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Preparation and Physical Properties of $BiMo_6S_8$ and $SbMo_6S_8$

NATHALIE CHEVREAU* AND DAVID C. JOHNSON†

E. I. DuPont de Nemours and Company, Experimental Station,
Wilimington, Delaware 19898

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The compounds $Me_1Mo_6S_8$ (Me = Bi, Sb) were prepared by low-temperature diffusion of Bi and Sb into the binary phase Mo_6S_8. The homogeneity range of the ternary elements is very narrow and centered about Me = 1.0, implying that the ternary metal is located at the origin position of the rhombohedral unit cell. The observed lattice parameters ($BiMo_6S_8$, $a_h = 9.194$, $c_h = 11.325$; $SbMo_6S_8$, $a_h = 9.122$, $c_h = 11.282$) are consistent with this hypothesis and suggest that these atoms enter the structure as trivalent cations. No superconducting transition is observed for these materials above 2 K. A small temperature-independent paramagnetism is present in the magnetic susceptibility of these compounds. The magnitude of this paramagnetism is less than that found in other ternary molybdenum chalcogenides with trivalent cations, suggesting that a reduced density of states is responsible for the observed lack of superconductivity. Attempts to prepare $MeMo_6(S_{1-x}Se_x)_8$ (Me = Sb and Bi) with $x > 0$ failed to yield ternary phases, instead producing mixtures of the unreacted ternary metal and the corresponding binary phase.

Introduction

The ternary molybdenum chalcogenides, $Me_yMo_6X_8$ (Me = Pb, Sn, Cu, Ln, etc.; $0 < y < 4$; X = S, Se, Te), have been extensively studied since their discovery by Chevrel *et al.* (*1*) as a result of their unusual physical properties. The physical properties vary substantially with the ternary metal. For instance, reentrant superconductivity and the coexistence of superconductivity and antiferromagnetism occur when the ternary metal is any one of several rare earths; high-temperature superconductivity and extremely high critical fields characterize these phases when Me is lead or tin; and low-temperature phase changes result when Me is a small and/or polarizable cation such as copper or indium (*2, 3*). These unusual properties are a consequence of the structure of these materials.

The main building block of the ternary molybdenum chalcogenides is the Mo_6X_8 unit in which eight chalcogen atoms sit at the corner of a distorted cube with six molybdenum atoms slightly above the face centers. Individual Mo_6X_8 units are rotated approximately 25° about the threefold axis of the cube so as to minimize the distance between the chalcogen atom of one cube and the molybdenum atom of an adjacent cube. The ternary Me atoms are positioned

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* Photosystems and Electronic Products Department.

† Author to whom correspondence should be addressed: Central Research and Development Department, E. I. DuPont de Nemours and Co., Experimental Station, Wilmington, Del. 19898.

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TABLE I

STARTING MATERIALS FOR $MeMo_6(S_{1-x}Se_x)_8$ SYNTHESIS

Element	Nominal purity (%)	Source
Sulfur	99.9999	Atomergic Chemetals Corp.
Selenium	99.9999	Atomergic Chemetals Corp.
Molybdenum	99.95	United Mineral and Chemical Corp.
Copper	99.999	Materials Research Corporation
Bismuth	99.99995	Alfa Products
Antimony	99.9999	Alfa Products

between Mo_6X_8 units either on the $\bar{3}$ axis (leading to a rhombohedral angle, α_r, less than 90°) or in a double belt of 12 tetrahedral sites around this position (α_r greater than 90°).

It was recently shown that it is possible to extract the copper ions in $Cu_2Mo_6X_8$ compounds using a solution of I_2 in acetonitrile to yield the binary compositions (*4*, *5*). Various metal atoms may then be diffused into the Mo_6X_8 phase at a temperature below the decomposition temperature of the binary phase. This technique has been exploited to produce several phases which cannot be formed via the usual high-temperature synthesis. $TlMo_6Se_8$ provides an excellent example of the unusual properties which can result from phases prepared in this manner; it has the highest superconducting critical temperature of any selenide Chevrel phase (*5*). We have recently used this technique to prepare several new ternary molybdenum chalcogenides. In this paper we report the low-temperature synthesis, lattice parameters, and physical properties of the previously unreported $SbMo_6S_8$ and $BiMo_6S_8$.

Experimental

I. Sample preparation. The initial starting materials for the preparation of these new phases were the binary materials, Mo_6X_8, which were prepared from $Cu_{1.8}Mo_6X_8$. The copper molybdenum chalcogenides were synthesized from ultrapure starting elements, purity and sources of which are shown in Table I. Prior to use, the molybdenum powder was reduced at 1000°C under a flow of hydrogen and stored in a vacuum desiccator until needed.

