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Preparation of a Chain-Type Composite Crystal, Ba_xTiS_3 (x = 1.00–1.05)

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Barium titanium sulfide, Ba_xTiS_3 (x = 1.00–1.05), has been prepared by the reaction of CS_2 with a mixture of $BaCO_3$ and TiO_2. The X-ray powder diffraction and electron diffraction patterns show that the structure is a chain-type composite crystal similar to Sr_xTiS_3 and $Ba_xFe_2S_4$. The structure consists of two interpenetrating cells, probably TiS_3 and Ba cells, which have the parameter a in common, whereas the parameter c is different (c_1 and c_2 in a hexagonal setting). c_1 shrinks with increasing Ba content, while c_2 expands. The electron diffraction spots and the X-ray powder diffraction peaks cannot be indexed because of an incommensurate structure; they were, therefore, indexed based on a four-dimensional formalism using the parameters a, c_1, and c_2. In the expression of the four-dimensional formalism, this sulfide is represented by a single structure with a homogeneity range of x = 1.00–1.05. © 1994 Academic Press, Inc.

INTRODUCTION

Some sulfides have recently received considerable attention, because they display structures called composite crystals. Two types of composite crystals are well known in the sulfides: layered composite crystals such as $(PbS)_{1.12}VS_2$ (1) and chain-type composite crystals such as $Ba_xFe_2S_4$ (2). In previous papers (3, 4), we reported that Sr_xTiS_3 was the latter type of structure. Prior to this work, it had been reported that $SrTiS_3$ is isostructural with $BaNiO_3$; however, the X-ray powder and electron diffraction patterns yielded extra peaks which could not be indexed to the $BaNiO_3$ type structure. The explanation for the extra peaks leads us to the conclusion that Sr_xTiS_3 crystallizes in the composite crystal, not in the $BaNiO_3$ type structure. The $SrTiS_3$-in-$BaNiO_3$ type structure contains two kinds of chains directed along the c axis in the hexagonal structure: the face-shared TiS_3 octahedra chain and the Sr chain. According to Refs. (3, 4), these two chains have different periodicities in the c direction. The different periodicities of the two chains generate the composite crystal. (In composite crystals in general, periodicity is not observed in the incommensurate direction of the structure. The word "periodicity" here represents the periodicity of the fundamental structure (5, 6).)

In the Ba–Ti–S system, the existence of a composite crystal is possible because of the similarity in the structures of $BaTiS_3$ and $SrTiS_3$ (7, 8). Three compounds have been reported so far in the Ba–Ti–S system: Ba_3TiS_5 (9), Ba_2TiS_4 (10), and $BaTiS_3$ (7). According to Hahn (7), the $BaTiS_3$ is isostructural with $BaNiO_3$; however, there was a serious discrepancy between the observed and calculated intensities of the X-ray powder diffraction peaks. Clearfield (8) studied the X-ray powder diffraction pattern of $BaTiS_3$ prepared under a CS_2 atmosphere at various temperatures. He also observed the poor agreement between the calculated and observed intensities, and concluded that this compound has a disordered $BaNiO_3$-type structure. Huster (11) studied the structure of the $BaTiS_3$ using a single crystal and reported that it has a $BaNiO_3$ type structure with R_F = 0.031.

This paper aims to report that Ba_xTiS_3 is a chain-type composite crystal and is the third example of this type of sulfide following $Ba_xFe_2S_4$ and Sr_xTiS_3.

EXPERIMENTAL

The starting materials $BaCO_3$ (99.9%) and TiO_2 (99.9%) were first dried in air at 100°C for 2 days to remove any absorbed water. The dried starting materials were mixed together in calculated amounts and placed in a furnace to which CS_2 was introduced with nitrogen gas. The starting materials in a silica boat were heated 750°C and kept at this temperature for 3 days. After cooling to room temperature, the sulfide thus obtained was sealed in an evacuated silica tube and heated at 900°C for 3 days. It was then quenched in water.

