Preparation of a New Strontium Titanium Sulfide Sr_xTiS_3 ($x = 1.05$–1.22) with Infinitely Adaptive Structures

MASANOBU SAEKI AND MITSUKO ONODA

National Institute for Research in Inorganic Materials,
1-1, Namiki, Tsukuba, Ibaraki, 305, Japan

A new strontium titanium sulfide, Sr_xTiS_3, has been prepared by the reaction of CS_2 with a mixture of $SrCO_3$ and TiO_2. The powder X-ray diffraction and the electron diffraction patterns showed that it has infinitely adaptive structures (or vernier structures) similar to $Ba_xFe_2S_4$. The crystal structure can be described as interpenetration of two subcells having a common a and two different c axes in a hexagonal setting of trigonal symmetry. One of the lattice dimensions along c, c_1, is from the TiS_3 part and another, c_2, is from the Sr part. In the composition range between $x = 1.05$ and $x = 1.22$ in Sr_xTiS_3, the c_1 expands while the c_2 shrinks with increasing x value. The X-ray diffraction peaks could be indexed using four integers. © 1993 Academic Press, Inc.

Introduction

Much attention has been paid toward composite crystals, the structures of which consist of plural units with different periodicities. For example, $(PbS)_{1.12}VS_2$ (*1, 2*) crystallizes in a structure with mutual stacking of a PbS layer with NaCl-type and a VS_2 layer with CdI_2-type. The structure is *incommensurate* in one direction parallel to the layers because of a difference in the lattice parameters of the PbS and VS_2. The structure, of course, is not composed from exact NaCl– and CdI_2-types. The PbS and VS_2 layers are distorted by the interaction of each other in the structure. Such a compound is called a layered composite crystal. Many sulfides like $(MS)_xM'S_2$ (M = rare earth atoms, Pb, Sn, or Bi; M' = Ti, V, Cr, Nb, or Ta; $x = 1.08$–1.23) belong to this type (*3–18*).

There is another type of composite crystal, which is composed of two chains, often called infinitely adaptive structures. $Ba_x Fe_2S_4$ (*19–30*) is a popular one and the only such example of a sulfide. The $Ba_xFe_2S_4$ has tetragonal symmetry and contains two chains directed along the c axis. One of them is an edge-shared iron sulfur tetrahedra chain, and another is a barium chain. The two chains have different basic periods, c_{FeS_2} from the FeS_2 chain and c_{Ba} from the Ba chain, and the lattice parameter c is represented by the common multiple of the c_{FeS_2} and c_{Ba}. The content of Ba varies in the range of $1.062 < x < 1.143$ in $Ba_xFe_2S_4$. The existence of the wide composition range is different from the layered composite crystal. In the traditional concept, there are an infinite number of structures in the composition range. The infinite number of structures originates from the elongating c_{FeS_2} and the shrinking c_{Ba} with increasing Ba content. The FeS_2 and Ba chains are incommensu-

rate mutually. The ratio c_{FeS_2}/c_{Ba} is dependent on the Ba content. Every composition in the range of $1.062 < x < 1.143$ produces a unique structure with no biphasic coexisting ranges.

This paper aims to report the existence of a similar type of composite crystal structure in the Sr–Ti–S system. The X-ray diffraction peaks of the sulfide have been indexed on the basis of four-dimensional formalism in order to uniformly treat the commensurate and incommensurate structures.

In the Sr–Ti–S system, the existence of $SrTiS_3$ has been reported by Hahn (31). The structure has been reported to be isotypic with $BaNiO_3$.

Experimental

The starting materials $SrCO_3$ (99.9%) and TiO_2 (99.9%) were, at first, dried in air at 100°C for 2 days to remove any absorbed water. (To confirm the removal of water, the starting materials were heated again in a furnace at 400°C, but no weight loss was detected.) The dried starting materials were mixed together in calculated amounts and placed in the furnace into which CS_2 was introduced with nitrogen gas. The starting materials were heated at 800°C for 3 days. After cooling to room temperature, the resulting compound was ground, followed by heating again in the same atmosphere at 800°C for 2 days. The specimen already attained constant weight during the first sulfurization. The second heating is, therefore, to confirm the perfect reaction. The sulfide thus obtained was sealed in an evacuated silica tube and heated at 900°C for 2 days. It was then quenched in water.

