

substance: chalcogenides of Ti, Zr, Hf

property: crystal structure, chemical bond, general characterization

Review papers on binary transition metal chalcogenides: [65H, 69W, 72J, 75W, 76R, 76W, 82G].

With the possible exception of Zr_2S_3 , Hf_2S_3 , and Hf_2Se_3 , all the semiconducting chalcogenide phases with M_{IV} cations formally contain these cations in their quadrivalent state. The several phases in the Ti – S system are shown in Fig. 1.

The stoichiometric compounds $\text{M}_{\text{IV}}\text{S}_2$ and $\text{M}_{\text{IV}}\text{Se}_2$ crystallize in the C6 layer structure of CdI_2 . The conduction bands are primarily cation-d bands, the valence bands anion- p^6 . The energy gap in TiS_2 is significantly smaller than those of ZrS_2 and HfS_2 ; in semimetallic TiSe_2 the gap has just vanished, and in metallic TiTe_2 the two bands overlap significantly. Stoichiometric TiS_2 has not been prepared; all samples are titanium-rich n-type $\text{Ti}_{1+x}\text{S}_2$, some interstitial titanium occupying the octahedral sites between TiS_2 layers. The lattice parameters increase linearly with x. The anomalous transport data of $\text{Ti}_{1+x}\text{Se}_2$ in the interval $100 \text{ K} < T < 200 \text{ K}$ and the change from n-type to p-type conductivity reflect a second-order phase transition at $T_{\text{tr}} \approx 200 \text{ K}$ and the semimetallic character of the compound. Holes in the Se:4p^6 valence bands are more mobile than electrons in the Ti:3d conduction bands. ZrS_2 exhibits a pronounced decrease in conductivity with increasing temperature in the interval $250 \text{ K} < T < 500 \text{ K}$ where the donor centers for extrinsic conduction are exhausted and intrinsic conduction is not significant.

The compounds $\text{M}_{\text{IV}}\text{S}_3$ crystallize in the ZrSe_3 structure. It contains linear chains of edge-shared trigonal prismatic sites held together by van der Waals forces. Each shaded triangle has a dimeric-anion base and a monomeric-anion apex to give a formal valence $\text{Zr}^{4+}\text{Se}^{2-}(\text{Se}_2)^{2-}$, and the empty antibonding orbitals of the $(\text{Se}_2)^{2-}$ unit have energies well above the bottom of the Zr:4d conduction band. Very little work has been done on the compounds Zr_2S_3 , Hf_2S_3 , and Hf_2Se_3 . If these compounds are semiconductors, as suggested, then we must anticipate the formation of dimeric cations capturing two electrons per dimer in a metal-metal bond having an energy near the top of the anion- p^6 valence band. Such cationic dimeric units are found in Mo_2S_3 [61J]. However, these compounds may prove to be metallic and without cationic dimerization.

References:

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Fig. 1.

Ti – S. Schematic pressure – composition diagram of the Ti – S system [67G]. y: atomic ratio S/Ti.

