

Synthesis of MoS_x ($5 > x > 6$) Amorphous Sulfides and Their Use for Preparation of MoS_2 Monodispersed Microspheres

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Amorphous binary sulfides MoS_5 , $\text{MoS}_{5.6}$, and MoS_6 have been prepared from the reactions in the solutions of common $(\text{NH}_4)_2\text{Mo}_2\text{S}_{12}$ precursor. Characterizations by X-ray diffraction, IR spectroscopy, and EXAFS suggest that all three sulfides have the structures similar to that of MoS_3 but contain more abundant S–S bonds. The $\text{MoS}_{5.6}$ sulfide obtained by means of reflux of the solution of $(\text{NH}_4)_2\text{Mo}_2\text{S}_{12}$ in acetone has uniform size spherical morphology. Thermal decomposition of $\text{MoS}_{5.6}$ leads to hollow spheres of MoS_2 .

Introduction

One of the current challenges for materials chemistry is to develop novel inorganic syntheses for the production of nanoscopic solids not available by conventional solid-state reactions. To accomplish this goal, reactions of chemically homogeneous precursors at low temperatures are used. Currently, investigation of the control of size and form of solids particles on different length scales is a rapidly developing field (recently coined definitions are “panoscopic materials”¹ or “chemistry of form”²). Elaboration of monodispersed hollow spheres or core shell particles of inorganic solids or polymers are of great interest because of the rich diversity of possible applications for such materials.³

Recently, we used soft chemistry methods to prepare MoS_2 , which is an important compound for catalysis and lubricants. MoS_2 was prepared in the aqueous or organic solvent solutions, with the goal of obtaining fine dispersions of pure⁴ or surfactant-stabilized⁵ MoS_2 materials. We observed also that the amorphous molybdenum polysulfide might form hollow microtubules.⁶

Trying to rationalize the preparations described in ref 6, we found that the key intermediate product, capable of producing solids with original morphology, is thiodimolybdate $\text{Mo}_2\text{S}_{12}^{2-}$. Here, we report on the reactions of ammonium thiodimolybdate in the solutions, leading to the new binary molybdenum sulfides MoS_x ($x = 5–6$) and we describe the technique allowing us to obtain uniform size MoS_2 microspheres.

Experimental Section

The starting compound applied for the syntheses was $(\text{NH}_4)_2\text{Mo}_2\text{S}_{12}$ (ATDM). ATDM was prepared using a literature

method.⁷ The product purity was controlled by means of powder X-ray diffraction (XRD), IR spectroscopy, and chemical analysis.

To prepare the $\text{MoS}_{5.6}$ solid, 0.001 mol of ATDM (0.61 g) was refluxed with 200 mL of acetone for 6 h. After the reflux, a dark suspension was formed. The brown powder ($\text{MoS}_{5.6}$) was collected, washed with CS_2 and acetone, dried in air, and kept in argon. To obtain MoS_2 , the $\text{MoS}_{5.6}$ solid (ca. 0.5 g) was heated in a nitrogen flow of 100 cm^3/min at 773–1073 K for 1 h.

To prepare the MoS_6 sulfide, 0.28 g of ATDM was dissolved in 20 mL of dimethylformamide (DMF); 0.2 g of iodine dissolved in 30 mL of DMF was added. The immediate formation of a precipitate was observed. The precipitate MoS_6 was filtered and subsequently washed with DMF, CS_2 , and acetone and dried in argon.

To obtain the MoS_5 sulfide, 0.3 g of ATDM was dissolved in 100 mL of water and then 25 mL of 1 M HCl was added. The dark precipitate was filtered, washed, and dried in argon.

MoS_3 was obtained as described above for MoS_5 , but $(\text{NH}_4)_2\text{MoS}_4$ (0.23 g) was applied instead of ATDM.

Infrared spectra were recorded in air, using KBr disks on a BRUKER Vector 22 FT IR spectrometer. X-ray diffraction patterns were recorded on a diffractometer SIEMENS D500 by using Ni-filtered $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (SEM) images were obtained on a Hitachi S800 microscope. High-resolution transmission electron microscopy was carried out on a JEOL 2010 device. The EXAFS measurements were performed at the Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE), on the XAS2 spectrometer (line D21). The measurements were carried out in the transmission mode at the Mo K edge from 19900 to 21000 eV at 8 K. The EXAFS data were treated with SEDTEM⁸ and FEFF⁹ programs. Thermal analysis was carried out using a SETARAM device under nitrogen flow. The solids were heated from room temperature to 1023 K at a rate 5 K min^{-1} .