The contents of Sr and Ti were calculated from the amounts of the starting materials. The sulfur content was determined from the weight change between the starting material and the resulting sulfide.

Powder X-ray diffraction data were collected with a step-scan procedure on a Phil-ips PW 1800 diffractometer using counterside monochromatized $CuK\alpha$ radiation. Electron diffraction patterns were taken for crushed particles using a 100-kV electron microscope (Hitachi 500-type).

The density of the specimen was obtained by measuring the buoyancy in carbon tetrachloride. About 0.5 g of the specimen with fine particles was placed in a bottle, the volume of which was about 2 ml and the weight of which was 1.5 g. The bottle and the specimen in carbon tetrachloride were kept at reduced pressure to remove any bubbles attached to the specimen and on the surface of the bottle. The buoyancy was obtained by measuring the weight of the specimen in air and in carbon tetrachloride at 25 ± 0.1°C.

Results

Figure 1 shows the powder X-ray diffraction pattern of the specimen obtained by sulfurization of the mixture with Sr/Ti = 1.14. (The diffraction angle in Fig. 1 is given by 2θ.) In the composition of Sr/Ti = 1.05 and 1.22, identical diffraction patterns were obtained, except for drift of the peak position. This suggests that this sulfide has a homogeneity range. The gravimetric analysis showed that the sulfur content of the specimens can be expressed as $Sr_xTiS_{2.98\pm0.07}$. The specimen was contaminated with SrS in the composition richer in Sr than 1.22, and contaminated with an unknown phase in the composition poorer in Sr than 1.05. The samples, therefore, were single phase within the composition range of $x = 1.05-1.22$ at 900°C.

Not only weak peaks but also some strong peaks in Fig. 1 are not indexed with the lattice parameters of the $BaNiO_3$-type structure reported by Hahn (31). The electron diffraction photograph (Fig. 2) is complex and reveals incommensurate features. A careful examination of the photographs led us to the conclusion that the diffraction
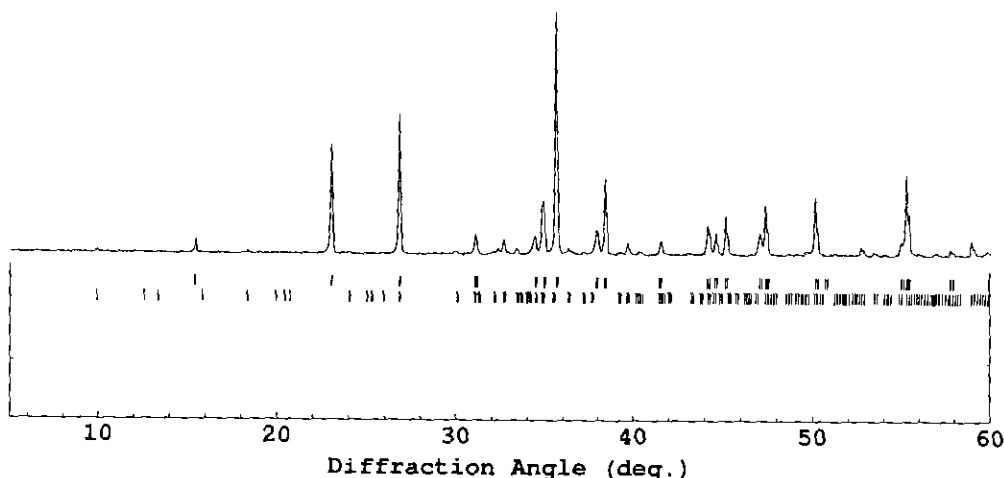
FIG. 1. X-ray diffraction pattern of $Sr_{1.15}TiS_3$. The upper tick marks indicate the calculated positions of the peaks with $m = 0$ or $l = 0$, and the lower tick marks indicate the positions calculated for the peaks with $m \neq 0$, $l \neq 0$, and either $|l|$ or $|m| \leq 3$, respectively.

spots consist of some prominent spots from two subcells and many weak spots which are considered to be satellites. The ED photographs and the powder X-ray diffraction measurements suggest that the sulfide has composite crystal and infinitely adaptive structures. Based on this assumption, an at-

FIG. 2. Electron diffraction pattern.

tempt was made to index the X-ray diffraction pattern in a hexagonal setting with the four-dimensional formalism.

