

Amorphous Precursors for Low-Temperature Preparation of Chevrel Phases $M_x\text{Mo}_6\text{S}_8$ and Their Tungsten Analogues

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Received August 30, 1994; accepted November 22, 1994

High-yield preparations of the amorphous ternary salts $\text{Na}_{2x}(\text{Mo}_6\text{S}_8)_x \cdot y\text{MeOH}$ (with $x = 1.0$ to 1.5 , $y = 4$ to 5) and $\text{Na}_{2.1}(\text{W}_6\text{S}_8)\text{S}_{1.05} \cdot 5.4\text{MeOH}$ have been devised by reaction of $M_6\text{Cl}_{12}$ ($M = \text{Mo}$ or W) with NaSH and NaOBu in various ratios in refluxing n -BuOH for $M = \text{Mo}$ and in refluxing MeCN for $M = \text{W}$. Characterization of these amorphous materials by chemical and spectroscopic methods (IR, Raman, PES) shows that the $(M_6\text{S}_8)^0$ cluster units are present. Vacuum thermolysis of the amorphous $\text{Na}_{2x}(\text{Mo}_6\text{S}_8)_x \cdot y\text{MeOH}$ first produces poorly crystalline NaMo_6S_8 by disproportionation at 800°C and well-crystallized NaMo_6S_8 at $\geq 900^\circ\text{C}$. The amorphous tungsten compound disproportionates to W and WS_2 at $\geq 200^\circ\text{C}$. Ion exchange of the sodium material in methanol with soluble M^{2+} and M^{3+} salts ($M = \text{Sn}$, Co , Ni , Pb , La , Ho) produces the $M_{2x/n}^{n+}(\text{Mo}_6\text{S}_8)_x \cdot y\text{MeOH}$ compounds. For tungsten, only exchange with SnCl_2 in THF was examined and resulted in $\text{Sn}_x(\text{W}_6\text{S}_8)_x \cdot y\text{MeOH}$. Conversion of $\text{Sn}_x(\text{Mo}_6\text{S}_8)_x \cdot y\text{MeOH}$ to poorly crystalline Chevrel phase, SnMo_6S_8 , was achieved by reduction under H_2 at 600°C . Well-crystallized SnMo_6S_8 resulted at higher temperatures. Conversion of $\text{Sn}_x(\text{W}_6\text{S}_8)_x \cdot y\text{MeOH}$ to SnW_6S_8 was not successful. © 1995 Academic Press, Inc.

of this network in either large cation (e.g., Pb^{2+} , Sn^{2+} , or La^{3+}) or small cation (e.g., Li^+ , Cu^+ , or Ni^{2+}) sites (7). Electron transfer from the cations gives formal charges of -1 to -4 on the $\text{Mo}_6\text{Y}_8^{n-}$ anionic network, and consequently metal cluster electron counts of 20 to 24 can be realized (8). The 20-electron case is realized in the binary phases Mo_6Y_8 , in which the sulfide is metastable and must be prepared by indirect means (9); the selenide and telluride members are stable and easily prepared by direct combination of the elements (10).

Up to the present time, there has been no report concerning the successful preparation of the tungsten analogues W_6Y_8 or $M_x\text{W}_6\text{Y}_8$. It is generally understood that these compounds must be unstable with respect to disproportionation (into W and WY_2 or W , WY_2 , and $M\text{Y}_{n/2}$). Thus, if success is to be achieved, preparation of the tungsten analogues must be pursued using low-temperature approaches. We have been successful in developing the chemistry of molecular complexes $M_6\text{S}_8\text{L}_6$ for both the molybdenum (11) and tungsten (12) cluster units and have sought to apply this in the development of low-temperature routes to the ternary phases $M_x\text{Mo}_6\text{S}_8$ and $M_x\text{W}_6\text{S}_8$. Such routes could also lead to methods for the deposition of films, coatings, and highly dispersed or high-surface area solids useful in electronic or catalytic applications.

