shows that, in the HF–SbF_5 system, the rate of protonation increases more rapidly than linearly with the excess SbF_5. Furthermore, Brouwer and co-workers,[28] on the basis of kinetic measurements and studies of mechanisms of protonation, have proposed an acidity scale in which the HF·SbF_5 solution is more acidic than the 9HF·SbF_5 mixture. These observations are in agreement with our findings since we have shown that addition of SbF_5 leads quickly to the depolymerization of the protonated HF chains and that the most acidic entities $H_3F_2^+$ and H_2F^+ are formed in HF–SbF_5 solutions with concentration above 40 mol % in SbF_5. These ions may therefore play a similar role to that of $H_5O_2^+$ and H_3O^+ species in aqueous acid solutions.

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Registry No. HF, 7664-39-3; SbF_5, 7783-70-2; $H_3F_2^+$, 72258-82-3; $CsSb_2F_{11}$, 23751-61-3; $CsSbF_6$, 16949-12-5.

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Effect of Chalcogen Nonstoichiometry on Superconductivity in Chevrel-Phase Tin Molybdenum Sulfides[1]

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The ternary molybdenum chalcogenides, $M_xMo_6X_8$ (M = Pb, Sn, rare earth elements; X = S, Se), usually called Chevrel phases,[2] are of special interest because of high superconducting critical temperatures,[3] high critical fields,[4] and coexistence of magnetic order and superconductivity.[5] Unfortunately, the materials are almost never prepared pure, and there are numerous discrepancies in the literature arising from failure to control stoichiometry. Not only is the content of ternary element M variable but also the ratio of molybdenum to chalcogen can be made greater than the ideal 6/8 value.

As part of a continuing program to investigate the chemical control of superconductivity, we have recently examined a large body of data on Chevrel phases to discover, if possible, the reason for the wide variability in reported parameters. Even for a single phase, e.g., $PbMo_6S_8$, reported T_c's ranged from 9.8 to 14.7 K. We found that T_c is a very sensitive function of the lattice parameters. Indeed, when the materials were grouped according to the formal charge on the ternary element M, T_c turned out to be a linear function of the hexagonal crystallographic c/a ratio.[6] In this communication, we report the result of a deliberate effort to enhance the superconducting critical temperature of $SnMo_6S_8$ by driving it off stoichiometry and thereby raising its c/a ratio.

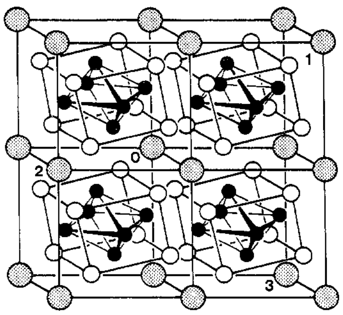

Figure 1. Idealized version of $SnMo_6S_8$ structure: black circles, Mo; white circles, sulfur; shaded circles, Sn.

Experimental Section

Preparation of Samples. Samples of $SnMo_6S_{8-x}$ were prepared by direct synthesis from ultrapure starting elements: Sn (99.999 95%, from Alfa Division, Ventron Corp.), Mo (99.95%, from United Mineral and Chemical Corp.), and S (99.9999%, from Atomergic Chemetals Corp.). The molybdenum powder was treated with hydrogen for 24 h at 1000 °C and stored in a helium Dri-Lab until needed. Amounts of elements appropriate for forming a series of materials with x = 0, 0.5, 1.0, 1.5, and 2.0 were weighed into silica tubes and the tubes degassed to 10^{-6} torr and then sealed. The tubes were wrapped in heavy Kanthal wire and heated together in a box furnace. Furnace temperature was slowly raised to 1000 °C over the course of 7 days, allowing the molybdenum and sulfur to prereact without thermal runaway. After 24 h at 1000 °C, the sample tubes were quenched in air and vigorously shaken to homogenize the sample. They were immediately reheated to 1200 °C, left to react for 24 h, and then air quenched.

