The Preparation of Ti_5S_8

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Ti_5S_8 (12R type), which had never been prepared in a pure state, was obtained as a single phase by the chemical-transport method. The conditions for the preparation were determined experimentally. The existence range of the phase was examined for composition and temperature.

Several phases have been reported in the TiS–TiS_2 composition range, namely, TiS (2H), Ti_8S_9 (9R), Ti_4S_5 (10H), Ti_3S_4 (21R), Ti_2S_3 (4H), Ti_5S_8 (12R), and TiS_2 (2H). (The designations in parenthesis indicate the structures in the Ramsdell notation.) Of these, the TiS phase is of the NiAs-type, while TiS_2 is of the CdI_2-type, structure. Both have a hexagonal close packed of sulfur. However, the intermediate phases have complex structures involving both the hexagonal and cubic packing of sulfur and varying stacking sequences, with a specific titanium-to-sulfur ratio. Titanium atoms are situated in the octahedral holes of the sulfur packing.

In spite of many reports on titanium sulfide, its phase diagram has not yet been established because of the variation in experimental data reported by many investigators, as has been pointed out by Jeannin[1] or Kjekshus and Pearson.[2] Furthermore, Tronc and Huber[3] reported that, at the composition of $Ti_{1.18}S_2$, there are many structures with different periods in the c-direction, *e.g.*, polytypism. These observations have indeed indicated that the titanium–sulfur system is complicated.

The existence of Ti_5S_8 has been reported by Jeannin,[4] Flink *et al.*,[5] and Tronc and Huber,[3] although it was not prepared by any of them as a single phase. They obtained it as a mixture with other structures, like Ti_2S_3 (4H type). We ourselves were not able to prepare Ti_5S_8 from the respective elements sealed in an evacuated silica tube. However, Ti_5S_8 was obtained as a single phase by the chemical-transport method when iodine was used as the transport agent. The aim of this paper is to describe the experimental conditions needed to obtain Ti_5S_8 as a single phase.

The preparation conditions of Ti_5S_8 will first be described, and then procedure for the identification of the obtained Ti_5S_8. Finally, the range of composition and temperature of Ti_5S_8 will be shown.

Results

Preparation Conditions. The preparation of Ti_5S_8 was performed according to the following procedure. The titanium sulfide (1.5 g), the composition and structure of which will be described later, and the iodine (0.15 g) were sealed in an evacuated silica tube 150 mm in length and 12 mm inner diameter. The tube was held in a horizontal resistance furnace, where the high-temperature end was set at 600 °C and the low-temperature end at 500 °C. The titanium sulfide was transported from the low- to the high-temperature side. The transported titanium sulfide was then deposited as plate-shaped, grey-black crystals.

To prepare Ti_5S_8 in a pure form by chemical transport, several important factors had to be ascertained: (1) the preparation temperature of the starting material, (2) the composition of the starting material, (3) the transport temperature, and (4) the iodine concentration. The specimen obtained by chemical transport was influenced by the following factors.

The Effect of the Preparation Temperature of the Starting Material. The synthesis of the titanium sulfide used as the starting material was carried out according to the following procedure. Titanium metal powder (purity, 99.0%) and sulfur (purity, 99.9999%) were mixed together in a calculated ratio; the mixture was then allowed to react for a few days at 350 °C, after which the temperature was raised to 500—900 °C. With respect to the composition in the range from $Ti_{1.38}S_2$ to $Ti_{1.16}S_2$, at 500 °C the structure of the specimen was of the 2H type; at 600—700 °C, a disordered stacking of the sulfur layers was detected, and above 800 °C the 4H type was the result. The 2H type specimen prepared at 500 °C might have been heterogeneous because of the incomplete reaction.

By using the 2H type as the starting material, the transport was found to take place, but when the starting materials prepared at a temperatures above 600 °C were used, transport did not occur. The reason for this was not clear. However, it can be seen from Table 1 that whether or not the transport take place is dependent on the crystal structure of the starting material.

The Effect of the Composition of the Starting Material. How the transport was influenced by the composition of the starting material was then examined. The curve in Fig. 1 shows the transport rate *versus* the composition of the starting material. As can be seen

TABLE 1. RELATION OF THE PREPARATION TEMPERATURE OF THE STARTING MATERIAL AND AVERAGE TRANSPORT RATE

Iodine concentration: 5.96 mg cm^{-3}, transport time: 144 h, composition of the starting material: $Ti_{1.21}S_2$, temperature: 500 °C (low-temperature end)→600 °C (high-temperature end).

