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Crystal Chemistry of Wylieite-Type Phosphates. Frédéric Hatert^a, André-Mathieu Franolet^a, Encarnación Roda-Robles^b, Miguel Galliski^c. ^aLaboratory of Mineralogy, University of Liège B-18, B-4000 Liège, Belgium. ^bDept. Mineralogy and Petrology, Universidad del País Vasco/EHU, Apdo. 644, E-48080 Bilbao, Spain. ^cLANIGLA-CONICET, C.C. 330 Avda. A. Ruiz Leal s/n, Parque Gral. San Martín, (5500) Mendoza, Argentina.
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The wylieite group of minerals consists of Na-Mn-Fe-Al-bearing phosphates which exhibit a crystal structure topologically similar to the alluaudite structure. However, the ordering of cations in the wylieite structure induces a splitting of the M(2) and X(1) sites of alluaudite into the M(2a) M(2b) and X(1a) X(1b) positions. Consequently, the $C2/c$ space group of alluaudite transforms into $P2_1/n$ in wylieite, with no significant change of the unit-cell parameters, and with a structural formula which corresponds to $X(2)X(1a)X(1b)M(1)M(2a)M(2b)(PO_4)_3$.

In granitic pegmatites, wylieite-type phosphates display chemical compositions ranging from $Na_2(Mn,Fe^{2+})Fe^{2+}Al(PO_4)_3$ to $Na(Mn,Fe^{2+})Fe^{3+}Al(PO_4)_3$, with Ca or Mn replacing Na on the X(2), X(1a) and X(1b) sites, Mg replacing Fe on the M(2a) site, and Mg or Fe^{3+} replacing Al on the M(2b) site, where represents a lattice vacancy. The name wylieite corresponds to $Na_2MnFe^{2+}Al(PO_4)_3$, while the name rosemaryite designates the more oxidized compositions, such as $NaMnFe^{3+}Al(PO_4)_3$. The prefix ferro- is then added if Fe^{2+} dominates in the M(1) site, thus leading to ferrowylieite, $Na_2Fe^{2+}Al(PO_4)_3$, and to ferrosemaryite, $NaFe^{2+}Fe^{3+}Al(PO_4)_3$. The name qingheite has been introduced for the Mg-rich equivalent of wylieite, $Na_2MnMgAl(PO_4)_3$.

Single-crystal structure refinements of ferrosemaryite from the Rubindi pegmatite, Rwanda ($R_1 = 2.43\%$, $a = 11.838(1)$, $b = 12.347(1)$, $c = 6.2973(6)$ Å, $\beta = 114.353(6)^\circ$), of rosemaryite from the Buranga pegmatite, Rwanda ($R_1 = 4.01\%$, $a = 12.001(2)$, $b = 12.396(1)$, $c = 6.329(1)$ Å, $\beta = 114.48(1)^\circ$), of wylieite from the Buranga pegmatite ($R_1 = 2.74\%$, $a = 11.954(2)$, $b = 12.439(2)$, $c = 6.406(1)$ Å, $\beta = 114.54(1)^\circ$), and of qingheite from the Santa Ana pegmatite, Argentina ($R_1 = 2.65\%$, $a = 11.878(3)$, $b = 12.448(2)$, $c = 6.438(2)$ Å, $\beta = 114.49(1)^\circ$), indicate that Al is predominant on the M(2a) site, not on the M(2b) site as observed in ferrowylieite. The morphologies of the X(1a) and X(1b) crystallographic sites correspond to a distorted octahedron and to a distorted cube, respectively. The [7+1]-coordinated X(2) site of rosemaryite is a very distorted gable disphenoid, similar to the A(2)' site of the alluaudite structure.

The structural features of rosemaryite, ferrosemaryite, wylieite, and qingheite are compared to those of other natural and synthetic wylieite-type phosphates, and the role played by Al to stabilize the wylieite structure is discussed in detail.