INTRODUCTION

The Chevrel phases of the general formula $M_x\text{Mo}_6\text{Y}_8$ ($M =$ ternary metal cation, $1 \leq x \leq 4$, $Y = \text{S}$, Se , or Te), are an important class of compounds because of their interesting chemical and physical properties. Among these are numerous examples of high H_{c2} superconductors (1), ordered magnetic phases (2), solid electrolytes (fast ion conductors) (3), and hydrodesulfurization catalysts (4). Structurally the compounds consist of three-dimensionally interlinked Mo_6Y_8 cluster units sharing chalcogenide ions between bridging and terminal positions (5) as indicated by the formulation $(\text{Mo}_6\text{Y}_2^i\text{Y}_{6/2}^{i-a})\text{Y}_{6/2}^{a-i}$ (6). The interlinking joins each cluster with six adjoining cluster units in a rhombohedral (sometimes lower symmetry) stacking. The ternary metal ions M^{n+} , with $n = 1$ to 4 , find positions within the interstices

EXPERIMENTAL PROCEDURES

$(\text{Mo}_6\text{Cl}_8)\text{Cl}_4$ (13) and $(\text{W}_6\text{Cl}_8)\text{Cl}_4$ (12) were prepared by methods described in the literature. NaSH was prepared by reaction of H_2S with NaOEt in ethanol according to the method described by Brauer (14). $\text{NaO-}n$ -Bu was obtained by the reaction of sodium metal with 1-butanol and used as the solid after vacuum removal of the solvent. All solvents were purified and dried prior to use according to accepted procedures. Manipulation of all air-sensitive materials was conducted under Ar or N_2 atmospheres or on the vacuum manifold.

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Syntheses

Preparation of $\text{Na}_{2x}(\text{Mo}_6\text{S}_8)\text{S}_x(\text{MeOH})_y$. The following reaction is given as representative of the preparative process. $\text{Mo}_6\text{Cl}_{12}$ (4.00 g, 4 mmole), NaSH (2.69 g, 48 mmole), and NaOBu (2.30 g, 24 mmole) were weighed in the drybox and transferred to a Schlenk reaction flask equipped with a water-cooled condenser. By syringe, 75 ml of 1-butanol was added to the reactants. The mixture was refluxed for 2–3 days. After cooling, a black solid and faint yellow solution were separated by filtration. The solid was extracted with methanol for several days to remove the NaCl by-product, and the remaining solid was dried *in vacuo*. The resulting black solid (4.15 g, 93% yield) showed no evidence of Cl by chlorine analyses. The presence of sodium was confirmed by photoelectron spectroscopy (PES). Also, it was observed that the sodium and methanol contents showed some degree of variability from one reaction to another. The product was found to be insoluble and amorphous to X rays. IR (Nujol, cm^{-1}): $\nu(\text{C}-\text{O})_{\text{MeOH}}$ 969 (br), $\nu(\text{Mo}-\text{S})$ 381 (br). *Anal.* Calcd for $\text{Na}_{2.8}(\text{Mo}_6\text{S}_8)\text{S}_{1.4}(\text{MeOH})_{4.2}$: Na, 5.98%; Mo, 53.50%. Found: Na, 5.98%; Mo, 53.43%; Na/Mo₆ = 2.80.

Preparation of $\text{Na}_{2x}(\text{W}_6\text{S}_8)\text{S}_x(\text{MeOH})_y$. W_6Cl_{12} (2.34 g, 1.53 mmole), NaSH (1.02 g, 18.2 mmole), and NaOEt (0.625 g, 9.2 mmole) were loaded in a Schlenk reaction flask equipped with a water-cooled condenser. By distillation, 50 ml of acetonitrile was added to the reactants and the mixture was refluxed for 3–4 days. A black solid and a faint yellow solution were separated by filtration. The solid was extracted with methanol for several days to remove the NaCl by-product, and the remaining solid was dried *in vacuo*. The product (2.06 g) showed an absence of Cl by chlorine analyses. The presence of sodium was confirmed by PES. The product was found to be slightly soluble in methanol and amorphous to X rays. IR (Nujol, cm^{-1}): $\nu(\text{C}-\text{O})_{\text{MeOH}}$ 960 (br), $\nu(\text{W}-\text{S})$ 376. *Anal.* Calcd for $\text{Na}_{2.1}(\text{W}_6\text{S}_8)\text{S}_{1.05}(\text{MeOH})_{5.4}$: Na, 2.98%; W, 68.19%. Found: Na, 3.02%; W, 66.50%; Na/W₆ = 2.12.