Powder X-ray Diffraction. X-ray diffraction photographs were made by using a 114.6-mm diameter Debye–Scherrer camera with nickel-filtered copper Kα radiation. Line positions were measured with a precision better than 0.05 mm. Intensities were estimated visually. Angles and d spacings were calculated by the Straumanis method, correcting for film shrinkage and camera radius uncertainty. Lines were assigned hkl indices with aid of a Fortran program that calculated line positions and intensities from single-crystal data. Because Chevrel-phase X-ray patterns typically show hundreds of lines, many of which are uniformly weak (especially for $\theta_{hkl} > 30°$), an iterative procedure was used. Well-resolved lines in the front reflection region were indexed and used to calculate an initial set of lattice parameters. These new lattice parameters were used to generate line positions for the 120 most intense reflections. Increasing θ_{hkl} were indexed, and the process was repeated until all lines were identified. Final lattice parameters and errors were calculated by using Cohen's least-squares fitting for indexed lines between 30 and 90°.

Superconducting Transition Determination. Onset of superconductivity was measured by Meissner Flux expulsion by using an apparatus described elsewhere.[7] The detection system is a primary coil with two opposed external secondary coils wound symmetrically about it. The sample sits in one of the secondary coils and transition to the superconducting state is seen as a large off-null signal. Temperature was measured with a calibrated germanium resistance thermometer from CryoCal, which was checked against the boiling point of helium and the transition temperatures of lead and niobium. T_c was taken as the temperature at which the inductive transition was half complete. The width of the transition was taken as the difference between the temperature at which the transition was 10% complete and the temperature at which it was 90% complete.

Results and Discussion

The Chevrel phases are usually rhombohedral and crystallize in the space group $R\bar{3}$. As shown in Figure 1, which is an idealized version of $SnMo_6S_8$, the central feature of the structure is the Mo_6S_8 unit, which can be visualized as an octahedron of molybdenum atoms with each triangular face of the octahedron capped by a sulfur atom. The quasi-cubic unit Mo_6S_8 is located in a nearly cubic array of the ternary atoms Sn, except that the Mo_6S_8 unit is rotated ~20° about

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(1) This research was sponsored by the Air Force Office of Scientific Research under Grant No. 74-2583 and was supported in part by the National Science Foundation and the Materials Science Center at Cornell University.

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Table I. Crystal Data for $SnMo_6S_{8-x}$

nominal x	a, Å	c, Å	c/a	impurity
0	9.174 (1)	11.367 (3)	1.2391 (5)	Mo_2S_3
0.5	9.175 (4)	11.395 (3)	1.2419 (9)	Mo
1.0	9.180 (13)	11.395 (11)	1.241 (3)	Mo
1.5	9.175 (3)	11.395 (3)	1.2420 (7)	Mo + unidentifiable phase
2.0	9.176 (2)	11.397 (4)	1.2420 (7)	Mo + unidentifiable phase

Table II. Superconductivity Data for $SnMo_6S_{8-x}$

nominal x	c/a	T_c, K	ΔT_c, K
0	1.2391	11.25	1.32
0.5	1.2419	13.56	1.51
1.0	1.2423	13.48	1.49
1.5	1.2420	13.32	1.64
2.0	1.2420	14.46	1.18

the $\bar{3}$ axis which is the body diagonal of the ternary element cube.

Though the materials are rhombohedral (the rhombohedral angle rarely deviates more than a degree from 90°), they may also be indexed hexagonally. In Figure 1, the hexagonal c unit vector goes from the origin at atom 0 to atom 1 and coincides with the $\bar{3}$ axis. The two a unit vectors are perpendicular to c along the face diagonals of adjacent unit cells, from the origin to atom 2 and atom 3.

Sergent and co-workers[8] found that the transition temperatures of different $PbMo_6S_8$ samples approached a similar value as the annealing time at 1100 °C was increased. The $SnMo_6S_{8-x}$ samples discussed here were quenched after a single heat treatment without annealing in hopes of freezing samples far off stoichiometry. The products were visually inhomogeneous. All but $SnMo_6S_8$ contained massive silver-white crystals, as well as the gray-black powders characteristic of the Chevrel phases. Debye–Scherrer X-ray photographs demonstrated that the silver-white crystals were molybdenum. Evidently the reaction conditions cause the fine Mo powder to form macroscopic crystals.

