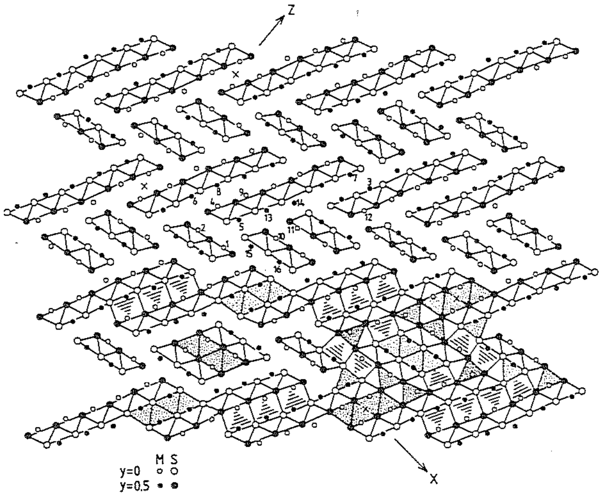
08.2–34 THE STRUCTURE AND HIGH RESOLUTION ELECTRON MICROSCOPE STUDY OF $Sn_6Sb_{10}S_{21}$. By John B. Parise and Piers P.K. Smith, Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, Australia.

The tin antimony sulphide $Sn_6Sb_{10}S_{21}$, previously reported as $SnSb_2S_4$ (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, β = 96.21(1)°, V = 3598.1(5) $Å^3$ 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 $(M_4S_6)_n$. 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 $(M_{10}S_{12})_n$ band and facing the leading edge of a $(M_4S_6)_n$ band, 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.



Projection of the structure of $Sn_6Sb_{10}S_{21}$ on (010)

08.2–35 A MOLYBDENUM (IV) PHOSPHATE WITH A TUNNEL STRUCTURE $TlMo_2P_3O_{12}$. 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-P-Mo-O (A = K, Rb, Tl), a new molybdenum phosphate $TlMo_2^{IV}P_3O_{12}$ was isolated, besides the molybdenyl phosphate $KMo_2^{V}P_3O_{13}$ (Leclaire et al., J. Solid State Chem. (1983) 48, 147). This compound crystallizes in an orthorhombic cell of space group 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 θ/λ)). The MoO_6 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 1.485(11) Å to 1.618(8) Å. The framework $Mo_2P_3O_{13}$ can be described as built up from corner-sharing PO_4 tetrahedra and MoO_6 octahedra. Three structural units are observed : PO_4 tetrahedra, diphosphate groups P_2O_7, and two-corner sharing octahedra Mo_2O_{11} units. 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 $KMo_2P_3O_{13}$. However the 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 $KMo_2P_3O_{13}$ by the fact that all the oxygen atoms of the MoO_6 octahedra are not isolated but form Mo_2O_{11} units. The potassium and rubidium oxides have also been synthesized : they are isostructural.

08.2–36 NEW TETRAHEDRA IN SILICON OXYNITRIDE COMPOUNDS : SiO_2N_2 AND SiO_3N. By G. Roult+, P. Bacher+, C. Liébaut+, R. Marchand++, P. Goursat+++, Y. Laurent++.
+ 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 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 differenciate clearly between oxygen and nitrogen atoms. The obtained compounds are :

Formula	Structure type	Lattice symmetry	Space group
$Ln_2Si_3O_3N_4$	melilite	Tetragonal	$P\bar{4}2_1m$
$LnSiO_2N$	wollastonite	monoclinic	C 2/c
$Ln_4Si_2O_7N_2$	cuspidine	monoclinic	$P2_1/c$
$Ln_{10}Si_6O_{24}N_2$	apatite	hexagonal	$P6_3$

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_3N_4 nitride and in the ternary silicon nitrides. The mixed SiN_3O tetrahedron exists in the Si_2N_2O oxynitride and in the A^ISiON compounds (A^I = alcaline) with LiSiON type structure.