Two-gram samples of $Cu_{1.8}Mo_6(S_{1-x}Se_x)_8$ ($x = 0$–1 in 10 steps) were prepared from the elements and placed in previously degassed silica tubes, which were degassed again at 10^{-6} Torr and sealed. All sealed tubes were placed together in a box furnace, the temperature of which was uniformly and slowly raised to 1050°C over the course of 5 days. After 24 hr at 1050°C the samples were cooled in air and the tubes vigorously shaken to homogenize the contents. They were then immediately reheated to 1100°C, kept there for 48 hr, and then air-cooled. The sample tubes were opened in a helium "Dri-Lab" and the samples thoroughly ground. After being resealed in new degassed silica tubes the samples were heated to 1200°C for 96 hr and finally air-cooled. The resulting materials were fine, homogenous gray–black powders.

After the $Cu_{1.8}Mo_6(S_{1-x}Se_x)_8$ samples were characterized by X-ray diffraction, the powders were added to a solution of I_2 (50-fold excess) in acetonitrile under an argon atmosphere and sealed. The solution containing the powdered material was then stirred for 48 hr at 60°C. The following reaction occurs during this period:

$$Cu_{1.8}Mo_6X_8 + 0.9I_2 \rightarrow Mo_6X_8 + 1.8CuI \quad (1)$$

The resulting powdered samples, Mo_6X_8, were washed with acetonitrile and dried. All the lines in the powder X-ray diffraction pattern were indexed and the resulting lattice parameters are given in Table II. These lattice parameters lie within the range of previously published values for the binary solid solution (*6*, *7*).

TABLE II

LATTICE CONSTANTS AND THEIR STANDARD DEVIATIONS FOR THE $Mo_6(S_{1-x}Se_x)_8$ SOLID SOLUTION

Composition	a_r (Å)	a_r (deg)	a_h (Å)	c_h (Å)	c/a	V_r (Å^3)
Mo_6S_8	6.436(3)	91.24(2)	9.200(4)	10.902(4)	1.184	266.4(1)
$Mo_6(S_{0.9}Se_{0.1})_8$	6.439	91.36	9.214	10.883	1.181	266.7
$Mo_6(S_{0.8}Se_{0.2})_8$	6.462	91.66	9.270	10.863	1.171	269.4
$Mo_6(S_{0.7}Se_{0.3})_8$	6.473	91.75	9.293	10.864	1.168	270.8
$Mo_6(S_{0.6}Se_{0.4})_8$	6.515	91.93	9.367	10.898	1.163	276.0
$Mo_6(S_{0.5}Se_{0.5})_8$	6.532	92.01	9.399	10.909	1.160	278.2
$Mo_6(S_{0.4}Se_{0.6})_8$	6.557	92.04	9.437	10.946	1.159	281.4
$Mo_6(S_{0.3}Se_{0.7})_8$	6.581	91.96	9.466	11.001	1.162	284.5
$Mo_6(S_{0.2}Se_{0.8})_8$	6.616	91.90	9.511	11.072	1.164	289.1
$Mo_6(S_{0.1}Se_{0.9})_8$	6.655	91.82	9.560	11.154	1.166	294.3
Mo_6Se_8	6.665	91.74	9.569	11.188	1.169	295.7

Appropriate amounts of Sb and Bi were then added to the binary phases to prepare 1-g samples of these new phases. The samples were sealed in previously degassed silica ampoules and heated to 480°C for the sulfur-rich compositions and 520°C for the selenide compositions. After 7–14 days at these temperatures, the samples were air-cooled. Unreacted antimony, bismuth, and the binary phase were present in the samples containing selenium. The sulfide end members were homogeneous, single phase, gray–black powders and there was no evidence of unreacted ternary metal.

II. Powder X-ray diffraction. X-Ray diffraction photographs were taken by using a 114.6-mm-diameter Debye–Scherrer camera with nickel-filtered Cu$K\alpha$ radiation. Lines were indexed with the aid of a Fortran program that calculated the positions and intensities of possible reflections from available single-crystal data. A least-squares fit, with corrections for absorption and camera radius error, was performed using all lines with $\theta(hkl) > 30°$ that could be indexed unambiguously. The procedure yields lattice parameters with errors of less than one part per thousand.