From the point of view of the three-dimensional formalism, this compound may present an infinite number of structures. A very slight change in Sr content leads to a change of the subcell periodicity and the formation of a different structure. Some of the specimens crystallize in commensurate and some others in incommensurate structures. In the case of commensurate structures, indexing in the three-dimensional formalism is possible but sometimes lead to misindexing because of the large lattice constant. Indeed, the incommensurate structure cannot be indexed in the three-dimensional formalism.

In the four-dimensional formalism, this compound can be treated as a single phase with a homogeneity range in which the lattice parameters given as the parameters of each subcell change continuously with the composition. Therefore, this treatment, which gives better understanding of the titled sulfide, is used below.

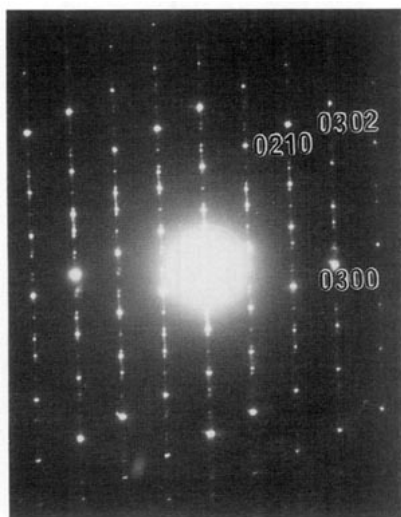At first, we adopt the unit vectors in the

TABLE I

INDICES AND CALCULATED AND OBSERVED VALUES OF d SPACINGS, AND OBSERVED INTENSITIES FOR $Sr_{1.15}TiS_3$ (a = 11.490 Å, c_{TiS_3} = 2.990 Å, and c_{Sr} = 5.197 Å)

h	k	l	m	d_{calc}	d_{obs}	I_{obs}
1	0	1	$\bar{2}$	8.90	8.93	<1
1	1	0	0	5.74	5.73	5
2	0	$\bar{1}$	2	4.83	4.82	<1
1	1	0	$\bar{1}$	3.854	3.850	43
2	1	1	$\bar{2}$	3.696	3.697	<1
3	0	0	0	3.317	3.313	53
3	0	$\bar{3}$	6	2.965	2.967	2
2	2	0	0	2.873	2.871	10
2	1	1	$\bar{3}$	2.777	2.778	1
3	1	$\bar{4}$	7	2.759	2.757	3
3	1	$\bar{1}$	2	2.733	2.732	7
3	1	2	$\bar{3}$	2.675	2.673	3
0	0	0	2	2.599	2.598	12
3	1	$\bar{1}$	1	2.569 ⎫	2.563	33
2	0	$\bar{1}$	0	2.563 ⎭		
2	2	0	1	2.514	2.513	100
4	0	1	$\bar{2}$	2.468	2.468	4
4	0	$\bar{2}$	4	2.413	2.414	2
1	1	0	2	2.368	2.367	17
2	1	1	0	2.340	2.340	32
3	1	$\bar{1}$	3	2.293	2.293	2
3	2	$\bar{1}$	$\bar{2}$	2.268	2.268	5
3	2	$\bar{2}$	3	2.234 ⎫	2.234 ⎫	3
3	2	$\bar{2}$	4	2.225 ⎭	2.228 ⎭	
4	1	0	0	2.172 ⎫	2.170	8
3	2	1	$\bar{1}$	2.171 ⎭		
3	0	0	2	2.046	2.047	18
3	1	$\bar{1}$	0	2.028	2.028	10

reciprocal lattice common to the two subcells. They are the common hexagonal a and b axes and two different c axes (c_1 and c_2).