The Ba and Ti contents were calculated from the initial amounts of the respective starting materials. The sulfur content was determined from the weight change between the starting material and the resulting sulfide. The specimens prepared were found to be slightly deficient in sulfur, i.e., $Ba_xTiS_{2.93\pm0.02}$.

X-ray powder diffraction data were collected with a step-scan procedure on a Philips PW 1800 diffractometer using automatic divergence slit and counter-side mono-

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chromatized Cu$K\alpha$ radiation. Electron diffraction patterns were obtained for crushed particles using a 100 kV electron microscope (Hitachi 500-type).

RESULTS

X-Ray Powder Diffraction and Electron Diffraction Patterns

Almost all reflections of the X-ray powder diffraction patterns of Ba_xTiS_3 (x = 1.00–1.05) can be indexed to a hexagonal cell with lattice parameters of a = 6.76 Å and c = 5.7 Å. The lattice parameters agree with those of the $BaNiO_3$ type structure. However, some very weak peaks which cannot be indexed are observed in enlarged diffraction patterns. These peaks disappear with the appearance of an adjacent phase, and the variation of these peak positions with the Ba content correlated with that of the main peaks. This suggests that the weak peaks come from the structure which generates the main peaks, and the extra peaks are neither from adjacent phases nor from impurities. In fact, as will be described later in this paper, these weak peaks and main peaks could be indexed with the same cell.

Figure 1a is an electron diffraction pattern of x = 1.00. The strong spots can be indexed to the hexagonal cell, and they agree with those of the $BaNiO_3$ type structure. While, as shown in Fig. 1a, there are some additional weak diffraction spots which cannot be indexed. Each of the weak spots consists of a pair of spots which are only slightly separated. As shown in Fig. 1b, which is a pattern of x = 1.04, each extra weak spot is clearly separated into two or three spots, and the separation is larger than that of Fig. 1a. The degree of separation of these weak spots depends on the barium content. The electron diffraction patterns of Figs. 1a and 1b reveal a very large c periodicity and suggest that $Ba_xTiS_{2.93}$ is a composite crystal. The reasons this sulfide may be a composite crystal are as follows: (1) The distance between the main spots along c^* axis is not a simple integral multiple of the distance between the satellites; i.e., the structure is suggested to be incommensurate. (2) The variation in the distance between satellites along c^* axis is sensitive to Ba content while the variation of the distance between the main diffraction spots is not similarly. (3) As will be described later in this paper, the extra peaks in the X-ray and electron diffraction patterns can be explained by the