Temp/°C	Structure	Transport rate/mg h^{-1}
500	TiS_2(2H) type	0.8
600	Random	Negligibly small
700	Random	Negligibly small
800	Ti_2S_3(4H) type	0
900	Ti_2S_3(4H) type	0

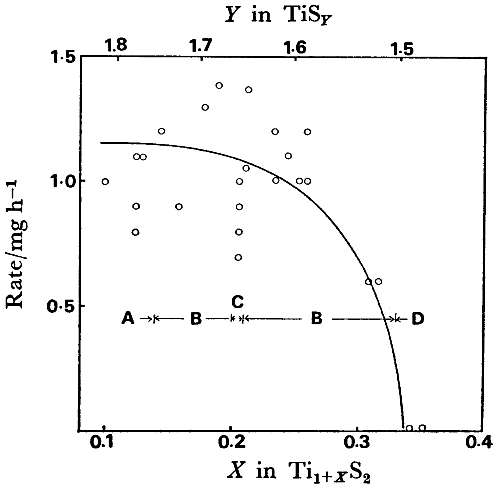

Fig. 1. Average transport rate versus composition of the starting material. (Iodine concentration: 5.96 mg cm^{-3}, transport time: 144 h, temperature: 500 °C(low temperature side)→600 °C(high temperature side)). A: Phase with disordered stacking of sulfur layers, B: mixed phase of Ti_2S_3 and Ti_5S_8, C: single phase of Ti_5S_8, D: no transport took place.

Table 2. Relation of the transport temperature and transported crystals

Iodine concentration: 5.96 mg cm^{-3}, transport time: 144 h, composition of the starting material: $Ti_{1.21}S_2$.

Temp/°C	Transported crystal
400→500	—
500→600	Ti_5S_8
600→700	$Ti_5S_8+Ti_2S_3$
700→800	$Ti_5S_8+Ti_2S_3$

from this figure, the titanium sulfide was not transported by using a starting material whose composition was poorer in sulfur than $Ti_{1.33}S_2$. The transported crystals were composed of a mixed phase consisting of Ti_2S_3 and Ti_5S_8 when $Ti_{1.33}S_2$–$Ti_{1.22}S_2$ was used as the starting material. A single phase of Ti_5S_8 resulted when $Ti_{1.21}S_2$ was used. A mixed phase of Ti_2S_3 and Ti_5S_8 resulted when $Ti_{1.19}S_2$–$Ti_{1.14}S_2$ was used and a phase with disordered stacking of sulfur layers when a specimen richer in sulfur than $Ti_{1.13}S_2$ was used.

Therefore, Ti_5S_8 in a pure form was obtained by using a starting material whose composition was $Ti_{1.21}S_2$. The sulfur content of the transported crystals was always found to be smaller than that of the starting materials.

The Effect of the Transported Temperature. The transport was carried out at various temperatures in order to determine the most suitable temperature conditions. As can be seen in Table 2, Ti_5S_8 was obtained in a pure form only at the temperature of 500 °C (low temperature side)→600 °C (high temperature side). At any temperature above this, the transported crystals were found to be two phases consisting of Ti_5S_8 and Ti_2S_3. From the observation of the electron diffractometry, it was found that the needle-shaped crystal was Ti_2S_3, and the plate-shaped one, Ti_5S_8.

On the contrary, the transport was found no longer to take place at temperature below 500 °C (low temperature end)—600 °C (high temperature end).

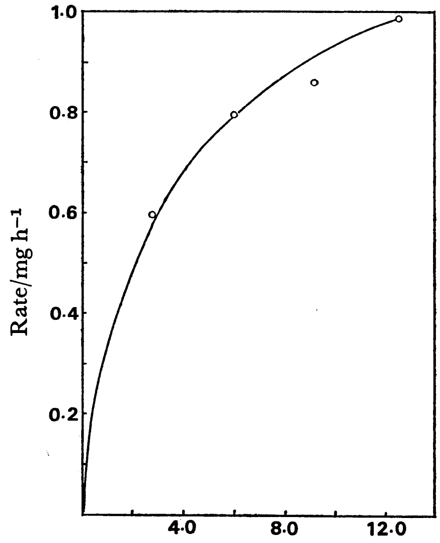

Fig. 2. Average transport rate versus iodine concentration. (Transport time: 144 h, composition of the starting material: $Ti_{1.21}S_2$, temperature: 500 °C (low temperature side)→600 °C (high temperature side)).

