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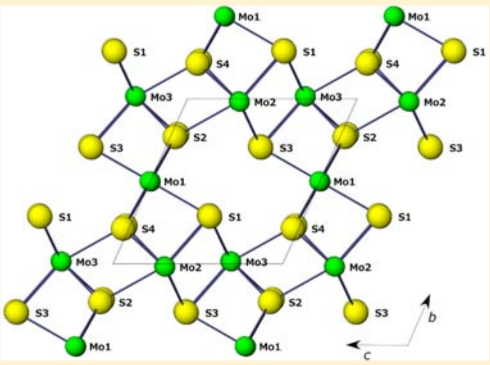
New Polymorph of Mo_3S_4 Prepared using a High-pressure Synthesis Technique: Crystal Structure, Electronic Property, and Band Calculation

Hiroshi Fukuoka,* Kumi Masuoka, Teruhiko Hanaoka, and Kei Inumaru

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Ⓢ *Supporting Information*



ABSTRACT: A new polymorph of Mo_3S_4 was synthesized at 13 GPa and 1450 °C from a stoichiometric mixture of elements. It crystallizes in a triclinic unit cell (space group $P\bar{1}$ (No. 2)) with cell constants of $a = 6.364(2)$ Å, $b = 6.608(2)$ Å, $c = 6.809(2)$ Å, $\alpha = 103.899(3)$ °, $\beta = 117.753(3)$ °, $\gamma = 103.958(3)$ °, and $V = 224.25(13)$ Å^3. The structure of Mo_3S_4 is composed of edge- and face-sharing MoS_6 octahedra. It was closely related to the structure of MMo_2S_4 type compounds (M = V, Cr, Fe, and Co). Mo_3S_4 can be regarded as a derivative with M = Mo. The calculated density of 6.160 g/cm^3 was much larger than 5.191 g/cm^3 of famous polymorphic Mo_6S_8 (Chevrel phase). Mo_3S_4 was metallic and did not show any superconducting transition down to 2 K. The bond-valence sums suggested that Mo_3S_4 can be classified in the class III−B of mixed-valence compounds; all Mo ions have a similar nonintegral valence. Electronic structure calculations revealed that the conduction band of Mo_3S_4 contains much contribution of the relatively narrow Mo 4d bands as well as the bands composed of hybridized Mo4d−S3d orbitals.

■ INTRODUCTION

Transition metals (M) often form M_3S_4 type sulfides having the Cr_3S_4 structure or its related ones, which are composed of corner- and face-sharing MS_6 octahedra. The M sites in the structures can be substituted by a different kind of transition element (M′), and this leads to ternary sulfides $M'_xM_{3-x}S_4$.[1−12] In the compounds, the site distribution of M and M′ atoms for the original M sites depends on the combination of the elements. In some compounds M and M′ atoms exclusively occupy different original M sites, and in other cases those atoms randomly occupy all or some original M sites.

Molybdenum is known to form $M'Mo_2S_4$ compounds with some 3*d* elements such as V, Cr, Fe, and Co.[7−12] Their structures are closely related to that of Cr_3S_4. However, the binary molybdenum sulfides Mo_3S_4 with the Cr_3S_4 structure have never been reported. Instead, molybdenum forms a famous Chevrel compound Mo_6S_8 (= Mo_3S_4).[13−16] The Chevrel compounds including ternary AMo_6X_8, where A is guest species and X = S and Se, attract much attention due to their unique structure (Mo_6 clusters). Most of them show interesting physical properties such as superconductivity with very high upper critical field H_{c2} and reentrant superconductivity.[17−24]

The guest-free compound Mo_6S_8 is usually prepared by the reactions of $NiMo_6S_8$ or $CuMo_6S_8$ with dilute mineral acids, or by anodic oxidation of these ternary compounds.[13,14] It contains large empty channels, since the guest atoms in Chevrel compounds are situated in large spaces among the Mo_6 cluster. Such a hollow structure would reduce the stability of lattice energy. This would be a reason why it is difficult to prepare Mo_6S_8 directly from molybdenum and sulfur. Here a question arises: why binary molybdenum sulfide Mo_3S_4 with the Cr_3S_4-like structure does not exist. One plausible reason is that Mo_2S_3 is thermodynamically very stable and Mo_3S_4 disproportionates into Mo_2S_3 and S at ambient pressure.