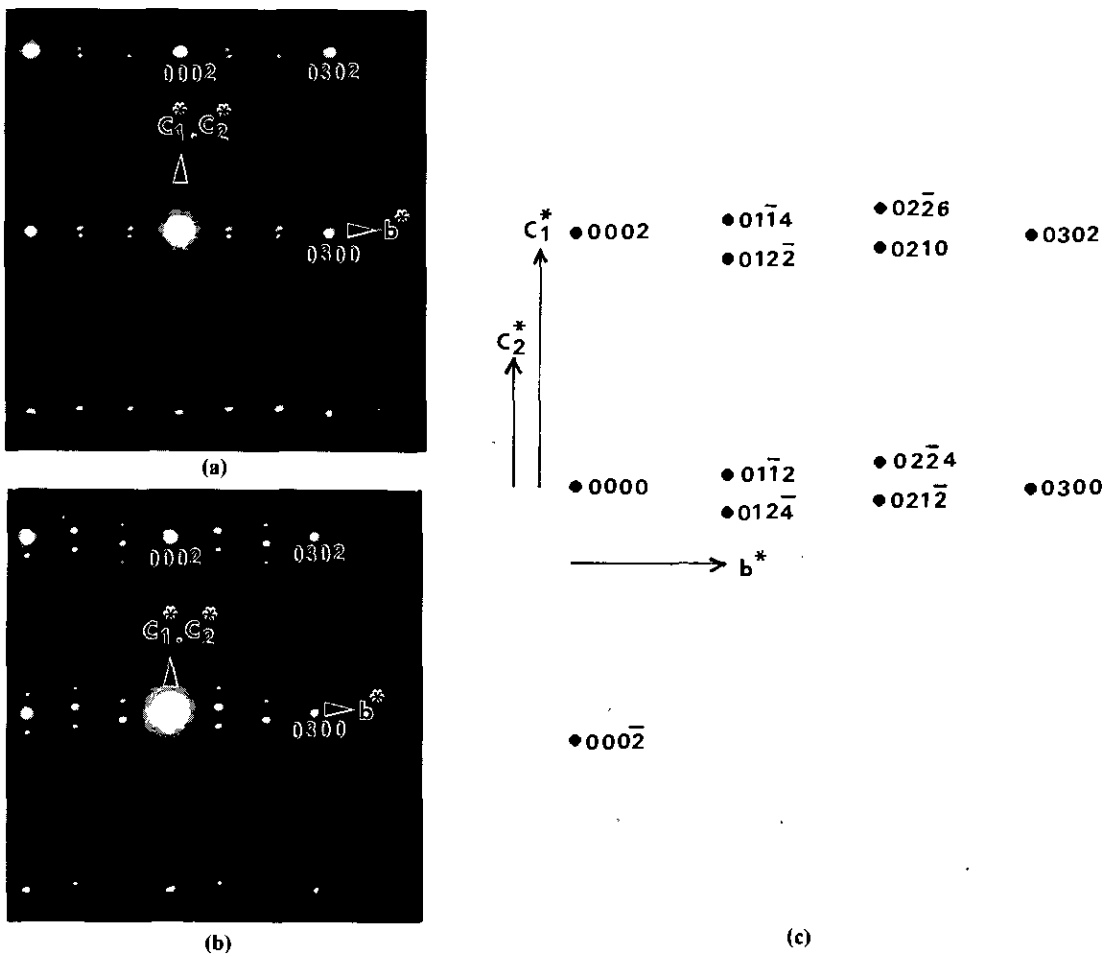

FIG. 1. Electron diffraction patterns: (a) x = 1.00; (b) x = 1.04 in Ba_xTiS_3; (c) schematic drawing of (a).

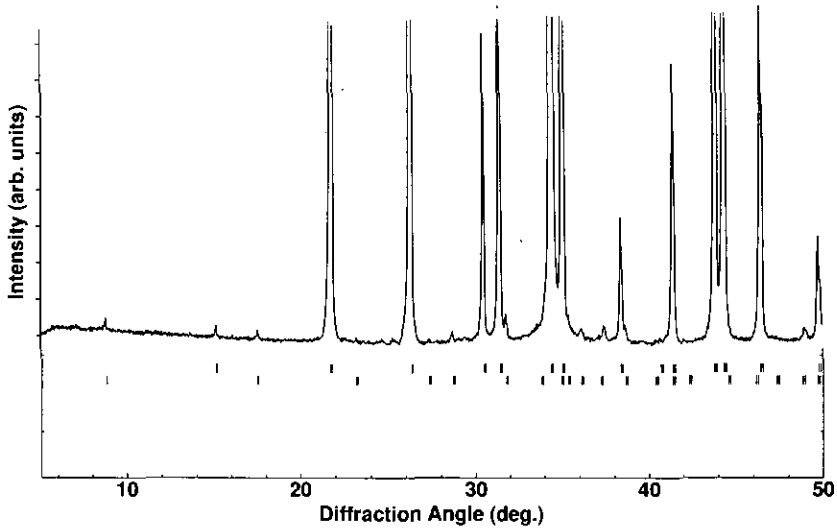

FIG. 2. X-ray diffraction pattern of $Ba_{1.043}$. The upper tick marks indicate the calculated positions of the peaks with $m = 0$ or $l = 0$, and the lower tick marks indicate the positions calculated for the peaks with $m \neq 0$, $l \neq 0$, and either l or $m = 1$, respectively.

composite crystal model. The variation of the lattice parameters with the Ba content is also reasonable for the composite crystal model.