Results and Discussion

The nonstoichiometric sulfide $\text{MoS}_{5.6}$ produced by means of reflux of ATDM acetone solution have monodisperse spherical morphology.

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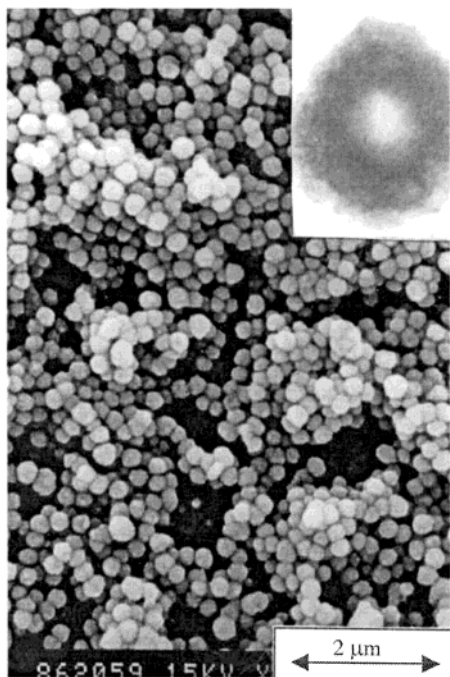


Figure 1. SEM image of the MoS₂ obtained from the MoS_{5.6} solid after heating at 1073 K under Ar flow. Insert: TEM image of one sphere.

Chemical analysis for the solid dried in air gives 32.8 wt % Mo, 61.2 wt % S, and 0.2 wt % N (calculated for MoS_{5.6}: 34.9 wt %, Mo 65.1 wt % S). The size of the spheres is in the range from 200 to 300 nm, with a mean value of ca. 250 nm. The MoS_{5.6} solid is DRX amorphous and has a featureless IR spectrum with only one broad line at 533 cm⁻¹.

Nearly uniform size weakly agglomerated spheres persist after thermal decomposition of MoS_{5.6} in an inert gas flow (Figure 1). For the solid treated at 673–1073 K in argon, XRD and chemical analysis confirm that pure MoS₂ is obtained. TEM study suggests that the majority of the MoS₂ microspheres are hollow, whereas their walls consist of randomly oriented MoS₂ stacks. According to the BET measurements, the MoS₂ spheres obtained at 773 K have a relatively high specific surface area of 76 m²/g.

Monodisperse spherical morphology of MoS_{5.6} may be explained by the fact that this solid is formed in the solution by slow nucleation and highly isotropic growth under the conditions near equilibrium. Indeed, the MoS_{5.6} suspension was obtained only after several hours of reflux. In contrast, shapeless amorphous solids are always produced by instant precipitation; such is the case of MoS₃ prepared by acidification of thiomolybdate solution or the samples of MoS₅ and MoS₆ sulfides (discussed below).

The MoS_{5.6} sulfide obtained possesses original morphology, but it is a nonstoichiometric compound with unclear chemical identity. Moreover, its preparation though well reproducible is carried out by means of boiling of ATDM acetone solution in air, which may include various interactions of ATDM with air moisture and oxygen as well as autodecomposition. The MoS_{5.6} composition suggested, however, that the simple binary sulfides with an integer sulfur-to-molybdenum atomic ratio of 5 or 6 may exist. Tungsten chalcogenides of

similar stoichiometry have been described earlier.^{10,11} Therefore, we tried to synthesize such binary sulfides from the same ATDM precursor, but using more rational preparation techniques.

