

Keywords: sodalite, gallium, substitution**P.10.06.7***Acta Cryst.* (2005). **A61**, C382**Hydrothermal Crystallization and Characterization of R⁺³: AlPO₄ Zeolites, where R=Ce, Pr and Nd**

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Zeolites are the most important technological materials made up of framework of aluminosilicates, aluminophosphates, vanadophosphates, silicoaluminophosphates and so on. In the recent years the interest is being extended greatly from the molecular sieves to selective catalysis, gas adsorption, nanoparticle hosts, atmospheric ecosystems, etc. These aluminophosphate molecular sieve zeolites have uni-, two-, and three-dimensional channels which are obtained hydrothermally in the presence of organic amines as structure directing agents. VPI-5 is an important aluminophosphate molecular sieve with 18 tetrahedral rings and free diameter of 12.1 Å. In this paper, the authors discuss the synthesis of R⁺³: aluminophosphate, where R=Ce, Pr and Nd. The addition of R⁺³ into the aluminophosphate framework not only enhances the stability of the framework, but also enlarges the pore diameter, which helps in the sieving of large molecules. Further, the efficiency of the catalytic activity can be elevated. The materials obtained have been subjected to a systematic characterization using Powder XRD, IR, SEM, BET and Positron Annihilation Life time measurements. The preliminary investigation shows that the following results: FTIR spectra show that the R⁺³ is inserted into the AlPO₄ pores. Cell volume has increased considerably with the insertion of R⁺³ elements into zeolite framework. Consequently the surface area decreased. Positron annihilation lifetime spectroscopy data show that micro void content increases as the surface area decreases.

Keywords: AlPO₄ zeolites, hydrothermal crystallization, rare earth elements**P.10.06.8***Acta Cryst.* (2005). **A61**, C382**Gallium Substitution in Aluminosilicate Halide Sodalites**

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In the Na₈[AlSiO₄]₆X₂ sodalite system (X = Cl, Br, I) the aluminium atoms were partially substituted with gallium progressively. The synthesised products represented the new composition Na₈[Al_{1-y}Ga_ySiO₄]₆X₂ (0 ≤ y ≤ 1). Gallium concentrations for different compositions were calculated using X-ray powder data Rietveld refinements and ²⁹Si MAS NMR spectroscopy. The lattice parameters increased [1, 2] linearly from [AlSiO₄]₆ to [GaSiO₄]₆ framework matrix. The Al/Ga-O distance was found as an average magnitude [2], which increases with increasing gallium concentration while the Si-O distance remained almost constant at 162.8 pm (σ ~ 2), 163.4 pm (σ ~ 3) and 162.6 (σ ~ 2) for the chloride, bromide and iodide sodalite, respectively. The increasing average tilt of the framework Al/GaO₄ and SiO₄ tetrahedra led to Na-O and Na-X distances shortening as a consequence of increasing gallium content in the trivalent site of the framework. The degree of framework oxygen s-hybridisation was observed linearly correlated to average T-O distances. In the XRD patterns no clear hints for domain formation of aluminium and gallium enriched parts in the crystals were observed. However, the ²⁹Si MAS NMR spectra showed clearly a non statistical distribution of the different Si-(OT₄) surroundings for bromide and iodide sodalites (y ~ 0.30 – 0.70). In the chloride sodalite series, aluminium and gallium were observed statistically distributed throughout the crystals.

[1] Perlmutter M. S., Todd L. T., Farrell E. F., *Mat. Res. Bull.*, 1974, **9**(1), 65.**P.10.06.9***Acta Cryst.* (2005). **A61**, C382**Na/K and Na/Li Substituted Aluminosilicate Nitrate Cancrinites**

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Cancrinites are the original class of microporous materials with so called ε-cages of sixring and fourring formed by TO₄-units (here T = Al, Si) and thereby including larger channels through the structures. We report here on synthesis and characterisation of the new forms of Na/K, Na/Li substituted cancrinities. The sodium form Na_{6+x}[Al₆Si₆O₂₄](NO₃)_x(H₂O)_y (TG => x ≈ 1, y ≈ 3) was directly prepared by soft chemical methods [1]. This form has been used as mother compound together with LiNO₃ and KNO₃ solutions under synthesis conditions obtaining the appropriate Li and K form. The lattice parameter (Tab. 1) show increased values with increasing cation size. This is explained by a decrease of the tilt angle of rigid TO₄-unit as defined here and supported by results of Rietveld refinements of X-ray powder data and infrared investigations.