Indexing of the Electron Diffraction Spots

In composite crystals, some of the specimens crystallize in commensurate, and others crystallize in incommensurate structures. In the case of the commensurate structures, indexing based on a three-dimensional formalism is possible, but because of the large lattice constant, sometimes leads to incorrect indexing. Indeed, an incommensurate structure cannot be indexed based upon the three-dimensional formalism. A four-dimensional formalism should, therefore, be used to index the spots in this case.

According to de Wolf (5) and Janner and Jannsen (6), a simple periodicity can be assigned to this kind of structure, if it is assumed that the reciprocal lattice points exist in imaginary four-dimensional space. The reciprocal spots we observe are projected from imaginary four-dimensional space onto three-dimensional space. Under this assumption, four axes, a^*, b^*, c_1^*, and c_2^*, were used to index the ED spots, as shown in Fig. 1c. The two axes, c_1^* and c_2^*, are perpendicular to the a^* and b^* axes in a hexagonal setting. The c_2^* is the projection from the fourth axis in the imaginary four-dimensional space to the c_1^* axis. Both the c_1^* and c_2^* axes are, therefore, in identical directions, but with different values. The diffraction spots are indexed by employing four integers $hklm$ based upon the four axes. The diffraction spots were classified into two types. One type consists of the main spots, which are reflections from the cell and are indexed with $hkl0$ or $hk0m$. The other type of spot consists of the satellites originating from modulation and indexed with $hklm$, where both l and m are nonzero. The satellites are indexed by the summation of the vectors of the two main spots. For example, $02\bar{1}2$ in Fig. 1c is indexed by the summation of $000\bar{2}$ and 0210.

In this way, all spots in Fig. 1a can be assigned as main spots ($hkl0$ and $hk0m$), and first- and second-order satellites, i.e., either l or $m \leq 2$, as is shown in Fig. 1c. From the indexing, it was found that the unit cell can be represented by simple periodicity with a four-dimensional formalism. The lattice parameters obtained are $a = 11$, $c_1 = 3$, and $c_2 = 5$ Å.

Indexing of the X-ray Powder Diffraction Peaks

The X-ray powder diffraction peaks were indexed with the lattice parametes a, c_1, and c_2 obtained from the electron diffraction pattern. In the hexagonal setting in the four-dimensional formalism, the plane interval d is given by

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

where $a^{*2} = (4/3)(1/a)^2$, $c_1^* = 1/c_1$ and $c_2^* = 1/c_2$. c_2^* is a vector projected from the fourth axis onto the third axis.

All of the X-ray powder diffraction peaks in Fig. 2 were indexed with the four-dimensional formalism using the hexagonal axes ($a = 11.490(3)$, $c_1 = 2.990(2)$, $c_2 = 5.197(2)$Å), according to the reflection conditions $-h + k + l = 3n$ for general $hklm$, and $m = 2n$ for $h0lm$. In Fig. 2, the upper row of tick marks indicate the calculated positions of the main peaks whose indices are represented by $hklm$, where l or $m = 0$, and the lower tick marks indicate the positions for the peaks of the satellites whose indices are given by $hklm$, where both l and m are nonzero.

As is seen in Fig. 2, all of the strong peaks are assigned to the main peaks, and the weak peaks are assigned to the satellites. Only first order satellites (m or $l = 1$) were given with the tick marks in the figure, and all the observed satellites belong to the first and second order, as is listed in Table 1.

Figure 3 gives the relationship between the lattice parameters and barium content. The parameters a and c_1 expand with increasing barium content while c_2 shrinks. From the lattice parameters, it was found that Ba_xTiS_3 exists in the composition range $x = 1.00$–1.05. Table 1 gives the indices $hklm$, d_{calc}, d_{obs}, and I_{obs}.

