

08.2-31 SYSTEMATIC STRUCTURE INVESTIGATION OF THE THIO-, SELENO- AND TELLUROHALOGENIDES OF As, Sb AND Bi. By G. Voutsas, A. Papazoglou, A. Stergiou and P. Rentzeperis, Applied Physics Laboratory, Aristotle University of Thessaloniki, Thessaloniki, Greece.

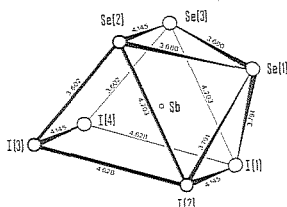
Several  $A_m^V B_m^{VI} C_p^{VII}$  compounds, with  $A=As, Sb, Bi$  -  $B=S, Se, Te$  and  $C=Cl, Br, I$ , show interesting physical properties, whose theoretical explanation necessitates an accurate structure determination. Single crystals were obtained from the gaseous phase in evacuated quartz tubes or hydrothermally under high pressure. The prepared Sb and Bi compounds are of the form ABC, whereas from As only the compound  $As_5Te_7I$  could be prepared so far. Cell dimensions and intensities were measured on an automatic Philips diffractometer. Most of the Sb and Bi thio- and selenohalogenides crystallize with the space group Pnmm, whereas the tellurohalogenides belong to different space groups, e.g. C2/m for SbTeI and  $As_5Te_7I$ . Representative cell dimensions are:

SbSeI :  $a = 8.6862, b = 10.3927, c = 4.1452$  Å

SbTeI :  $a = 13.7008, b = 4.2418, c = 9.2005$  Å,  $\beta = 128.631^\circ$

$As_5Te_7I$  :  $a = 14.560, b = 4.0354, c = 13.865$  Å,  $\beta = 110.564^\circ$

In all the investigated Sb and Bi compounds these atoms are seven-coordinated by four halogen and three S, Se or Te atoms in the form shown in the figure for SbSeI. The



further linkage of these composite polyhedra has led so far to two related but distinct structure types, represented by SbSeI and SbTeI respectively. In SbSeI the composite polyhedron (prism+pyramid) is linked to a symmetry-equivalent one by a common Se, Se edge of their pyramids. This double-polyhedron system is repeated along the c axis, forming an infinite double chain  $\{Sb_2Se_4I_2\}_n$  which is further linked to each of four similar chains by a common  $(I, I)_n$  row parallel to c.

In SbTeI the composite polyhedron is linked to a symmetry-equivalent one by the four I atoms. Thus, the two prisms of the individual polyhedron have a common face and actually form a single prism with a  $Te_2I_2$  parallelogram base. This double-polyhedron unit is linked to adjacent translation equivalent units along the b axis by common  $Te_2I_2$  prism bases, forming infinite  $\{Sb_2Te_4I_4\}_n$  chains. These chains are further linked to adjacent parallel chains by Te atoms to form plate-like blocks along the c-axis, which are held together by weak Te, I bonds.

The structure of  $As_5Te_7I$  constitutes a new third type. Three of the five As atoms are octahedrally coordinated by six statistically distributed (Te, I) atoms, whereas the other two are surrounded by a composite polyhedron of Te atoms, similar to the one described previously. One  $As(Te_5I)_6$  octahedron is linked to two neighbouring octahedra on either side by a common (Te, I), (Te, I) edge and they in turn are linked each to a composite  $As_5Te_7$  polyhedron. The block is repeated along the b axis forming infinite bands, which are held together by weak As, Te bonds.

The proposed structures explain very well the needle-like growth and brittleness of the crystals and also their soft-mode Raman and infrared spectra.

08.2-32 COMPARATIVE STUDIES ON  $Ag_2O_nX$  ( $X = NO_3^-, F^-, SO_4^{2-}, BF_4^-, ClO_4^-$ ). By B. Standke and M. Jansen, Inst. f. Anorg. Chem., Univ. Hannover, FRG.

