



Soviet-era science, translated into English

**A. V. GOROKH, L. N.
RUSAKOV, A. A.
SAVINSKAYA**

1964

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196401.02030>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

CRYSTALLOGRAPHY

A. V. GOROKH, L. N. RUSAKOV, A. A. SAVINSKAYA

SYNTHESIS AND CHARACTERIZATION OF MOLYBDENUM SESQUISULFIDE (Mo_2S_3)

(Presented by Academician N. V. Belov on 18 I 1964)

During the thermal dissociation of molybdenite, an intermediate sulfur compound is formed, to which, on the basis of chemical analysis, the formula Mo_2S_3 has been assigned ⁽¹⁾. Neither an optical nor an X-ray characterization of this compound has been given up to the present time ⁽²⁻⁴⁾. In this connection, we carried out the synthesis of molybdenum sesquisulfide and determined some of its physical constants.

As starting materials we used molybdenum powder (99.9%) and stick sulfur in a ratio of 2 : 3. The weighed portions (Mo 9.6 g, S 4.8 g) were thoroughly mixed and sealed in a quartz ampoule under vacuum. The prepared mixture was heated and held at temperatures of 500° for 6 hr, 900° for 14 hr, and 1400° for 15 min. As a result, the molybdenum and sulfur reacted completely, forming a homogeneous, crystalline, granular aggregate of molybdenum sesquisulfide.

Macroscopically, Mo_2S_3 is a crystalline substance of lead-gray color with a metallic luster. The streak is gray. The crystals are elongated-prismatic, and in cross section have the shape of a rhombus with angles between adjacent faces equal to 40 and 140°. Often the acute angles in the rhombic prism are truncated by faces of the pinacoid (010). On the basis of the morphological features of the crystals, it may be concluded that molybdenum sesquisulfide crystallizes in the orthorhombic system, in the rhombodipyramidal symmetry class ($3L_2^2PC$).

The hardness of Mo_2S_3 on the Mohs scale is 5. The microhardness varies within the range from 350 to 510 kg/mm². The prism and pinacoid faces have the lower hardness, and transverse sections of the crystals the higher. The specific gravity, determined by the pycnometric method, is 5.75.

In polished sections in reflected light, molybdenum sesquisulfide has a yellowish-cream color and clearly visible birefractance. The reflectivity is high (30-40%) and somewhat different for different faces. The anisotropy is strong (Fig. 1), with orange and greenish-blue color effects.

The reagents HNO_3 , HCl , H_2SO_4 , and aqua regia do not act on the polished surface of Mo_2S_3 crystals.

When Mo_2S_3 was heated without access of air to a temperature of 1600°, its

Fig. 1

Figure 1: Fig. 1

Fig. 2a and 2b

Figure 2: Fig. 2a and 2b

dissociation with formation of a metallic phase was observed. Consequently, at normal pressure Mo_2S_3 dissociates before melting.

The crystal lattice of molybdenum sesquisulfide is similar to the lattice of antimonite Sb_2S_3 . The interplanar spacings are given in Table 1.

In order to check whether molybdenum sulfides lower than Mo_2S_3 are formed, we sintered mixtures of molybdenum with sulfur in ratios of 1 : 1, 1.5 : 1, and 2 : 1 under conditions analogous to those described above. In all cases the products obtained consisted of Mo_2S_3 and residues of unreacted molybdenum, with the molybdenum sesquisulfide in direct contact with the metal. In some areas, accumulations of grains were encountered.

To the article by A. V. Gorokh, L. N. Rusakov, A. A. Savinskaya

Fig. 1. Microphotograph of an aggregate of Mo_2S_3 grains. Reflected light, nicols +, 300 \times

Fig. 2. Character of the distribution of metallic particles (white) in molybdenum sesquisulfide. *a* –450 \times , *b* –1350 \times

Mo_2S_3 saturated with the finest (~ 0.001 mm) molybdenum particles. These particles had a rounded, elongated, or dendrite-like shape and were strictly uniformly distributed in the grains of the sesquisulfide (Fig. 2). Their quantitative content was always close and averaged 28% of the volume of the enclosing grains.

Table 1

Interplanar spacings of Mo_2S_3 .
Fe anticathode, $D = 57.3$ mm

No.	I^*	d/n	No.	I	d/n	No.	I	d/n
1	w.	5.97	16	v. w.	2.15	31	v. w.	1.53
2	s.	5.38	17	w.	2.11	32	v. w.	1.515
3	w.	4.19	18	med.	2.08	33	v. w.	1.49
4	v. w.	3.28	19	w.	2.02	34	med. s.	1.44
5	v. w.	3.09	20	s.	1.95	35	w.	1.40
6	med.	2.98	21	med.	1.91	36	med.	1.38
7	w.	2.79	22	w.	1.88	37	med. s.	1.35
8	w.	2.70	23	v. w.	1.85	38	w.	1.30
9	v. w.	2.58	24	w.	1.83	39	w.	1.278

No.	I^*	d/n	No.	I	d/n	No.	I	d/n
10	w.	2.53	25	s.	1.70	40	v. w.	1.235
11	w.	2.44	26	w.	1.68	41	w.	1.205
12	v. w.	2.33	27	v. w.	1.64	42	med.	1.186
13	s.	2.28	28	w.	1.62	43	s.	1.164
14	w.	2.22	29	w.	1.59	44	v. w.	1.157
15	w.	2.20	30	v. w.	1.56	45	w.	1.138

* W. = weak, v. w. = very weak, med. = medium, s. = strong.

Such a regular distribution of metallic inclusions is due to the simultaneous crystallization of the metal and the sesquisulfide from the melt. This is also supported by the fact that precipitates of Mo_2S_3 saturated with metallic particles are, as a rule, located in the spaces between pure Mo_2S_3 crystals, playing the role of a cementing bond.

Consequently, with an excess of molybdenum relative to the stoichiometric content for Mo_2S_2 , a liquid sulfide phase arose in the mixtures already at temperatures below 1400° . Judging from the quantitative content of metallic particles in the grains of the sesquisulfide, its composition corresponded to the formula Mo_4S_3 .

Molybdenum in this melt was naturally present in the form of ions of lower (below 3+) valences. On cooling, these ions decomposed with the formation of metallic particles and simultaneous crystallization of molybdenum sesquisulfide.

Thus, it may be concluded that in the Mo–S system no sulfide lower than Mo_2S_3 is formed.

Chelyabinsk Scientific Research
Institute of Metallurgy

Received
5 XII 1963

REFERENCES CITED

1. C. L. McCabe, Trans. AIME, **203**, 61 (1905).
2. A. N. Zelikman, O. E. Krein, ZhFKh, **29**, issue 11, 2081 (1955).
3. A. N. Zelikman, L. V. Belyaevskaya, ZhNKh, **1**, issue 10, 2239 (1956).
4. Ya. N. Gerasimov, A. N. Krestovnikov, S. A. Shakhov, *Chemical Thermodynamics in Nonferrous Metallurgy*, 3, Moscow, 1963.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.