Preparation of $M_{2x/n}^{n+}(\text{Mo}_6\text{S}_8)\text{S}_x$ and $\text{Sn}_x(\text{W}_6\text{S}_8)\text{S}_x$ by ion exchange. The general procedure for the ion-exchange reaction involved the transfer in the drybox of weighed amounts of $\text{Na}_{2x}(\text{Mo}_6\text{S}_8)\text{S}_x(\text{MeOH})_y$ (1.00 g) and a five- to sixfold excess of the metal salt ($M\text{Cl}_2$ for $M = \text{Sn}, \text{Co}, \text{Ni}$; $M\text{Cl}_3$ for $M = \text{Ho}, \text{La}$; $\text{Pb}(\text{NO}_3)_2$) into a 100-ml Schlenk reaction flask, and then 30 ml of methanol was vacuum-distilled onto the solids. After the mixture was stirred at room temperature for 1–2 days, a black solid and a faint yellow solution were obtained. The resulting solid was extracted with solvent distilled from the filtrate in order to remove the NaCl by-product and any unreacted metal salt. After drying under dynamic vacuum, a black powder was obtained. The product was found to be insoluble and amorphous to X rays. IR (Nujol, cm^{-1}): $\nu(\text{C}-\text{O})_{\text{MeOH}}$ 980

(br), $\nu(\text{Mo}-\text{S})$ 383 (br). *Anal.* Calcd for $\text{Sn}_{1.2}(\text{Mo}_6\text{S}_8)\text{S}_{1.2}(\text{MeOH})_{4.6}$: Sn, 12.27%; Mo, 49.61%. Found: Sn, 12.18%; Mo, 49.59%; Sn/Mo₆ = 1.19. *Anal.* Calcd for $\text{Co}_{0.8}(\text{Mo}_6\text{S}_8)\text{S}_{0.8}(\text{MeOH})_{3.9}$: Co, 4.58%; Mo, 55.89%. Found: Co, 4.54%; Mo, 55.82%; Co/Mo₆ = 0.79. *Anal.* Calcd for $\text{Ni}_{1.0}(\text{Mo}_6\text{S}_8)\text{S}_{1.0}(\text{MeOH})_{4.4}$: Ni, 5.52%; Mo, 54.11%. Found: Ni, 5.34%; Mo, 54.04%; Ni/Mo₆ = 0.97. *Anal.* Calcd for $\text{La}_{0.6}(\text{Mo}_6\text{S}_8)\text{S}_{0.9}(\text{MeOH})_{5.4}$: La, 7.23%; Mo, 51.69%. Found: La, 7.24%; Mo, 51.66%; La/Mo₆ = 0.58. *Anal.* Calcd for $\text{Ho}_{0.3}(\text{Mo}_6\text{S}_8)\text{S}_{0.45}(\text{MeOH})_{4.4}$: Ho, 4.77%; Mo, 55.52%. Found: Ho, 4.98%; Mo, 55.58%; Ho/Mo₆ = 0.31.

$\text{Sn}_x(\text{W}_6\text{S}_8)\text{S}_x$ was prepared in a similar manner to the molybdenum analogues, except tetrahydrofuran (THF) was used as the solvent instead of methanol. Then the product was extracted with methanol in order to remove the NaCl. The black product is amorphous to X rays. IR (Nujol, cm^{-1}): $\nu(\text{C}-\text{O})_{\text{MeOH}}$ 958 (br), $\nu(\text{W}-\text{S})$ 376.

Conversion to $\text{Na}_x\text{Mo}_6\text{S}_8$ and SnMo_6S_8 . $\text{Na}_{2x}(\text{Mo}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ was placed in a Pyrex ampoule with joints for connection to the vacuum manifold. The ampoule was then furnace heated to 500°C under a dynamic vacuum of 10^{-4} Torr to remove the bound methanol. In attempts to prepare the desired sodium Chevrel phase, the samples were then loaded into fused silica vessels and sealed *in vacuo* for annealing at 800, 900, and 1100°C for 2–5 days. Examination of $\text{Na}_{2x}(\text{W}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ was also explored by heating *in vacuo* and under flowing H_2 at temperatures up to 200°C.

A different route was used to prepare the tin Chevrel phase, SnMo_6S_8 . The $\text{Sn}_x(\text{Mo}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ sample was heated under flowing H_2 over the range from 500 to 1000°C. In all cases, the sample was placed into an alumina boat inside a quartz tube. The material was then furnace-heated to the desired temperature while under a flowing H_2 gas stream. Similar attempts were examined with the tungsten compound $\text{Sn}_x(\text{W}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$, by heating at 200°C under flowing H_2 .