Keywords: phosphate minerals; wylieite group; crystal chemistry

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Holtite from Szklary, Poland. Sylwia Zelek^a, Adam Pieczka^b, Katarzyna Stadnicka^a. ^aFaculty of Chemistry, Jagiellonian University, Krakow, Poland. ^bFaculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Krakow, Poland.
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Holtite is very rare borosilicate mineral with a complex and a various chemical composition. It has been found in pegmatites in only three places in the world: Greenbushes - Australia [1]; Kola Peninsula - Russia [2] and Szklary - Poland [3]. The crystal structure has been already determined for single crystals originated from two of these occurrence (Australia [4], Russia [5, 6]), whereas the preliminary crystal structure for the holtite from Poland was announced in 2008 [7]. Recently three types of holtite from Szklary were isolated (yellow, amber, brown). For the amber, needle-shaped holtite crystals two kinds of the unit cell could be recognized: orthorhombic one with the lattice parameters $a=40.980(2)$, $b=23.6661(8)$, $c=4.6979(2)$ Å and hexagonal one: $a=23.6944(7)$, $c=4.7012(2)$ Å. The holtite, isostructural with $Si_3B[Al_{6.75}O_{17.25}(OH)_{0.75}]$ (dumortierite), has SiO_4 tetrahedra partially replaced by SbO_3 or AsO_3 triangular pyramids. Additionally, Al cations in the octahedral positions are partially substituted by Ta or Ti cations. The characteristic features of the holtite structure is the presence of both cation and anion vacancies. The structural work on the amber single crystals together with a possible twinning consideration is in progress.

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Keywords: holtite; mineral crystal structure; crystal twinning

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Layered Brownmillerites in the System of Manganese-Containing Alumino-Ferrites. Hannes Krüger^a, Stefan Stöber^b, Marina Sulzbachner^a, Herbert Pöllmann^b, Volker Kahlenberg^a. ^aInstitute of Mineralogie and Petrography, University of Innsbruck. ^bFaculty of Geoscience, University of Halle-Wittenberg.
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The system $Ca_2Fe_2O_5$ - $Ca_2Mn_2O_5$ - $Ca_2Al_2O_5$ was investigated by many authors (see [1] and citations therein), due to its relevance for the chemistry of cements. Single-

crystal growth experiments using a flux of CaCl_2 [2] produced crystals of a rare structure type, which has only been found in $\text{Sr}_3\text{NdFe}_3\text{O}_9$ [3] so far. The structure was solved and refined in space group *Amma*, with $a=5.32$, $b=26.64$, $c=5.47\text{\AA}$. The chemical composition determined from the structure refinement is $\text{Ca}_4\text{Al}_{0.24}(\text{Fe},\text{Mn})_{2.76}\text{O}_9$. Preliminary EDX results show a Fe/Mn ratio of approximately 77/23, which suggest that at least all the Mn is 4+, and possibly oxygen vacancies are present.

Barrier et al. [3] described the structure type as an intergrowth between the brownmillerite and the K_2NiF_4 structures. It also can be addressed as a *layered brownmillerite*. The structure type shows separated blocks of the brownmillerite-type. Each block has three layers: octahedral-tetrahedral-octahedral. The structural model in *Amma* requires disorder of right- and left-handed tetrahedral chains. $\text{Ca}_4\text{Al}_{0.24}(\text{Fe},\text{Mn})_{2.76}\text{O}_9$ shows rods of diffuse intensity in the XRD pattern. Their distribution suggests that the tetrahedral chains are alternating within the layers and the layers are stacked with disorder due to two possible translation vectors between the layers.

