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book reviews

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Structural Crystallography of Inorganic Oxysalts. By S. V. Krivovichev. Vol. 22, **IUCr Monographs on Crystallography**. Oxford University Press, 2009. Price (hardback) GBP 65.00. ISBN 978-0-19-921320-7.

Almost a century ago X-ray crystallography began with the structure determination of sodium chloride by W. L. Bragg. Since then thousands of crystal structures have been determined and filed into databanks. At present, the Inorganic Crystal Structure Data File (ICSD) contains almost 120 000 entries. To investigate correlations between the chemical composition of inorganic substances on the one hand, and their crystal structures, chemical and physical properties on the other, several classification methods have been developed.

Early classifications were based on the linkage of cation-centred coordination polyhedra $[AX_n]$ with n = 3 or 4 into zero-, one-, two- and three-dimensional structural units. Here the $A-X$ bonds are the strongest bonds in the structure, *i.e.* those in which the A cations are small, the X anions are relatively small and the A cations have valences greater than 3 if X is oxygen. Such $[AX_n]$ polyhedra can share corners but not edges or faces, because of the repulsive forces between the high-valent A cations in neighbouring polyhedra (Pauling's third rule). The most elaborate of these classifications are those of the silicates and borates. To classify not only such classes of inorganic substances but much larger groups of inorganic substances, in addition to the cation-centred coordination polyhedra with the strongest $A-X$ bonds, those with the next strongest bonds are taken into consideration. This allows one to include larger cations and anions and those of lower valence and $[AX_n]$ polyhedra with $n > 4$ into the classification scheme.

Later it was discovered that structures containing 'additional' oxygen anions that are not linked in strong $[AX_n]$ polyhedra can be classified on the basis of anion-centred coordination polyhedra $[XA_m]$. Here, X is O^{-II} or sometimes N^{-III}, and A are, in particular, the lone-pair cations Pb^{II} and Bi^{III}, the lanthanide cations Ln^{III} and Cu^{II}, but also Be^{II}, Zn^{II}, Ca^{II} and Sr^{II}. Owing to the lower valence of the central X and, in most cases, longer $A-X$ distances, repulsive forces between X anions are relatively weak. As a consequence, anion-centred $[XA_m]$ polyhedra cannot only share corners but also edges and faces. This leads to a much larger diversity of structural units than are known, for example, in the case of silicates or borates.

In a similar way, anion-centred $[XA_6]$ octahedra are used to describe, in particular, cubic and hexagonal antiperovskites such as $(SO_4)F^{[6]}Na_3$, $CeO^{[6]}Na_3$, $AsN^{[6]}Mg_3$ and the superconductor $MgC^{[6]}Ni_3$.

It has recently been shown that a number of highly symmetric inorganic structures with large cations can be described as dense packings of cations with anions filling interstices between the large cations.

Sergey Krivovichev has made substantial contributions to several of these classifications. In his book he describes all of them lucidly, illustrating them with a large number of polyhedron plots, simplified schematic drawings and graph representations of the structures. He gives a clear survey of the vast number of inorganic oxysalts and their analogues. The number of structures that are listed in tables is impressive.

The book is divided into six chapters. Chapter I: basic concepts (5 pages); Chapter II: graph theory applied to low-dimensional structural units (88 pp); Chapter III: topology of framework structures (68 pp); Chapter IV: anion topology approach (10 pp); Chapter V: alternative approaches (42 pp); Chapter VI: dimensional reduction in inorganic oxysalts (11 pp).

It is most satisfying that the entirety of the presented classification schemes, despite their somewhat dry formalism, clearly reflects the crystal-chemical relations between the compounds. The book is recommended to anyone who wants to obtain an insight into more than just a small, restricted family of compounds.

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