Physical Methods

Infrared spectra (4000–200 cm^{-1}) were recorded with a Bomem MB-102 Fourier transform infrared spectrometer equipped with CsI optics. Samples were prepared as Nujol mulls and mounted between CsI windows. Raman spectra were obtained with a Spex Triplemate spectrometer with a Princeton Applied Research Corp. intensified SiPD detector cooled to -40°C . The excitation source was a Coherent Ar⁺ 200 series laser (514.5 nm) and the scattered radiation was collected in a backscattering geometry. The laser power at the sample was approximately 20 mW, and the integration time was 200 sec. The Raman spectra were obtained at room temperature from solid samples packed in capillary tubes. Photoelectron (PE) spectra were col-

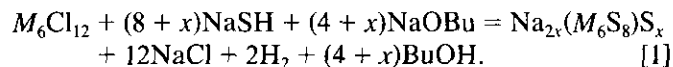
lected with a Physical Electronics Industries 5500 multi-technique surface analysis system, and the binding energies were calibrated with C 1s binding energy (BE) of 284.6 eV. Powder X-ray diffraction (XRD) data were obtained with a Philips ADP3520 θ - 2θ diffractometer using $\text{CuK}\alpha$ radiation. The air-sensitive samples were loaded into a specially designed sample holder and sealed while in the drybox.

Molybdenum was determined gravimetrically as the 8-hydroxyquinolate (15) and tungsten was determined as the trioxide. Chlorine was determined by potentiometric titration with a standardized silver nitrate solution. Sodium was determined by atomic absorption using a Perkin-Elmer 305B spectrometer. Cobalt, lanthanum, and holmium were separated prior to the molybdenum oxime analyses as insoluble oxides and fired to constant weight. Tin was separated from molybdenum and determined as the oxide (16). Nickel was determined as the dimethylglyoxime complex (17).

RESULTS AND DISCUSSION

Preparation of Sodium Salts $\text{Na}_{2x}(\text{M}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$

The most important result of this research involves the preparation of the sodium salts, $\text{Na}_{2x}(\text{M}_6\text{S}_8)\text{S}_x$, of both the molybdenum and tungsten M_6S_8 cluster units. Although an excess of NaSH is always used to ensure complete sulfidation of the M_6Cl_{12} starting materials, higher ratios of NaSH/ M_6Cl_{12} promote greater values of x . The reactions appear to proceed by the equation



In all cases, the use of excess NaSH assures oxidation of the cluster units to the 20-electron neutral cluster core $(\text{M}_6\text{S}_8)^0$. Formation of these sodium salts results from coordination of sulfide ions in the terminal positions of the cluster units. Since the NaCl by-product is removed from the precipitated materials with methanol washing, some methanol is retained by coordination in the terminal positions or incorporated in the lattice. Compounds of the general formula $\text{Na}_{2x}(\text{M}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ are thus obtained, with y in the range from 4 to 5. Furthermore, these materials are amorphous and generally quite reactive in air.

Close control of the value of x is difficult. For three different reactions with the same reaction ratios of 1 : 12 : 6 (M_6Cl_{12} : NaSH : NaOBu), the observed values of x were 0.85, 1.2, and 1.4. For the reaction ratios 1 : 11 : 7, $x = 1.15$ and for the ratios 1 : 15 : 7, $x = 1.5$. Thus, for the compositions $\text{Na}_2(\text{M}_6\text{S}_8)\text{S}$ and $\text{Na}_3(\text{M}_6\text{S}_8)\text{S}_{1.5}$, desired in the subsequent ion-exchange with M^{2+} and M^{3+} cations, the reaction ratios of 1 : 11 : 7 and 1 : 15 : 7, respec-

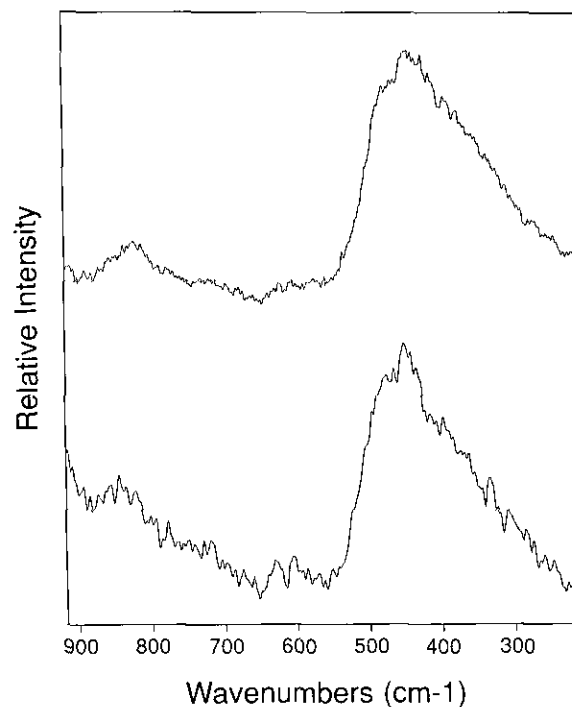


FIG. 1. Raman spectra of amorphous materials, $(\text{Mo}_6\text{S}_8)(\text{PrNH}_2)_{6-x}$ (top) and $\text{Na}_2(\text{Mo}_6\text{S}_8)\text{S} \cdot y\text{MeOH}$ (bottom).