Molybdenum sulfides with sulfur contents higher than that in MoS₂ have never been prepared in the crystalline form. The molecular precursor often used to obtain molybdenum sulfide materials is (NH₄)₂MoS₄.^{4–6} Thermal decomposition of this salt in an inert gas or in hydrogen at 673–773 K leads to the formation of dispersed MoS₂. Acidification of (NH₄)₂MoS₄ solutions leads to the precipitation of amorphous MoS₃ sulfide:



No consensus has been reached in the literature on the structure of MoS₃, even concerning the number of molybdenum atoms in the basic structural unit. Hibble et al., who carried out the most detailed study on this compound, using EXAFS and neutron diffraction, suggested a chainlike structure of MoS₃,^{12,13} but recently accepted the model proposed earlier by Müller et al.¹⁴ in which Mo trimers are the principal building blocks of the structure.¹⁵

Besides MoS₃, a nonstoichiometric sulfide, MoS_{4.7}, has been obtained from the reaction of Mo(CO)₆ with sulfur and studied by EXAFS.¹⁶ Moreover, Khudorozhko et al. claimed to obtain amorphous MoS₄ sulfide as an intermediate of ATDM thermal decomposition.¹⁷ Later, Hibble and Feaviour found that poorly crystalline Mo₃S₁₂ and amorphous Mo₃S_{13.5} are formed in the thermal decomposition of ammonium thiomolybdates.¹⁸

A wide variety of different polythiomolybdates are described in the literature,^{19,20} but only few of them were used as precursors for materials preparation because with only a few exceptions they are rather difficult to obtain in a pure state and easily decompose. Thiotri-molybdate (NH₄)₂Mo₃S₁₃ is stable and readily available and was applied as a precursor for heterogeneous catalysts.²¹ Leist et al. have studied the thermal decomposition of hydrated (NH₄)₂Mo₂S₁₂ and (NH₄)₂-Mo₃S₁₃ to obtain dispersed molybdenum sulfide.²² The final decomposition product in all cases is poorly crys-

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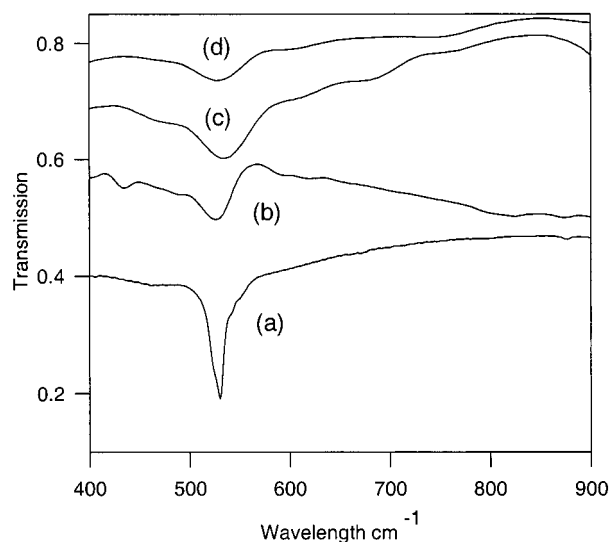
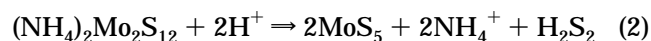


Figure 2. IR spectra of ATDM (a), MoS₅ (b), MoS_{5.6} (c), and MoS₆ (d).

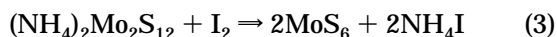
talline MoS₂. However, the solids obtained from ATDM in the solution have never been studied.

From the analogy with reaction 1 of monothio salt, we suggested that other, more rich in sulfur binary molybdenum sulfides might be available from the acidic hydrolysis of ATDM. Indeed, acidification of (NH₄)₂-Mo₂S₁₂ leads to the precipitation of amorphous stoichiometric sulfide MoS₅ (chemical analysis found: 35.1 wt % Mo, 58.5 wt % S; Mo/S atomic ratio 5.003; calculated for MoS₅: 37.6 wt % Mo and 62.4 wt % S; the total percentage of Mo and S is 93.6 wt %, lower than 100 wt % because of the adsorbed impurities and occluded solvent). This sulfide shows in the IR spectrum only a strong line at 536 cm⁻¹ similar to that of the S–S bonds feature in MoS₃,²³ but placed at a slightly higher frequency (Figure 2).



Note that in the purely acid–base reaction 2, no change of the formal oxidation state of sulfur occurs; therefore, hydrogen disulfide should be formed.

