Preparation of TaS₃ under High Pressure

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Monoclinic TaS_3 is prepared without the coexistence of the orthorhombic TaS_3 and TaS_2 under high pressure in a cubic anvil device. Lattice parameters are $a = 9.552$ Å, $b = 3.345$ Å, $c = 14.925$ Å and $\beta = 109.98°$. The compound is a semiconductor with transitions at 200 and 250 K.

Introduction

Among the transition metal chalcogenides of group IV and V, their di- and trichalcogenides are the compounds containing relatively large amounts of chalcogen. These compounds have highly anisotropic structural units separated by rather large distances, generally of the order of the van der Waals radii (*1*). The dichalcogenides have layered structural units in which the transition metal ions reside between two hexagonally close-packed chalcogen layers. These metal ions are either in sites of octahedral symmetry or in ones of trigonal prismatic symmetry. On the other hand, a general feature of the structures of the trichalcogenides is a linear stacking of trigonal prisms of chalcogen atoms parallel to the chain axis with the transition metal atom located at about the center of the prism. The structural anisotropy results in a very high anisotropy in the electronic, vibrational, and mechanical properties. Thus these compounds attract attentions of the people who are interested in low-dimensional properties. They are usually prepared by heating the mixtures of metal and chalcogen in a sealed tube. It is difficult to obtain these compounds as single phase

because di- and trichalcogenides crystallize together in the same reaction vessel and frequently contaminate each other.

In this paper, we report the application of high-pressure technique to obtain TaS_3 or the compound containing more amount of sulfur than trisulfide as a single phase. As a result we could obtain a modification of TaS_3 which is different from that prepared by the usual sealed-tube method.

Experimental

Tantalum and sulfur powders were mixed in desired ratios. The mixtures were placed inside carbon heaters separated by BN sleeves. These assemblages were inserted in pyrophyllite cubes and subjected to high-temperature–pressure conditions using a cubic anvil device. The reactions were conducted for 30 min under the conditions summarized in Table I. On the other hand, the mixture of Ta and S with a ratio Ta/S = ¼ was also sealed in an evacuated quartz tube and heated in a temperature gradient of 700°C/620°C for 1 week. Fibrous TaS_3 crystals were obtained and hexagonal platelets of TaS_2 were also observed in the same reaction tube. The products were characterized by X-ray powder diffractometry, electrical conductivity and TG-DTA.

Results

The products obtained under respective conditions listed in Table I were black and metallic lustrous compounds. X-Ray diffractometry showed that the unknown phase X was obtained in the runs 1–7 and TaS_2 was obtained in run 8. However, in run 7 coexisting Ta was observed. The phase X has the chemical composition nearly of TaS_3 judging from the mixing ratios of the starting powders. To remove excess sulfur from the products, all products for the runs from 1–5 were sealed in evacuated tubes and heated at 160°C for 1 week. Excess sulfur was deposited at a cooler end of the sealed tubes. No change was observed in X-ray diffraction patterns after the heating, but a very small amount of TaS_2 appeared after the further heating. Differential thermal analysis was conducted up to 1000°C in air on the purified product with the heating rate of 10°C/min. Small exothermic peaks were observed at about 300 and 400°C. Gradual weight loss began above 200°C and the total weight loss up to 1000°C was about 22%. The sample had converted to Ta_2O_5 due to the heating. The calculated weight loss is 21% for the conversion from TaS_3 to Ta_2O_5.