tively, are the most suitable. Less information about the control of x is available at the present time for the tungsten materials.

The best results for the preparation of the molybdenum salts has been found with use of butanol as a solvent. However, in the preparation of the analogous tungsten compounds, butanol was found to cause slight decomposition as evidenced by the presence of bands at 450 and 500 cm^{-1} in the IR spectra. This decomposition is minimized when the reactions are conducted in acetonitrile. Fortunately, the sulfidation of W_6Cl_{12} is more facile than that of $\text{Mo}_6\text{Cl}_{12}$, which makes the lower temperature of refluxing acetonitrile (82°C) advantageous.

IR spectra for the sodium salts show strong bands at 381 and 376 cm^{-1} , characteristic of the M -S stretching mode of T_{1u} symmetry for the Mo_6S_8 and W_6S_8 cluster units, respectively. Raman spectra of the amorphous $\text{Na}_{2x}(\text{M}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ also show a broad emission centered at 450 cm^{-1} , arising from the Mo-S stretching modes. The sharp Raman mode of A_{1g} symmetry at $415 \pm 3 \text{ cm}^{-1}$, characteristic of crystalline $(\text{M}_6\text{S}_8)\text{L}_6$ derivatives (11), cannot be seen in the spectra of amorphous materials. A comparison of the broad bands in the Raman spectra of the amorphous $\text{Na}_{2x}(\text{M}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ and the partially deligated $(\text{M}_6\text{S}_8)(\text{PrNH}_2)_{6-x}$ (18) is shown in Fig. 1.

Perhaps the most useful spectroscopic data are provided by Mo 3d and W 4f photoelectron spectra. The W 4f PES of $\text{Na}_{2.1}(\text{W}_6\text{S}_8)\text{S}_{1.05} \cdot (\text{MeOH})_{5.4}$ is shown in Fig. 2,

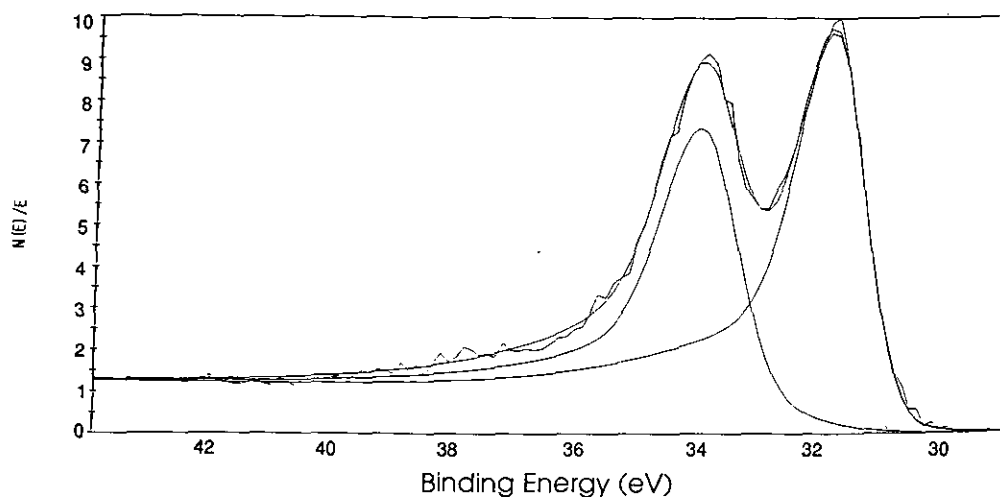


FIG. 2. W 4f photoelectron spectrum of $\text{Na}_{2.1}(\text{W}_6\text{S}_8)\text{S}_{1.05}(\text{MeOH})_{5.4}$.