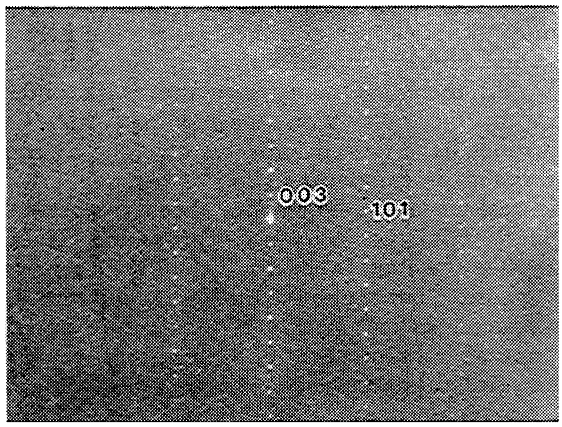

Fig. 3. Electron diffraction photograph of Ti_5S_8 obtained by the chemical transport method.

The Effect of the Iodine Concentration. In order to determine the most suitable conditions, the transport was carried out at various iodine concentrations. The results are shown in Fig. 2, where the transport rate increases with the increase in the iodine concentration. Crystals with stacking faults were produced at concentrations of more than 12 mg cm^{-3}.

Identification by Means of Electron and X-Ray Diffractometry. Figure 3 shows an electron diffraction pattern taken from a crystal fragment obtained by grinding a transported crystal. The incident beam was directed parallel with the [010] direction. The distance of the repeating unit along the c-axis in the hexagonal setting was found to be 34 Å, containing 12 layers. The systematic absence, $-h+k+l=3n$, in-

Table 3. Indices, calculated, and observed d-spaces and intensities

h	k	l	d_{calcd}	d_{obsd}	I_{calcd}	I_{obsd}
0	0	6	5.709	5.719	64	*247
1	0	−2	2.928	2.929	21	26
0	0	12		2.857		*9
1	0	4	2.808	2.811	16	12
1	0	−5	2.727	2.728	51	44
1	0	7	2.540	2.542	98	94
1	0	−8	2.442	2.443	62	68
1	0	10	2.245	2.246	100	100
1	0	−11	2.150	2.151	9	12
1	0	13	1.972	1.973	7	6
0	0	18	1.903	1.904	3	*15
1	0	−14	1.889	1.889	54	50
1	0	16	1.737	1.737	19	18
1	1	0	1.716	1.717	87	*59
1	0	17	1.668	1.668	21	26
1	1	6	1.643	1.639	10	9
1	0	19	1.541	1.541	6	9
1	0	20	1.484		4	
2	0	2	1.481			
2	0	−4	1.464		2	
2	0	5	1.452		5	
0	0	24	1.427	1.428	14	*65
2	0	−7	1.422	1.418	12	9
2	0	8	1.404	1.403	8	9
1	0	22	1.379		2	
2	0	−10	1.363	1.363	15	21
2	0	11	1.341		2	
2	0	−13	1.244		1	
1	1	18	1.274	1.274	4	6
2	0	14	1.270	1.270	11	6

* Indicates the indices affected by the preferred orientation.

dicates the rhombohedral symmetry of the structure. Therefore, the structure of this crystal may be referred to as a 12R type using Ramsdell notation, this is consistent with the structure of Ti_5S_8 as described by Flink *et al.*,[5] and Tronc and Huber.[3]

The powder X-ray diffraction pattern of the Ti_5S_8 sample (composition, $Ti_{1.31}S_2$) obtained by crushing the transported crystals was taken by the counter-diffractometer technique using Ni-filtered Cu $K\alpha$ radiation. The pattern was indexed on the basis of the hexagonal cell (a=3.431 and c=34.25 Å), where the systematic absence, $-h+k+l\neq 3n$, is consistent with the case of the electron diffraction. Powder X-ray diffraction intensities were calculated for the structure model by Tronc *et al.*[6] for the composition of $Ti_{1.31}S_2$ (Ti_5S_8 phase) with an overall temperature factor of B=1.0. The intensities, calculated and observed, are listed in Table 3. These do not agree with each other for the 00l and 110 peaks because of the preferred orientation in the sample. The reliability factor R, defined by $R=\Sigma|I_{obsd}-I_{calcd}|/\Sigma|I_{obsd}|$, was 0.39; this was excessive. However, the R-value estimated by eliminating the 00l and 110 peaks, which were affected by the preferred orientation, was 0.14. Therefore, this specimen was identified as Ti_5S_8 (12R type), as has previously been reported by Tronc *et al.*[6]

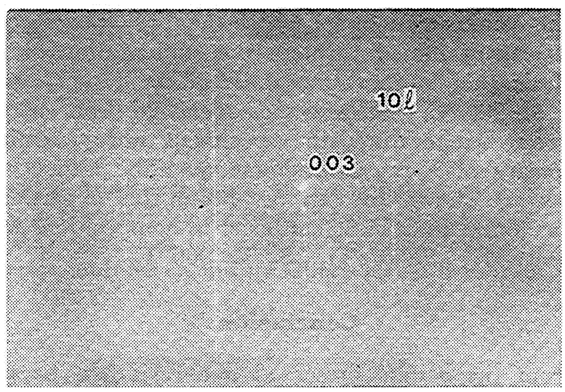

Fig. 4. Electron diffraction photograph of the specimen annealed at 1200 °C.

