

## 08.01 – Inorganic Crystal Chemistry

## MS-08.01.01 INORGANIC STRUCTURE SYSTEMATICS:

AIM – WAYS – PROSPECTS. By F. Liebau, Mineralogisches Institut der Universität Kiel, Germany.

I. **AIM:** The *aim* of structure systematics is to arrange the vast number of inorganic structures in such a way that relationships between them are easily recognized. Depending on the kind of relationships considered, different classification principles have to be chosen.

II. **WAYS:** Structures consist of *atoms spatially arranged* to balance *attractive and repulsive forces between them*. Consequently, there are various ways for systematic classification.

1) **General approaches** compare (i) lattice dimensions ( $a_s, b_s, c_s, \alpha, \beta, \gamma$ ), (ii) lattice symmetry (space groups), (iii) atomic coordinates ( $x, y, z$ ) of Wyckoff positions, and (iv) frequency, degree, and chemistry of occupation of Wyckoff positions.

Each of these criteria may be *identical, similar, or dissimilar*, depending upon the degree of deviation from identity. Increasing degree of deviation of one or other of these criteria and deviations of an increasing number of these criteria from identity are responsible for decreasing structural similarities [Lima de Faria et al., *Acta Cryst.* A46 (1990) 1].

2) A purely **geometrical approach** [Hellner, *Z.Krist.* 175 (1986) 227] uses point configurations (*Bauverbände*) to classify inorganic crystal structures. These *Bauverbände* are described by invariant lattice complexes and coordination polyhedra.

3) **Chemical approaches** consider structures as networks of atoms linked by chemical bonds and classify structures according to the topology of their linkages. Within a structure the bond strength distribution can either be (i) homogeneous (e.g. He, Cu, diamond, NaCl, SiO<sub>2</sub>, ...) or (ii) inhomogeneous (e.g. H<sub>2</sub>, CO<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, GaMo<sub>5</sub>O<sub>8</sub>, ...). Crystals with inhomogeneous bond strength distribution are classified according to the topology of their *strongest* bonds and subdivided according to the arrangement of their *next strongest* bonds, etc.

For silicates a systematic classification has been developed which is based on [SiO<sub>n</sub>] polyhedra ( $n=4,6$ ) and the way they are linked to form larger silicate anions [Liebau, *Structural Chemistry of Silicates*. Springer, Heidelberg 1985]. This classification can be extended to structures with other [BX<sub>4</sub>] tetrahedra and structures with [BX<sub>6</sub>] octahedra. Since the classification parameters used are correlated with atomic properties of the cations and non-silicate anions, *indirect* allowance is made for the contribution of weaker bonds within the structure.

Hawthorne [*Z.Krist.* 192 (1990) 1; 201 (1992) 183], in contrast, treats octahedrally coordinated cations and OH<sup>-</sup> in structures with [BX<sub>4</sub>] tetrahedra, *directly*, at the expense of simplicity.

Parthe and Chabot [*Acta Cryst.* B46 (1990) 7] developed a classification for structures with tetrahedral groups, including those with defect tetrahedra and tetrahedral complexes containing homoatomic bonds, by making use of valence electron concentrations.

4) **Crystal chemical formulae**, based on the systems described above, give detailed structural information and have been strongly recommended by the IUCr [Lima de Faria et al., *l.c.*].

III. **PROSPECTS:** To improve *general structure systematics*, Schmahl [*Z.Krist.* 191 (1990) 23] and Burzlaff and Rothammel [*Acta Cryst.* A48 (1992) 483] began developing methods to quantify structure similarities. Improvements for *specific classes of substances or structures* such as 3-dim. framework compounds

MS-08.01.02 THE INFLUENCE OF CHEMISTRY ON INORGANIC STRUCTURE. I.D. Brown\*, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1.

Only recently have quantitative theories of inorganic structure become available. Two models are currently popular, the ionic (two body potential) model (Burnham, C.W. (1990) *Am. Miner.* 75, 443-463) and the chemical bond (bond valence) model (Brown, I.D. (1992) *Acta Cryst.* B48, 553-572). The **ionic model** calculates the total energy of a crystal by summing the contribution from every atom pair. Once suitable potential functions have been found, the model can be used to explore the energies of a variety of possible atomic arrangements. It can be used to predict crystal structures and explore diffusion and other properties. The **bond valence model** is the inorganic equivalent of the chemical bond model widely used in organic chemistry. A solid is treated as an infinite network of atoms linked by bonds which obey certain simple empirical rules. Given the topology of this network, chemically ideal bond lengths can be predicted. In most cases these are the distances observed, but anisotropies in the valence shell electrons and steric constraints sometimes result in bond lengths that are different from the ideal. The ionic and bond valence models are complementary; the bond valence model is easy to use and gives insights into the chemistry but only the ionic model gives energies.

A theorem of the bond valence model is the valence matching principle which shows why it is the cation that determines the framework structure in aluminosilicates (Hawthorne, F.C. (1985) *Am. Mineral.* 70 455-473). Water molecules enter into structures either to mediate the bonding between mismatched cations and anions (Hawthorne, F.C. (1992) *Z. Krist.* 201 183-206) or to occupy space that would otherwise be empty (Brown, I.D. & Duhlev, R. (1991) *J. Solid State Chem.* 95, 51-63). Some structures, notably those related to perovskite, have bonds that are strained from their chemically ideal values by non-bonded repulsions, the requirements of packing, or the need for commensurability between different parts of the structure. Strain, detected by the failure of the bond valences around an atom to add up to the atomic valence, can be relaxed by changes in the lengths of other bonds, distortions that may lower the crystallographic symmetry, stabilization of unusual oxidation states, or the replacement of strained atoms by vacancies or atoms of a different kind. The consequences of strain affect the chemical and physical properties in important and increasingly predictable ways.

Both models still have problems. Except for the simplest structures, it is not yet possible to predict the structure of a compound directly from its chemical formula, though once the topology of the structure is known, both methods can, in most cases, determine the bonding geometry to within a few picometres. A notable exception occurs for atoms whose partially-filled valence shell leads to an intrinsic distortion of its coordination environment. These cases require a quantum mechanical treatment, though it is possible that the classical models can be adapted to reflect the observed behaviour of these atoms.