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book reviews

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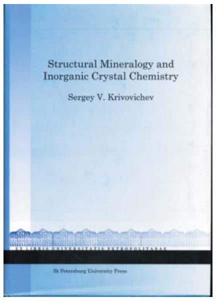

Structural Mineralogy and Inorganic Crystal Chemistry. By Sergey V. Krivovichev. St Petersburg University Press, 2009. Pp. 398. (Hardbound) Price unknown. ISBN 978-5-288-05004-6.

> This book is devoted to a description of crystal structures of inorganic compounds and, in particular, of minerals, that is, of crystalline substances that constitute the surface and interior of our planet. Understanding their structures is essential for our understanding of the formation and evolution of Earth in geological time. Recently, a new paradigm has emerged that considers minerals as potential advanced materials that can serve as prototypes for the synthesis of new compounds with important technological properties.

The quoted paragraph is taken from the foreword of the book and summarizes well the content which develops through an impressive collection of complex inorganic crystal structures that have been studied in only a decade by Sergey Krivovichev and his group, at the Department of Crystallography of St Petersburg State University. The title of the book could appear pretentious, with the chapters only based practically on the author's results. Instead, after carefully considering the content, one realises that in this monograph the author has simply reversed the usual procedure: instead of writing chapters dedicated either to strategies for solving complex structures or to the crystal-chemical properties of inorganic crystal structures embedding examples in the background, the author exposes methods and crystal chemistry *via* the discussion of a wide variety of crystal structures. The task assumed by the author is efficaciously accomplished also because the book is not just a collection of published papers. In fact, even if the original articles are still recognizable and correspond to sections of the book, they have been reworked focusing on specific properties and methods. To facilitate this purpose, experimental details are concentrated in the notes given at the end of the book, except special cases where the details are essential to understand the main text. The content is grouped into three chapters, each one devoted to a class of inorganic structures.

Chapter 1 (110 pages) is titled 'Structural mineralogy' and describes the structures of minerals chemically belonging to oxides, oxychlorides, sulfates, phosphates, arsenates, selenites and silicates. Several structures are very complex and their solution and crystal-chemical discussion represent valuable examples of structural mineralogy.

Chapter 2 (50 pages) is titled 'Lead minerals and inorganic compounds' and reports the structures of carbonates, nitrates, oxychlorides, sulfates, vanadates, phosphates, arsenates and chromates. This chapter represents *de facto* an overview of the crystal chemistry of lead and, in particular, shows how useful the description of structures is in terms of anion-centred polyhedra – a method proposed by Krivovichev *et al.* $\sim$ 10 years ago – in the case of very distorted cation polyhedra like those of Pb^{2+}.

Chapter 3 (70 pages) is titled 'Uranium minerals and inorganic compounds' and illustrates the structures of uranium compounds with relevance to uranium mineralogy and radioactive waste disposal; materials science aspects related to the chemistry of uranium are discussed. With reference to their topology, the structures are classified as compounds with open topologies (coordination polyhedra share corners) and compounds with dense heteropolyhedral layers formed by polyhedra that share edges. In the latter case, the author adopts the method of anion topology to correlate the structure of layers occurring in different compounds. The anion topology is constructed by removing cations and anions that are not bonded to at least two cations within the layer.

Theoretical contribution to and discussion of topological aspects in inorganic structures are favourite topics of the author, who recently developed them in a book titled *Structural Crystallography of Inorganic Oxysalts* and belonging to the series of *IUCr Monographs on Crystallography*. In the present monograph one can find paradigmatic examples related to these topics. Apart from the above mentioned chapter 3, the following sections deal especially with the topology of the structures: connectivity diagrams in cafetite and rimkorolgite; topology and geometrical isomerism in compounds with laueite-type heteropolyhedral sheets and derivatives of these sheets (*e.g.* mitryaevaite); analysis of topology in microporous jonesite; interpretation of the structure of several lead compounds as based on a periodic sheet of anion-centred (OPb_4) tetrahedra affected by different degrees of vacancies; discussion of the topology of the $[(UO_2)(MoO_4)_2]^{2-}$ sheets according to a graph that is parent to at least 35 different sheet topologies observed in crystal structures of inorganic oxysalts; common topology of the $(UO_2)(AO_4)_2$ sheet (A = Cr, Mo) in ten compounds where, however, the layer symmetry is different (note that in the layer group symbols the lattice type should be indicated by lower case and not a capital letter).

