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THE CRUCIAL ROLE OF HALOGEN ATOMS IN THE FORMATION OF Ta_2S_2C*

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Summary

The successful preparation of Ta_2S_2C at 1150 °C has been found to be intimately linked to the presence of halogens in the reaction. Adventitious chlorine obtained either through the use of excess carbon or of graphite crucibles was apparently responsible for previously successful reactions. The purposeful introduction of catalytic amounts (0.01 wt.%) of C_6Cl_6, C_6Br_6 or I_2 into reactions containing stoichiometric amounts of tantalum, carbon and sulfur produces quantitative yields of Ta_2S_2C as measured by X-ray diffraction. Resistivity measurements made on a sintered pellet show Ta_2S_2C to be metallic between 300 and 4 K with a room temperature resistivity of approximately $2.2 \times 10^{-3}\ \Omega$ cm.

1. Introduction

The recent success observed in preparing zirconium, scandium and rare earth halide clusters by the inclusion of an interstitial atom in the cluster center [1 - 6] lead us to explore the possibility of applying this concept to the preparation of so far unreported niobium and tantalum chalcogenide clusters. As kinetic difficulties were initially encountered with reactions from mixtures of the elements or binary compounds even at temperatures as high as 1200 °C, an effort was made to locate ternary compounds in which the metal, chalcogen and interstitial atoms were all contained to use as starting materials. Ta_2S_2C appeared to be an ideal candidate [7]. Structurally, Ta_2S_2C is a layered material composed of tightly bound two-dimensional slabs containing five close-packed layers sequenced S–Ta–C–Ta–S. These slabs are in turn held together by relatively weak van der Waals interactions which give Ta_2S_2C a graphitic character. From an alternate point of view, namely as a precursor material, the structure can be viewed as a two-dimensional condensation of carbon-centered Ta_6S_{12} cluster units.

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*Dedicated to Professor LeRoy Eyring on the occasion of his 70th birthday.

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Ta_2S_2C was initially reported [7] as a product of the reaction of a 1:1:1 mixture of tantalum, sulfur and carbon at 1200 °C. Later reports in the literature [8] indicated that the compound could be prepared in pure form by the reaction of stoichiometric amounts of tantalum, sulfur and carbon in a graphite crucible (in an evacuated silica jacket) at 1200 °C. Our initial reactions utilizing stoichiometric quantities of reactants in evacuated silica tubes at 1180 °C failed to yield even traces of Ta_2S_2C by X-ray powder diffraction; only binary tantalum sulfides and carbon were observed. Subsequent reactions run under identical conditions but using a graphite crucible to hold the reactants in the sealed silica tube produced Ta_2S_2C in an essentially quantitative yield. The role of the graphite crucible and the subsequent discovery of the importance of halogen atoms in the preparation of Ta_2S_2C are the subjects of this paper.

2. Experimental details

All reactions were carried out in evacuated silica tubing using stoichiometric amounts of tantalum powder (Wah Chang Albany; purity, 99.9%), sulfur powder (Atomergic Chemicals Corporation; purity, 99.9999%) and spectroscopic grade carbon powder (National Carbon Co., Division of Union Carbide). Graphite crucibles were obtained from Ultra Carbon Corporation. Trace amounts of halogens were introduced into the reactions through the use of C_6Cl_6, C_6Br_6 (Aldrich; purities, 97% and 98% respectively) or I_2 (Fisher; purity, 99.99%). Reactions which were heated to temperatures greater than 1150 °C were "double sealed" in evacuated silica tubes, *i.e.* the silica reaction tube was itself sealed within an evacuated silica jacket. "Double sealing" reduced the devitrification of the inner reaction tube and the subsequent potential for fracture on cooling.

All products were opened in air and characterized by X-ray powder diffraction. Conductivity measurements were made using a standard four-probe technique on pressed pellets that had been sintered at 1180 °C for 24 h.

3. Results and discussion

The apparent importance of the graphite crucible in the formation of Ta_2S_2C leads us to study the reaction in greater detail with the anticipation that a better understanding of the reaction might lead not only to a better preparatory method for Ta_2S_2C but also to potential methods for the preparation of heteroatom-centered niobium and tantalum clusters. A variety of functions that the graphite crucible could potentially assume in the formation of Ta_2S_2C were considered. The most obvious ones, a need for excess graphite or a layered substrate for nucleation purposes, were eliminated by reactions utilizing up to a twofold excess of carbon powder or contained within a layered BN crucible. A clue indicating the importance of a gaseous carbon-containing species became apparent from reactions in which the graphite crucible was used as the sole source of carbon.