Figure 1 shows X-ray diffraction diagrams for both TaS_3 prepared under pressure and obtained in a sealed tube. Both diagrams are a little complicated, but that for TaS_3 prepared by the sealed-tube method can be indexed as orthorhombic $C222_1$, which was reported by Bjerkelund and Kjekshus (2). Diffraction lines for $h00$ and $0k0$ are intense because of sample orientation. A very small amount of TaS_2 coexists with this phase. TaS_3 obtained under high pressure is indexed as monoclinic, and its X-ray diffraction data are presented in Table II. The lattice parameters were determined as follows by a least-squares method using the computer program LCLSQ compiled to "CRC" system

TABLE I

REACTION CONDITIONS OF THE SYSTEM Ta–S

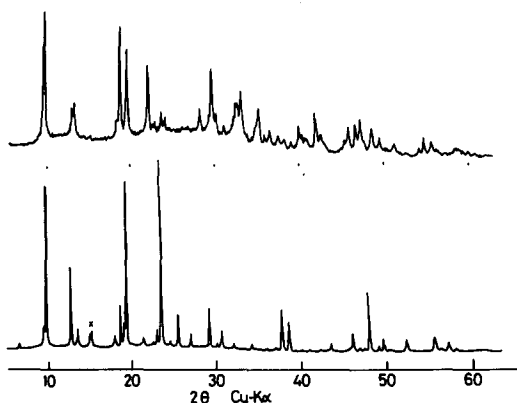| Run	Ta/S ratio	Temperature (°C)	Pressure (GPa)	Product
1	1/10	700	2	Phase X
2	1/6	900	1	
3	1/4	900	3	
4	1/4	900	1	
5	1/4	700	2	
6	1/3	700	2	
7	1/2.8	700	2	Phase X, Ta
8	1/2	700	2	TaS_2

FIG. 1. X-Ray powder diffraction diagrams for both TaS₃ prepared under pressure (above) and in a sealed tube (below). The reflections marked with × are assigned to the coexisting TaS₂.

of Osaka University; $a = 9.552$, $b = 3.345$, $c = 14.925$ Å and $\beta = 109.98°$. The X-ray density of 6.18 g/cm³ was obtained. There have been reported orthorhombic and monoclinic modifications of TaS₃ prepared in sealed ampoule. The crystal data of TaS₃ obtained under pressure are summarized in Table III comparing with those of other modifications of TaS₃.

Electrical resistivities were measured using the four-point contact method in the temperature range 77–290 K on a disk of TaS₃ prepared under pressure and on a fibrous TaS₃ crystal obtained in a sealed tube. The results are shown in Fig. 2. The orthorhombic phase was semiconductive. Metallic temperature dependence already reported by other investigators (4) could not be observed in the present study. The monoclinic phase was a semiconductor having a resistivity of 5×10^{-2} ohm cm at room temperature. Two phase transitions were observed at around 200 and at 250 K.

Orthorhombic TaS₃ was pressed under 2 GPa for 30 min at room temperature and 700°C to know the relation between the monoclinic and the orthorhombic phases. No phase change could be observed at room temperature, but orthorhombic TaS₃

TABLE II

X-RAY POWDER DATA FOR MONOCLINIC TaS₃

hkl	d_{obs}	d_{calc}	I
100	9.0267	8.9491	s
10$\bar{2}$	6.7679	6.7528	w
101	6.6216	6.5920	w
102	4.7841	4.7835	w
003	4.6839	4.6756	s
200	4.4778	4.4745	s
20$\bar{3}$	3.9867	3.9832	m
10$\bar{4}$	3.7292	3.7259	w
103	3.6671	3.6623	w
20$\bar{4}$	3.3794	3.3764	vvw
010	3.3347	3.3453	vvw
202	3.2959	3.2960	vvw
110	3.1389	3.1335	w
30$\bar{3}$	3.0243	3.0271	w
11$\bar{2}$	2.9857	2.9976	s
104	2.9434	2.9414	w
20$\bar{5}$	2.8571	2.8563	vw
203	2.7902	2.7913	vvw
11$\bar{3}$	2.7584	2.7602	vw
21$\bar{1}$	2.7338	2.7369	w
013	2.7257	2.7206	w
21$\bar{2}$	2.6875	2.6933	s
21$\bar{3}$	2.5629	2.5617	w
211	2.5383	2.5378	m
11$\bar{4}$	2.4906	2.4892	vw
105 20$\bar{6}$	2.4479	2.4488 2.4427	w
204	2.3883	2.3918	vw
40$\bar{2}$ 21$\bar{4}$	2.3761	2.3798 2.3764	vw
006	2.3375	2.3378	vw
31$\bar{1}$	2.2950	2.2912	vvw
30$\bar{6}$	2.2451	2.2509	w
11$\bar{5}$ 310	2.2265	2.2267 2.2264	w
303	2.2004	2.1973	w
213 40$\bar{5}$	2.1430	2.1432 2.1419	m
20$\bar{7}$	2.1176	2.1187	w
401	2.1002	2.1005	w
30$\bar{7}$ 31$\bar{5}$	2.0111	2.0120 2.0115	vvw
11$\bar{6}$	1.9906	1.9914	w
21$\bar{6}$	1.9742	1.9728	m
41$\bar{2}$	1.9383	1.9392	m
01$\bar{6}$ 41$\bar{1}$	1.9159	1.9163 1.9158	m
50$\bar{3}$	1.9031	1.9026	w
31$\bar{6}$	1.8671	1.8675	m

