

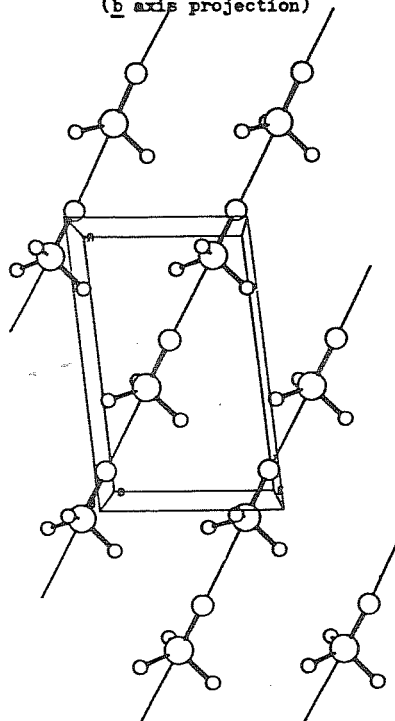
We have, for the first time, established the existence of SiO_2N_2 tetrahedra in the pyrosilicate group $\text{Si}_2\text{O}_7\text{N}_4$ during the structural study of the melilite compound $\text{Ln}_2\text{Si}_3\text{O}_7\text{N}_4$. The third silicon atom presents a SiN_4 nitrided environment.

When calcium is substituted by lanthanide in CaSiO_3 , LnSiO_3N compounds are obtained. The cyclic Si_3O_9 group of the wollastonite is replaced by the $\text{Si}_3\text{O}_6\text{N}_3$ entity with existence of $\text{Si}_2\text{O}_2\text{N}_2$ tetrahedra.

The $\text{Ca}_4\text{Si}_7\text{O}_{17}\text{F}_2$ cuspidine belongs to the sorosilicate family. The substitution of calcium by lanthanide leads to the $\text{Ln}_4\text{Si}_7\text{O}_{17}\text{N}_2$ oxynitrides. Nitrogen doesn't take the fluorine position but is linked to silicon. In the $\text{Si}_2\text{O}_5\text{N}_2$ group the formation of SiO_3N tetrahedra can be observed.

So, as the SiO_4 , SiN_4 and SiON_3 tetrahedra were already well known, we have pointed out for the first time the evidence of the SiO_2N_2 and SiO_3N tetrahedra.

Figure 1. Packing diagram for silyl fluoride (b axis projection)



08.2-37 THE CRYSTAL STRUCTURE OF SILYL FLUORIDE
AT 96K, by Alexander J. Blake, E.A.V. Ebsworth and Alan J. Welch, Department of Chemistry, University of Edinburgh, Scotland, EH9 3JJ.

A sample of silyl fluoride was sublimed into a Pyrex tube which was then sealed. On cooling the sample on a Weissenberg camera equipped for low-temperature work, a liquid appeared from which a single crystal was grown. Space group ($P2_1/n$) and unitcell parameters were determined before the crystal was transferred - without melting or other phase change - to an Enraf-Nonius CAD4 diffractometer for data collection. Accurate unitcell parameters were obtained by least-squares refinement (G.S. Pawley, J. Appl. Cryst. 1981, 14, 357-361) against an X-ray powder profile for the compound obtained by microdensitometry of a film recorded on a Guinier-Simon low-temperature camera.

The structure of silyl fluoride consists of chains of molecules formed by strong F...Si interactions. The F...Si distance of 2.8941(12) Å is well within the sum of the corresponding van der Waals' radii (3.45 Å). The Si - F...Si and F...Si - F angles are 146.03(7) and 178.65(6)° respectively. Perhaps surprisingly, there are no close F...H contacts. The Si has 4 + 1 coordination and a concomitant lengthening of the Si - F bond in the crystal (1.6045(12) Å) as compared with the gas phase value of 1.59465(4) Å (S. Craddock, personal communication) is observed. Full details will be presented for silyl fluoride and for related compounds.

08.2-38 ON THE NON-HOMOGENEITY OF THE PHASE COMPOSITION OF URINARY CALCULI.
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As the result of the investigations which we have conducted using powder methods on a X-ray diffractometer, we have found that several parts / outer part, central part, nucleus / of the same kidney stone - may have a different phase composition /Tab. I/. This fact is not fully and satisfactorily examined and described in the literature yet. Non-homogeneity of the composition can also effect the quantitative determination of the composition. The stone can be composed from two substances only /e.g. from WEW and WED/ but the quantitative relation of these components in the outer part and in the central part of the stone can be different. There are also such cases, in which one finds in the renal of the same patient a few stones with different phase composition /Tab. II/.

The accurate data will be published in Polski Tygodnik Lekarski / Polish Magazine of Medicine/. The abbreviations applied in this abstract are as follows: WEW - whewellite, WED - weddellite, HAPA - hydroxyl-apatite, STRU - struvite, UA - uric acid.

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.

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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 M_2X_{136} type, only the MX-compounds are observed. Their common unit is the X_4^{4-} tetrahedrane anion 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 ($\text{P}\bar{4}3n$, $a=12.734(1)$ Å); RbGe ($\text{P}\bar{4}3n$, $a=13.198(3)$ Å) and CsGe ($\text{P}\bar{4}3n$, $a=13.654(5)$ 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 $\text{Pa}\bar{3}$ (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 $\text{CsK}_6\text{NaGe}_8$ ($\text{Pa}\bar{3}$, $a=12.879(3)$ Å).

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