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 o rdered 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 *Institute of Inorganic Chemistry, Novosibirsk, 630090, Russia.

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) - $4s, 6o, 5y, 4t2c, 8do, 6p, 4t$; 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.
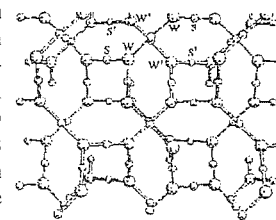
ANA-framework structure genesis is discussed in terms of template approach. An important feature not noted before is that a large-volume W (or W+S) components form two enantiomorphous interpenetrating 3-

dimensional 3-connected 10-gon nets (of a $(10,3)$-a type after A.F.Wells) acting as a template. For $N_W/N_T = 1/3$ it is this network which provides uniform interaction between template W (or W+S) components and $TO_{4/2}$ framework constituents. Conventionally one can subdivide the whole tetrahedral framework into two subsystems as if generated by different W,S subnets.

PS08.00.09 CRYSTAL CHEMISTRY OF SYNTHETIC 1:3 SILICATE AND GERMANATE PYROXENES M. Behruzi, E. Banerjea-Appel, F.D. Scherberich and Th. Hahn. Institut fuer Kristallographie, RWTH Aachen, D 52056 Aachen, Germany.

Binary systems of the type $LiAlGe_2O_6$-$LiGaGe_2O_6$ show peritectic melting and increase of the melting temperatures with increasing atomic number of the three valent cations (Fe, Sc, In). All 1:3 pyroxenes crystallize only in the monoclinic form with the exception of $LiScGe_2O_6$ and $LiInGe_2O_6$ which can be synthesized in the monoclinic and orthorhombic enstatite types. The orthorhombic forms are the low temperature phases and undergo a sluggish but complete transition to the monoclinic form; the reverse transition is much more sluggish.

The monoclinic germanates show a rapid and reversible phase transition from the low temperature form (mostly P21/c) to the high temperature form (C2/c). The phase transitions give rise to a discontinuous increase of the a, c and ß but decrease of the b axis. Furthermore, the symmetrically non-equivalent tetrahedral chains become equivalent and the tetrahedral chains stretch.

Special features of monoclinic pyroxenes: 1) The observed M^{3+}-O bond lengths are 0.985 of the calc. bond lengths . 2) The Li-O and Na-O bond lengths differ for the corresponding silicates and germanates 3) They are a linear function of the M^{3+}-O bond lengths. 4) The c axes of the Li and Na silicates are equal and a linear function of the M^{3+}-O. 5) The c-axes of the germanates are larger than those of the corresponding silicates. They are also a linear function of M^{3+}-O; for C2/c they are larger than for P21/c.

PS08.00.10 INORGANIC STRUCTURAL CHEMISTRY WITH CRYSTALLOGRAPHIC DATABASES. G.Bergerhoff and M.Berndt, University of Bonn, Germany

Application of a clearcut definition for the concept of isotypism to the crystallographic databases allows to find new and old relations between inorganic crystal structures. First of all data have to be standardized in order to get a uniform description of crystal structures. We started to apply STRUCTURE TIDY, the procedure of L.M.Gelato and E.Parth (J.appl.Cryst. 20 (1987) 139-143), to the ICSD (Inorganic Crystal Structure Database). But there are limits of this method if cell dimensions or coordinates are near specific values. In a second step, therefore, all structures within an isopointal group are compared with each other. The structural difference between structure (1) and structure (2) is now the degree Δ of isotypism, which is zero for complete coincidence (m = multiplicity).

$$\Delta = (((2^{1/2} * \Delta(c))+1) * \Delta(d)) - 1$$

where is $\Delta(c) = (\sum (m * ((x_1-x_2)^2 + (y_1-y_2)^2 + (z_1-z_2)^2)^{1/2})) / \sum m$ $\Delta(d) = a_1^2 * b_2 * c_2 / a_2^2 * b_1 * c_1$ where $a_1 > a_2, b_2 > b_1, c_2 > c_1$ $\Delta(c)$ is the weighted mean difference of the coordinates of both structures, $\Delta(d)$ combines the relation between the cell dimensions of both structures. Δ is calculated and reduced to the minimum value by selecting the best fitting set of equivalent coordinates and cell choice. The comparison by means of the Δ value can also be expanded beyond the limits of an isopointal group. In course of the indexing process of the database the minimal Δ value is stored as a retrieval parameter in the revised version SICS (Standardized Inorganic Crystal Structures) of the ICSD. The user now can choose any structure and ask for isotypes within a preselected Δ range. For the effectivity of this way of retrieval several examples are given. This algebraic procedure has the advantage not to be dependent on theories of bonding and connections. For a real impression of the structures compared we use DIAMOND, a graphics system easily used in connection with the databases. Further information you may find in WWW: http://www.rhrz.uni-bonn.de/~unc442/diamond.html

PS08.00.11 STUDIES ON THE TEMPERATURE DEPENDENCE OF ELECTROCONDUCTIVITY FOR CRYSTALS OF PHLOGOPITE AND FLUOROPHLOGOPITE. Y.V. Ezhova, F.A. Scherbachenko, V.A. Karnakov, N.A. Hlopenko, Irkutsk State University, Irkutsk, Russia

The specific conductivity of natural (phlogopite) and synthetic (fluorophlogopite) micas has been studied as a function of temperature. This allowed to establish activation energies and a nature of charge carriers responsible for current in crystals under investigation.

The conductivity of Phlogopites in the temperature range 300-500 K is associated with aqua-pellicle impregnations and is characterized by activation energy of 0.15-0.20 ev. In the range 500 - 900 K the carriers are loosely bound ions of impurities with activation energy of 0.3- 0.4 ev. Above 900 K the activation energy is about 3.0 ev and the charge carriers are most likely fluorine ions.

Within the considered interval of temperatures specific conductivity of fluorophlogopites is by two orders of magnitude lower than those of phlogopites. The differences in the magnitude and character of conductivity for these species of mica are explained by a high thermoresistance of fluorophlogopite. The latter is due to a substitution of hydroxygroups by fluorine ions, more firmly bound to lattice, and due to the nearly complete absence of molecular water in fluorophlogopite.

PS08.00.13 DETERMINATION OF SPACE GROUP AND STRUCTURE FOR SYNTHETIC SVABITE: $Ca_5(AsO_4)_3F$. P. Goodman, A. Schwartzman, School of Physics, University of Melbourne, Parkville, Vic. Australia 3052, B.Rodier, F. Lincoln, Department of Chemistry, University of Western Australia, Nedlands, W.A. Australia 6009; T.J. White, Ian Wark Research Institute, University of South Australia, The Levels, S.A., Australia 5098.

Although the structure of fluoro-apatite was established some 50 years ago[1], the chemical analogue with As replacing P has never been investigated structurally, due primarilly to the fact that in its native form it is associated with numerous cation impurities. In this paper we present evidence to show that the As substitution causes the space group to shift from $P6_3/m$ to $P6_322$, as a result of a shift of the heavier cation from special to general positions. The structural change has been investigated in the solid solutions $Ca_5(As_xP_{1-x}O_4)_3F$, and it appears that the change occurs for x > 0.5, although a complete phase diagram has yet to be described.

Investigative methods include CBED and Rietveld refinements of powder x-ray data.

[1]C.A.Beevers and D.B.McIntyre (1946) Mineralogical Mag. **27**, 870.