Pre-reacted equal molar mixtures of tantalum and sulfur placed in a $\frac{1}{2}$ in diameter graphite crucible were converted quantitatively to Ta_2S_2C in 5 - 7 days at 1180 °C. In fact, Ta_2S_2C was formed even when the TaS mixture was not in physical contact with the crucible. Although CO, potentially formed by the reaction of the carbon crucible with the SiO_2 reaction tube at 1180 °C, or hydrocarbons evolved from the crucible on heating seemed likely gas phase species, purposeful addition of these species to reactions without graphite crucibles failed to facilitate the formation of Ta_2S_2C. Carbon disulfide or other carbon subsulfides also appear to be unlikely since their formation should occur just as readily from a powdered mixture of tantalum, sulfur and carbon as from the reaction of S_x with a graphite crucible wall.

Two additional clues helped to unravel the role of the graphite crucible. Close examination of a number of the carbon crucibles used in Ta_2S_2C reactions revealed very small crystals of TaS_2 and Ta_2S_2C growing on the outside wall of the crucible. In other words there was movement of not only carbon but also tantalum through the gas phase. Second, the industrial processing of graphite crucibles was examined [9, 10]. Intrinsic to both processes — the transport of tantalum and the purification of graphite — is the presence of chlorine. The chemical transport of TaS_2 by halogens is well known and proceeds according to the reaction [11]

$$2TaS_2(s) + 5X_2(g) \rightleftarrows 2TaX_5(g) + 2S_2(g)$$

Removal of metal impurities from molded graphite pieces through volatilization of metal halides involves a high temperature firing in a chlorine atmosphere. Apparently some chlorine is retained in the graphite after this purification process, most probably not as elemental Cl_2, but as Cl bonded to C at grain boundaries or other defects. Indeed, reactions containing stoichiometric amounts of tantalum, sulfur and carbon and catalytic amounts of C_6Cl_6 (less than 0.1 wt.%) produced excellent yields of Ta_2S_2C in 5 - 7 days at 1180 °C without the use of a graphite crucible. Subsequent reactions have shown that both bromine and iodine will also catalyze the reaction.

Interestingly, even carbon crucibles outgassed under vacuum at high temperatures still retain enough chlorine to prepare Ta_2S_2C. Although the chemical species actually involved in the chemical transport of carbon have not been identified, the role of the halogen does appear to be catalytic. The extremely small amounts of chlorine used, which correspond to less than 1 chlorine atom per 20 carbon atoms, and the observation of small amounts of $TaCl_5$ in the air-quenched product strongly suggest a catalytic role for chlorine rather than incorporation into the compound. Attempts to reduce the reaction temperature to lower than 1100 °C were not successful.

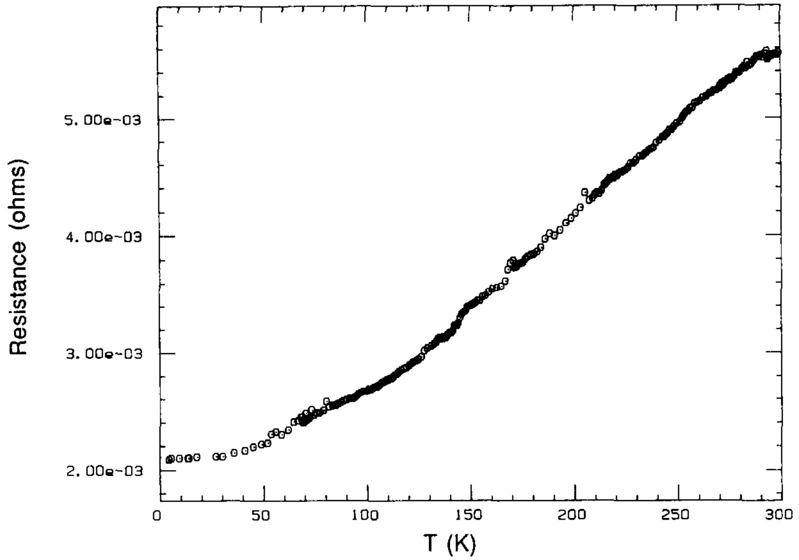

Fig. 1. The resistance of a Ta_2S_2C sintered pellet is plotted as a function of temperature from 300 to 4.2 K. The small fluctuations from a smooth curve are due to system noise.

Electronically, Ta_2S_2C should be metallic with one electron per tantalum occupying the Ta d band. Conductivity measurements were made from 300 to 4.2 K on a pressed-and-sintered pellet. The results illustrated in Fig. 1 clearly show Ta_2S_2C to be metallic with a room temperature resistivity of approximately 2.2×10^{-3} Ω cm. As in other layered compounds the resistivity is expected to be anisotropic. The value reported here is believed to be close to the average resistivity since the pellet is polycrystalline. Many quasi-two-dimensional metals, such as TaS_2, exhibit structural phase transitions driven by charge density wave instabilities [12]. While such transitions usually produce dramatic changes in the electrical properties, no such changes are seen in Ta_2S_2C at temperatures below 300 K.

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