

Table I

patient nr	phase composition	
	outer part	central part
1	WEW	HAPA+UA
2	WED+WEW	WEW+HAPA+UA
3	WEW+WED	WEW
4	HAPA+STRU	WEW+HAPA
5	WEW+WED+HAPA+STRU	WEW+HAPA+UA
6	WEW+HAPA	HAPA
7	WEW+WED	WEW+WED+HAPA+UA+STRU

Table II

patient nr and stone nr	phase composition	patient nr and stone nr	phase composition
I-1	WEW+WED	III-1	WEW
I-2	WEW	III-2	WEW+WED+UA
I-3	WEW+HAPA	IV-1	HAPA+STRU
II-1	WEW+HAPA+UA+STRU	IV-2	HAPA+STRU+WEW
II-2	WEW+HAPA+STRU		

coordinate respectively.

The second compound, $\text{BaTiAl}_5\text{O}_{12}$ is orthorhombic, $a = 4.862(1)$, $b = 7.136(2)$, $c = 13.598(3)$ Å, Pnn2. Its structure consists of ribbons of octahedra joined by sheets of tetrahedra to form parallel 'six-sided' tunnels. The barium ions in the tunnels are ten-coordinate.

In the first structure the tunnels are interconnected whereas in the second they are not. A full description of the structures will be presented together with their relevance to the SYNROC process.

References:

1. Ringwood, A.E. Safe Disposal of high level nuclear reactor wastes: A new strategy. Australian National University Press, Canberra (1978); and Ringwood, A.E., Kesson, S.E., Ware, N.G., Hibberson, W.O. and Major, A. *Geochem. J.*, **13**, 141 (1979)
2. Kesson, S.E. *Rad. Waste Manag. and the Nuclear Fuel Cycle*, **4**, 1, 53 (1983); and Kesson, S.E., Sinclair, W.J. and Ringwood, A.E. *Nucl. Chem. Waste Manag.*, In press, 1984.
3. G.D. Fallon and B.M. Gatehouse, *J. Solid State Chem.*, **49**, 59 (1983)
4. Guha, J.P., Kolar, D. and Volavsek, B. *J. Solid State Chem.*, **16**, 49 (1976); and Guha, J.P., *J. Solid State Chem.*, **34**, 17 (1980)

08.2-39

NEW STRUCTURES IN THE $\text{BaO-Al}_2\text{O}_3\text{-TiO}_2$ SYSTEM OF SIGNIFICANCE TO THE SYNROC PROCESS

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Interest in the alkaline earth aluminium titanates, especially the $\text{BaO-Al}_2\text{O}_3\text{-TiO}_2$ system, has heightened due to the work of Professor Ringwood and coworkers (1) on their proposed SYNROC process for the long term storage of radwaste. SYNROC consists principally of three minerals, hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{15}$), perovskite (CaTiO_3) and zirconolite ($\text{CaZrTi}_2\text{O}_7$). Each of these synthetically formed mineral species has been shown to incorporate different radwaste ions in varying proportions (2).

The structure of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ was determined recently (3) and shown to contain blocked tunnels or cavities of the hollandite type in which barium ions are situated, and as a result of this finding other phases that might be of significance to the SYNROC process have been sought.

The structures of two compounds in the $\text{BaO-Al}_2\text{O}_3\text{-TiO}_2$ system, whose compositions were previously known but whose crystal systems and symmetries had been incorrectly reported (4), have been determined. The first, $\text{Ba}_3\text{TiAl}_9\text{O}_{20}$ is monoclinic, $a = 15.631(4)$, $b = 11.373(2)$, $c = 4.981(1)$, $\beta = 107.77(2)^\circ$ C2/m. The structure consists of sheets of corner-shared AlO_4 tetrahedra, two deep, linked by corner-sharing to parallel ribbons of edge-shared octahedra. Each ribbon forms part of four separate tunnels of two different types. One is 'five-sided' and the other 'six-sided'; both accommodate barium ions that are ten- and eight-

08.2-40 NEW COMPOUNDS WITH Ge_4^{4-} TETRAHEDRANE-ANIONS. By J. Llanos, R. Nesper and H.G. von Schnering, Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80.

I-IV-compounds of Na, K, Rb and Cs are not precisely characterized up to now [1,2,3,4]. Besides some clathrate compounds of the M_2X_6 and $\text{M}_{24}\text{X}_{136}$ type, only the MX-compounds are observed. Their common unit is the X_4^{4-} tetrahedraneanion which is always coordinated by four metal atoms in form of a distorted cubane M_4X_4 . Different crystal structures arrive from different cubane packings [5]. We have reinvestigated precisely NaGe (P2/c, $a=12.373(4)$, $b=6.668(3)$, $c=11.498(3)$ Å, $\beta=120.21(2)^\circ$); KGe (P43n, $a=12.734(1)$ Å); RbGe (P43n, $a=13.198(3)$ Å) and CsGe (P43n, $a=13.654(5)$ Å) to discuss the cubane geometry in different structures [6]. Moreover new ternary germanides of alkaline metals with the composition $\text{M}_2\text{M}'_{1-x}\text{Ge}$ have been prepared and investigated. Two new structure types occur which contain new arrangements of cubanes and exhibit the special character of the Na- Ge_4 interaction.