In the four-dimensional description, each reflection is expressed by

$$q = ha_1^* + ka_2^* + lc_1^* + mc_2^*,$$

where a_1^* and a_2^* are the reciprocal bases corresponding to a and b. c_1^* and c_2^* are reciprocal to c for the first and the second subcells, respectively.

The distance from the origin of the reciprocal lattice d^* is given by

$$d^* = 1/d = [(h^2 + hk + k^2)a^{*2} + (lc_1^* + mc_2^*)^2]^{1/2},$$

where $a^{*2} = 4/3(1/a)^2$, $c_1^* = 1/c_1$, $c_2^* = 1/c_2$, and d is the plane interval and is related to the diffraction angle by the Bragg equation.

All of the powder X-ray diffraction peaks in Fig. 1 were indexed with the four-dimensional formalism (*32*) in the hexagonal axis (a = 11.490(3) Å, c_1 = 2.990(2) Å, and c_2 = 5.197(2) Å) according to the reflection conditions; for general $hklm$, $-h + k + l = 3n$; for $hk0m$, $h - k = 3n$. The reflection conditions reveal a trigonal symmetry.

In the composite crystal, the structure is modulated through the interactions between the subcells (*33*). The satellites in the ED
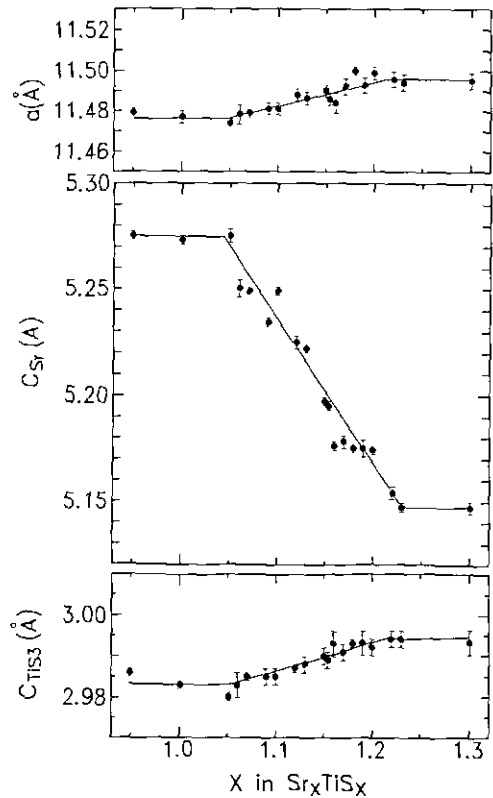

FIG. 3. Lattice parameters c_{TiS_3}, c_{Sr}, and a vs x in Sr_xTiS_3.

and X-ray diffraction patterns originate from the modulation. It is considered that the strong peaks are from the subcells, and weak peaks are due to the satellites. In Fig. 1, the upper tick marks indicate the calculated positions of the peaks with $m = 0$ or $l = 0$, and the tick marks at the bottom indicate the positions calculated for the peaks with $m \neq 0$, $l \neq 0$, and either $|l|$ or $|m| \leq 3$. Only one peak, $d = 2.757$ Å, was not indexed with $|l|$ and/or $|m|$ less than 4, but the peak position agrees with that of $(31\overline{4}7)$, as is shown in Table I in which the indices $(hklm)$, d_{calc}, d_{obs}, and I_{obs} are listed. From the indexing in Table I, we can understand which cell the diffraction peaks come from. For example, $(hk00)$ is from the projection along c_1 and c_2 of the two subcells, $(hkl0)$ is from the first subcell, $(hk0m)$ is from the second subcell, and $(hklm)$ is a satellite, where both l and m are not zero. Almost all peaks can be assigned to the main peaks and to the first-, second-, and third-order satellites (either $|l|$ or $|m| \leq 3$). This means that the modulation in the structure can be represented approximately by the summation of the first, second, and third harmonics in the Fourier decomposition.

