08. INORGANIC AND MINERALOGICAL CRYSTALLOGRAPHY


Several $A^mB^nC^i$ compounds, with $A=As, Sb, Bi; B=S, Se, Te$ and $C=CI,Br,I$, 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 $AB_2$, whereas from As only the compound $ASTe_7$ 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 $Pnm$, whereas the tellurohalogenides belong to different space groups, e.g. $C2/m$ for $SbTeI$ and $AAsTe_7I$.

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, $\alpha=88.56^\circ$

$AAsTe_7I$ : $a=14.56$, $b=4.0354$, $c=13.85$, $\alpha=110.56^\circ$

In all the investigated Sb and Bi compounds these atoms are seven-coordinated, whereas As 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 $(Sb,Se)_n$ 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 $Te_1$ parallelogram base. This double-polyhedron unit is linked to adjacent translation units along the $b$ axis by common $Te_1$ prism bases, forming infinite $(Sb,Te_1)_n$ 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-Te bonds. The structure of $AAsTe_7I$ constitutes a new third type. Three of the five As atoms are octahedrally coordinated by six statistically distributed $(TeI)_n$ atoms, whereas the other two are surrounded by a composite polyhedron of Te atoms, similar to the one described previously. One $AsTe_1I$ octahedron is linked to two neighbouring octahedra on either side by a common $(Te_1,I)_n$ edge and they in turn are linked each to a composite $ASTe_7$ 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 $Ag_2O_3X\cdot X=N_2^-, F^-$, $SO_4^2$-, $BF_4^-$, $ClO_4^-$. By H. Stanek 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 three of unsure structure due to missing single crystal x-ray data. The series of compounds $Ag_2O_3X$ ($X=N_2^-, F^-, SO_4^2-, BF_4^-$ and $ClO_4^-$) has been studied by us [J. Chem. Phys. (1963) 322, 286/96; A.C. Gossard, D.K. Hinderer, M.B. Robins, W.A. Roubel 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 $Ag_2O_3X$ compounds have the same $AgO$ structure containing complex anions in cage-like voids (I. Náray-Szabó, G. Avgary and P. Szabó, Acta Crystallogr. (1965) 19, 180), the site structure of origin from the point symmetries of the anions. This causes disorder of the $X$ anions. All structure determinations performed so far are unsatisfactory with respect to this part of the structure (C.H. Woot, K. Wüth, E. Heuer, A. Ch. Thiele, Z. Kristallogr. (1966) 122, 1/3). The occupation 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 $(Sb,Se)_n$ 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 $Te_1$ parallelogram base. This double-polyhedron unit is linked to adjacent translation units along the $b$ axis by common $Te_1$ prism bases, forming infinite $(Sb,Te_1)_n$ 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-Te bonds.

The structure of $AAsTe_7I$ constitutes a new third type. Three of the five As atoms are octahedrally coordinated by six statistically distributed $(TeI)_n$ atoms, whereas the other two are surrounded by a composite polyhedron of Te atoms, similar to the one described previously. One $AsTe_1I$ octahedron is linked to two neighbouring octahedra on either side by a common $(Te_1,I)_n$ edge and they in turn are linked each to a composite $ASTe_7$ 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.