tungusite, fedorite, K- and Z-phases, and some modified structures of minehillite and baratovite. The various sets of module combination present polytypic and OD modifications differing in layer stacking, which is defined by the symmetry operations of translation, rotation, reflection and inversion relating successive modules, presenting unit cells in multiplicity relationships. Both modular systems provide an useful and powerful way for understanding the relationships between polymorphs, polytypes, OD structures, and polysomes. They also show the efficiency of the modular approach in description, analysis and derivation of both existing and hypothetical crystal structures.

MS08.00.07 VARIABLE TEMPERATURE ANALYSIS OF COMPOUNDS CONTAINING DISORDERED PERCHLORATE COUNTER IONS. Leanne M. Cook & Jan C. A. Boeyens, Center for Molecular Design, Chemistry Department University of the Witwatersrand, Private Bag 3, WITS 2050, South Africa

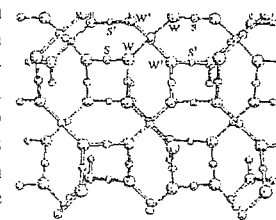
More often than not sodium perchlorate is used to facilitate crystallisation. To counterpoise large cations an equally large anion is required to promote closepacking. Although the perchlorate ion is only of medium size, it always seems to fill the void adapting its geometry accordingly. This is commonly interpreted as static disorder which is locked in at the time of crystal growth. However, this is not easily distinguishable from dynamic disorder, unless it's analysed as a function of temperature. Study of a macrocycle at room temperature [1] and at 130K [2], revealed that the disorder of the macrocycle is unaffected by cooling but that the perchlorate favoured one arrangement when cooled. The more rigid environment appeared to impose more structure on disordered perchlorate ions in the crystal. This suggested that the perchlorate be considered as structureless in solution and to assume [3] a tetrahedral shape in the solid state at a low temperature. An extensive search of the Cambridge Database revealed ordered and disordered perchlorates and it is not always easy to distinguish between the two instances. Investigation of the relationship of the free volume and the degree of disorder reveals that the larger the available space for the perchlorate ion, the higher the degree of disorder that results. A program [4] that calculates the volume of the molecule was then used to calculate the free available volume from the total cell volume. Comparisons of structures at room temperature and at low temperature demonstrate the relationship between the free volume available and the degree of disorder displayed by the perchlorate ion.

References:

1. Boeyens, J.C.A.; Oosthuizen, E.-L. J. Cryst. Spectr. Res. 1992, 22, 3-7
2. Boeyens, J.C.A.; Oosthuizen, E.-L. J. Chemical Crystallography, Vol.24, No 12, 815-816, 1994.
3. Woolley, R.G. J. Mol. Struct. 1991, 230 (76), 17-46.
4. Taverner, B.C. 1995, Personal communication.

PS08.00.08 TEMPLATE NETWORK AND SITE SYSTEMATICS OF EXTRAFRAMEWORK ATOMS IN THE ANALCIME-LEUCITE STRUCTURE TYPE Bakakin V.V.*, Seryotkin Yu.V., Fursenko B.A., Belitsky I.A. Institute of Mineralogy and Petrography, Novosibirsk, 630090, Russia
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The analcime-leucite structure family (ANA-type) comprises more than 70 natural and synthetic compounds. The (pseudo)cubic cell parameters lie in the range from 12.6 to 14 Å. 12 space groups are known. The general formula for the group can be expressed as: $(L_{16})W_{16}S_{24}[T_{48}O_{96}]$, where $[T_{48}O_{96}]$ - tetrahedral framework of the ANA-topology, L (from Lithium) - positions with coordinations (by anions): 3l, 3n, 4t, 6o; S (from Sodium) - 4s, 6o, 5y, 4r2c, 8do, 6p, 4t; W (from Water) - 6o6c, 6o3c, 6p3c. More than 20 various combinations of L-, S-, W-site occupations existing in real compounds (both natural and modified) are presented. A comparative analysis of 30 ANA-type compounds for which the full crystal structure data are available demonstrates existing variations in composition and/or symmetry in the family. The correlations were found between cell volume, $(T-O)_{avr} < (T-O-T)_{avr}$, and ionic radii R_S and R_W .



ANA-framework structure genesis is discussed in terms of template approach. An important feature not noted before is that a large-volume W (or W+S) components form two enantiomorphous interpenetrating 3-