

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 (CuK_α - 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

sectional groups of the two individuals, in their respective orientations, obtained across a plane which corresponds to the composition plane of the twin.

The second case needs the use of *lattice complexes*, which are types of crystallographic orbits generated by atoms in a crystal structure under the action of the symmetry operations of the space group.

When part of the atoms of an individual of a twin have a continuation across the twin interface, the individuals have a substructure in common, which corresponds to a lattice complex. If a crystal structure is composed of lattice complexes some of which have an eigensymmetry higher than the space group, these can be invariant under the action of the twin operation(s) and govern thus the formation of the twin.

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Keywords: lattice complexes; subperiodic groups; twinning

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Non-MDO 4-layer Ferrophlogopite from Ruiz Peak (New Mexico). Massimo Nespolo^a, Isabella Pignatelli^a. ^aCRM² UMR-CNRS 7036, Institut Jean Barriol, Nancy-Université, France.

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In this study we investigated a crystal of ferrophlogopite from a rhyodacite lava flow at Ruiz Peak (New Mexico), belonging to the same rock hand specimen previously investigated by Ross et al. [3]. The analysis of the single-crystal X-ray diffraction pattern, obtained with an Oxford SuperNOVA microsource using CuK α radiation, shows four reflections in the 1/10 Å⁻¹ period of the 1M basic structure along the non-family rows: the crystal is thus a non-MDO 4-layer polytype. The cell parameters are $a = 5.3194(3)$ Å, $b = 9.2107(5)$ Å, $c = 39.828(5)$ Å, $\alpha = 90^\circ$, $\beta = 92.537(5)^\circ$, $\gamma = 90^\circ$. The stacking sequence has been obtained by PID analysis [4] and it can be expressed by RTW symbols $2 \bar{2} \bar{2}2$ [3], Z symbols 1353 [7] and OD symbols 2040 [2] in the homo-octahedral approximation. It is the first time that this polytype is found in the Ruiz Peak sample, although it was discovered in a Ti-biotite by means of oblique-texture electron diffraction [6] and indicated with the $4M_3$ Ramsdell symbol. The atomic coordinates of the structural model have been obtained from those of the 1M polytype from the same sample, by applying the PID stacking vectors. The space-group type, as obtained from the stacking sequence, would be $C2/c$, but the intensities distribution reveals a triclinic structural symmetry. This lower symmetry can be due to the desymmetrization of the OD layers and/or to the cation ordering in the octahedral sheets [1]. $C2/c$ is therefore the maximal space-group type for this polytype whereas the correct space-group type is a triclinic *translationengleiche* subgroup of it. Consequently the Ramsdell symbol $4M_3$, previously used to indicate this stacking sequence [3, 5, 6], should actually be modified

in 4A to take into account the structural symmetry. The structural refinement is in course and the preliminary results confirm the stacking sequence obtained by PID analysis.

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The Misfit Layer Structure of Franckeite. Emil Makovicky^a, Václav Petříček^b, Michal Dušek^b, Dan Topa^c. ^aUniversity of Copenhagen. ^bCzech Academy of Sciences Prague. ^cUniversity of Salzburg.

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Franckeite from San Jose, Bolivia, nominally $Pb_{4.6}Ag_{0.2}Sn_{2.5}Sb_2Fe_{0.8}S_{12.6}$, consists of alternating pseudo-hexagonal (H) and pseudotetragonal (Q) layers. The triclinic crystal structure has a pronounced one-dimensional transversal wave-like modulation and a non-commensurate layer match in two dimensions. The Q layer is an MS layer (M=Pb, Sn²⁺, Sb.), four atomic planes thick, with a 5.820 Å, b 5.872 Å, and the layer-stacking vector c 17.367 Å. The lattice angles are α 94.98°, β 88.43°, γ 89.97°; the modulation vector $q = 0 a^* + 0.1286 b^* - 0.0284 c^*$. The H layer is a single-octahedral MS₂ layer (M = Sn⁴⁺, Fe.) with a 3.672 Å, b 6.275 Å, c 17.447 Å, α 95.25°, β 95.45°, γ 89.97°; the modulation vector is $q = 0 a^* + 0.1374 b^* - 0.0304 c^*$. Length of the modulation vector is 45.67 Å; the match of centred (sub)cells in this b direction, 15.5 Q : 14.5 H, occurs at 91.00 Å, a double of the modulation vector plus a structurally important difference $\Delta = 0.34$ Å. The a and b vectors of both subsystems are parallel; the c vectors diverge. 5D superspace refinement was performed in the superspace group C-1, using 7260 observed reflections. It resulted in the overall R(obs) value equal to 0.113. The Q layers are composed of two tightly-bonded double-layers, separated by an interspace hosting lone electron pairs. Average composition of cations on the outer surface was refined as $Pb_{0.9}(Sn,Sb)_{0.1}$ whereas that of cations covering the interspace with lone electron pairs, with a typical configuration analogous to that observed in orthorhombic SnS, corresponds to $Sn(Sb)_{0.64}Pb_{0.36}$. Iron is dispersed over Sn⁴⁺ sites in the H layer. Franckeite does not form cylindrical aggregates (as does related cylindrite) because of the increased thickness of the Q layer.

Keywords: modulated structure; misfit layer structure; Pb-Sn-Sb-Fe sulphide; franckeite