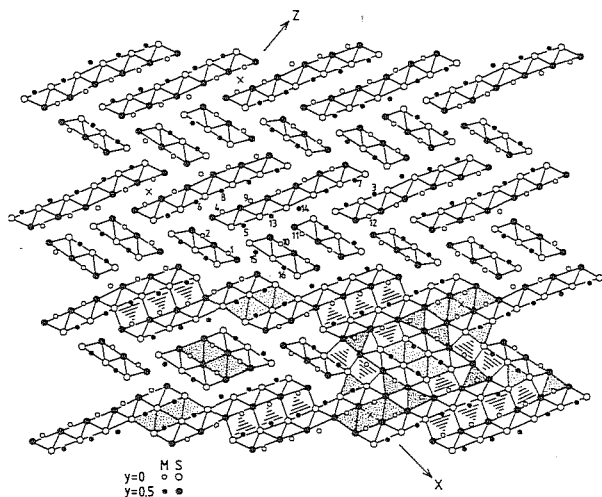


**08.2-34** THE STRUCTURE AND HIGH RESOLUTION ELECTRON MICROSCOPE STUDY OF  $\text{Sn}_6\text{Sb}_{10}\text{S}_{21}$ . By John B. Parise and Piers P.K. Smith, Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, Australia.

The tin antimony sulphide  $\text{Sn}_6\text{Sb}_{10}\text{S}_{21}$ , previously reported as  $\text{SnSb}_2\text{S}_4$  (Wang and Eppelsheimer, Chem. Erde (1975) 34S, 201), crystallizes in the monoclinic space group  $C2/m$  with  $a = 44.995(5)$ ,  $b = 3.9023(5)$ ,  $c = 20.613(3)$  Å,  $\beta = 96.21(1)^\circ$ ,  $V = 3598.1(5)$  Å<sup>3</sup> and  $Z = 4$ . The structure solved from single crystal X-ray data using direct methods consists of bands of edge-sharing half-octahedra that extend parallel to [010] (Fig. 1); two bands have composition  $(\text{M}_4\text{S}_6)_n$ . These bands are clearly imaged in high resolution electron microscope images taken along the [010] direction. With the exception of M(14), the coordination polyhedra of all the metal atoms (see lower right corner of Fig. 1) may be considered as monocapped trigonal prisms. The coordination of M(14), at the middle of an  $(\text{M}_{10}\text{S}_{12})_n$  band and facing the leading edge of a  $(\text{M}_4\text{S}_6)_n$  band, is a bicapped trigonal prism. Typically M-S distances in the prisms are distributed as follows:  $1 \times 2.53$  Å,  $2 \times 2.65$  Å,  $2 \times 3.03$  Å with M(14) ( $2 \times 2.71$  Å,  $1 \times 2.79$  Å and  $1 \times 3.16$  Å) again being the exception.



Projection of the structure of  $\text{Sn}_6\text{Sb}_{10}\text{S}_{21}$  on (010)

**08.2-35** A MOLYBDENUM (IV) PHOSPHATE WITH A TUNNEL STRUCTURE  $\text{TlMo}_2\text{P}_3\text{O}_{12}$ . By A. Leclaire, J.C. Monier and B. Raveau, Laboratoire de Cristallographie, Chimie et Physique des Solides, L.A. 251, ISMRA-Université de Caen, 14032 Caen Cedex, France.

During the investigation of the systems  $A\text{-P-Mo-O}$  ( $A = \text{K}, \text{Rb}, \text{Tl}$ ), a new molybdenum phosphate  $\text{TlMo}_2\text{P}_3\text{O}_{12}$  was isolated, besides the molybdenyl phosphate  $\text{KMo}_2\text{P}_3\text{O}_{13}$  (Leclaire et al., J. Solid State Chem. (1983) 48, 147). This compound crystallizes in an orthorhombic cell of space group  $\text{Pbcm}$  with  $a = 8.8364(6)$ ,  $b = 9.2553(7)$  and  $c = 12.2889(11)$  Å. Its structure was refined to  $R = 0.055$  and  $R_w = 0.062$  ( $w = f(\sin \theta/\lambda)$ ). The  $\text{MoO}_6$  octahedra and  $\text{PO}_4$  tetrahedra are almost regular. The Mo-O distances range from 1.855(2) Å to 2.048(10) Å and the P-O bonds range from 1.485(11) Å to 1.618(8) Å. The framework  $\text{Mo}_2\text{P}_3\text{O}_{13}$  can be described as built up from corner-sharing  $\text{PO}_4$  tetrahedra and  $\text{MoO}_6$  octahedra. Three structural units are observed:  $\text{PO}_4$  tetrahedra, diphosphate groups  $\text{P}_2\text{O}_7$ , and two-corner sharing octahedra  $\text{Mo}_2\text{O}_{11}$  units. This framework delimits large tunnels where the  $\text{Tl}^+$  ions are located. The  $\text{Tl}^+$  ions are off-centered in the tunnels, this is to be compared to the displacement of  $\text{K}^+$  in the oxide  $\text{KMo}_2\text{P}_3\text{O}_{13}$ . However the  $\text{Tl}^+$  ions are close to the walls of the tunnels: every ion forms three bonds with the oxygen atoms, ranging from 2.820(17) Å to 2.840(12) Å. It differs also from  $\text{KMo}_2\text{P}_3\text{O}_{13}$  by the fact that all the oxygen atoms of the  $\text{MoO}_6$  octahedra are not isolated but form  $\text{Mo}_2\text{O}_{11}$  units. The potassium and rubidium oxides have also been synthesized: they are isostructural.