The oxidation of DMF solution of ATDM by iodine provides a route to another stoichiometric sulfide MoS₆ (chemical analysis data found: 31.2 wt % Mo, 63.3 wt % S; S/Mo atomic ratio 6.08; calculated for MoS₆: 33.3 wt % Mo and 66.6 wt % S; the sum of Mo and S contents is 94.5% and again short of 100% because of the occluded solvent). The solution pH drops after the reaction from its initial value of 7.5 to 2 probably because of ammonium iodide formation according to reaction 3:



The IR study shows that the obtained amorphous black sulfide MoS₆ contains abundant S–S bonds, which give in the IR spectrum a broad line centered at 530 cm⁻¹.

The first question concerning these sulfur-rich amorphous sulfides was obviously whether they are really

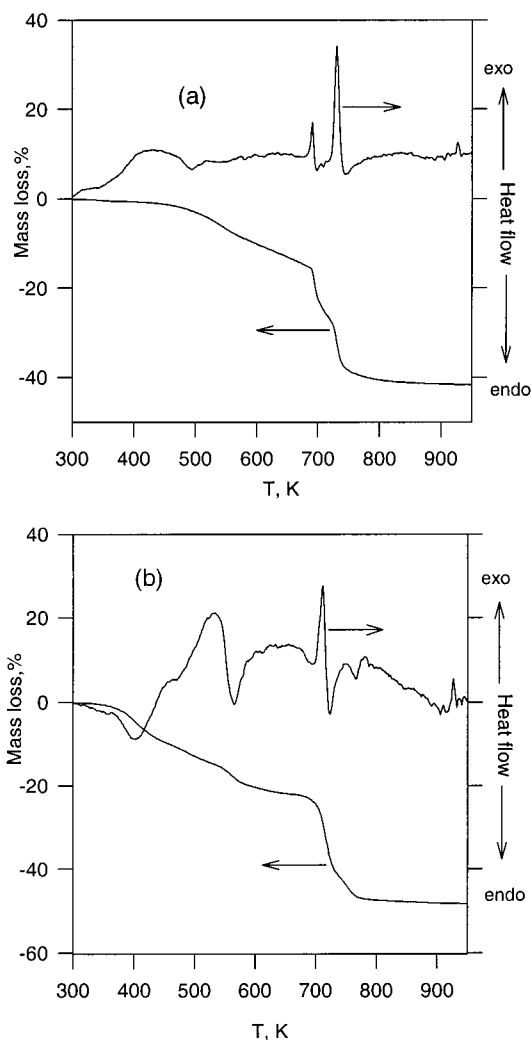


Figure 3. TG curves of MoS₅ (a) and MoS₆ (b) for thermal decomposition in N₂ at 5 K min⁻¹.

new individual compounds and not just the intimate mixtures of sulfur and MoS₃. For this reason we applied in our preparations thorough washing with CS₂, which would remove all eventual impurities of occluded sulfur. In fact, after evaporation of the CS₂ used for washing, no sulfur residual was observed, in agreement with reactions 2 and 3. Being prepared in the solutions at low temperatures, the solids are highly dispersed and contain non-negligible amounts of adsorbed or occluded solvent, which varies between 5 and 8 wt %. However, the Mo-to-S atomic ratio in MoS₅ and MoS₆ is stoichiometric within the limits of accuracy of our analytic techniques (0.1–0.2 wt %). Both solids are not soluble in any available organic solvents. According to SEM, both MoS₅ and MoS₆ have shapeless morphology.

Thermal analysis of the MoS₅ and MoS₆ under nitrogen flow shows the stepwise elimination of sulfur (Figure 3). Both sulfides decompose, producing MoS₂ in the temperature range 673–740 K. The total mass loss for MoS₅ is 42 wt %; the calculated value for MoS₅ to MoS₂ transformation is 37.5 wt %. For MoS₆ the total mass loss found was 47.6 wt % and the calculated 44.4 wt %. Several weight percentage points of mass loss occur below 200 °C, which can be attributed to the loss of adsorbed solvents and moisture. Both solids show the most important inflection point on the TG curves near

