8. INORGANIC AND MINERALOGICAL CRYSTALLOGRAPHY


Several \( A^\beta B^\gamma C^\delta \) compounds, with \( A = \text{As, Sb, Bi} \) and \( C = \text{Cl, Br, I} \), 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 \( \text{AsTe}_7 \) and \( \text{SeTe}_7 \) are seven-coordinated by four halogen and three Te atoms, similar to the one described previously. The preparation of \( \text{AsTe}_7 \) and \( \text{AsSeTe}_7 \) has been reported previously.

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

8.2–32 COMPARATIVE STUDIES ON \( \text{Ag}_2\text{O}_{6}X \) = \( \text{NO}_2 \), \( \text{F}^+ \), \( \text{SO}_4^{2-} \), \( \text{BF}_4^{-} \), \( \text{ClO}_4^{-} \). By H. Stannett 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 \( \text{AgO} \) which is only preparable in the form of a powder, and thus of unsure structure due to missing single crystal x-ray data. The series of compounds \( \text{Ag}_2\text{O}_x \text{X} = \text{NO}_2 \), \( \text{F}^+ \), \( \text{SO}_4^{2-} \), \( \text{BF}_4^{-} \), and \( \text{ClO}_4^{-} \) (I. Náray-Szabó and K. Pópp, Z. Anorg. Allg. Chem. (1963) 222, 186/95; A.C. Gossard, D.K. Hinde, M.B. Robins, W.A. Roesler and T.H. Geballe, J. Am. Chem. Soc. (1967) 89, 7121/3). The latter compounds show unusual structural properties; div- 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 oxygen against all the \( \text{Ag}_2\text{O}_x \text{X} \) compounds have the same \( \text{AgO} \) structure containing complex anions in cage-like voids (I. Náray-Szabó, G. Angy and P. Szabó, Acta Crystallogr. (1965) 19, 180), the site structure of Ag 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 (D. Moret, E. Daniel, P. Philippot, Ch. Maurin, C. Daniel, Moret, Philippot, Maurin J. Solid State Chem. (1997) 22, 385). When this compound is prepared by thermal decomposition of \( \text{Ag}_2\text{TeO}_4 \) (M. H. Tuan, 573 K), the phase is orthorhombic (Kratzschvihl, Jensovsky, Acta Crystallogr. (1977) B33, 2596) \( \beta \) phase. From the point of view of chain packing these structures are very similar: a longitudinal translational sliding of two groups of two chains of magnitude 0.3 Å leads to the presence of two different types of channels in the \( \beta \) phase and consequently to different locations for the cations. An irreversible phase transition (953 K) changes the \( \beta \) phase into the \( \alpha \) one. This temperature is very near the temperature of decomposition of the \( \beta \) phase giving \( \text{Ag}_2\text{TeO}_4 \).