

substance: tungsten oxides

property: general characterization

The W-O phase diagram is complex (Fig. 1) with a number of oxides in the range $\text{WO}_2 - \text{WO}_3$. The phase WO_2 has a narrow stoichiometry range. The neighbouring phase $\text{W}_{18}\text{O}_{49}$ ($\text{WO}_{2.72}$) also has an apparently very small homogeneity range [69M, 76P]. The structure of $\text{W}_{18}\text{O}_{49}$ is not related to the homologous shear-plane structures, but is a compromise between the WO_2 and WO_3 structures [50M].

Homologous series of the general formula $\text{W}_n\text{O}_{3n-(m-1)}$ are derived from the ReO_3 structure by shearing along the $\{10m\}$ planes (Fig. 2). The series with $m = 2$ has been explored by electron microscopy [74B, 74S]. It has not proved possible, however, to isolate any pure $\text{W}_n\text{O}_{3n-1}$ phase. Weak reduction gives both $m = 2$ and $m = 3$ series and heavier reduction favours the latter. Sintering weakly reduced WO_3 at 1273 K gives $\text{W}_{30}\text{O}_{89}$ ($\text{WO}_{2.966}$) and $\text{W}_{26}\text{O}_{76}$ ($\text{WO}_{2.923}$) and values of n as low as 14 ($\text{W}_{14}\text{O}_{41}$, $\text{WO}_{2.929}$) have been observed. The series $m = 3$ is better characterized; $\text{W}_{20}\text{O}_{58}$ and $\text{W}_{25}\text{O}_{73}$ are well known, though values of n from 12 to 28 have been found [69A].

The end-member of the homologous series, WO_3 , has a very small homogeneity range. Pure WO_3 can only be made under high oxygen pressures [77G]. As usually prepared, WO_3 is slightly oxygen deficient, though true point defects appear only to be found for $x \leq 10^{-4}$ in WO_{3-x} [70S]. For values of $x > 10^{-4}$ condensation of these point defects to form shear planes is found [76T].

References:

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Fig. 1.

WO_x . Pressure-composition diagram at 1450 K. Inset shows incongruent evaporation of WO_{3-x} above 1550 K [63A].

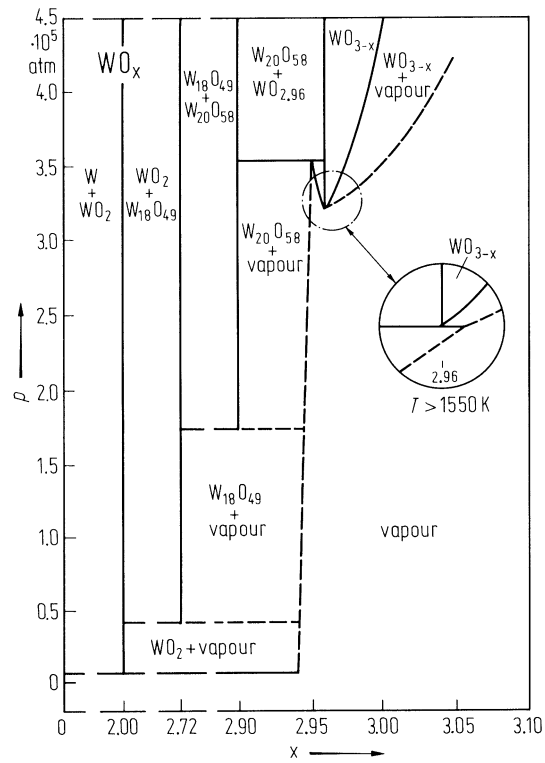


Fig. 2.

WO₃. Idealized projection of the structures of (a) {102} CS planes, (b) {103} CS planes and (c) a {101} shear plane in an idealized matrix [77I].