Besides the cases mentioned above where emphasis is given to the topology of structures and an almost ubiquitous discussion based on bond-valence calculations, the content of the book can be usefully classified according to the other structural, crystal-chemical and physical properties of the structures. The following list gives examples of this possible classification.

(i) Physical properties: negative thermal expansion in melanothallite; magnetism due to the crystallographically independent positions of Cu^{I} and Cu^{II} in allochalcoselite.

(ii) Twinning: cafetite, mereheadite, rimkorolgite, nacaphite, tyrolite, jonesite, shafranovskite, diversilite-(Ce), yuksporite, $Pb_7O_4(OH)_4Cl_2$, blixite, spriggite, $(UO_2)Mo_2O_7(H_2O)_2$, $Ag_{10}[(UO_2)_8O_8(Mo_5O_{20})]$, $Tl_2[(UO_2)(MoO_4)_2]$, β-$Cs_2[(UO_2)_2(MoO_4)_3]$, $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)$, $K_4[(UO_2)_3(CrO_4)_5](H_2O)_8$, $[CH_6N_3]_3[(UO_2)_2(SeO_4)_2(H(SeO_4)_2)](H_2O)_2$. The solution of this large number of twinned structures has been mainly attained thanks to modern software dedicated to the detection of twinning from diffraction patterns. In several cases, however, only the intuition of the authors could deconvolute the diffraction patterns of twins and also illustrate the procedure with figures. Regrettably, only the simple twins by merohedry are classified in terms of reticular theory; for the more complex cases of twinning by reticular (pseudo)merohedry, only the matrix relating the two individuals is normally given, without specifying the symmetry of the sublattice that is responsible for twinning and fixing the twin index and obliquity.

(iii) Polytypism: discussion of nacaphite and related structures in terms of polytypes based on antiperovskite units; two polytypes of tyrolite; chlorite-like polytypism in glagolevite; two polytypes of $Ag_2[(UO_2)W_2O_8)]$.

(iv) Polysomatism: polyphite based on nacaphite-like and *HOH* heterophyllosilicate modules.

(v) Polymorphism: dimorphism of parageorgbokiite and georgbokiite; two topologically related modifications of $Cs_2[(UO_2)_2(MoO_4)_3)]$; *in situ* study of the phase transition in $[C_6H_{16}N]_2[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_2$; dimorphism of $Mg_2[UO_2)_3(SeO_4)_5](H_2O)_{16}$.

(vi) Chemical bond: lone electron pair stereoactivity of the Tl^{+} cation.

(vii) Layered structures: weakly linked layers of possible interest for materials science in tyrolite; undulated tetrahedral–octahedral 2:1 layers in shafranovskite; novel phyllosilicate-like layer in armbrusterite; organic inorganic layered uranyl selenates.

(viii) Microporous structures: in the titanosilicate jonesite the presence of a sheet which is also observed in heterophyllosilicates and of a porous double layer similar to that occurring in rhodesite; yakovenchukite-(Y) based upon a novel type of microporous octahedral–tetrahedral framework; a new type of broken zeolites framework in thornasite.

(ix) Nanostructured inorganic actinide compounds, *i.e.* compounds with nanoscale clusters and other structural units (including nanotubes).

The description of the structures is accompanied by appropriate and well dimensioned figures; despite being only black and white, their meaning is very clear thanks also to the accompanying detailed captions. An exhaustive list of references, complete with titles and 30 pages long, allows the interested reader to easily search for further data. It is really a pity that a subject index reporting at least the names of minerals and chemical formulae of the compounds is missing.

Some printing mistakes and flaws have been detected, but their occurrence is perhaps unavoidable in a book of ~ 400 pages. For example: the caption of Fig. 104 refers to colours that probably were present in the original paper; in some cases the year of a reference given in the text is not accompanied by the appropriate letter shown in the alphabetical list [*e.g.* on pages 221 and 225 to the year 2008 shown for Krivovichev's publications a letter (a, b, c or d) must added]; the value of the β angle is missing for the monoclinic structure of Note [28].

On the whole the scientific standard of the book is high and the thoroughly discussed examples of crystal structures complement well the traditional monograph that the author has published with the IUCr series mentioned above. Together, the two books represent an undoubtedly useful reference for researchers working in the field of the crystallography of inorganic materials. In particular, they can inspire materials scientists looking for tailored new materials, mineralogists in their characterization of some exotic new minerals, as well as physicists and chemists studying the properties of the crystalline state. Finally, if a book is useful for researchers that means it can also be a textbook for advanced courses, in this case devoted to the crystallography of inorganic compounds.

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