TABLE III

LATTICE PARAMETERS OF TaS₃ MODIFICATIONS

	Orthorhombic (Ref. (3))		Monoclinic (this work)	Monoclinic (Ref. (6–8))
a (Å)		36.804	9.522	9.515
b (Å)		15.173	3.345	3.3412
c (Å)		3.340	14.925	14.912
β (°)			109.98	109.99
V (Å³)		1865.15	446.8	445.5
Z		24		6
Space group		$C222_1$		$P2_1/m$

was converted to monoclinic TaS₃ and a small amount of TaS₂ at 700°C. When the monoclinic phase was heated at 700°C in an evacuated tube for 2 days, it was partly changed to the orthorhombic phase and excess sulfur deposited in a cooler end of the tube. After further heating at 700°C for 4 days, the sample decomposed to TaS₂.

Discussion

Zirconium triselenide has the simplest crystal structure among the group of transition metal trichalcogenides (1). The chains of [ZrSe₆] trigonal prism extend along the b axis as illustrated in Fig. 3. They are shifted by $b/2$ each other and crosslinked by the bonding Zr with Se in the neighboring chains to form a layer of ZrSe₃ in the a–b plane. The layers are separated in the order of van der Waals radii. There are two kinds of Se in the trigonal prism of [ZrSe₆]. A triangle of Se is made of a pair (Se–Se)²⁻ and a Se²⁻ ion. It is well known, as can be appreciated from the crystal structure, that ZrSe₃ is effectively $Zr^{4+}(Se_2)^{2-}Se^{2-}$. This compound is a diamagnetic semiconductor.
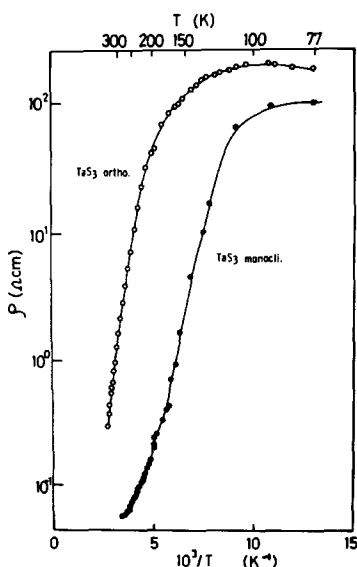

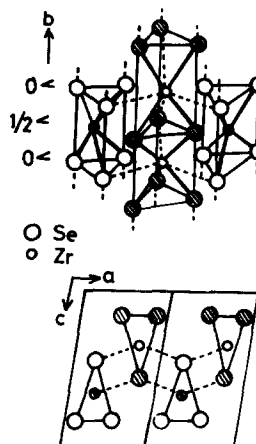FIG. 2. Temperature dependences of electrical resistivities for orthorhombic and monoclinic TaS₃.