The compounds M_7NaGe_8 crystallize cubic in Pa3 (K_7NaGe_8 , $a=12.684(1)$ Å; Rb_7NaGe_8 , $a=13.165(1)$ Å; Cs_7NaGe_8 , $a=13.472(3)$ Å) with $Z=4$. They contain the linear $\text{M}_3\text{Ge}_4\text{-Na-Ge}_4\text{M}_3$ unit, which exhibits the geometry of a corner-shared double cubane M_3NaGe_4 . One of the large cations M stays without direct contact to Ge_4 , preserving the MX composition. The structure of such compounds is therefore represented by a quaternary aristotype $\text{M}'\text{M}''_6\text{NaX}_8$, which could be rationalized in $\text{CsK}_6\text{NaGe}_8$ (Pa3, $a=12.879(3)$ Å).

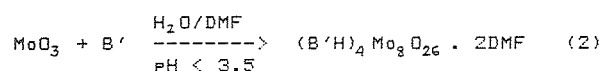
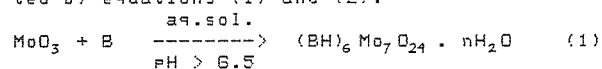
The compound $\text{Cs}_2\text{Na}_2\text{Ge}_4$ crystallizes with a new structure type, which is related to the NaPb-

structure ($P2_1/n$, $a=12.969(7)$, $b=9.782(4)$, $c=8.517(4)$ Å, $\beta=106.31(4)$). The central unit is a onedimensional infinite chain $\frac{1}{2}[\text{Na}_2/\text{NaCsGe}_4]$ which consists of linked cubanes $\{[\text{NaCsGe}_4] - \text{Na} - [\text{Ge}_4\text{CsNa}] - \text{Na}\}$ in trans-arrangement. A further Cs atom stays without direct contact to the Ge_4 -units and preserves again the composition MX. The structure of this compound is represented by the formula $\text{Cs}\frac{1}{2}[\text{CsNaNa}_2/\text{Ge}_4]$.

- [1] L.M. Dennis and N.A. Skow, *J. Am. Chem. Soc.* **52**, 2369 (1930)
 [2] W. Klemm und E. Hohmann, "Alkalisilizide, Alkaligermanide, ihre Darstellung und einige wichtige Eigenschaften", Januar 1946
 [3] E. Busmann, *Z. Anorg. Allg. Chem.* **313**, 90 (1961)
 [4] J. Witte und H.G.v. Schnering, *Z. Anorg. Allg. Chem.* **327**, 260 (1964)
 [5] R. Nesper, H.G.v. Schnering, *Z. Krist.* **162**, 202 (1983)
 [6] J. Llanos, Dissertation, Universität Stuttgart (1984)

08.2-41 SYNTHESSES AND CRYSTAL STRUCTURES OF AMINOPYRIDINIUM POLYMOLYBDATES. By J. M. Gutiérrez-Zorrilla^a, P. Román^a, C. Esteban-Calderón^b, M. Martínez-Ripoll^b and S. García-Blanco^b. a) Dept. Química (Inorgánica) Univ. del País Vasco, Aptdo. 644, Bilbao, Spain, b) Dept. Rayos X, Instituto Rocasolano CSIC, Serrano 119, Madrid-6, Spain.

Aminopyridinium hepta- and octamolybdates have been prepared in aqueous or $\text{H}_2\text{O}/\text{DMF}$ solutions. Preparation of these compounds can be formulated by equations (1) and (2):



B = 2-aminopy (i), 3-aminopy (ii), 4-aminopy (iii), 2-amino-3-methylpy (iv), 2-amino-4-methylpy (v), 2-amino-5-methylpy (vi) and 2-amino-6-methylpy (vii)
 B' = 2-aminopy (viii). (py = pyridine)

Single crystals of (i), (iii), (iv), (vi) and (viii) have been obtained. Crystal data for (i) are: $(\text{C}_5\text{H}_7\text{N}_2)_6 \text{Mo}_7 \text{O}_{24} \cdot 3\text{H}_2\text{O}$ $a=14.8161(4)$, $b=17.5073(4)$, $c=20.8492(6)$ Å, $\beta=107.503(2)^\circ$, $V=5153.7(3)$ Å³, $Z=4$, $P2_1/n$, $D_0=2.15$ $D_x=2.17$ g cm⁻³, $R=0.030$, $wR=0.034$ for 4959 observed reflexions. The structure contains isolated $(\text{Mo}_7\text{O}_{24})_6^-$ anions linked to the 2-aminopyridinium cations and water molecules through hydrogen bonds of N-H...O and O-H...O type. Crystal structures of (iii), (iv), (vi) and (viii) are in progress.

