08.2-34 THE STRUCTURE AND HIGH RESOLUTION ELECTRON MICROSCOPY STUDY OF SnSb$_2$S$_4$. By John B. Parise and Pierre 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 SnSb$_2$S$_4$, previously reported as SnSb$_2$S$_4$ (Wang and Eppelheimer, Chem. Erde (1975) 348, 201), crystallises in the monoclinic space group C2/m with a = 44.955(3), b = 9.0223(5), c = 20.613(3) Å, β = 96.21(1)°, V = 3598.1(5) Å$^3$ and 2 = 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 [M$_4$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 noncapped trigonal prisms. The coordination of M(14), at the middle of an [M$_4$S$_6$]$_n$ band and facing the leading edge of a SnSb$_2$S$_4$ tetrahedron, is a bicapped trigonal prism. Typically M-S distances in the prisms are distributed as follows: 1 = 2.53 Å, 2 = 2.65 Å, 2 = 3.03 Å with M(14) (2 = 2.71 Å, 1 = 2.79 Å and 1 = 3.16 Å) again being the exception.

08.2-35 A MOLYBDENUM (IV) PHOSPHATE WITH A TUNNEL STRUCTURE TlMo$_6$P$_2$O$_{12}$. By A. Leclaire, J.C. Monier and B. Raveau, Laboratoire de Cristallographie, Chimie et Physique des Solides, L.A. 251, INSA-Université de Caen, 14032 Caen Cedex, France.

During the investigation of the systems A-P-MoO$_3$ (A = K, Rb, Tl), a new molybdenum phosphate TlMo$_6$P$_2$O$_{12}$ was isolated, besides the molybdanyl phosphate KMo$_6$P$_2$O$_{12}$ (Leclaire et al., J. Solidal State Chem. (1983) 48, 147). This compound crystallises in an orthorhombic cell of space group Pbcm with a = 8.8364(6), b = 9.2533(7) and c = 12.2890(11) Å. Its structure was refined to R = 0.053 and R$_p$ = 0.062 (w = f(sin θ/λ)). The Mo$_6$O$_{12}$ octahedra and 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 1.435(11) Å to 1.618(8) Å. The framework Mo$_6$P$_2$O$_{12}$ can be described as two corner-sharing PO$_4$ tetrahedra and Mo$_6$O$_{12}$ octahedra. Three structural units are observed: PO$_4$ tetrahedra, diphosphate groups P$_2$O$_7$, and two-corner-sharing octahedra Mo$_6$O$_{12}$. This framework delimits large tunnels where the Tl$^+$ ions are located. The Tl$^+$ ions are off-centered in the tunnels, this is to be compared to the displacement of K$^+$ in the oxide KMo$_6$P$_2$O$_{12}$. However the Tl$^+$ ions are close to the walls of the tunnels: every ion forms three bonds with the oxygen atoms, ranging from 2.020(17) Å to 2.840(12) Å. It differs also from KMo$_6$P$_2$O$_{12}$ by the fact that all the oxygen atoms of the Mo$_6$O$_{12}$ octahedra are not isolated but form Mo$_6$O$_{12}$ units. The potassium and rubidium oxides have also been synthesized: they are isocrystallographic.


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 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
--- | --- | --- | ---
Ln$_2$Si$_2$O$_2$N$_4$ | melilite | Tetragonal | P 4 2 1 m
Ln$_2$SiO$_4$N | wollastonite | monoclinic | C 2/c
Ln$_2$Si$_2$O$_2$N$_2$ | cuspidine | monoclinic | P 2 1/c
Ln$_4$Si$_3$O$_6$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 SiO$_4$ tetrahedra are well known in silica and silicate compounds and the SiN$_4$ tetrahedra in the Si$_3$N$_4$ nitride and in the ternary silicon nitrides. The mixed SiN$_x$O$_{1-x}$ tetrahedra exist in the Si$_3$N$_4$ nitride and in the A$_2$Si$_x$ON compounds (A = alkaline) with LISION type structure.