We have, therefore, investigated the reaction of molybdenum and sulfur under high-pressure conditions. High pressure synthesis is one of the most powerful methods to produce new materials. We have applied this technique on the preparation of new materials in silicide, germanide, and sulfide systems.[25−30] It sometimes enables us to produce unique structures that cannot be obtained under ambient pressure.[29,30] In the previous studies, we succeeded in preparing four new chromium sulfides.[31,32] Their structures were solved and refined by X-ray single crystal analysis. Recently, interesting vanadium sulfides with a Cr_3S_4 related structure have been prepared under high pressure by Klein et al.[33]

In the present study, we have successfully obtained the target compound Mo_3S_4, whose structure is closely related to that of Cr_3S_4. This is the first polymorph of the Chevrel compound Mo_6S_8. We report the high-pressure synthesis, structure, electrical property, and band structure calculations of the new binary sulfide Mo_3S_4.

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■ EXPERIMENTAL SECTION

Synthesis. A mixture of Mo (Rare Metallic co. Ltd. 99.99%) and S (Rare Metallic Co. Ltd. 99.999%) with a molar ratio of 3: 4 was well ground with an agate mortar, and was placed in an h-BN cell. It was heated at 1450 °C under a pressure of 13 GPa using a multi anvil press. After the reactions, the samples were quenched to room temperature. The detailed assembly of our high-pressure cell and the press was described elsewhere.[34]

Characterization. The products were characterized by X-ray powder diffraction (XRD) measurements with a Bruker AXS D8 Advance diffractometer with Ni-filtered Cu Kα radiation. The structure analysis was carried out on a single crystal with a size of $0.02\times 0.04 \times 0.06$ mm^3. The X-ray diffraction data were collected using a Bruker APEX II CCD area detector diffractometer with graphite-monochromated Mo Kα radiation at room temperature. The total exposure time was 4 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.[35] Data were corrected for absorption effects using the multiscan method (SADABS).[36] The ratio of minimum to maximum apparent transmission was 0.859. The structure was solved and refined using the Bruker SHELXTL software package.[37]

Chemical compositions of the products were examined by an electron probe micro analyzer (EPMA) (JEOL JCMA-733). Temperature dependence of electrical resistivity was measured from 300 to 2 K by the four-probe method with silver paste contacts using Quantum Design MPMS-5.

The band structure calculation was performed using the WIEN2k package with a general potential LAPW code.[38,39] Some parameters used were as follows: RMT, 2.40 for Mo and 2.06 for S; Gmax, 12; RMT × kmax, 9; number of k points, 2000.

■ RESULTS AND DISCUSSION

We obtained black polycrystalline bulk products from the high-pressure and high-temperature reactions. A powder XRD pattern of the product prepared by a reaction of Mo and S at 13 GPa and 1450 °C is shown in Figure 1. The main diffraction peaks could not be assigned to any known compounds, though some peaks of Mo_2S_3 and Mo were detected as minor products. The peak pattern of the unknown phase is very similar to those of $CoMo_2S_4$ and VMo_2S_4.[7−12] The new phase is stable at ambient pressure and moisture at room temperature.

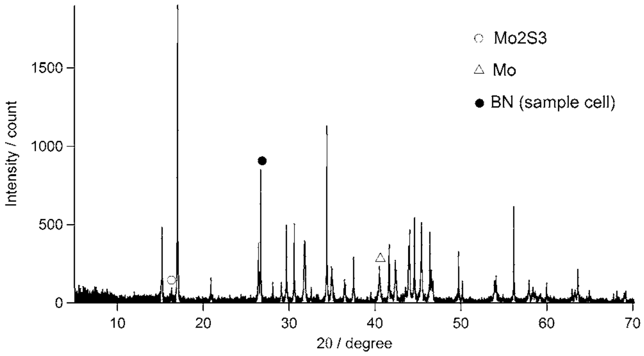

Figure 1. Powder XRD pattern of a new compound with small amounts of impurities; ○: Mo_2S_3, Δ: Mo, and ●: BN (used as the reaction cell).

Figure 2 shows an image obtained by electron probe microanalysis. The composition of the main phase was determined to be Mo/S = 3:4.1, and the unknown phase was regarded as a new polymorph of the well-known Chevrel phase Mo_6S_8. Small amounts of Mo_2S_3 and Mo were also detected. Additionally, a tiny amount of an unknown phase with the composition of Mo_2S was found.