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Keywords: diffuse scattering; stacking faults

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Solid Solutions of $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ as a Base of New Multifunctional Materials. Pavel Teslenko^a, Larisa Reznitchenko^a, Olga Razumovskaya^a, Yuri Kabirov^a, Michael Kupriyanov^a. ^a*Department of Physics, Southern Federal University, Rostov-on-Don, Russia.*

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Solid solutions (SS) of $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ (BFMO) pose a great interest as a base of new materials simultaneously possessing ferroelectric and magnetic properties and high phase transition temperature values into paraelectric and/or paramagnetic states. At present there is contradictory information on properties of phases of the system, as the formation of stable crystal phases of PBMO depends from synthesis conditions greatly. As a result, the study of peculiarities of SS of $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ($0 \leq x \leq 0.5$ c $\Delta x=0.05$) at various synthesis conditions is of interest. The SS were synthesized with the use of solid solution reactions in two steps with intermediate grinding that provided the completeness of the reactions and the homogeneousness of the synthesized substance. As base reagents the high purity oxides were used. The X-ray study of samples was performed with the use of full-profile powder analysis ($\text{CuK}\alpha$ - radiation). As a result, the present phases, their concentrations and cell sizes were determined. The concentration of the main phase ($\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$) with perovskite structure varied from 49 to 98% for different compositions and was dependent from synthesis temperature values. Bi_2O_3 and $\text{Bi}_2(\text{Fe}/\text{Mn})_4\text{O}_9$ parasite phases have been

detected. The monotonous changes of cell parameters of $\text{Bi}(\text{Fe}/\text{Mn})\text{O}_3$ with rhombohedral phase of BiFeO_3 with the increase of x evidence the consecutive replacement of Fe ions with Mn ions. $T_1=790^\circ\text{C}$, $\tau=10\text{h}$, $T_2=800^\circ\text{C}$, $\tau=10\text{h}$ was chosen to be the optimal temperature & time mode. The XRD study of the samples has shown that with the increase of Mn concentration in BFMO from $x=0.05$ to $x=0.35$ the monotonous decrease of cell parameters and, corresponding to it, of cell volumes is observed. This evidences, most definitely, the changes of chemical bonds Fe-O and Mn-O in perovskite structure with the formation of ordered structure clusters. The insignificant increase of sub-cell volumes at $x>0.35$ corresponds with this theory. It is also possible to assume that the physical properties in BFMO compositions with $0.3 \leq x \leq 0.4$ would be extreme.

Keywords: ferroics; solid-state reactions; XRD

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Investigation of the Structure Role in the Formation of Twins. Giovanni Ferraris^a, Massimo Nespolo^b. ^a*Dpt Sci Min Petr, University Torino, Italy.* ^b*CRM² UMR-CNRS 7036 Institut Jean Barriol, Nancy Université, France.*

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The reticular theory of twins assumes that a good lattice restoration, as is the prerequisite to have a good structural match, is the *necessary* condition for the formation of a twin. This is however not a *sufficient* condition, because the structure is not obliged to have the full symmetry of its lattice (merohedral crystals). In fact, for a twin to be able to form, a (partially) coherent interface must exist, where a structural continuity is realized between the individuals sharing that interface and allows the same structure to develop along at least two different but crystallographically related directions.

Several exceptions apparently contradicting the reticular theory are known in the literature, but these are normally explained by the theory of hybrid twins, where the coexistence of concurrent sublattices is taken into account [1,2].

To go beyond the reticular theory and include the role of the structures, two possibilities are here analysed.

1. Twins fully sharing only a slice of structure at the interface: the symmetry of this slice probably governs the relative orientation of the individuals.
2. Twins share a subset of atoms, (especially larger ones) and the symmetry of the subset is higher than the intersection symmetry of the structure of the individuals in their respective orientations. The additional symmetry operations of this subset may map the individuals onto each other and create a common substructure in the individuals.

For twins sharing only a slice of structure, a systematic approach would require the use of *diperiodic groups* and *sectional layer groups of space groups*, analyzed in Volume E of the *International Tables for Crystallography*. The slice shared by a pair of individuals should have a diperiodic group that is a supergroup of the intersection of the