The lattice parameters in Fig. 3 were calculated from the diffraction peaks indexed using the previous method. In Sr_xTiS_3, c_1 expands while c_2 shrinks with increasing x value. The first and second subcells may be then attributed to the TiS_3 and Sr parts, respectively, and the variation of the lattice parameters ($c_1 = c_{TiS_3}$, $c_2 = c_{Sr}$) shown in Fig. 3 are reasonable for the various compositions. From the lattice parameters, it is found that Sr_xTiS_3 exists in the $x = 1.05$–1.22 composition range.

The observed density for $Sr_{1.15}TiS_3$ is 3.51 g/cm³ (the average of two measurements 3.50 and 3.52 g/cm³), compared with the calculated one of 3.57 g/cm³ ($V = 341.8$ Å³, $Z = 3$).

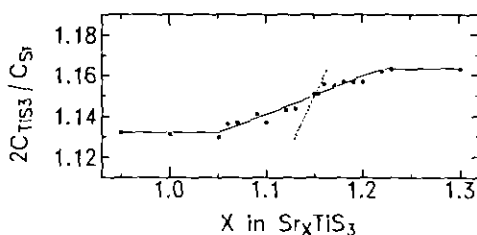In general, the chemical composition of the composite structures can be estimated

FIG. 4. $2c_{TiS_3}/c_{Sr}$ vs composition.

from the ratio of the lattice parameters. In the present case, when Sr_xTiS_3 is represented by $Sr_p(TiS_3)_q$, where p and q are integers, the lattice parameter c becomes $c = qc_{TiS_3} = (1/2)pc_{Sr}$. In the last term, not pc_{Sr} but $(1/2)pc_{Sr}$ was adopted, because it is presumed from the sizes of the subcells that the first subcell contains three TiS_3 molecules while the second subcell contains six Sr atoms. Hence, x in Sr_xTiS_3 is given by $x = p/q = 2c_{TiS_3}/c_{Sr}$, since a_1 and a_2 are common in both subcells. Therefore, the composition, $x = Sr/Ti$, should be given by the $2c_{TiS_3}/c_{Sr}$.

Figure 4 shows the relation of the composition calculated from $x = 2c_{TiS_3}/c_{Sr}$ and the nominal composition. They do not agree with each other except for $x = 1.15$. The dotted line stands for the case in which the calculated composition agrees with nominal one. In $Ba_xFe_2S_4$, Nakayama et al. (23) also observed this inconsistency, and he postulated the existence of Ba and Fe vacancies. In the present work, more experiments are necessary to confirm this. There is another problem about lattice parameters, that is, the lattice parameters are dependent on the temperature and sulfur pressure during preparation. This problem was also pointed out in $Ba_xFe_2S_4$ (19, 23). The crystal structure of the Sr_xTiS_3 is now in progress.

Conclusion

A new strontium titanium sulfide Sr_xTiS_3 ($x = 1.05$–1.22) has been prepared. It has

infinitely adaptive structures, and the X-ray diffraction peaks were indexed with the four-dimensional formalism, with a common a and b and two different c axes, c_1 and c_2, in a hexagonal setting. The c_1 elongates slightly and c_2 shrinks with increasing Sr content.