which illustrates that only one type of tungsten atom is necessary to fit this spectrum. The derived binding energies of 30.8 ($4f_{7/2}$) and 33.0 eV ($4f_{5/2}$) are characteristic of the W_6S_8 unit and compare with the $4f_{7/2}$ BEs of 31.2 eV for $(\text{W}_6\text{S}_8)(\text{PET}_3)_6$ (19), 32.7 eV for WS_2 , and 35.4 eV for WO_3 . PES data for the molybdenum compounds, including $\text{Na}_{2x}(\text{M}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$, are given in Table 1. The Mo $3d_{5/2}$ BE of 227.2 eV for the latter is in agreement with the BEs of 227.5 ± 0.4 eV observed for the materials prepared from this sodium salt by ion-exchange. For comparison, the Mo $3d_{5/2}$ of MoS_2 is 229.5 eV. This 2.0-eV difference in BE makes MoS_2 easily detectable when it occurs as an impurity. None of the compounds listed in Table 1 showed evidence for the presence of MoS_2 .

Ternary Salts Prepared by Ion Exchange

The preparation of the ternary compounds $M_{2x/n}^{n+}(\text{Mo}_6\text{S}_8)\text{S}_x$ and $\text{Sn}_x(\text{W}_6\text{S}_8)\text{S}_x$ by ion exchange from the sodium salts could be accomplished by stirring the latter with appropriate salts of the desired cations in methanol

for the molybdenum compounds and THF for the tungsten compound. Slow decomposition of the tungsten cluster is again observed in methanol, which makes the use of THF as an alternate solvent desirable. Complete exchange after about 1 day of stirring the reaction mixture was verified by PES analysis, which showed the absence of Na in any of the products. Even though reactions were started with materials of composition near $\text{Na}_2(\text{M}_6\text{S}_8)\text{S} \cdot y\text{MeOH}$, only the compounds $\text{Sn}_{1.2}(\text{Mo}_6\text{S}_8)\text{S}_{1.2}(\text{MeOH})_{4.6}$ and $\text{Ni}_{1.0}(\text{Mo}_6\text{S}_8)\text{S}_1(\text{MeOH})_{4.4}$ could be verified as having the expected composition for replacement of all Na^+ by Sn^{2+} or Ni^{2+} . In the other cases, loss of coordinated sulfide evidently also occurred during the ion-exchange process and the products thus achieved a lower M^{n+} /cluster ratio than indicated by the initial Na stoichiometry. This was especially noticeable with the holmium salt, which only resulted in 46% of the expected Ho^{3+} content. In all cases, the ion-exchanged materials retained four to five methanol molecules per cluster unit. The exact composition of the $\text{Sn}_x(\text{W}_6\text{S}_8)\text{S}_x$ compound is unknown except that the PES analysis verified the absence of Na and the presence of Sn.

TABLE 1
Binding Energies (eV) from Photoelectron Spectra of Ternary Sulfides $M_{2x/n}^{n+}(\text{Mo}_6\text{S}_8)\text{S}_x^a$

Compound ^b	Mo $3d_{3/2}$	Mo $3d_{5/2}$	S $2s$	S $2p_{3/2}$	S $2p_{1/2}$	M^c
NaMoS	227.2	230.4	225.0	160.6	161.8 sh	—
CoMoS	227.9	231.1	225.8	161.3	162.5 sh	779.0
NiMoS	227.7	230.8	225.6	161.0	162.2 sh	852.8
SnMoS	227.5	230.6	225.4	161.8 br	—	487.0
PbMoS	227.7	230.8	225.4	161.6 br	—	137.4
LaMoS	227.7	230.9	225.9	161.6 br	—	838.0
HoMoS	227.2	230.5	225.0	161.1 br	—	—

^a Values adjusted to C 1s binding energy of 284.6 eV; br, broad, sh, shoulder.

^b For actual compositions, see Experimental.

^c $M = \text{Co}$ or Ni , $2p_{3/2}$; $M = \text{Sn}$ or La , $3d_{5/2}$; $M = \text{Pb}$, $4f_{7/2}$.