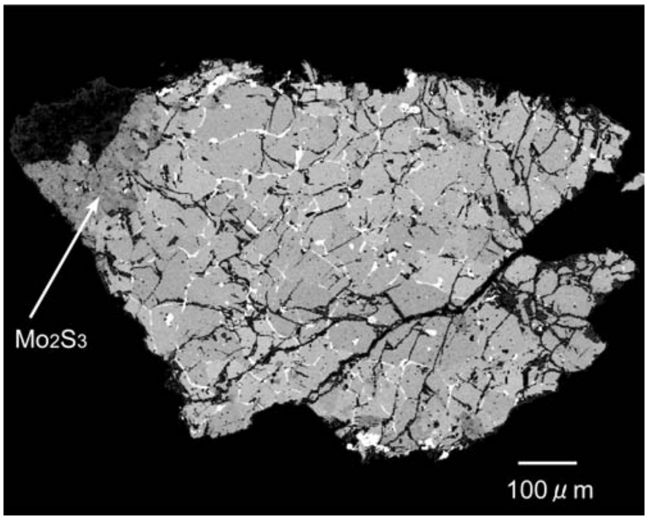

Figure 2. Composition image of the Mo_3S_4 sample by EPMA. Black lines are cracks on the sample surface. White areas mainly correspond to Mo metal. Gray area except for that pointed by an arrow shows the composition of Mo/S = 3:4.1.

To determine the crystal structure, we performed single crystal structure analysis. We picked up more than 10 crystals from the as-prepared products to determine the cell constants, and finally obtained a crystal with the size of 0.02 × 0.04 × 0.06 mm suitable for the structure determination. The crystallographic data and atomic and thermal displacement parameters of Mo_3S_4 are listed in Tables 1 and 2. Mo_3S_4 crystallizes in a triclinic unit cell (space group $P\overline{1}$ (No. 2)) with cell constants of a = 6.364(2) Å, b = 6.608(2) Å, c = 6.809(2) Å, α = 103.899(3) °, β = 117.753(3) °, γ = 103.958(3) °, and V = 224.25(13) Å^3. The powder X-ray diffraction peaks in Figure 1 can be indexed with these lattice constants. Calculated lattice constants using the diffraction data of Figure 1 are a = 6.364(3) Å, b = 6.604(2) Å, c = 6.808(3) Å, α = 103.93(3) °, β =

Table 1. Crystallographic Data and Details on the Structure Determination of Mo_3S_4

Formula	Mo_3S_4
Formula weight	416.06
Space group	$P\overline{1}$ (No. 2)
a/Å	6.364(2)
b/Å	6.608(2)
c/Å	6.809(2)
α/°	103.899(3)
β/°	117.753(3)
γ/°	103.958(3)
V /Å^3	224.25(13)
Z	2
Crystal size (mm)	0.02 × 0.04 × 0.06
Diffractometer	Bruker APEX-II CCD
Radiation (graphite monochromated)	Mo Kα
μ(Mo Kα)/mm^{-1}	9.923
2θ limit	47
No. of observed unique reflections	652
No. of variables	64
$R1$, $wR2$ for all data	0.0224, 0.0589
Godness of fit, S	1.137
Largest diff. peak and hole	1.73/−1.53

Table 2. Atomic Coordinates and Thermal Displacement Parameters for Mo_3S_4

atom	*x*	*y*	*z*	*Ueq*
Mo1	0.27920(10)	0.00147(8)	0.50321(9)	0.0083(2)
Mo2	0.45364(10)	0.48276(8)	0.18129(9)	0.0048(2)
Mo3	0.97490(10)	0.48563(8)	0.19147(9)	0.0049(2)
S1	0.5307(2)	0.2127(2)	0.9482(2)	0.0056(2)
S2	0.0542(2)	0.2693(2)	0.4722(2)	0.0057(2)
S3	0.9837(2)	0.7946(2)	0.0635(2)	0.0059(2)
S4	0.4454(2)	0.7149(2)	0.5320(2)	0.0053(2)

117.70(2) °, γ = 103.96(3) °, and V = 224.2 (2) Å^3. They are identical to the above values within the experimental error.