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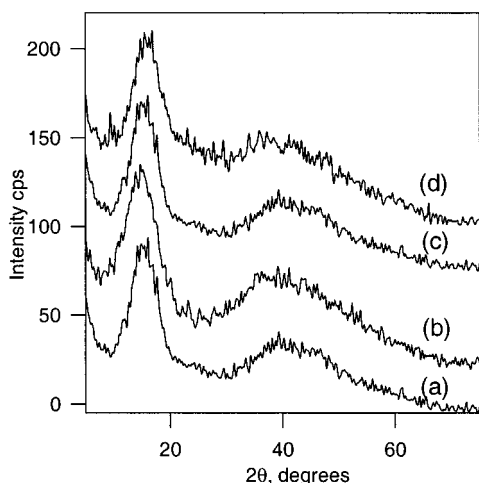


Figure 4. XRD patterns of MoS₃ (a), MoS₅ (b), MoS_{5.6} (c), and MoS₆ (d).

the stoichiometry MoS₄, reported earlier as an intermediate compound of ATDM decomposition, which forms above 550 K. The MoS₄ stoichiometry is somewhat critical because above it a smooth change of sulfur content occurs whereas below this composition rapid loss of sulfur with sharp thermal effects occurs. Further formation of the MoS₃ compound seems to be related to the inflection on the descending part of mass loss curves, near 710–720 K. Narrow exothermal events are observed for crystallization of MoS₂ from both amorphous sulfides. The temperature of complete removal of sulfur with the formation of MoS₂ (730–740 K) is somewhat higher than reported by Hibble for decomposition of thiopolymolybdates probably because of a higher heating rate applied by us. The sharp transition from MoS_{4+x} to MoS_{2+x} near 720 K was observed by Brito et al., who also used relatively rapid heating (10 K min⁻¹).²⁴

If we assume that MoS₅ and MoS₆ are respectively formed according to “purely acid base” and “purely redox” reactions 2 and 3, then the chemical composition of MoS_{5.6} suggests that the formation of this solid follows an intermediate route between (2) and (3), including both acid–base and oxidative transformations.

Obtained from the same precursor under soft conditions and having close chemical compositions, three solids under study probably have certain structural similarities. Less obvious is that they all seem to be structurally similar to the MoS₃ sulfide. Indeed, though virtually amorphous, all the MoS_x samples ($x = 5, 5.6$, and 6), showed in the XRD patterns two broad maxima at 2θ of 15° and 42°, placed at the same angles as those for the MoS₃ solid (Figure 4).

Moreover, the IR spectra of all solids (Figure 2) show the single S–S stretching band at 530–536 cm⁻¹, similar to that of starting ATDM. Note that the splitting of the S–S band into two bands at 510 and 545 cm⁻¹ reported by Hibble for the products of ATDM decomposition has not been observed in our specimens, either in sulfur-rich sulfides or in MoS₃. This splitting is characteristic for the formation of trimeric Mo₃S₁₃²⁻ or (Mo₃S₁₂) species. It occurs probably at high temperatures because of the ammonia that evolved in the

Table 1. Results of Mo Shell EXAFS Fitting in Our Samples and Literature Data for Some Reference Compounds

compound ^a	$R(S)^a$	$N(S)^b$	$A/\text{\AA}^2$ ^c	$R(\text{Mo})^a$	$N(\text{Mo})^b$	$A/\text{\AA}^2$ ^c
MoS ₆	2.44	5.9	0.005	2.78	0.69	0.002
MoS _{5.6}	2.44	6.2	0.005	2.76	0.75	0.002
MoS _{4.7} (ref 12, 80 K)	2.44	7.33	0.008	2.78	1.33	0.002
MoS ₃ (this work)	2.44	6.1	0.005	2.77	0.95	0.002
MoS ₃ (ref 12, 80 K)	2.43	6	0.012	2.75	1	0.004

^a Interatomic distance, Å. ^b Coordination number. ^c Debye Waller parameter.