III. Superconducting transition determination. The transition to the superconducting state was monitored using an ac mutual-inductance apparatus described elsewhere (*8*). In this device the detection system consists of a primary coil with two opposed secondary coils wound symmetrically about it. The sample is placed in one of the secondary coils, and onset of superconductivity is signaled by an imbalance between the secondary coils resulting from an abrupt increase in magnetic shielding in the sample coil. Temperature is measured using a calibrated CryoCal germanium thermometer, which was checked against the boiling point of helium and the transition temperatures of lead and niobium.

IV. Magnetic susceptibility. Magnetic susceptibilities were measured from 2 K to room temperature by the Faraday technique using an apparatus described previously (*9*). The balance was calibrated using $HgCo(SCN)_4$ as a standard. Samples were held in Spectrosil quartz buckets. All samples were run over a range of fields (5–10 kG); susceptibilities were found to be field independent. The reported susceptibilities have been corrected for the susceptibility of the quartz buckets.

Results and Discussion

The attempts to diffuse antimony and bismuth into Mo_6S_8 and Mo_6Se_8 produced sur-

TABLE III

LATTICE CONSTANTS AND THEIR STANDARD DEVIATIONS FOR $BiMo_6S_8$ AND $SbMo_6S_8$

Compound	a_r (Å)	α_r (deg)	a_h (Å)	c_h (Å)	c/a	V_r (Å^3)
$BiMo_6S_8$	6.513(3)	89.78(2)	9.194(4)	11.325(4)	1.232	276.3(1)
$SbMo_6S_8$	6.471(3)	89.62(2)	9.122(4)	11.282(4)	1.236	270.9(1)

prisingly different results. All of the selenide samples contained unreacted ternary metal and Mo_6Se_8, while the sulfide samples appeared homogeneous. The X-ray results confirmed these observations, indicating that the new ternary phases $BiMo_6S_8$ and $SbMo_6S_8$ were formed. Attempts to vary the ternary metal stoichiometry from unity, which was shown to yield a continuous single-phase product for $Hg_xMo_6S_8$ ($0 < x < 1$) (*6*), resulted in two-phase samples with either unreacted ternary metal or unreacted Mo_6S_8 depending upon which was in excess relative to the ternary composition $Me_{1.0}Mo_6S_8$. The lattice parameters obtained did not vary with the stoichiometry and are given in Table III.

In order to determine the solubility limit of the bismuth and antimony in a system containing varying amounts of selenium, we investigated the diffusion of antimony and bismuth into the solid solution $Mo_6S_{8-x}Se_x$. All of the fired samples with Se contained unreacted ternary metal and unreacted binary phase. X-Ray patterns confirmed that only the compositions $BiMo_6S_8$ and $SbMo_6S_8$ formed ternary phases.

The antimomy and bismuth systems are in some respects similar to the mercury system investigated by Tarascon *et al.* (*4*). The authors found that $Hg_yMo_6S_8$ formed a single-phase product for $0 < y < 1$ but the corresponding selenide phase did not form. They also studied the diffusion of mercury into the binary solid solution $Mo_6(S_{1-x}Se_x)_8$ and reported that the amount of mercury which can be inserted into this solid solution decreases rapidly with increasing x (*6*). The antimony and bismuth phases differ from the mercury samples because they have a single stable composition, $Me_{1.0}Mo_6S_8$. Since the selenide phase is unstable and the ternary metal content cannot be reduced below $Me_{1.0}Mo_6S_8$, the formation of the mixed chalcogen ternary compositions is not possible.

The oxidation states assumed by bismuth and antimony in these ternary systems can be inferred from crystallographic parameters. Yvon (*2*) has pointed out that the cell volume in the ternary molybdenum chalcogenides increases rapidly with the size of the ternary ion. According to the sulfide crystal radii determined by Shannon (*10*), Bi^{3+} has a radius similar to La^{3+} with the eightfold coordination found in the ternary molybdenum chalcogenides. The crystal radii for Sb^{3+} can be extrapolated from the same tables and is similar to that of Gd^{3+}. The volumes of the bismuth and lanthanum molybdenum sulfides are similar (828.9 and 826 Å^3, respectively), and likewise the observed volumes for the antimony and gadolinium phases are also very similar (813 and 814 Å^3, respectively). The agreement between these volumes leads us to believe that both antimony and bismuth enter the ternary molybdenum chalcogenide structure as tripositive cations.

