

MS15-P26 New chain diborate $\text{TmH}[\text{B}_2\text{O}_5]$ and its relation to $\text{GdH}[\text{B}_2\text{O}_5]$: group-subgroup relation. A. P. Zorina, E. L. Belokoneva, O.V. Dimitrova, *Lomonosov Moscow State University, geological faculty, Moscow, Russia*
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Pale-green plate single crystals of new compound $\text{TmH}[\text{B}_2\text{O}_5]$ were obtained under hydrothermal conditions at $T=270^\circ\text{--}280^\circ\text{C}$ and $P\sim 70$ atm. with the components weight ratio $\text{Tm}_2\text{O}_3:\text{B}_2\text{O}_3=1:1$. Mineralizers Cl^- and HCOOH were presented in the solution at concentration of ~ 20 wt.%. This phase crystallizes also with Yb and Ho. The structure was determined without preliminary knowledge of chemical formula. Unit cell dimensions $a=6.82$, $b=8.61$, $c=11.43$ Å, $\beta=91.4$, and experimental intensities were determined using Xcalibur S diffractometer equipped with CCD area detector. The data were integrated using Crys-Alis program. The structure was solved using Patterson method in CSD package in a space group $C2/c = C_{2h}^6$ and refined in SHELXL-97 package. In $\text{TmH}[\text{B}_2\text{O}_5]$ structure two independent polyhedra: BO_4 -tetrahedron and BO_3 -triangle are connected via corners in a chain $2:[1\text{T}+1\Delta]^{8-}$. It is chain diborate in accordance with the borate systematic [1]. No other borates exhibit such unique chain unit. Chains are elongated in b -axis direction and are on two levels on c -axis. The new $\text{TmH}[\text{B}_2\text{O}_5]$ -structure is similar to diborate $\text{GdH}[\text{B}_2\text{O}_5]$ investigated earlier [2] which has monoclinic symmetry with other unit cell. Both structures demonstrate equal pseudosymmetry described in common unit cell by orthorhombic supergroup $Cmca$. The deviation from orthorhombic to monoclinic systems in the structures is visualized by displacements of REE-atoms from special positions. "Layer" with the chains, disposed on L of a -axis, has local orthorhombic pseudogroup $Cmcb$, subgroup of $Cmca$, and all its symmetry elements belongs to the "layer", thus the triangles are in mirror plane and tetrahedra are divided by m -plane into two equal parts. Combination of the "layers" in pairs is realized by other symmetry elements which correspond to orthorhombic space group $Pbna$, other subgroup of $Cmca$. The multiplicities of both groups are equal and there are no variants in pairs determined by symmetry relation in accordance to OD-theory [3]. The origin of existence of two structural models is in the difference in ionic radii of the elements at the middle and at the end of the REE-elements row. Different displacements from pseudo-mirror plane provide better coordination environment in every case. Pseudosymmetry relations determine twinning, typical for Tm and Gd-diborates. Crystal structures of two new minerals penobsquisite $\text{Ca}_2\text{Fe}[\text{ClB}_9\text{O}_{13}(\text{OH})_6]\text{Cl}\cdot 4\text{H}_2\text{O}$ [4] and walkerite $\text{Ca}_{16}(\text{Mg},\text{Li})_2[\text{B}_{13}\text{O}_{17}(\text{OH})_{12}]_4\text{Cl}_6\cdot 28\text{H}_2\text{O}$ [5] contain in complicate anionic groups diborate chains, which are combined with other blocks up to frameworks.

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MS15-P27 Metasideronatrite-1M, $\text{Na}_2\text{Fe}(\text{SO}_4)_2(\text{OH})\cdot\text{H}_2\text{O}$: a new polytype from Mežica (Slovenia). Fernando Cámara,^a Marco E. Ciriotti,^b ^a*Dipartimento di Scienze della Terra, Università di Torino, Torino, Italy,* ^b*Associazione Micromineralogica Italiana, Devesi-Cirič, Italy*
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According to [1] metasideronatrite $[\text{Na}_2\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})\cdot\text{H}_2\text{O}]$ - the first dehydration product of sideronatrite $[\text{Na}_2\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})\cdot 3\text{H}_2\text{O}]$ - is orthorhombic, space group $Pbmm$, with $a=7.3959(8)$, $b=16.0979(15)$, $c=7.1607(8)$ Å, $V=852.5(2)$ Å³, $Z=4$. Following [2] sideronatrite may present two OD polytypes: sideronatrite-2O, $P2_12_12_1$, $a=7.265$, $b=7.120$, and $c=20.522$ Å, $V=1061.5$ Å³; and sideronatrite-2M, $P2_1/c$, $a=7.265$, $b=7.120$, $c=20.828$ Å, $\alpha=99.84^\circ$, $V=1061.5$ Å³. Nevertheless, the monoclinic ordered polytype has not been described so far and the structural model is only based on OD theory [3]. An exploratory study of samples coming from the dumps of the Mežica mines, Mežica (Slovenia), revealed the presence of a new polytype of metasideronatrite, along with intermixed crystals of d'ansite-(Fe) $(\text{Na}_{21}\text{Fe}^{2+}(\text{SO}_4)_{10}\text{Cl}_3)$ and d'ansite-(Mg) $(\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3)$. A quick indexing of the cell results in a monoclinic symmetry with $a=7.416$, $b=7.1440$, $c=32.237$ Å, $\beta=96.57^\circ$, $V=1696.8$ Å³, thus a sort of super cell of metasideronatrite. Careful inspection of the reciprocal space showed the presence of a twin $[100](001)$ with $a=7.423(2)$, $b=7.151(3)$, $c=8.469(3)$ Å, $\beta=109.06(4)^\circ$, $V=424.9(2)$ Å³. Intensity data was obtained in a thin flake (ca. 30 μm thick) showing no streaks along c^* and the structure was solved with direct methods in the space group $P2_1/m$ and refined by full matrix least-squares ($R=5.6\%$ and $R_w^2=11.3\%$ on 935 reflections with resolution of 0.77 Å⁻¹ from both twin elements, twin ratio $0.458(3):0.542$). The observed topology contains infinite $[\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})]^{2-}$ octahedral-tetrahedral chains of the type $[\text{M}(\text{TO}_4)_2\varphi]$ with a 7.15 Å repeat running parallel to the b axis. Columns of $\text{NaO}_5(\text{H}_2\text{O})$ polyhedra, running also parallel to b axis, complete corrugated (001) slabs, linked just by strong hydrogen bonds [$\text{Ow-H}\dots\text{O}_2=2.78(1)$ Å, $\text{Ow-H-O}_2=167.6(5)^\circ$]. This is in agreement with the observed $\{001\}$ cleavage. The observed slabs and geometry of polyhedra match those observed in orthorhombic metasideronatrite by [1]. The main difference is the alternation of the slabs in the orthorhombic polytype upside up and upside down, where in the monoclinic polytype all the slabs point in the same direction. Thus the observed topology can be related to the theoretical natrosiderite-2M proposed by [2], by removal of two (H_2O) groups. Incidentally, it is close related to the basic OD layer crystallographic parameters described by [2], i.e.: $a=7.265$ and $b=7.120$, and symmetry defined by the layer group $P2_1/m$, while the width $c_0=10.261$ Å is reduced by the different staking sequence. Na-Na distance is $3.257(4)$ Å, slightly shorter than in the orthorhombic polytype. The finding of the monoclinic polytype of metasideronatrite supports the monoclinic model for sideronatrite and its formation by hydration of metasideronatrite-1M is under investigation.

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