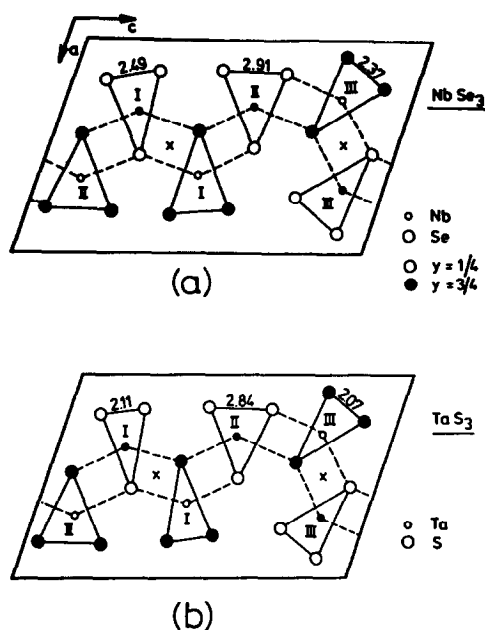FIG. 3. Crystal structure of ZrSe₃. Open circles are at 0 and shaded ones are at $\frac{1}{2}b$.

FIG. 4. The monoclinic structure of NbSe₃ (a) and TaS₃ (b) projected along [010]. The Se–Se and S–S distances are indicated in angstroms.

Other trichalcogenides have crystal structures similar to that of $ZrSe_3$. For example, $NbSe_3$ shows a reduction of crystal symmetry because of the strains within and between the $[NbSe_6]$ trigonal prisms. There are three kinds of trigonal prisms in a unit cell as shown in Fig. 4a (5, 6).

The structure of orthorhombic TaS_3 has not yet been determined. The unit cell is large and contains 24 chains (2). There might be a more or less continuous spread of the S–S bonding in the different chains due to the large number of chains in the unit cell as recently predicted by Roucau et al. (7). Meerschaut et al. found that a monoclinic TaS_3 which is isostructural to $NbSe_3$ can be prepared together with orthorhombic one as a minor phase (3). The unit cell of this monoclinic structure is determined as shown in Fig. 4b (8). It has three kinds of six chains. There are two short distances S–S of 2.07 and 2.11 Å leading to a covalent bonding $(S_2)^{2-}$ and a long one of 2.84 Å. Columns I and III respectively form pairs

and they are interconnected through column II. It is not clear whether TaS_3 prepared in the present study is exactly the same as that found by Meerschaut et al. (3). They seem to be very similar judging from their lattice constants. The application of static pressure to the preparation of TaS_3 enhanced the structural regularity. TaS_3 prepared under pressure has only three kinds of S–S bonding but the orthorhombic phase has a distribution of S–S bonding.

On the other hand, the relationship between orthorhombic and monoclinic phases might be explained by nonstoichiometry. A nonstoichiometry in trichalcogenides has already been considered by Jellinek et al. (8). A simple model is proposed assuming a replacement of some $(S_2)^{2-}$ groups by S^{2-} ions in the $MS(S_2)$ formula. This would lead to a sulfur-deficient MS_{3-x}. The vapor pressure of sulfur is not so high in a sealed tube. In this case, the sulfur-deficient phase might be obtained. However, the sulfur vapor pressure can be raised high enough to obtain the stoichiometric trichalcogenide in a small reaction chamber of cubic anvil device. The high-pressure phase of TaS_3 has an X-ray density of 6.18 g/cm³ which is larger than 5.92 g/cm³ for the orthorhombic phase (2).

The semiconductive properties of the present monoclinic TaS_3 might be explained as a one-dimensional conductor having a Peierls transition temperature at about 250 K. Peierls transition has already been observed on the orthorhombic TaS_3 by several investigators (4, 10). The transition is not clear in the present study and it seems to be sample dependent. Some of the samples showed the broad transition from metal to semiconductor above 300 K. However, two transitions were observed at 250 and 200 K in the monoclinic phase.

In conclusion, a monoclinic TaS_3 is prepared as a dense form under pressure higher than 1 GPa without the coexistence of the orthorhombic phase.

Acknowledgment

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