The crystal structure of Mo_3S_4 is presented in Figure 3. The structure is completely different from that of the Chevrel phase. Mo_3S_4 is composed of edge and face sharing MoS_6 octahedra, while an octahedral Mo_6 cluster is the structural unit of the Chevrel phase. The calculated density of Mo_3S_4 is 6.161 g/cm^3, which is much larger than 5.191 g/cm^3 of the Chevrel phase. The new Mo_3S_4 is a high-pressure phase and cannot be prepared under ambient pressure.

The structure of Mo_3S_4 is constructed with crystallographically independent three molybdenum and four sulfur sites. It is closely related to that of the Cr_3S_4 structure, which can be regarded as a cation-deficient NiAs structure. The NiAs structure contains hexagonally closed-packed anion layers, and cations occupy all octahedral sites between the anion layers. In the Cr_3S_4 structure, half of the octahedral layers are cation deficient, and the fully and half occupied layers are alternately stacked up to form the whole structure. Therefore, the Mo2 and Mo3 sites in the fully occupied layers of Mo_3S_4 form MoS_6 octahedra sharing three edges and one face, while the Mo1 sites in the half occupied layers form octahedra sharing two opposite faces as shown in Figure 3a.

Mo_3S_4 also can be seen as a derivative of $M'Mo_2S_4$ type compounds with the case of M′ = Mo. Their structures are very similar to each other. The Mo1 site in Mo_3S_4 corresponds to the guest cation (M′) site in $M'Mo_2S_4$ compounds. The lattice symmetry for Mo_3S_4 (triclinic) is, however, lower than those for $M'Mo_2S_4$ compounds (monoclinic). The Mo1(Mo3) and Mo2(Mo4) sites in $CoMo_3S_4$ (monoclinic, *Cc*) are merged into the Mo2 (Mo3) site in Mo_3S_4.

The difference in crystal system is possibly caused by the difference of the charge distribution among cations. In $M'Mo_2S_4$ compounds, the oxidation state of M′ ions is 2+ and the charge distribution for cation sites is M'^{2+} [Mo^{3+}, Mo^{3+}]. In contrast to it, Mo_3S_4 is a mixed valence compound. We tried to estimate the charge distribution of molybdenum ions using the bond-valence sum (BVS) method. Mo−S distances in Mo_3S_4 are in the range of 2.373(2) to 2.617(2) Å. We calculated the valence V for each molybdenum site using the equations

$$V = \sum s$$

and

$$s = (R/R_0)^{-N}$$

where R_0 = 2.167 and N = 5.8 according to the review of Brown.[40,41] The BVSs for the Mo2 and Mo3 sites are +2.87 and +2.85, respectively. The BVS for the Mo1 site is +2.97, which is slightly larger than those for the Mo2 and Mo3 sites. The difference between them, however, are very small and Mo_3S_4 can be categorized into Class III−B, that is, all Mo sites have almost the same oxidation number (+2.66).

The fact that Mo_3S_4 shows almost temperature-independent paramagnetism (2.0×10^{-6} emu g^{-1}) offers evidence for this categorization. This type of magnetism is well-known as Pauli paramagnetism for metal compounds. The *d* electrons in Mo_3S_4 would be delocalized through *d*-bands and become itinerant electrons. The detailed electronic structure of Mo_3S_4 is discussed below using the results of band calculations.

The total value of BVSs for all sites (+8.69) is larger than +8 calculated from the composition. This discrepancy would be due to the fact that Mo_3S_4 was prepared under very high pressure conditions. For such compounds, a larger R_0 value should be used for the average Mo−S distance.[42]

Figure 4 shows the temperature dependence of the electrical resistivity of Mo_3S_4 measured on a sample prepared by polishing the obtained bulk product with sandpaper. Mo_3S_4 is metallic like a Chevrel compound Mo_6S_8 as it can be expected

