

Mineralogical Crystallography

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Crystallography remains, for mineralogy, one of the main sources of information on natural crystalline substances. A description of mineral species shape is carried out according to the principles of geometric crystallography; the crystal structure of minerals is determined using X-ray crystallography techniques, and physical crystallography approaches allow one to evaluate various properties of minerals, etc. However, the reverse comparison should not be forgotten as well: the crystallography science, in its current form, was born in the course of mineralogical research, long before preparative chemistry received such extensive development. It is worth noting that, even today, investigations of the crystallographic characteristics of minerals regularly open up new horizons in materials science, because the possibilities of nature (fascinating chemical diversity; great variation of thermodynamic parameters; and, of course, almost endless processing time) are still not available for reproduction in any of the world's laboratories. This Special Issue is devoted to mineralogical crystallography, the oldest branch of crystallographic science, and combines important surveys covering such topics as: discovery of new mineral species; crystal chemistry of minerals and their synthetic analogs; behavior of minerals at non-ambient conditions; biomineralogy; and crystal growth techniques.

We hope that the current set of reviews and articles will arouse genuine interest among readers and, perhaps, push them to their own successful research in the field of mineralogical crystallography.

1. Crystal Chemistry of Minerals and Their Synthetic Analogs

Gurzhiy et al. [1] reviewed the crystal chemistry of the family of natural and synthetic uranyl selenite compounds, paying special attention to the pathways of synthesis and topological analysis of the known crystal structures. Crystal structures of two minerals were refined. The H atoms positions belonging to the interstitial H₂O molecules in the structure of demesmaekerite, Pb₂Cu₅[(UO₂)₂(SeO₃)₆(OH)₆](H₂O)₂, were assigned. The refinement of the guilleminite crystal structure allowed the determination of an additional site arranged within the void of the interlayer space and occupied by an H₂O molecule, which suggests the new formula of guilleminite to be written as Ba[(UO₂)₃(SeO₃)₂O₂](H₂O)₄. This paper could be regarded as the first review on the mineralogy and crystal chemistry of the named group of compounds.

Tyumentseva et al. [2] studied the alteration of the uranyl oxide hydroxy-hydrate mineral schoepite [(UO₂)₈O₂(OH)₁₂](H₂O)₁₂ at mild hydrothermal conditions in the presence of sulfate oxyanions, which resulted in the crystallization of three novel compounds.

Comparison of the isotypic natural and synthetic uranyl-bearing compounds [1,2] suggests that formation of all uranyl selenite and of the majority of uranyl sulfate minerals requires heating, which most likely can be attributed to the radioactive decay. The temperature range could be assumed from the manner of the interpolyhedral linkage.

2. Discovery of New Mineral Species

Pekov et al. [3] discovered the new hydrous aluminum chloroborate mineral krasnoshteinite ($\text{Al}_8[\text{B}_2\text{O}_4(\text{OH})_2](\text{OH})_{16}\text{Cl}_4 \cdot 7\text{H}_2\text{O}$), with a zeolite-like microporous structure and a three-dimensional system of wide channels containing Cl^- anions and weakly bonded H_2O molecules. The crystal structure of krasnoshteinite is also remarkable due to the presence of a novel insular borate polyanion $[\text{B}_2\text{O}_4(\text{OH})_2]^{4-}$.

Britvin et al. [4] reported on the crystal structure of natural Ca-Mg-phosphate stanfieldite, $\text{Ca}_7\text{M}_2\text{Mg}_7(\text{PO}_4)_{12}$ ($M = \text{Ca}, \text{Mg}, \text{Fe}^{2+}$), derived from the pallasite meteorite Brahmin for the first time. The authors reviewed the existing analytical data and showed that there is no evidence that the phosphor base with the formula $\text{Ca}_3\text{Mg}_3(\text{PO}_4)_4$ exists.

3. Behavior of Minerals at Non-Ambient Conditions

Comodi et al. [5] studied the transformation of the crystal structure of galenobismutite, PbBi_2S_4 , under pressure up to 20.9 GPa. The structure undergoes reversible and completely elastic transitions. The size and the shape of Bi- and Pb-centered polyhedra suggest that the high-pressure structure of galenobismutite can host Na and Al in the lower mantle, which are incompatible with the periclase or perovskite crystal structures.

Hydrous coesite crystals, a high-pressure SiO_2 polymorph, were synthesized with various B^{3+} and Al^{3+} contents and in situ high-temperature Raman and FTIR spectra were collected at ambient pressure by Miao et al. [6]. Crystals were observed to be stable up to 1500 K. Al substitution significantly reduces the H^+ concentration in coesite, so the mechanism is controlled by oxygen vacancies, while the B incorporation may prefer the electrostatically coupled substitution ($\text{Si}^{4+} = \text{B}^{3+} + \text{H}^+$).

4. Biomineralogy

Izatulina et al. [7] studied the effect of bacteria that are present in human urine on the crystallization of oxalate and phosphate mineral phases, the most common constituents of renal stones. It was shown that the inflammatory process will contribute to the decrease in oxalate supersaturation in urine due to calcium oxalate crystallization, while the change in urine pH and the products of bacterial metabolism will be of major importance in the case of phosphate mineralization.

Rusakov et al. [8] reported on the mechanisms of Sr-to-Ca substitution in the structures of calcium oxalate minerals that were found in lichen thalli on Sr-bearing apatite rock. It was shown that the incorporation of Sr ions is less preferable than Ca into the structures of whewellite and weddellite, and substitution rates are slightly higher for weddellite than for whewellite, which is most likely caused by the denser manner of the interpolyhedral linkage in the latter structure.

Five Cactaceae species were studied using various experimental techniques to characterize the biomineral composition within their different tissues by De la Rosa-Tilapa et al. [9]. Calcium carbonates and silicate phases were detected along with common calcium oxalates.

5. Crystal Growth Techniques

Konopacka-Lyskawa [10] reviewed the state of the art of the vaterite crystallization techniques. Vaterite is known to be the least thermodynamically stable anhydrous calcium carbonate polymorph, very rarely found in nature. However, synthetic vaterite has large potential in pharmacology and manufacturing. Well-known classical and new methods used for vaterite precipitation were discussed with particular attention to the parameters affecting the formation of spherical particles.

Tang and Yi-Liang [11] revealed that specific geochemical microenvironments and the bacterial activities in the long-lived volcanic hot springs from Kamchatka result in the development and preservation of the complex pyrite crystal habits. Application of similar techniques to other systems may help in the identification of biogenic iron sulfides in sediments on Earth and other planets.

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