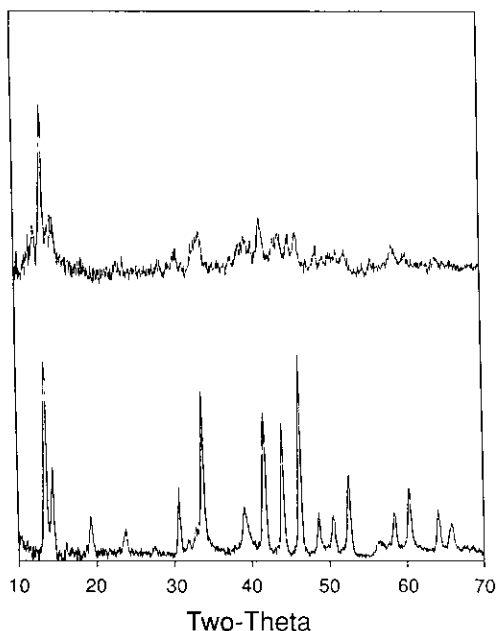


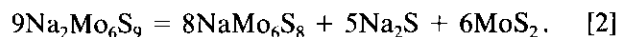
FIG. 3. X-ray powder diffraction pattern for NaMo_6S_8 prepared from $\text{Na}_2(\text{Mo}_6\text{S}_8)\text{S} \cdot y\text{MeOH}$ after annealing at 800°C (top) and 900°C (bottom).

By analogy to the results for the molybdenum compound, complete exchange of Sn for Na would provide a material of composition $\text{Sn}_{1.05}(\text{W}_6\text{S}_8)\text{S}_{1.05} \cdot y\text{MeOH}$.

Bands at 376 and 381 cm^{-1} in the IR spectra of the $\text{Sn}_x(\text{M}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ materials reflect the presence of the W_6S_8 and Mo_6S_8 cluster units, respectively. Likewise, the constant Mo $3d$, S $2s$, and S $2p$ BEs derived from the PE spectra of the ternary molybdenum compounds, given in Table I, show the unchanging presence of the $(\text{Mo}_6\text{S}_8)^0$ cluster unit. Similarly, the W $4f_{7/2}$ BE of 30.9 eV for $\text{Sn}_x(\text{W}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ agrees with the values given above for $\text{Na}_{2x}(\text{W}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ and $(\text{W}_6\text{S}_8)(\text{PET}_3)_6$.

Conversion to Crystalline NaMo_6S_8

After removal of bound methanol from $\text{Na}_{2x}(\text{Mo}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ *in vacuo* at 500°C , further annealing at higher temperatures ultimately leads to formation of the polycrystalline NaMo_6S_8 Chevrel phase. Annealing at 800°C results in the broad XRD lines shown in Fig. 3a. Annealing at lower temperatures fails to provide crystalline material, while annealing at 900°C results in markedly improved crystallinity as observed in Fig. 3b. In these materials, the strongest line of MoS_2 at $2\theta = 14.5^\circ$ appears in all samples annealed below 1100°C . This MoS_2 line did not appear in a sample annealed at 1100°C . Notably, no lines of Na_2S or Mo_2S_3 could be detected in these XRD patterns. On the basis of the approximate starting composition $\text{Na}_2\text{Mo}_6\text{S}_9$, we expect a disproportionation to occur, as given in



Thus, poorly crystalline MoS_2 should be seen as a product of the annealing. However, the Na_2S formed in this reaction probably reacts with the fused silica vessel and is removed from the mixture. The reason for the disappearance of the strongest line of MoS_2 in the sample annealed at 1100°C is not apparent.

The lattice parameters calculated from the XRD data of the sample annealed at 900°C , $a_H = 9.202(3)$ and $c_H = 11.227(6)\text{ \AA}$, are in reasonably good agreement with the values given by Gocke *et al.* (20) for $\text{Na}_1\text{Mo}_6\text{S}_8$: $a_H = 9.231$ and $c_H = 11.321\text{ \AA}$. For comparison, the lattice parameters for Mo_6S_8 were reported as $a_H = 9.192$, $c_H = 10.889\text{ \AA}$, and for $\text{Na}_3\text{Mo}_6\text{S}_8$ as $a_H = 9.897$, $c_H = 10.725\text{ \AA}$. On the basis of these lattice parameters, we formulate the product as NaMo_6S_8 in Eq. [2]. The conversion of the $\text{Na}_{2x}(\text{Mo}_6\text{S}_8)\text{S}_x$ precursor to crystalline NaMo_6S_8 at 800°C is noteworthy, since much higher temperatures are generally needed for direct synthesis of the Chevrel phase compounds (1).