Acknowledgments

References

1. M. Onoda, K. Kato, Y. Gotoh, and Y. Oosawa, *Acta Crystallogr. Sect. B* **46**, 487 (1990).
2. Y. Gotoh, M. Goto, K. Kawaguchi, Y. Oosawa, and M. Onoda, *Mater. Res. Bull.* **25**, 307 (1990).
3. K. Kato, I. Kawada, and T. Takahashi, *Acta Crystallogr. Sect. B* **33**, 3437 (1977).
4. E. Makovicky and B. G. Hyde, *Struct. Bonding* **46**, 101 (1981).
5. L. Otero-Diaz, J. D. Fitzgerald, T. B. Williams, and B. G. Hyde, *Acta Crystallogr. Sect. B* **41**, 405 (1985).
6. L. Guemas, P. Rabu, A. Meerschaut, and J. Rouxel, *Mater. Res. Bull.* **23**, 1061 (1988).
7. G. A. Wiegers, A. Meetsma, R. J. Haange, and J. L. de Boer, *Mater. Res. Bull.* **23**, 1551 (1988).
8. Y. Oosawa, Y. Gotoh, and M. Onoda, *Chem. Lett.*, 523 (1989).
9. G. A. Wiegers, A. Meetsma, S. van Smaalen, R. J. Haange, J. Wulff, T. Zeinstra, J. L. de Boer, S. Kuypers, G. van Tendeloo, J. van Landuyt, A. Amelinckx, A. Meerschaut, P. Rabu, and J. Rouxel, *Solid State Commun.* **70**, 409 (1989).
10. A. Meerschaut, P. Rabu, and J. Rouxel, *J. Solid State Chem.* **78**, 35 (1989).
11. Y. Gotoh, M. Onoda, M. Goto, and Y. Oosawa, *Chem. Lett.*, 1281 (1989).
12. A. Meetsma, G. A. Wiegers, R. J. Haange, and J. L. de Boer, *Acta Crystallogr. Sect. A* **45**, 285 (1989).
13. S. Kuypers, G. van Tendeloo, J. van Landuyt, and S. Amelinckx, *Acta Crystallogr. Sect. A* **45**, 291 (1989).
14. Y. Gotoh, M. Onoda, K. Uchida, Y. Tanaka, T. Iida, H. Hayakawa, and Y. Oosawa, *Chem. Lett.*, 1559 (1989).
15. S. van Smaalen, *J. Phys.: Condens. Mater.* **1**, 2791 (1989).
16. K. Kato, *Acta Crystallogr. Sect. B* **46**, 39 (1990).
17. G. A. Wiegers, A. Meetsma, R. J. Haange, S. van Smaalen, J. L. de Boer, A. Meerschaut, P. Rabu, and J. Rouxel, *Acta Crystallogr. Sect. B* **46**, 324 (1990).
18. J. Wulff, A. Meetsma, S. van Smaalen, R. J. Haange, J. L. de Boer, and G. A. Wiegers, *J. Solid State Chem.* **84**, 118 (1990).
19. I. E. Grey, *J. Solid State Chem.* **11**, 128 (1974).
20. I. E. Grey, *Acta Crystallogr. Sect. B* **31**, 45 (1975).
21. J. T. Hoggins and H. Steinfink, *Acta Crystallogr. Sect. B* **33**, 673 (1977).
22. H. Boller, *Monatsh. Chem.* **109**, 975 (1978).
23. N. Nakayama, K. Kosuge, and S. Kachi, *J. Solid State Chem.* **33**, 267 (1980).
24. J. S. Swinnea and H. Steinfink, *J. Solid State Chem.* **32**, 329 (1980).
25. N. Nakayama, K. Kosuge, and S. Kachi, *J. Solid State Chem.* **36**, 9 (1981).
26. N. Nakayama, K. Kosuge, and S. Kachi, *Chem. Scr.* **20**, 174 (1982).
27. J. S. Swinnea and H. Steinfink, *J. Solid State Chem.* **41**, 114 (1982).
28. J. S. Swinnea and H. Steinfink, *J. Solid State Chem.* **41**, 124 (1982).
29. A. C. Holladay and L.-R. Eyring, *J. Solid State Chem.* **64**, 113 (1986).
30. M. Onoda and K. Kato, *Acta Crystallogr. Sect. B* **47**, 630 (1991).
31. H. Hahn and U. Mutschke, *Z. Anorg. Allg. Chem.* **288**, 269 (1956).
32. P. M. de Wolff, T. Janssen, and A. Janner, *Acta Crystallogr. Sect. A* **37**, 625 (1981).
33. A. Janner and T. Janssen, *Acta Crystallogr. Sect. A* **36**, 408 (1980).