There are some crystallographic differences between the bismuth and antimony phases and the corresponding rare earth phases of similar radii. The hexagonal c_h axes for the antimony and bismuth phases are shorter than those observed for $GdMo_6S_8$ and $LaMo_6S_8$ by 0.07 and 0.16 Å, respectively, and the a_h axes are correspondingly longer than observed in the rare earths by 0.03 and 0.07 Å, respectively. In this respect, these new ternary phases are similar to $AgMo_6S_8$ which also has a shorter c_h axis and a larger a_h axis than one would expect from the ionic radius of Ag^{1+}.

The crystal structure of $AgMo_6S_8$ indicates that the silver cations are delocalized off the $\bar{3}$ axis. The thermal parameters describe an elliptical surface for the cation. This delocalization from the origin allows the Mo_6S_8 units to come closer to each other, reducing the c_h axis while correspondingly increasing the a_h axis. The delocalization is caused by the high polarizability of the silver cation (*2*).

The differences in the bonding of the antimony and bismuth in the ternary molybdenum chalcogenides when compared to corresponding rare earth phases partially result from the larger electronegativities of antimony and bismuth. The increased electronegativities of antimony and bismuth relative to the rare earths lead to more covalent bonding between the ternary atom and the sulfide cage which surrounds the ternary element in these compounds. Also, bismuth and antimony are more polarizable than the rare earth ions. As demonstrated by the silver system, a polarizable cation tends to be delocalized from the origin position, resulting in a shorter c_h axis and longer a_h axis.

Previous researchers have attempted to correlate various physical parameters (especially the superconducting critical temperature, T_c) with changes in crystallographic parameters. Early work by Shelton (*11*), Marezio (*12*), and others (*13*) suggested that T_c is directly related to the unit cell volume, while other researchers (*14, 15*) have proposed that a strong correlation exists between the rhombohedral angle α_r and T_c, with T_c decreasing as α_r increases. Subsequent data indicate that such simple correlations are not valid when all of the ternary molybdenum chalcogenides are considered together. A more confined correlation was proposed by Delk and Sienko (*16*) who suggested that by grouping the ternary molybdenum chalcogenides according to the formal valence of the ternary element, a correlation exists between the hexagonal c_h/a_h ratio (or equivalently α_r) and the observed superconducting transition temperatures. The unusual crystallographic behavior observed in the bismuth and antimony systems led us to investigate the superconducting properties of these materials.

From volume considerations we would expect $BiMo_6S_8$ to superconduct near 7 K ($LaMo_6S_8$; $T_c = 7$ K) and $SbMo_6S_8$ to superconduct near 4 K. From the c_h/a_h relationship suggested by Delk and Sienko (*16*), we would expect transition temperatures in the 2–3 K region. Unfortunately, no evidence of superconductivity was found for either $SbMo_6S_8$ or $BiMo_6S_8$ above 2 K. This result is quite surprising since almost all of the ternary molybdenum chalcogenides investigated to date with rhombohedral symmetry and a large cation have been found to be superconducting. We suspect that the lack of superconductivity in these phases results from the modified bonding of antimony and bismuth to the Mo_6S_8 network which we will discuss below.

In the BCS theory of superconductivity (*17*), the superconducting critical temperature T_c is given by

$$kT_c = \langle h\omega \rangle \exp(-1/NV), \quad (2)$$

where $\langle \omega \rangle$ is the mean phonon frequency, N is the density of states at the Fermi level, and V is the electron–phonon coupling constant. In changing the ternary cation in a ternary molybdenum chalcogenide from lanthanum to bismuth or antimony, all trivalent cations, the T_c drops from 7 to below 2 K. This drop is either due to a decrease in the density of states, a change in the phonon frequency, or a decrease in the electron–phonon coupling constant. All of these factors will be altered by changes in the bonding of the ternary cation.

The increased a_h and decreased c_h axes imply that the Mo_6S_8 units are closer together in $SbMo_6S_8$ and $BiMo_6S_8$ than in La Mo_6S_8. This reduction in intercluster mo-

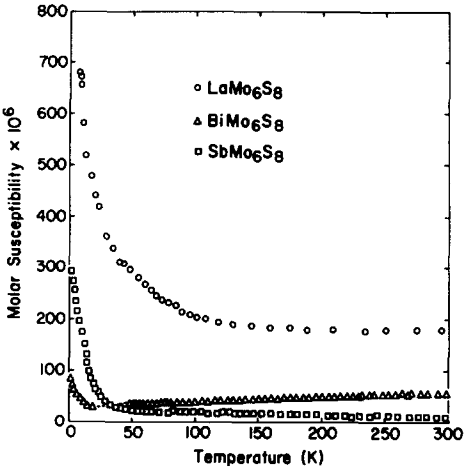

FIG. 1. The molar susceptibility of $Me\mathrm{Mo_6}X_8$ (Me = La, Bi, and Sb) as a function of temperature.

lybdenum distances broadens the conduction band, reducing the density of states at the Fermi level and therefore T_c. Additionally, the increased bonding between cluster units will raise the intercluster vibrational energies affecting both the electron–phonon coupling and the mean phonon frequency. To probe the effect of these crystallographic changes on the density of states and indirectly on the electron–phonon coupling, the magnetic susceptibilities of the antimony, bismuth, and lanthanum compounds were investigated.