Conversion to Crystalline SnMo_6S_8

In order to obtain the SnMo_6S_8 Chevrel phase from the ion-exchanged precursor, $\text{Sn}_{1.2}(\text{Mo}_6\text{S}_8)\text{S}_{1.2}(\text{MeOH})_{4.6}$, conversion under flowing H_2 was utilized. At lower temperatures, $\leq 500^\circ\text{C}$, the bound methanol was lost. Reduction and conversion of the amorphous precursor were examined at successively higher temperatures from 500 to 1000°C . Formation of poorly crystalline SnMo_6S_8 was first observed after 6 hr at 600°C , as indicated by the broad lines in Fig. 4a. After 6 hr at 700°C , the XRD lines were sharp and exhibited about the same bandwidth as those from conversion at 1000°C (Figs. 4b and 4c). In all cases, the appearance of the two strongest lines of Mo indicated that reduction of SnMo_6S_8 was occurring simultaneously with its formation. Production of Mo should be accompanied by the formation of Sn, but the latter was only observed in the XRD for the sample reduced at 700°C .

The lattice parameters calculated from the XRD data of the sample heated at 700°C under flowing H_2 , $a_H = 9.188(3)$ and $c_H = 11.366(6)\text{ \AA}$, are again in reasonable agreement with the values given by Chevrel *et al.* (21) for the single crystal determination of SnMo_6S_8 , $a_H = 9.206$ and $c_H = 11.363\text{ \AA}$. Thus we find that the SnMo_6S_8 Chevrel phase can be produced from the precursor at temperatures as low as 600°C , but under flowing H_2 its formation is always accompanied by reduction to Mo metal. To avoid the latter reduction, an appropriate partial pressure of H_2S should be included in the gas flow.

Attempted Conversion to Crystalline $M_x\text{W}_6\text{S}_8$

Upon heating $\text{Na}_{2.1}(\text{W}_6\text{S}_8)\text{S}_{1.05}(\text{MeOH})_{5.4}$ at 130°C *in vacuo* for 3 days, the sample suffered only partial loss of

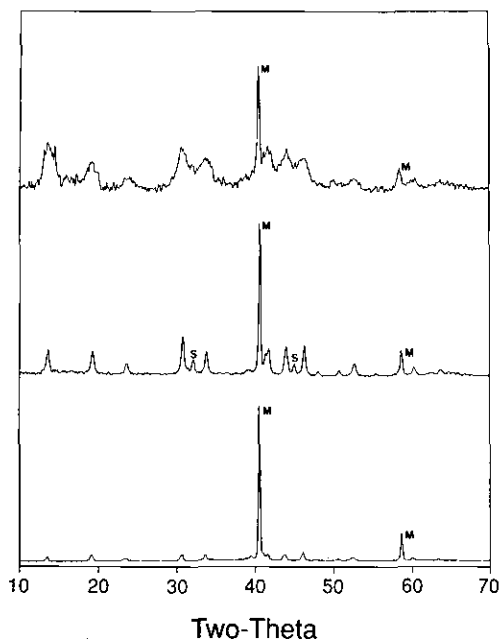


FIG. 4. X-ray powder diffraction patterns for SnMo_6S_8 prepared from $\text{Sn}(\text{Mo}_6\text{S}_8)\text{S} \cdot y\text{MeOH}$ by hydrogen reduction at 600 (top), 700 (middle), and 1000°C (bottom). Reflections marked with M and S indicate those arising from Mo and Sn metals, respectively.

bound methanol, but both the IR and PE spectra showed that the W_6S_8 cluster unit survived. However, heating a separate sample at 300°C for 1 day resulted in decomposition and formation of W and WS_2 , according to both PES and IR data. Heating at 200°C under flowing H_2 also resulted in the formation of W and WS_2 . Thus formation of the metastable crystalline $\text{Na}_x\text{W}_6\text{S}_8$ must be effected at a temperature less than 200°C if it is to succeed. Efforts to convert $\text{Sn}_x(\text{W}_6\text{S}_8)\text{S}_x \cdot y\text{MeOH}$ to the Chevrel phase analogue also failed, with decomposition resulting from reaction under H_2 at 200°C.

ACKNOWLEDGMENTS

We thank Jim Anderegg for aid with the PE spectra. This work was supported by the U.S. Department of Energy, Office of Basic Energy

Sciences, through Ames Laboratory operated by Iowa State University under Contract W-7405-Eng-82.

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5. The Mo_6Y_8 cluster unit is composed of six Mo atoms bonded to form an octahedron. The bridging ligands Y which cap the faces of the octahedron are each bonded to three Mo atoms. Each Mo atom can form one additional bond directed radially outward from the cluster to a terminal ligand.
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8. Here the MCE consists of only the electrons remaining in the 4d orbitals of Mo and used for Mo-Mo bonding after the valence levels of the S atoms are filled.
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