

Editorial

Editorial for the Special Issue Modularity and Twinning in Mineral Crystal Structures

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Ferraris et al. [1] systematically reviewed mineral phases whose crystal structures can be described as built up by periodic stacking at atomic scale of either one (usually) module (polytypes) or more modules—M, M', M'' ...—with different compositions (polysomes). Whereas a series of polytypes shows essentially a constant chemical composition, the members of a polysomatic series have different chemical compositions that depend on the ratio M/M'/M'' ... In a polysomatic series, the physical properties are a function of the chemistry of the modules and of their stacking; thus, tailoring of the properties is possible via synthesis of ad hoc compounds. A special class of polytypes is rationalized by the so-called order/disorder (OD) theory [2] that plays a basic role in most of the articles published in this special issue of Minerals.

Twinning, i.e., the oriented association of two or more crystals of a same compound, is considered a modular structure at macroscopic scale (see Chapter 5 in [1]). The members of a series both of polytypes and of polysomes usually have in common a supercell that, according to the reticular theory of twinning, favors the formation of twins.

The articles published in this issue show that polytypism, polysomatism, and twinning are fertile fields of research and their basic principles are powerful tools to solve and classify related crystal structures. The detection of twinned crystals is almost no longer a matter of morphological observation as it used to be in the past. This task is now left to algorithms that are routinely included in the software dedicated to the solution and refinement of the crystal structures.

However, research on twinning and its consequences on structure and properties of crystalline materials is a growing field and a frontier field concerning twin walls is reviewed in this issue by Salje [3]. The author shows that a specific type of twinning is a very common phenomenon in ferroelastic materials where the thin areas (twin walls or twin boundaries) between the twin domains yield characteristic physical and chemical properties. This category of crystal structures generates a large variety of properties. Some properties of the twin walls are discussed in the review article, such as their ability for chemical storage, and their structural deformations which generate polarity and piezoelectricity inside the walls. It is noteworthy that none of these effects exist in the adjacent domains of the twins because only their twin walls contain topological defects, such as kinks, and are strong enough to deform surface regions.

Instead, classical twinning is central in the articles contributed by Németh [4], Bindi and Morana [5], and Makovicky [6]. Via the analysis of electron diffraction patterns and high-resolution TEM images, the article [4] shows that the extra reflections occurring halfway between the Bragg reflections of glendonite, a calcite (CaCO₃) pseudomorph after ikaite (CaCO₃·6H₂O), are the consequence of microtwinning by reticular pseudomorphedry based on a pseudo-orthorhombic C-centered sublattice. The same diffraction features correspond to the so-called carbonate *c*-type reflections associated with Mg and Ca ordering, a phenomenon that cannot occur in pure calcite, as is the studied sample.

The article by Bindi and Morana [5] deals with the structural study of a low-temperature phase of the mineral spryite, (Ag_{7.98}Cu_{0.05})_Σ = 8.03(As⁵⁺_{0.31}Ge_{0.36}As³⁺_{0.31}Fe³⁺_{0.02})_Σ = 1.00S_{5.97},



Citation: Ferraris, G. Editorial for the Special Issue Modularity and Twinning in Mineral Crystal Structures. *Minerals* **2021**, *11*, 758. <https://doi.org/10.3390/min11070758>

Received: 7 July 2021

Accepted: 13 July 2021

Published: 14 July 2021

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a new natural sulfosalt recently described. At room temperature, spryite is orthorhombic, space group $Pna2_1$ with cell parameters $a = 14.984$, $b = 7.474$, $c = 10.571$ Å; in its structure As^{3+} and As^{5+} statistically occupy the same crystallographic position. X-ray diffraction data were collected at 30 K (helium cryostat) on the same sample previously characterized from a chemical and structural point of view at room temperature. At 30 K, spryite maintains the $Pna2_1$ space group, but shows an $a \times 3b \times c$ superstructure and twinning by reticular merohedry based on a hexagonal sublattice. The superstructure arises from the ordering of As^{3+} and (As^{5+}, Ge^{4+}) in different crystal–chemical environments. Recognition of twinning allowed solving and refining the crystal structure.

The twinning by merohedry of tetrahedrite–tennantite (point group $-43m$) is well known. In his article, Makovicky [6] investigates the structural aspect of this twinning and finds that it is related to defects which can occur during the growth of tetrahedrite crystals; consequently, the twinning is described as an order–disorder (OD) phenomenon. The author takes as unit OD layer a one-tetrahedron-thick (111) layer composed of six-member rings of tetrahedra that are stacked according to the sequence ABCABC. The sequence can be described by three consecutive tetrahedron configurations, named α , β , and γ . When the orientation of the component tetrahedra is uniform, the α , β , γ , α sequence builds the cage structure of tetrahedrite. If it happens that the tetrahedra of the β layer are rotated by 180° against those in the underlying α configurations and/or rotated α configuration follows after the β configuration (instead of γ), the defect allows the growth of the crystal structure according to a different orientation, i.e., a twinning is generated.

The use of the OD theory is also central in the articles by Aksenov et al. [7] and Topnikova et al. [8]. In [7], the crystal structures of compounds with the general formula $Cs\{^{[6]}Al_2[^{[4]}TP_6O_{20}]\}$ ($T = Al, B$) are analyzed. Microporous, heteropolyhedral MT frameworks, consisting of octahedra (M) and tetrahedra (T), occur in these structures; thus, they are suitable for the migration of small cations such as Li^+ , Na^+ , and Ag^+ . The studied structures display order–disorder (OD) character and are described using the same OD groupoid family and two kinds of nonpolar layers that alternate along the b direction and have common translation vectors a and c . Both ordered polytypes and disordered structures are obtained using the following symmetry operators: a 2_1 screw axis parallel to c , inversion centers, and a screw axis parallel to a .

Article [8] reports the crystal structure of a new silicate–germanate with formula $Rb_{1.66}Cs_{1.34}Tb[Si_{5.43}Ge_{0.57}O_{15}] \cdot H_2O$. However, for this special issue, the important part of the article is represented by the comparison of the investigated structure with those of other related layered natural and synthetic silicates. The comparison is based on a topology–symmetry analysis by OD approach. A wollastonite chain was selected as initial structural unit. Three symmetrical ways of forming ribbons from such chain and three ways of interconnecting the ribbons to form layers are described using symmetry groupoids. Finally, hypothetical variants of the described layers and ribbons are predicted.

In the last article [9], a family of layered vanadates, arsenates, and phosphates, including the minerals vésignéite and bayldonite, and synthetic analogous is investigated. Their structures are built by similar modules that consist of a central octahedral layer filled by Mn, Ni, Cu, or Co and adjacent $[VO_4]$, $[AsO_4]$, or $[PO_4]$ tetrahedra. These structures are discussed in terms of modular crystallography and are shown to form a mero-plesiotype polysomatic series, i.e., a series where a module is common to all the members of the series, whereas a second module is peculiar for each member (merotypy) and, at the same time, the common layer may be modified both in its chemical composition and, to some extent, in its topology (plesiotypy; see Chapters 1 and 4 of [1]).

The articles published in this issue offer a sound update of research fields where the concepts of modular crystallography are well alive and provide unique tools to understand and to solve problems of structural crystallography. To note that even if the OD theory is quite often applied to mineral phases, it has been successfully applied to molecular crystals too, as, e.g., exemplified by the articles [10–12]. Reference [11], besides reporting the OD

character of the crystals of 9,10 phenantrenequinone, illustrates the basic elements of the OD theory.

Data Availability Statement: Not applicable.

Conflicts of Interest: The author declares no conflict of interest.

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