The Preparation of Novel Metal-Rich Transition-Metal Sulfides and Selenides by High-Temperature Techniques*,†

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The techniques used for the preparation of metal-rich chalcides by high-temperature techniques are discussed. The two newest metal-rich compounds, two ternary metal-rich sulfides with novel structures, are described. © 1986 Academic Press, Inc.

Introduction

The preparation of new binary metal-rich sulfides and selenides with novel structures and stoichiometrics (Table I) has been accomplished by taking samples initially prepared at about 725 K in evacuated, sealed fused silica tubes to temperatures in excess of 1700 K. High-temperature techniques may yield new materials for two basic reasons. One is thermodynamic: the solid in question may form endothermically and endoentropically from neighboring phases and thus form spontaneously only when $T > \Delta H°/\Delta S°$. The other is kinetic: diffusion of

either transition metal or nonmetal in the compounds has activation energies for diffusion which fall roughly in the range of 70 to 140 kJ mole^{-1}, and thus the formation process is approximately 200 to 50,000 times faster at 1500 K than it is at 1000 K.

Experimental Technique

The technique used to achieve the high-temperature environment has generally been induction heating of a tungsten Knudsen cell under a high-vacuum (Fig. 1). This technique has two advantages that derive from the use of an open system. One advantage is that the stoichiometry of the solids can be varied and controlled. For example, in the Ta–S system, Ta_2S can be prepared by controlled decomposition of TaS_{2-x}:

$$2\ TaS_{2-x}(s) = Ta_2S(s) + (3 - 2x)\ S(g) \quad (1)$$
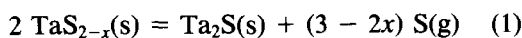
and Ta_6S can be prepared by controlled decomposition of $Ta_2S(s)$:

$$3\ Ta_2S(s) = Ta_6S(s) + 2\ S(s). \quad (2)$$
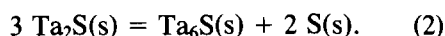
By quantitative study of the decomposition

TABLE I[a]

NEW BINARY METAL-RICH
SULFIDES AND SELENIDES

Ti_8S_3	α-V_3S
Ti_2S, Ti_2Se	β-V_3S
Zr_9S_2	$Nb_{14}S_5$
Zr_2S, Zr_2Se	$Nb_{21}S_8$
	Nb_2Se
Hf_2S	Ta_6S
	Ta_2S

[a] Ref. (5).

reactions it has been determined (1) that P_S over reaction (2) is, for example, 5.6×10^{-7} atm at 1750 K. This pressure provides a slow but useable loss of sulfur from a typical Knudsen cell.

The second advantage derives from the fact that the large dissociation energies of typical transition-metal oxides (e.g., 168 kJ/ mole for TiO (2)) result in large values of equilibrium constants for reactions such as the following example appropriate to TiS(s) preparation

Ti (in TiS) + O (impurity in TIS) = TiO(g)

for which the equilibrium constant is $K = P_{TiO}/X_{TiO}$. This is an example of the general phenomenon of "suboxide vaporization" that has been discussed previously (3) and is known in some cases such as TiS vaporization (4) to lead to substantial reduction of oxygen impurities during high-temperature sample preparation.

The use of tungsten as a container material has, in the case of sulfide preparation, the advantage that there are no stable sulfides of tungsten, either solid or gaseous, at temperatures above 1000 K under high vacuum. The most serious problems in the synthesis of transition-metal sulfides in a tungsten container is the solution of transition metals, such as Ti, V, etc., into the solid crucible. This is a relatively slow process, but nonetheless one that must be guarded

against in order to achieve precise stoichiometry.

The techniques of high-temperature chemistry, including both the Knudsen effusion and the arc-melting technique have been used in a series of studies investigating the synthesis of the binary metal-rich sulfides (and a few selenides) of the group III, IV, and V transition metals (Table I). The structures of these chalcides and those of a number of related metal-rich solids (phosphides, nitrides, carbides, oxides) are discussed in a 1978 review (5). Since that review appeared two new types of metal-rich compounds have been prepared. These compounds were all prepared by arc-melting pellets of Ta_2S and the appropriate transition-metal or by heating at about 1700°C for 10–20 hr in a tungsten container under a high vacuum.

Results

The structure type $(Ta_{6-x}M_x)S$ can be viewed as a substitutional solid solution of early 3d transition metal in Ta_6S. This
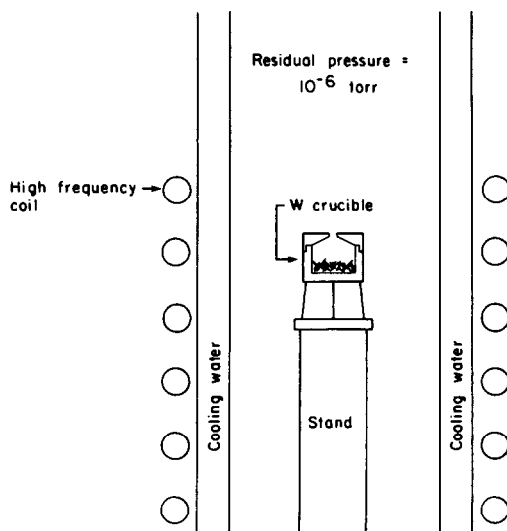