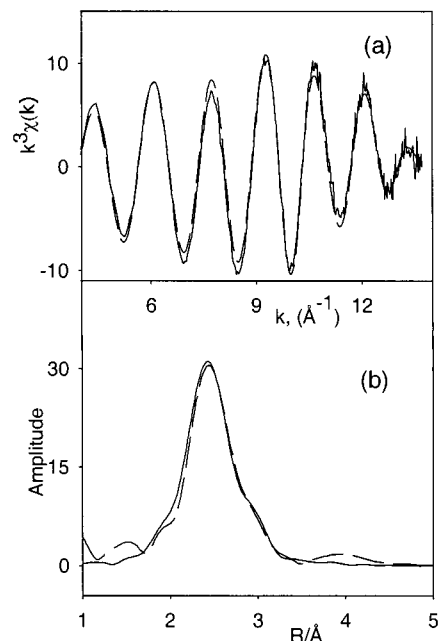


Figure 5. Mo K edge EXAFS data for MoS₆ measured at 8 K: k^3 weighted experimental and calculated interference curves (a), and the Fourier transform curves, corrected for the Mo–S first-shell backscattering (b).

decomposition, which might be similar to the action of a base in the solution. It seems that under the soft conditions applied in our preparations the bonded units of the initial ATDM are preserved. It is plausible that two types of amorphous MoS_x sulfides of similar composition but different properties may exist: those obtained from thermal decomposition of thiomolybdates and those precipitated by acidification of solutions. The former type have two bands in the S–S bond region; the latter have only one.

The only method to access direct structural information for the amorphous solids such as sulfides studied in this work is EXAFS spectroscopy. The EXAFS fitting results for Mo K edge are summarized in Table 1; an example of fit curves is depicted in Figure 5 for the MoS₆ specimen.

In agreement with other characterizations, the coordination of molybdenum seems to be similar in all the sulfides studied. The first shell consists of 5.9–6.2 sulfur atoms at 2.44 Å distance. In all cases, the presence of the Mo atoms in the second shell is necessary to obtain a satisfactory fit. The Mo–Mo distance varies slightly between 2.76 and 2.78 Å, whereas the CN varies from 0.69 to 0.95, which is borderline for the precision of EXAFS determination of CN for this kind of disordered compounds.

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On the basis of our EXAFS data, we cannot definitively rule out or confirm one of the existing models of the MoS_3 structure, but whatever is the true one, the Mo coordination in the MoS_x samples seems to be similar to that in MoS_3 because at the same initial assumption about Debye Waller and energy shift parameters, a very similar coordination of Mo is obtained. More precise conclusions are hindered by the lack of accuracy in the CN determination. Indeed, the CN values found in the EXAFS fits are strongly correlated with the Debye Waller parameter A . Since the last cannot be independently measured, no exact determination of CN is possible as well. Application of the A values found from the reference compounds with known coordination numbers is not correct in this case because both CN and static disorder may strongly differ between the reference compounds and the amorphous sulfides under study; therefore, not one of two correlated variables could be excluded. Variation of the A_S for the Mo–S shell within physically reasonable limits from 0.003 to 0.008 \AA^{-2} leads to the corresponding change of CN from 5 to 7. However, provided the A parameter is fixed at the same value for all samples, similar CN values are obtained in the fit (presented in Table 1 values of the Debye Waller parameter are fixed at the same value).

Concerning the structure of the Mo–S amorphous solids, the only thing which seems to be definitely established is that they contain some bonded Mo–Mo units, connected by the sulfur bridges. Even the structure of MoS_3 is still being discussed for many years.

From our data we suggest that MoS_5 , MoS_6 , and $\text{MoS}_{5.6}$ as well as the earlier described MoS_8 product⁶ contain the same Mo–Mo basic building units, but differ just by the abundance of the connecting S–S bonds. We should note however that our results suggest the continuity of properties in the sequence $(\text{NH}_4)_2\text{Mo}_2\text{S}_{12}$ – MoS_6 – MoS_5 – MoS_3 . As for the earlier reported data on the products of chemical excision from the amorphous MoS_3 ,^{14,15} we do not think that they give a decisive solution of the problem. Indeed, these results leave no doubt that Mo_3 units are extracted from MoS_3 by hydroxide or cyanide and not formed in the solution. However, that does not provide the evidence that these units are already present in the solid. Slow isotope exchange between ^{100}Mo - and ^{92}Mo -enriched species does not rule out the possibility of rearrangement during excision.

In conclusion, simple solution routes for the preparation of new binary Mo sulfides are reported. We believe that new Mo sulfides obtained by soft chemistry methods may be interesting for applications and as reference compounds for further fundamental studies because there is still no clarity concerning the structure of the amorphous Mo sulfides.

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