The fine gray-black powders were separated from the excess molybdenum and analyzed via X-ray diffraction. In each case, in addition to the desired phase, one or more impurity phases were detected. Table I lists the observed hexagonal lattice parameters as well as the impurities observed.

It is quite apparent that the listed stoichiometries are only nominal and the Chevrel phase composition is quite different. The a parameter is constant within experimental error. The c parameter increases as the nominal composition changes from $SnMo_6S_8$ to $SnMo_6S_{7.5}$, and then it remains constant. The increase in c suggests that vacancies are introduced in the special-position sulfur sites on the $\bar{3}$ axis. The fact that a remains constant suggests that there is no change in the occupancy of the general-position sulfur sites off the $\bar{3}$ axis.

The observed superconducting critical temperatures and the associated ranges are listed with the corresponding c/a ratios in Table II. It is gratifying to note that the transition temperature is pushed up 2–3 K when the phase is driven off stoichiometry. The value found for the last sample (14.46 K) is the highest T_c for a tin molybdenum sulfide yet reported.

The fact that the lattice parameters and transition temperatures are unchanged beyond $SnMo_6S_{7.5}$, and the presence of substantial quantities of unreacted molybdenum in the products, suggests that a phase boundary has been reached.

The width of the transition in these materials is a source of concern. The width is generally 20 times broader than the transition in niobium metal measured on the apparatus described above ($\Delta T_c = 0.060$ K for Nb). The presence of the impurity phases suggests that the problem may arise from inhomogeneity in the Chevrel phase. The lattice parameters presented here, on the other hand, are among the most precise data published for powder ternary molybdenum chalcogenides. Furthermore, the $PbMo_6(S_{1-x}Se_x)_8$ series, which we have also studied, show no contamination, yet the samples still exhibit broad transitions.

Summary

The series of materials $SnMo_6S_{8-x}$ has been synthesized from the elements and investigated by X-ray diffraction and superconducting critical temperature. The crystal data suggest that the special-position chalcogen sites on the $\bar{3}$ axis are chemically different from the other chalcogen sites. On going off stoichiometry, sulfur vacancies appear to be introduced on the special-position sites. The c/a ratio increases, and the superconducting critical temperature rises along with it. The phase boundary for $SnMo_6S_{8-x}$ appears to be at $SnMo_6S_{7.5}$.

Registry No. $SnMo_6S_8$, 39432-50-3.

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Crystal Data for Mixed-Anion Molybdenum Dichalcogenides

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The layered dichalcogenides[1] MoS_2 and $MoSe_2$ are of special interest as lubricants,[2] catalysts, and catalyst supports for hydrodesulfurization reactions,[3] precursors of intercalation superconductors,[4] and possible electrodes for photoelectrolysis.[5] In the pure, stoichiometric state they are moderate-gap semiconductors (1.75 eV for MoS_2 and 1.4 eV for $MoSe_2$),[5] presumably because the characteristic trigonal splitting of the d orbitals leads to filled d subbands. As part of a larger study on how small changes in chemical parameters affect superconductivity, we have had occasion to prepare the full solid solution series $MoS_{2-x}Se_x$ ($0 < x < 2$). The end compounds form both 2H and 3R polytypes. In each case, molybdenum atoms occupy trigonal-prismatic sites within the layers. In addition, in the system $MoS_{2-x}Se_x$, a continuous series of solid solutions can be prepared, all having the same 2H two-layer hexagonal structure (space group $P6_3/mmc$). We report in this communication the evolution of lattice parameters of the mixed-anion system.

Experimental Section

Preparation of Samples. A series of samples $MoSe_{2-x}Se_x$, where x varied from 0 to 2, was prepared by direct reaction of stoichiometric

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