As described above, the structure of Ba_xTiS_3 is represented in the four-dimensional formalism by a single structure with a homogeneity range of $x = 1.00$–1.05. On the other hand, from a three-dimensional viewpoint, the overall structure is described as an aggregation of an infinite number of structures. Each of the structures is composed of two penetrating cells whose lattice parameters are a and c_1 and a and c_2, respectively. Based on an analogy with the case of Sr_xTiS_3, the first and second cells may then be attributed to the TiS_3 and Ba cells, respectively. The lattice parameter c in the three-dimensional formalism is represented by a common multiple of $c_1(c_{TiS3})$ and $c_2(c_{Ba})$. The parameter $c_1(c_{TiS3})$ expands with increasing Ba content, whereas $c_2(c_{Ba})$ shrinks. Hence, a very slight change in Ba content leads to a change in the periodicity in the c-direction and the formation of a different structure. Therefore, in the three-dimensional formalism, this sulfide contains an infinite number of structures that originate from the different periodicity in the c-direction.

TABLE 1

Indices, Calculated, and Observed Values of d Spacings, and Observed Intensities for $Ba_{1.04}TiS_{2.93}$ ($a = 11.724(1)$, $c_1 = 2.959(1)$, $c_2 = 5.6948(1)$ Å).

h	k	l	m	d_{calc}	d_{obs}	$(I/I_0)_{obs}$
1	0	1	−2	10.06	10.04	2
1	1	0	0	5.862	5.855	3
0	2	1	−2	5.065	5.061	2
1	1	0	1	4.085	4.083	365
2	1	1	−2	3.832	3.831	2
3	0	0	0	3.385	3.383	393
2	1	1	−1	3.257	3.255	1
3	1	1	−3	3.107	3.105	2
2	2	0	0	2.9311	2.9293	66
0	0	0	2	2.8474	2.8465	97
1	3	1	−2	2.8138	2.8141	4
2	2	0	1	2.6062	2.6055	1000
1	1	0	2	2.5613	2.5601	95
1	3	1	−3	2.4861	2.4852	2
1	2	2	−2	2.4018	2.4006	3
2	1	1	0	2.3431	2.3427	46
3	0	0	2	2.1789	2.1791	99
4	1	0	1	2.0649	2.0651	237
2	2	0	2	2.0424	2.0425	237
3	3	0	0	1.9541	1.9540	150
2	3	2	−2	1.8577	1.8574	3
3	2	1	0	1.8302	1.8305	41

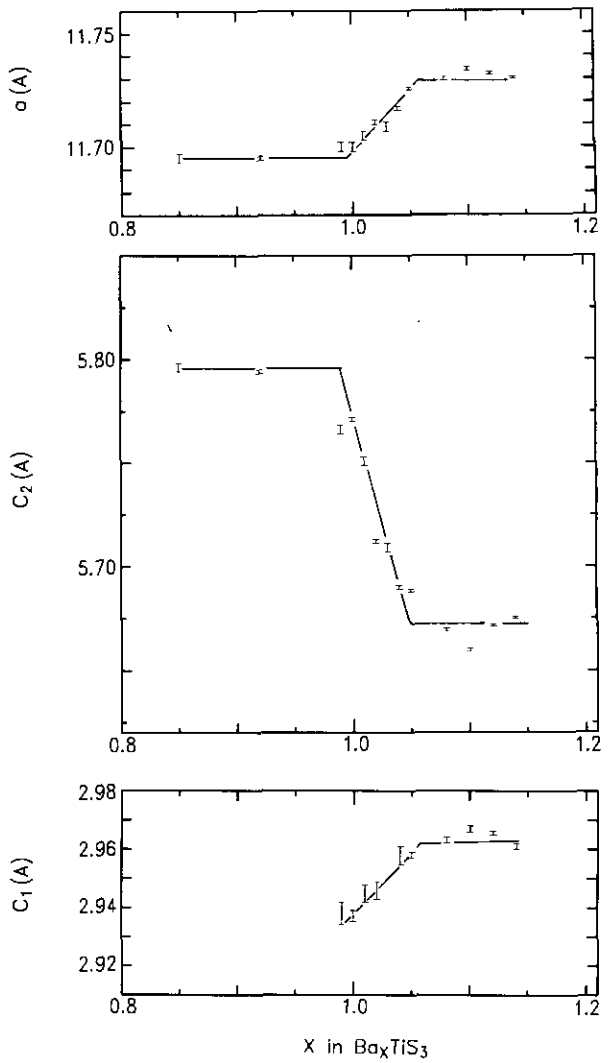

FIG. 3. Lattice parameters c_1 (or c_{TiS3}), c_2 (or c_{TiS3}), c_2 (or c_{Ba}), and a vs x in Ba_xTiS_3.