FIG. 1. Experimental apparatus for high-temperature synthesis of refractory solids in an inductively heated Knudsen cell.

structure type exhibits space group $C2/c$ with $a \cong 755$ pm, $b \cong 1290$ pm, $c \cong 507$ pm, and $\beta \cong 111.5°$. The structure type is known for M = V and Cr with on the order of 20% of the tantalum substituted by Cr or V. The structure of $Ta_{6-x}M_xS$ is similar to that of Ta_6S (Fig. 2), consisting of a close packing of metal columns made up of interpenetrating icosahedra and sulfur in some of the resulting interstices. In the case of $Ta_{4.74}V_{1.26}S$ the central tantalum atoms are about 60% substituted and the four shaded tantalum atoms in Fig. 2 are about 30% substituted and the remaining tantalum atom positions are unsubstituted. A major difference between Ta_6S and $Ta_{6-x}M_xS$ is in the relative vertical positioning of the column clusters, and a resultant difference in the sulfur coordination. In Ta_6S the sulfur is seven-coordinate in a monocapped trigonal prism, while the sulfur in $Ta_{6-x}M_xS$ is eight-coordinate (four fully occupied Ta positions and four partially occupied (30%) Ta positions).
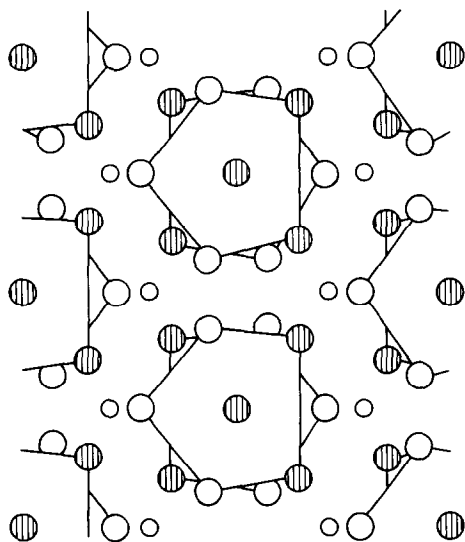

FIG. 3. View down the columns of tricapped trigonal prismatic M atoms in $M_2Ta_9S_6$ (M = Fe, Co, and Ni) and $Fe_2Nb_9S_6$. Shaded circles indicate atom positions at z = 0, unshaded circles indicate atom positions at z = 1/2.

The second of these ($M_2Ta_9S_6$ (6)) with M = Fe, Co, and Ni and $Fe_2Nb_9S_6$) occurs as a hexagonal network of MTa_9 tricapped trigonal prisms sharing capping atoms (Fig. 3) with sulfur on the exterior of the network and surrounding a large channel. The space group is $P\bar{6}2m$ with $a \cong 1030$ pm and $c \cong 329$ pm.

Discussion

The importance of these ternary compounds is that their existence extends to substitutional alloys and intermetallics the concept of metal modification through metal-rich compound formation. The metal-rich binary sulfides (Table I) provide a variety of metal–metal bonded structures which can be thought of as modified metals, i.e., metals modified structurally and electronically by interaction with a minority quantity of sulfur. $Ta_{6-x}M_xS$ and $M_2Ta_9S_6$ extend our knowledge of such materials to alloys and intermetallics.

The most important feature of the new

FIG. 2. View down the intermetallic columns of icosahedral coordinated metal atoms in $Ta_{6-x}M_xS$ (M = V, Cr). Shaded circles indicate positions that are jointly occupied by Ta and $3d$ element.
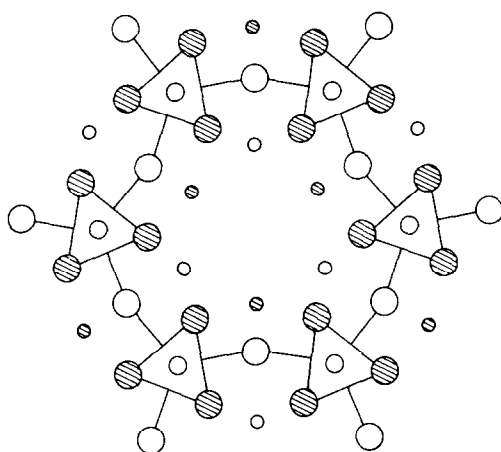
ternary compounds is their extensive metal–metal bonding. For example, the 12 metal atoms (six Ta only and six a distribution of Ta and M) surrounding the central metal in a distorted isocahedron in $Ta_{6-x}M_xS$ are at distances between 253 and 296 pm indicating substantial intermetallic bonding. In the $M_2Ta_9S_6$ compounds, $Ni_2Ta_9S_6$, for example, the Ni atom is in a tricapped trigonal prism, with six Ta neighbors at 249.5 pm forming a trigonal prism and three Ta capping atoms at 296.1 pm.

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