

In connection with crystal chemical studies of alkaline earth arsenates, $\text{BaZn}_2(\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$ was synthesized under hydrothermal conditions. Its crystal structure was investigated by single-crystal X-ray diffraction data from a merohedral twin.

$\text{BaZn}_2(\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$ crystallizes in space group $P2_1$: $a = 5.291(1)$, $b = 10.418(2)$, $c = 8.055(2)$ Å, $\beta = 95.33(3)^\circ$, $Z = 2$. The feldspar-like framework consists of ZnO_4 and AsO_4 tetrahedra which share corners. The central atoms Zn and As are arranged alternately, thus all O atoms of the framework are linked to a Zn and an As atom. The tetrahedra are connected to four- and eight-membered rings which are arranged to form channels in the direction of the a -axis. Parallel to these channels only the same kinds of tetrahedra are stacked above each other. Topologically related - but not identical - are e.g., paracelsian, $\text{BaAl}_2(\text{SiO}_4)_2$ [1], danburite, $\text{CaB}_2(\text{SiO}_4)_2$ [2], and $\text{BaZn}_2(\text{AsO}_4)_2$ [3]. The [8]-coordinated Ba atom (BaO_8 forms a tetragonal antiprism) and the water molecules are located in cavities centred in the larger channels. The H_2O molecule is linked to two Ba atoms; the acceptors of the hydrogen bonds are framework O atoms. Financial support of the Austrian science foundation (FWF) is gratefully acknowledged (Grant P15875-N03).

[1] Chiari *et al.*, *Am. Mineral.*, 1985, **70**, 969. [2] Sugiyama, Takéuchi, *Z. Kristallogr.*, 1985, **173**, 293. [3] Lucas *et al.*, *Canad. Mineral.*, 1998, **36**, 1045.

Keywords: $\text{BaZn}_2(\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$, hydrothermal synthesis, crystal chemistry of inorganic compounds

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Slabs from Cubic Sb_2O_3 Interspersed between Puckered BN-Type $\text{CuCl}_x\text{Br}_{1-x}$ Layers

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New compounds, $\text{CuSb}_2\text{O}_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$), were obtained from chemical reactions taking place in sealed evacuated silica tubes. The structure consists of slabs of cubic antimony(III) oxide and hexagonal puckered CuX layers.

The compounds crystallize in the monoclinic space group Cc, but pseudo merohedral mimetic twinning produces the Laue symmetry 6/mmm. Unphysical short distances precludes the solution in any hexagonal (or trigonal) space group, and this is fully resolved by considering a twinned solution.

The antimony atoms have tetrahedral $[\text{SbO}_3\text{E}]$ coordination, E being the stereochemically active $5s^2$ lone pair electrons. The antimony oxide cages, Sb_4O_6 , are slightly distorted but of the same type as found in cubic Sb_2O_3 .

The Sb_2O_3 slabs are interspersed between hexagonally packed CuX ($\text{X} = \text{Cl}, \text{Br}$) layers resembling the boron nitride hexagonal structure. The Cu atoms have distorted $[\text{CuX}_3\text{O}]$ tetrahedral coordination. The oxygen atom in each tetrahedron belongs to the nearest Sb_4O_6 cage. The CuX network is regularly distorted at the nodes in between the $[\text{CuX}_3\text{O}]$ tetrahedra.

Keywords: stereochemically active lone pair, Sb_4O_6 cages, puckered CuX network

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New Intermetallic Compounds Forming the $\text{Ca}_{11}\text{Ga}_7$ Structure Type