It may seem strange that only a few silver oxides with silver in a higher oxidation state than  $1^+$  are known. Examples are  $AgO$  (which is only preparable in the form of a powder, and thus of unsure structure due to missing single crystal x-ray data), and the series of compounds  $Ag_2O_nX$  ( $X = NO_3^-, F^-, SO_4^{2-}, BF_4^-,$  and  $ClO_4^-$ ) (I. Náráy-Szabó and K. Pöpp, Z. anorg. allg. Chem. (1963) 322, 286/96; A.C. Gossard, D.K. Hindermann, M.B. Robin, N.A. Kuebler and T.H. Geballe, J. Am. Chem. Soc. (1967) 89, 7121/3). The latter compounds show unusual structural properties: di- and trivalent silver atoms occupy one crystallographic site. Obviously a non integral oxidation state is realized. Furthermore the present  $Ag^+$  ions exhibit an unusual coordination of 8 against oxygen. All the  $Ag_2O_nX$  compounds have the same  $Ag/O$  structure containing complex anions in cage-like voids (I. Náráy-Szabó, G. Argay and P. Szabó, Acta Crystallogr. (1965) 19, 180), the site symmetry differing from the point symmetries of the anions. This causes disorder of the X anions. All structure determinations performed so far are unsure with respect to this part of the structure (C.H. Wong, T.H. Lu, C.N. Chen and T.I. Lee, J. inorg. nucl. chem. (1972) 34, 3257/9). As the occupation of this site influences the formal charge of the  $Ag_2O_n$  part of the structure, it was deemed necessary to undertake further investigations. The compounds were prepared as single crystals by anodic oxidation of the respective aqueous silver salt solutions at high current densities. It was thus possible to observe the oxidation product of an  $AgPF_6$  solution for the first time. The average structures were determined by single-crystal methods, and in order to establish, whether ordered phases exist, the low temperature behavior was investigated by Guinier-techniques.

08.2-33 SINGLE CRYSTAL STRUCTURE DETERMINATION OF  $S_rTe_eO_4$ . STRUCTURE ORGANISATION BY PACKING OF  $TeO_4$  CHAINS HELD TOGETHER BY CATIONS. J. Moret and J. Lapasset Groupe de Dynamique des Phases Condensées (LA 233) Place E. Bataillon, 34060 Montpellier Cedex. F.

The single crystal structure of  $S_rTe_eO_4$  (hydrothermal synthesis 643 K) confirms the powder study of Hottentot and Loopstra (Acta Cryst. (1979) B35, 728) : it has the same space group as  $\beta Na_2TeO_4$ . The atomic positions are identical to those of the powder study for  $S_r$  and  $Te$ . Only more accurate locations for the oxygen atoms are observed. The structure belongs to the  $X_{1/2}TeO_4$  and  $XII TeO_4$  type : these structures contain  $TeO_6$  octahedra which share edge, thus forming infinite  $TeO_4$  chains. Projection of the chains along their axis leads to a rectangular centered lattice; the lozenge shaped channels built by the chain projections contain the cations. Some of these compounds show a structural dimorphism :  $Na_2TeO_4$ , synthesised hydrothermally (603 K, pH = 10), is monoclinic ( $\alpha$  phase) (Daniel, Moret, Philippot, Maurin J. Solid State Chem. (1977) 22, 385). When this compound is prepared by thermal decomposition of  $Na_2H_4TeO_6$  (Na  $NO_3$  flux, 573 K), the phase is orthorhombic (Kratochvil, Jensovsky, Acta Cryst. (1977) B33, 2596) ( $\beta$  phase). From the point of view of chain packing these structures are very similar : a longitudinal relative gliding of two groups of two chains (order of magnitude 0.3 Å) leads to the presence of two different types of channels in the  $\alpha$  phase and consequently to different locations for the cations. An irreversible phase transition (953 K) changes the  $\alpha$  phase into the  $\beta$  one. This temperature is very near the temperature of decomposition of the  $\beta$  phase giving  $Na_2TeO_3$ .