08.2-42 SYNTHESIS AND CRYSTAL SYMMETRY OF A MONOCLINIC MODIFICATION OF $\text{MoO}_3 \cdot \text{H}_2\text{O}$. by J.L. Garin and M.A. Solar. Departamento² de Metalurgia, Universidad de Santiago de Chile, Santiago, Chile.

Molybdenum trioxide mono-hydrate is formed as an intermediate substance during thermal decomposition of some ammonium molybdates, the final product being anhydrous molybdenum trioxide. The compound has been reported in earlier literature, as having at least three different phases. The structure of the white modification or "α-molybdic acid", for instance, crystallizes with triclinic symmetry in the space group $P1$ (Bösch and Krebs (1975), *Acta Cryst.* **B30**, 1795).

The authors synthesized another modification of the compound, by leaching of molybdenite concentrate with nitric acid. Single crystals growing in well-shaped white needles were obtained. The chemical composition of the crystals, as determined by usual analysis techniques, was found to be very close to stoichiometry.

The crystal data for $\text{MoO}_3 \cdot \text{H}_2\text{O}$ were determined by recording three dimensional data on Weissenberg and Buerger precession photographs, using Ni-filtered Cu-radiation. The unit cell is monoclinic, with $a=9.720$ Å, $b=3.725$ Å, $c=7.179$ Å, $\beta=102.4^\circ$ and space group $P2_1/m$.

The calculated density, assuming four formula units in the unit cell, is 4.24 g cm⁻³. The measured value resulted to be 4.20 g cm⁻³.

From our results we can conclude that the compound under study discloses another white isomer of $\text{MoO}_3 \cdot \text{H}_2\text{O}$.

08.2-43 STRUCTURAL CHARACTERISTICS OF $\text{La}_2\text{Ge}^{\text{IV}}\text{Ge}^{\text{V}}\text{Ge}^{\text{VI}}\text{O}_9$ AND RELATIONSHIPS TO THE RARE EARTH ALUMINIUM GERMANATES OF THE TYPES $\text{RE}_2\text{Al}[\text{GeO}_4]_2\text{OH}$ AND $\text{REAlGe}^{\text{V}}\text{O}_5$. By K.-H. Klaska, M. Werk and O. Jarchow, Mineralogisch-Petrographisches Institut der Universität, Grindelallee 48, 2000 Hamburg 13, Germany.

Single Crystals of $\text{La}_2\text{Ge}^{\text{IV}}\text{Ge}^{\text{V}}\text{Ge}^{\text{VI}}\text{O}_9$ were synthesized hydrothermally at 800°C and 1500 bar. $\text{La}_2\text{Ge}^{\text{IV}}\text{Ge}^{\text{V}}\text{Ge}^{\text{VI}}\text{O}_9$ crystallizes in space group $A\bar{1}$ with $a=7.68_6$ Å, $b=5.71_2$ Å, $c=16.57_0$ Å, $\alpha=90.59^\circ$, $\beta=109.82^\circ$, $\gamma=88.72^\circ$ and $Z=4$. The direct method program MULTAN 80 was used for the structure determination. The structure is characterized by slightly distorted $[\text{GeO}_6]$ -octahedra, $[\text{GeO}_5]$ -tetragonal pyramids and $[\text{GeO}_4]$ -tetrahedra. To the best of our knowledge this is the first structure with three different coordination numbers of the Ge-atoms. The $[\text{GeO}_6]$ -octahedra join into chains parallel $[010]$ by sharing edges. Adjacent chains are cross-linked by pairs of edge-sharing tetragonal pyramids. In addition an inter-chain linkage is provided by insular $[\text{GeO}_4]$ -tetrahedra. The Ge-polyhedra form layers running in the a,b-plane. These layers are connected by La^{3+} -O bonds to a three-dimensional network. The new compound $\text{La}_2\text{Ge}^{\text{IV}}\text{Ge}^{\text{V}}\text{Ge}^{\text{VI}}\text{O}_9$ has a structure closely related to those of $\text{RE}_2\text{Al}[\text{GeO}_4]_2\text{OH}$ and $\text{RE}_2\text{AlGe}^{\text{V}}\text{O}_5$ (Jarchow, Klaska, Werk, *Z. Krist.* (1982) **159**, 65-67). All three structures are based on straight chains of edge-sharing octahedra.