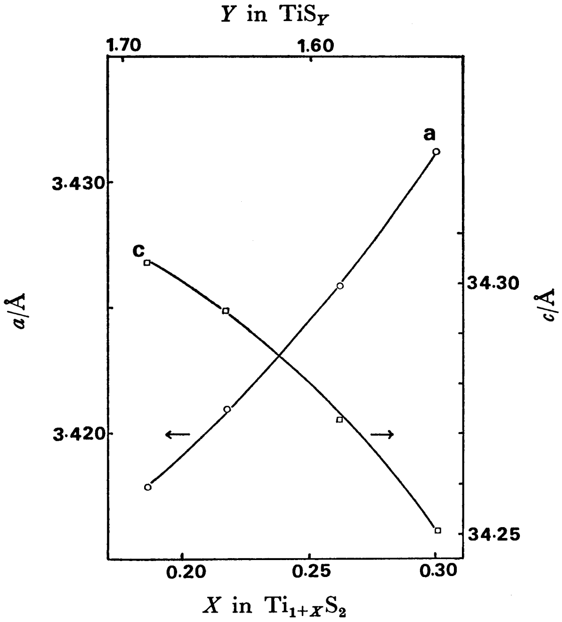

Fig. 5. Relation of the lattice constants and composition.

The information obtained from X-ray and electron diffractometry showed that the specimen prepared by the method described above was indeed a pure single phase and did not contain any other phases, like Ti_2S_3 (4H type) or TiS_2 (2H type).

Range of the Temperature and Composition in Which Ti_5S_8 Can Exist. The range of temperature and composition in which Ti_5S_8 can exist was also examined. At first, Ti_5S_8 (composition $Ti_{1.23}S_2$) was kept in evacuated tubes at 800, 900, 1000, 1100, and 1200 °C for 3 d. Disorder in sulfur stacking at 1100 °C and 1200 °C was found, although no change was detected in the specimens annealed below 1000 °C. Figure 4 is an electron-diffraction photograph of the specimen annealed at 1200 °C. In this figure, the diffusion for $h-k=3n\pm1$ shows disorder caused by sulfur stacking.[7] At 1100 °C, Ti_5S_8 began to change to another structure, but the rate of the transformation was so slow that a stable structure could not be ascertained at this temperature.

The composition range where the Ti_5S_8 phase could exist was examined through the sulfurization or desulufurization in the atmosphere of the H_2–H_2S mixture at 900 °C. After being quenched from 900 °C to room temperature, the specimens were examined by means of X-ray diffractometry. The lattice constants are shown in Fig. 5. From this experiment, it was found that Ti_5S_8 can exist in compositions from at least $Ti_{1.31}S_2$ to $Ti_{1.16}S_2$ at 900 °C.

Conclusion

From the results presented above, it can be concluded that: (1) Ti_5S_8 in a pure form can be prepared by the chemical transport method under the following conditions: transport agent; iodine (6—9 mg cm^{-3}), starting material; titanium sulfide (composition $Ti_{1.21}S_2$) prepared at 500 °C, transport temperature; 500 °C (low temperature end)→600 °C (high temperature end), and (2) Ti_5S_8 can exist over a large composition range at 900 °C.

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References

1) Y. P. Jeannin, "Problems of Nonstoichiometry," ed by A. Rabenau, North-Holland, Amsterdam (1970), p. 77.
2) A. Kjekshus and W. B. Pearson, "Progress in Solid State Chemistry," ed by H. Reiss, Oxford (1964), Vol. 1, p. 83.
3) E. Tronc and M. Huber, *J. Phys. Chem. Solids*, **34**, 2045 (1973).
4) Y. P. Jeannin, *Ann. Chim.*, **7**, 57 (1962).
5) E. Flink, G. A. Wiegers and F. Jellinek, *Rec. Trav. Chim. Pays-Bas*, **85**, 869 (1966).
6) E. Tronc, R. Moret, J. J. Legendre, and M. Huber, *Acta Crystallogr., Sect. B*, **31**, 2800 (1975).
7) M. Onoda and I. Kawada, *Acta Crystallogr., Sect. A*, **36**, 134 (1980).