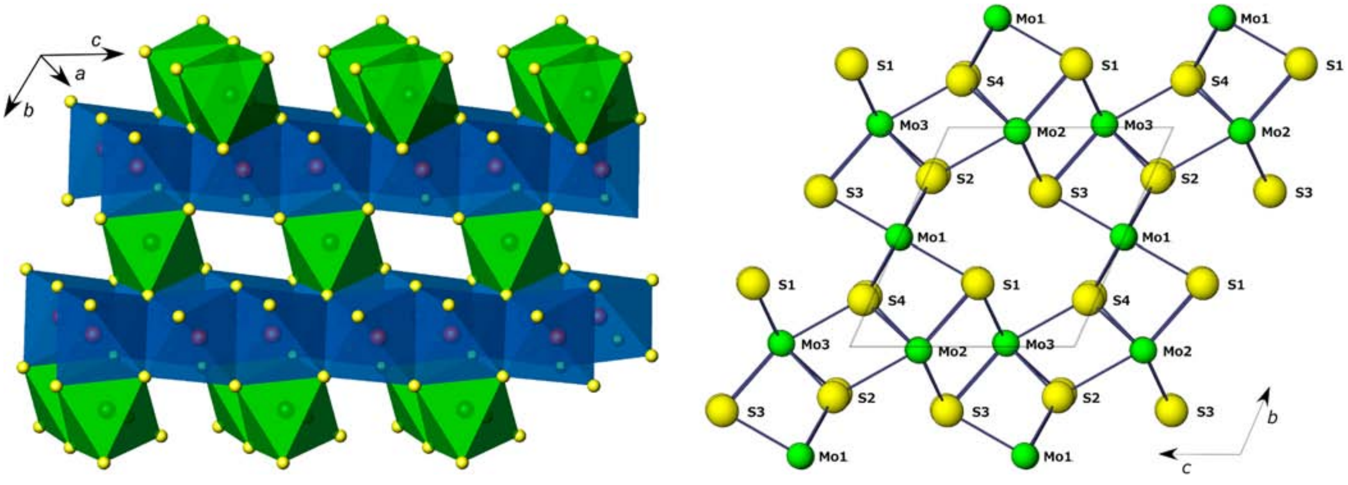

Figure 3. (a) Crystal structure of Mo_3S_4 depicted in a polyhedral model. Yellow spheres show sulfur atoms. Green polyhedra represent Mo1 octahedra, and blue ones represent Mo2 and Mo3 octahedra. (b) Ball and stick representation of the Mo_3S_4 structure projected along the *b*-axis. Green and yellow spheres show molybdenum and sulfur atoms, respectively.

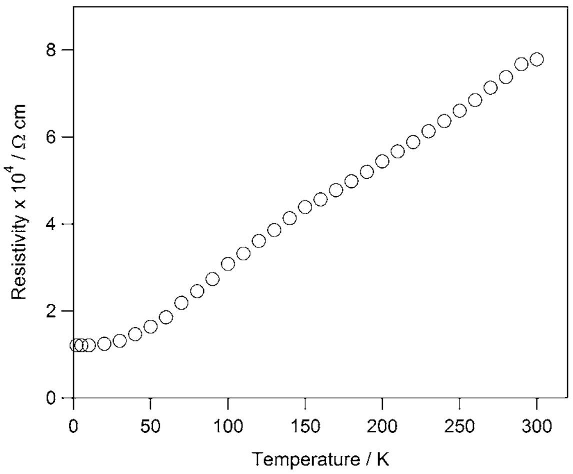

Figure 4. Temperature dependence of electric resistivity of Mo_3S_4.

from its magnetic property. Mo_3S_4 does not show any superconducting transition down to 2 K.

We calculated the electronic structure of Mo_3S_4 using a software program Wien2k. The calculated total and partial (Mo, S, and Mo 4d) density of states (DOS) are shown in Figure 5.

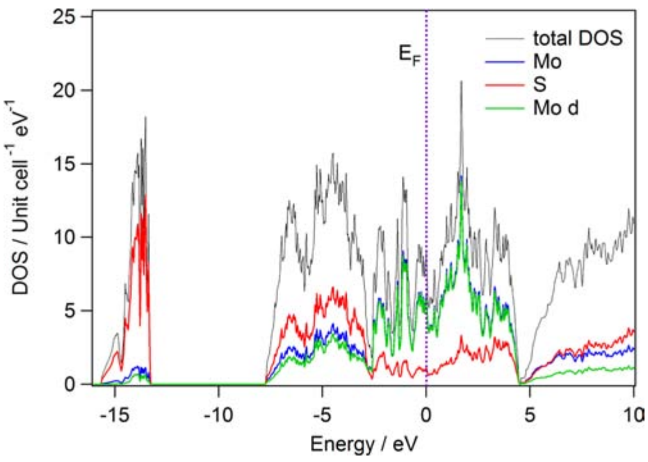

Figure 5. The total and partial DOS of Mo_3S_4. The total, Mo and S partial, and Mo-*d* partial DOS are displayed in black, blue, red, and green, respectively.