Table 1: Lattice parameter of the different cancrinite forms

Cancrinite form	a /pm	c /pm	V /10 ⁶ pm ³
Na/Li	1246.76(5)	501.92(3)	675.66(7)
Na	1265.89(2)	518.15(1)	719.08(3)
Na/K	1303.56(5)	535.65(2)	788.27(7)

[1] Buhl J.-Ch., Stief F., Fechtelkord M., Gesing Th.M., Taphorn U., Taake C., *J. Alloys Compd.*, 2000, **305**, 93.**Keywords:** cancrinite, substitution, synthesis**P.10.06.10***Acta Cryst.* (2005). **A61**, C382**The Crystal Structure of Sacrofanite, the 74 Å Phase of the Cancrinite Group**

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Sacrofanite, *a* = 12.903(2), *c* = 74.284(8) Å, space group *P* $\bar{6}2c$, is the largest member known to date of the cancrinite group, displaying a 28 layer stacking sequence along the *c* axis. The members of this group share some structural features with zeolites, their structural cages hosting extra-framework ions as well as H₂O molecules. The crystal structure of sacrofanite has been modeled on the basis of HRTEM images collected by means of a JEOL 4000EX microscope and processed with the program CRISP. The obtained model has been successfully refined vs. synchrotron radiation data (collected at the X-ray Diffraction Beamline at the Elettra facility, Trieste, Italy) up to *R* = 0.083 for 2426 reflections, with a resolution of 0.96 Å. The layer stacking sequence has Zhdanov symbol |12(8)21|12(8)21|, and corresponds to ABCABACACABACBACBACABABACABC..., where A, B and C stand for the positions of the six-member rings in each layer. The topological symmetry is *P6₃/mmc*; however the ordering of Si and Al in the tetrahedral sites reduces the symmetry to *P* $\bar{6}2c$. The resulting framework is formed by two sequences of four cancrinite cages and two sodalite cages along 0, 0, *z*, whereas sequences of one losod, one cancrinite, one losod, two sodalite, one liottite, and two sodalite cages develop along both 1/3, 2/3, *z* and 2/3, 1/3, *z*. These cages host extra-framework cations and anions, as well as water molecules. The crystal chemical formula of sacrofanite, as obtained from the refinement, is (Na,K)₉₈Ca₂₀(Si₈₄Al₈₄O₃₃₆)(SO₄)₂₆Cl₂·8H₂O.

Keywords: crystal structure, HRTEM, synchrotron radiation**P.10.08.1***Acta Cryst.* (2005). **A61**, C382**BaZn₂(AsO₄)₂·H₂O: A Framework Structure Related to Feldspar**

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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

P.10.08.2

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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, $\text{CuSb}_2\text{O}_3\text{X}$ ($X = \text{Cl}, \text{Br}$), 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 ($X = \text{Cl}, \text{Br}$) 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 $Fm\bar{3}m$, $a \approx 1620$ ($A = \text{Ca}$)/1750 pm ($A = \text{Sr}$)). 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 ($M(1) = \text{Al}, \text{Ga}, \text{In}, \text{Sn}, \text{Pb}$) 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 $M^{\text{III}}/M^{\text{IV}}$ compounds, the phase range reaches up to a maximum composition limit of $A_{11}[\text{M}(1)^{\text{III}}_4][\text{M}(2)^{\text{IV}}_3]$, 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.

[1] M. L. Fornasini, F. Merlo, *Z. Kristallogr.*, 1989, **187**, 111-115. [2] M. Wendorff, C. Röhr, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1768. [3] M. Wendorff, C. Röhr, *Z. Naturforsch.*, 2004, **59 b**, 619-628.

Keywords: alloy chemistry, trielides, tetrelides

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

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Alkalithiooxovanadates(V) $\text{A}_3\text{VS}_x\text{O}_{4-x}$ ($A = \text{Na}, \text{K}; x = 1-4$) [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

P.10.08.6

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