The magnetic susceptibilities of $Me\mathrm{Mo_6S_8}$ (Me = La, Bi, and Sb) are plotted as a function of temperature in Fig. 1. All of the susceptibilities reveal the presence of a Curie tail at low temperature due to the presence of paramagnetic impurities. The low-temperature data was fit to

$$\chi = C/(T + \theta) + \chi_0, \tag{3}$$

where C, θ, and χ_0 are assumed to be constant at very low temperature. We then assume that C and θ are temperature independent and in Fig. 2 we plot $\chi_p = \chi - \chi_d - C/(T + \theta)$, which represents the susceptibility corrected for the Curie tail and the diamagnetic cores. The curves obtained are not very sensitive to changes in the fitted parameters.

The susceptibilities in Fig. 2 are all paramagnetic and consist of the sum of several contributions: Pauli paramagnetism and Landau diamagnetism due to the conduction electrons and Van Vleck paramagnetism which results from the mixing of excited magnetic states with the ground state. Although we cannot separate these contributions from each other, we suggest that the variation of χ_p is mainly due to changes in the Pauli paramagnetism. This term is proportional to the density of states at the Fermi level (although it can also be enhanced by electron–electron effects). The susceptibility of $\mathrm{LaMo_6S_8}$ (a 7 K superconductor) is larger than those observed for $\mathrm{SbMo_6S_8}$ and $\mathrm{BiMo_6S_8}$ by 25%. This result suggests that the lack of superconductivity in the bismuth and antimony phases may be the result of a decreased density of states.

In addition, the magnetic susceptibilities of $\mathrm{BiMo_6S_8}$ and $\mathrm{SbMo_6S_8}$ are essentially temperature independent, while the susceptibility of $\mathrm{LaMo_6S_8}$ increases as the temperature decreases (the presence of this nonzero slope is not a function of the fitted

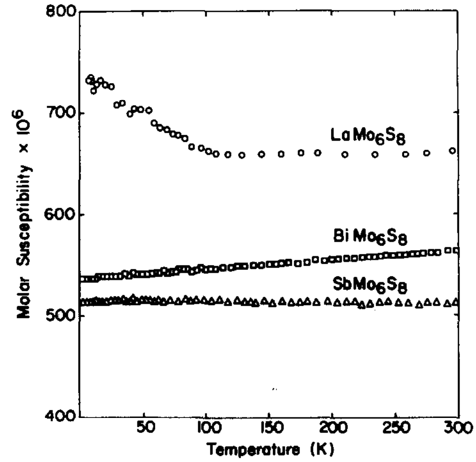

FIG. 2. The molar susceptibility of $Me\mathrm{Mo_6}X_8$ (Me = La, Bi, and Sb) corrected for diamagnetic cores and paramagnetic impurities as a function of temperature.

parameters from Eq. (3)). The negative temperature dependence of the $LaMo_6S_8$ susceptibility is commonly observed for many high-temperature superconductors, and it has been suggested that it is a result of electron–electron correlations (coupled through electron–phonon interactions) (*18*). If this is correct, then the electron–phonon coupling in these new antimony and bismuth molybdenum chalcogenides is reduced as a result of increased intercluster bonding.

In summary, the new ternary molybdenum chalcogenides $BiMo_6S_8$ and $SbMo_6S_8$ have been prepared via a low-temperature synthetic route. The lattice parameters indicate that both antimony and bismuth are trivalent in this structure and that the Mo_6S_8 units are closer together than in other trivalent Chevrel phases with cations of similar size. The smaller intercluster distance results from both the larger polarizability of bismuth and antimony relative to other trivalent cations and the increased covalency of the bismuth–sulfur and antimony–sulfur bonds when compared to the rare earth–sulfur bonds found in $LnMo_6S_8$ compounds. No superconductivity is observed, and magnetic susceptibility results suggest that the lack of superconductivity is due to a smaller density of states and a reduced electron–phonon coupling relative to superconducting trivalent ternary molybdenum chalcogenides.

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