Usually, the chemical composition of the composite structures can be estimated from the ratio of the lattice parameters. In the present case, when Ba_xTiS_3 is represented by $Ba_p(TiS_3)_q$, where p and q are integers, the lattice parameter c in the three-dimensional formalism becomes $c = qc_{TiS3} = (1/2)pc_{Ba}$. In the last term, not pc_{Ba} but $(1/2)pc_{Ba}$ was adopted, because it is presumed from the sizes of the unit cells that the first cell contains three TiS_3 molecules while the second cell contains six Ba atoms. Hence, x in Ba_xTiS_3 is given by $x = p/q = 2c_{TiS3}/c_{Ba}$, because a_1 and a_2 are common to both cells. Therefore, the composition, x = Ba/Ti, should be given by $2c_{TiS3}/c_{Ba}$.

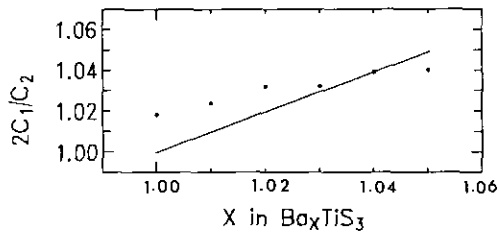

FIG. 4. $2c_1/c_2$ (or $2c_{TiS3}/c_{Ba}$) vs composition.

Figure 4 shows the relationship of the composition calculated from $x = 2c_{TiS3}/c_{Ba}$ and the nominal composition. These values do not agree with each other. The line in the figure represents the case in which the calculated and nominal compositions agree. In $Ba_xFe_2S_4$, Nakayama (12) also observed this inconsistency and postulated the existence of Ba and Fe vacancies.

The parameters $2c_1$ and c_2 need to have identical values at $x = 1.00$. In the experiments shown in Fig. 4, however, the former is a little larger than the latter. The disagreement is probably a result of the point defects. Therefore, two calculated densities were obtained from the two different cell volumes. They are 3.99 g/cm^3 (V = 349.0 Å^3, Z = 3) on the TiS_3 cell, and 4.06 g/cm^3 (V = 685.8 Å^3, Z = 6) on the Ba cell. The observed density for $Ba_{1.00}TiS_{2.93}$ is 4.03 g/cm^3, which is the average of four measurements 4.03, 4.03, 4.03, and 4.03 g/cm^3. A more detailed experiment is necessary to explain the value of the experimental density.

The lattice parameters are dependent not only on the Ba content but also on the sulfur content. The sulfur content in this work was fixed at $Ba_xTiS_{2.93}$ but it can vary from $Ba_xTiS_{2.79}$ to $Ba_xTiS_{2.97}$. Every specimen in this range consisted of composite crystal structure. Structure analysis using a single crystal is now in progress.

CONCLUSION

Prior to this work, $BaTiS_3$ had been described as being isostructural with $BaNiO_3$. However, in X-ray powder and electron diffraction patterns, some extra weak reflections exist which cannot be indexed to the $BaNiO_3$ structure. These reflections can be explained by satellites in the composite crystal. The diffraction patterns were indexed with a four-dimensional formalism, and the compound Ba_xTiS_3 can be described with a single structure with homogeneity range of x = 1.00–1.05.

In a three-dimensional atomic arrangement, the structure of Ba_xTiS_3 (x = 1.00–1.95) consists of two penetrating substructures, i.e., a TiS_3 cell and a Ba cell. The two cells have different fundamental periodicities, c_{TiS3} and c_{Ba}, in the c direction in a hexagonal setting. As c_{TiS3} and c_{Ba} vary with Ba content, an infinite number of structures with different periodicity are generated over the composition range of x = 1.00–1.05 in a three-dimensional formalism. Most of these structures crystallize in an incommensurate structure.

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