The total DOS confirmed the metallic property of Mo_3S_4. The band around −15 eV is mainly composed of S 3*p* orbitals. In contrast, the states at the vicinity of Fermi level (E_F) are mainly contributed by Mo 4*d* bands as well as hybridized bands between Mo 4*d* and S 3*p* orbitals.

It is noteworthy that $M'Mo_2S_4$ compounds except Mo_3S_4 are not metallic but semiconducting. Canadell and Vaqueiro et al. discussed the reason why $M'Mo_2S_4$ become semiconductors.[12,43] They concluded that a Peierls distortion is induced by half-filled t_{2g} block bands of Mo^{3+} ions. The distortion results in the opening of a gap at the E_F as well as the formation of diamond-type clusters of cations.

In the case of Mo_3S_4, the oxidation state of Mo ions is not 3+ but is a nonintegral value. Furthermore, large 4*d* orbitals can be overlapped to form more stable *d* bands than those of 3*d* metal $M'Mo_2S_4$ compounds. These would be the reasons why no Peierls distortion is induced in Mo_3S_4 and the metallic property is maintained at least down to 2 K. In fact, the unit cell of Mo_3S_4 is the most fundamental one and different from those for other $M'Mo_2S_4$ compounds.

The importance of M−M zigzag chains for metallic behavior was comprehensively discussed in several chalcogenides by Canadell et al.[43] To emphasize the Mo network in Mo_3S_4, a skeletal view of Mo_3S_4 structure is shown in Figure 6, where solid lines indicate Mo−Mo separations shorter than 3 Å. The distances between Mo1−Mo1, Mo2−Mo2, Mo2−Mo3, and Mo3−Mo3 are 2.836, 2.839, 2.830, and 2.815 Å, respectively. Interestingly, zigzag chains of $[-Mo2-Mo2-Mo3-Mo3-]_\infty$ can be seen in the structure but no dimerization is observed. This structural feature is very different from those for the $M'Mo_2S_4$ compounds as reported by Vaqueiro et al.[14] In these compounds, the Mo−Mo chains are deformed to make chains composed of diamond- and triangular-type clusters. Due to the distortion, the unit cell size of $M'Mo_2S_4$ is 4 times as large as that of Mo_3S_4. This is a Peierls distortion and the half-filled t_{2g} block bands of $M'Mo_2S_4$ form two split bands separated by a band gap. The absence of this type of distortion is probably the reason why only Mo_3S_4 becomes metallic.

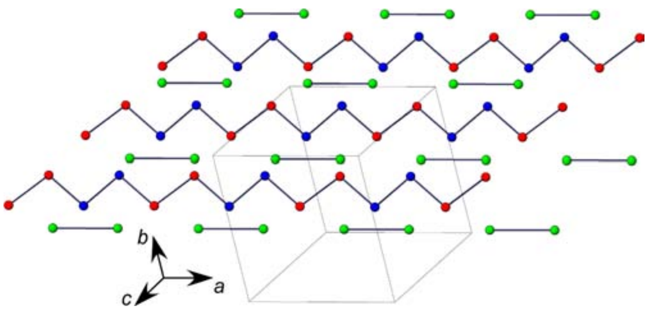

Figure 6. Arrangement of Mo atoms of Mo_3S_4 is shown in a skeletal presentation. The Mo1, 2, and 3 sites are shown by green, red, and blue balls, respectively. Solid lines indicate Mo−Mo separations shorter than 3 Å.

The arrangement of Mo1−Mo1 atoms shows alternately long and short separations along the *a* axis. The long separation of 3.529 Å is much longer than the short one. Therefore, the direct interaction of Mo1−Mo1 4d orbitals would have small contribution to the metallic property.

■ CONCLUSIONS

We succeeded in preparing a new binary molybdenum sulfide Mo_3S_4. It is the first polymorph of the famous Mo_6S_8 (Chevrel phase). The structure of Mo_3S_4 is closely related to those of $M'Mo_2S_4$ compounds and is composed of face- and edge-sharing MoS_6 octahedra. Mo_3S_4 is metallic in the range of 2 K to room temperature. The electronic structure calculation confirmed the metallic band structure, and BVS suggested it is a mixed valent compound categorized into the Class III−B.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic Information File. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +81-824-24-7742. Fax: +81-824-24-5494. E-mail: hfukuoka@hiroshima-u.ac.jp.

Notes

The authors declare no competing financial interest.

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