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The binary alkaline earth (A^{II}) trielides $\text{Ca}_{11}\text{Ga}_7$ [1] and $\text{Sr}_{11}\text{In}_7$ [2] crystallize with a singular structure type (cubic, space group $Fm\bar{3}m$, $a \approx 1620$ (A=Ca)/1750 pm (A=Sr)). Fourteen new ternary Ca and Sr trielides (M^{III})/tetrelides (M^{IV}) forming this structure type were synthesized from stoichiometric mixtures of the elements and characterized by single crystal x-ray diffraction. The structures exhibit isolated M(1) atoms (M(1)=Al, Ga, In, Sn, Pb) together with tetrahedral units $[\text{M}(2)_4]$, which are formed by the triel elements

exclusively. Remarkably, one of the four crystallographically independent A^{II} positions is – as in the pure element – coordinated by A partners of the same kind in a cuboctahedral arrangement. In the mixed $\text{M}^{\text{III}}/\text{M}^{\text{IV}}$ compounds, the phase range reaches up to a maximum composition limit of $\text{A}_{11}[\text{M}(1)^{\text{III}}_4][\text{M}(2)^{\text{IV}}]_3$, which nearly corresponds to a ionic description according to the Zintl concept (tetrahedral anions $[\text{M}^{\text{III}}_4]^{8-}$ isoelectronic to white phosphorus P_4 besides isolated noble gas isoelectronic anions $[\text{M}^{\text{IV}}]^{3-}$). In the case of the Sr/In/Pb compounds, even the Sr position coordinated by Sr only is substituted by Pb^{4+} . The stabilities and phase ranges of the compounds, which are influenced by geometric and electronic factors (investigated by FP-LAPW band structure calculations) will be discussed.

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Keywords: alloy chemistry, trielides, tetrelides

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Structure and Bonding in Thiooxovanadates $\text{A}_3\text{VS}_x\text{O}_{4-x}$ ($\text{A} = \text{Na}, \text{K}$; $x = 1-4$)

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Alkalithiooxovanadates(V) $\text{A}_3\text{VS}_x\text{O}_{4-x}$ ($\text{A} = \text{Na}, \text{K}$; $x = 1-4$) [1-3], amongst them the new compounds $\text{K}_3\text{VS}_3\text{O}$ (SG $P2_1/c$, $a = 1014$, $b = 685$, $c = 1195$ pm, $\beta = 93.2^\circ$, $R1 = 0.09$) and Na_3VSO_3 (SG $R3c$, $a = 863$, $c = 1235$ pm, $R1 = 0.02$) were synthesized via reactions in the melt starting from V, the alkaline metal (A), A_2S , A_2O and sulfur. The structures of all compounds contain similar ortho anions $[\text{VS}_x\text{O}_{4-x}]^{3-}$, each with a different ion packing. The bonding situation for all sodium compounds $\text{Na}_3\text{VS}_x\text{O}_{4-x}$ with $x = 1-4$ was investigated by raman spectroscopy and DFT bandstructure calculations. In order to study the influence of cations, measurements and calculations of sodium vanadates are compared to corresponding potassium compounds.

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Keywords: vanadates, structural relationships, band calculations

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New Oxoferrates of the Alkali Metals

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Regarding structural motifs, the oxoferrates of the alkali metals are closely related to the oxosilicates due to the rigid coordination of the oxometallate anions: the angles of Fe-O-Fe bonds connecting two FeO_4 -tetrahedra correlate strongly with the size of the alkali metal ions. An even greater structural variety of the ferrates arises from three major differences between Fe and Si: By assuming different oxidation-states, iron ions build FeO_4 -tetrahedra of different size and charge. FeO_4 -units with HS- d^4 - (Fe^{IV}) and HS- d^3 -configuration (Fe^{V}) show significant deviations from tetrahedral geometry due to Jahn-Teller distortion. Some ferrates of the heavier alkali metals even contain edge sharing tetrahedra. Our studies [1-3] yielded several novel phases illustrating the structural characteristics of the oxoferrate chemistry.

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Keywords: oxometallates, ferrates, structural relationships

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Rietveld Refinement of the Crystal Structure of the Novel Compound Ir₄Ga₁₁

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The binary Ir-Ga system is rich in phases, several with large unit cells and complex structures. The crystal structure of the novel compound Ir₄Ga₁₁ has been determined from high resolution synchrotron powder diffraction data from the ID31 beamline at ESRF in Grenoble. The space group is *Imam* with $a = 12.80562(4)$ Å, $b = 9.25303(3)$ Å and $c = 8.02187(3)$ Å.

Keywords: intermetallics compounds crystal structure, Rietveld structural refinement, synchrotron powder diffraction