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6R-TYPE OF Ti_2S_3 SYNTHESIZED IN AN H_2S-H_2 ATMOSPHERE

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A new type of Ti_2S_3 was prepared by reducing TiS_2 in an H_2S-H_2 atmosphere at 600°C. The structure is proposed to be of 6R-type, being composed of cubic-close-packed sulfur layers as well as the fully and partially occupied titanium layers. The ordering of titanium vacancies was suggested.

The phase relation in the titanium-sulfur system is not fully established[1-4], because the equilibrium state is not easily reached in this system and the structure of titanium sulfide is affected by the preparation method. An attempt was made to prepare the material through well defined procedures. The following is a report on a new structure type of Ti_2S_3 which is based on cubic-close-packed sulfur layers.

The powder of TiS_2 was first synthesized from titanium metal powder (purity 99.0%) and sulfur powder (99.9999%) in an evacuated silica tube. It was then put in a silica boat and heated at 600°C for 6 hours in a stream of gas mixture of H_2S and H_2, whose ratio was regulated to be 1:500, and then quenched. The composition of the product was determined by the measurement of weight-loss after it was oxidized to TiO_2 at 800°C in air. The powder X-ray diffraction pattern was taken by the counter-diffractometer technique using Ni-filtered CuKα radiation. The crystal fragments were obtained by crushing and electron diffraction patterns were taken from them.

The powder X-ray diffraction pattern of the sample $TiS_{1.49}$ consists of several strong peaks and many weak peaks. More than half of them, including all the strong peaks, could be indexed on the basis of a hexagonal cell as shown in Table 1. The unit cell dimension is a=3.440(1) and c=17.100(5) A. The systematic absences, $-h+k\pm l \neq 3n$, indicate the rhombohedral symmetry of the structure. The symmetry was confirmed by the electron diffraction pattern with an incident beam parallel to the [010] direction. The line broadening was observed for the peaks with $h-k \neq 3n$, and this must be due to the occurrence of stacking faults.

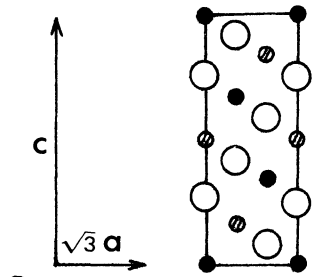
Based on the rhombohedral symmetry and the cell dimension, the structure is referred to as a 6R type using the Ramsdell notation.[5] Considering the structural features of titanium sulfides[2-4], a model of the atomic arrangement is derived in the space group $R\bar{3}m$: Six sulfur atoms in 6(c):$\pm(0,0,z)$;$\pm(2/3,1/3,1/3+z)$;$\pm(1/3,2/3,2/3+z)$;with z=0.25, three titanium atoms in 3(a):(0,0,0);(2/3,1/3,1/3);(1/3,2/3,2/3), and one titanium atom in 3(b):(0,0,1/2);(2/3,1/3,5/6);(1/3,2/3,1/6). It is based on a cubic-close-packed sulfur framework with the alternation of fully and partially occupied titanium layers (see Fig. 1).

Powder diffraction intensities were calculated for the structure model with an

Table 1. Powder X-ray diffraction data.

d_{obs}	d_{calc}	hkl	I_{obs}	I_{calc}	d_{obs}	d_{calc}	hkl	I_{obs}	I_{calc}
5.72	5.70	003	34	18	2.444	2.444	$10\bar{4}$	100	100
5.16*			7		2.245	2.246	$10\bar{5}$	23	5
4.97*			4		2.07**				
4.73*			1		1.901	1.900	009	6	1
4.40*			1		1.887	1.889	107	8	3
2.97**					1.737	1.737	$10\bar{8}$	29	29
2.936	2.935	101	13	11	1.719	1.720	110	69	28
2.85**					1.67***				
2.814	2.813	$10\bar{2}$	3	1	1.646	1.646	113	6	3
2.73***					1.484	1.484	$20\bar{1}$	4	1
2.64***					1.425	1.425	$00\underline{12}$	12	5
2.57*			2		1.407	1.406	$20\bar{\underline{4}}$	18	13
2.54***									

* Weak peak suggesting the presence of a supercell.
** Broad peak due to faulted 2H-Ti_2S_3.
*** Broad peak due to faulted 12R-Ti_2S_3.



○ sulfur site
● fully occupied titanium site
⊘ partially occupied titanium site

Fig. 1. A section through a hexagonal (110) plane.

overall temperature factor (B=1.0). Observed and calculated intensities are qualitatively compatible (see Table 1), but the R-value, defined by $R=\Sigma|I_{obs}-I_{calc}|/\Sigma I_{obs}$, could not be less than 0.33. The possible reasons for the apparently insufficient agreement may be; (1) the occurrence of stacking faults in the structure,[6] (2) the overlap of the peaks from the faulted 2H- and 12R-type Ti_2S_3 mentioned below and (3) the preferred orientation in the powder sample.

The weak peaks marked by stars in Table 1 are not assigned to the 6R-type structure. Some of them can be indexed on the basis of a rectangular supercell ($a'=\sqrt{3}a$, $b'=3a$ and $c'=2c$). The corresponding weak spots were observed in the electron diffraction pattern with an incident beam parallel to the [001] direction. This suggests the presence of the ordering of titanium atoms and vacancies in the partially occupied titanium layers as was observed in the $(4H)_2$- and $(4H)_3$-type structures of Ti_2S_3.[7-9] The rest of the weak peaks in the powder X-ray diffraction pattern are very broad and they can be indexed by assuming the presence of faulted 2H-Ti_2S_3[10], and faulted 12R-Ti_2S_3[4].

The specimen was sealed in an evacuated silica tube and heated for 3 days at 1200°C. It transformed to 4H-type which has already been reported[3,4] for the composition near Ti_2S_3.

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