**08.2-36** NEW TETRAHEDRA IN SILICON OXYNITRIDE COMPOUNDS:  $\text{SiO}_2\text{N}_2$  AND  $\text{SiO}_2\text{N}$ . By G. Roult<sup>+</sup>, P. Bacher<sup>+</sup>, C. Liébaud<sup>+</sup>, R. Marchand<sup>++</sup>, P. Goursat<sup>+++</sup>, Y. Laurent<sup>++</sup>. DRF/DN, CEN-G, CEA, 85X, 38041 Grenoble Cedex, France. ++ Lab. de Chimie Minérale, L.A. 254, 35042 Rennes Cedex. +++ Lab. des Céramiques, L.A. 320, 87061 Limoges Cedex.

The densification of silicon and aluminium oxynitride ceramics so called "Sialons" is made easier by using additives such as metallic oxides. When the lanthanide oxides are used, a lot of compounds have been prepared belonging to the  $\text{Ln-Si-O-N}$  system. The structural study has been resolved by multicomponent profile analysis of time-of-flight neutron diffraction data. By this technique it is possible to differentiate clearly between oxygen and nitrogen atoms. The obtained compounds are:

Formula	Structure type	Lattice symmetry	Space group
$\text{Ln}_2\text{Si}_3\text{O}_5\text{N}_4$	melilite	Tetragonal	$P \bar{4} 2_1 m$
$\text{LnSiO}_2\text{N}$	wollastonite	monoclinic	$C 2/c$
$\text{Ln}_4\text{Si}_2\text{O}_7\text{N}_2$	cuspidine	monoclinic	$P 2_1/c$
$\text{Ln}_{10}\text{Si}_6\text{O}_{24}\text{N}_2$	apatite	hexagonal	$P 6_3$

Except the apatite type, the ordered arrangement between oxygen and nitrogen in the coordination tetrahedra around the silicon atoms leads to new types of tetrahedra.

In fact, the  $\text{SiO}_4$  tetrahedra are well known in silica and silicate compounds and the  $\text{SiN}_4$  tetrahedra in the  $\text{Si}_3\text{N}_4$  nitride and in the ternary silicon nitrides. The mixed  $\text{SiN}_2\text{O}$  tetrahedron exists in the  $\text{Si}_2\text{N}_2\text{O}$  oxynitride and in the  $\text{A}^1\text{SiON}$  compounds ( $\text{A}^1 = \text{alcaline}$ ) with  $\text{LiSiON}$  type structure.

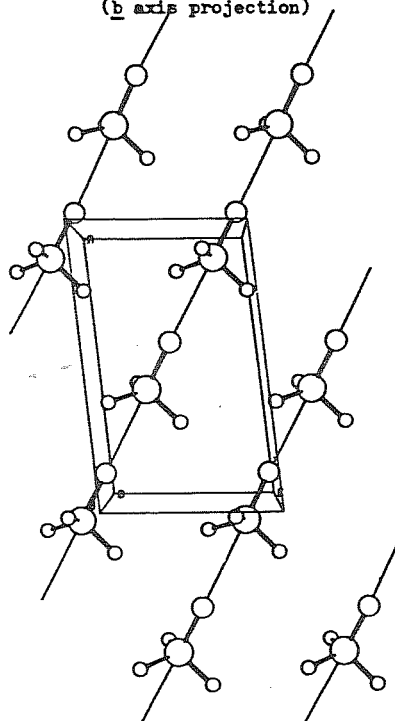
We have, for the first time, established the existence of  $\text{SiO}_2\text{N}_2$  tetrahedra in the pyrosilicate group  $\text{Si}_2\text{O}_7\text{N}_4$  during the structural study of the melilite compound  $\text{Ln}_2\text{Si}_3\text{O}_7\text{N}_4$ . The third silicon atom presents a  $\text{SiN}_4$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

When calcium is substituted by lanthanide in  $\text{CaSiO}_3$ ,  $\text{LnSiO}_3\text{N}$  compounds are obtained. The cyclic  $\text{Si}_3\text{O}_9$  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  $\text{SiO}_3\text{N}$  tetrahedra can be observed.

So, as the  $\text{SiO}_4$ ,  $\text{SiN}_4$  and  $\text{SiON}_3$  tetrahedra were already well known, we have pointed out for the first time the evidence of the  $\text{SiO}_2\text{N}_2$  and  $\text{SiO}_3\text{N}$  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.