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Composite Crystals $BaTiS_y$ (y = 2.70–2.93)

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Barium titanium sulfide, $BaTiS_y$ ($y = 2.70$–2.93), has been prepared in atmospheres in which the sulfur partial pressures are controlled. The electron diffraction spots and the X-ray powder diffraction peaks of the sulfide could not be indexed because of large periodicity. The diffraction pattern was, however, indexable on the basis of hexagonal setting (trigonal system) with the lattice parameters of a, c_{TiS_3}, and c_{Ba} when four-dimensional formalism was employed. In the four-dimensional formalism, the structure could be represented as a single structure with homogeneity range of $BaTiS_{2.70}$–$BaTiS_{2.93}$. From the view point of three dimensional formalism, the structure of the sulfide consists of two penetrating hexagonal subcells. The lattice parameter a in the hexagonal setting is common to both subcells while c has different values, c_{TiS_3} and c_{Ba}. The c_{TiS_3} increases with decreasing sulfur content, while c_{Ba} decreases. As the lattice parameter c is given by $c = pc_{TiS_3} = qc_{Ba}$, where p and q are integers, there is an infinite number of structures with different c parameters in the composition range of $BaTiS_{2.70}$–$BaTiS_{2.93}$.

INTRODUCTION

It has been reported that many sulfides have a composite crystal structure which consists of two penetrating subcells. These sulfides are classified into two kinds of structures. One of them is a layered composite crystal such as PbS $(VS_2)_{1.12}$ (1), and the other is a chain-type composite crystal such as Sr_xTiS_3 (2, 3), $Ba_xFe_2S_4$ (4), and Ba_xTiS_3 (5).

$BaTiS_3$ belonging to chain-type composite crystals has been known to be isostructural with $BaNiO_3$ (6–8). However recently, Saeki and Onoda (5) revealed the existence of extra satellites in the electron and X-ray powder diffraction patterns of $BaTiS_3$. The explanation of these satellites led to the conclusion that $BaTiS_3$ is a composite crystal, and not isostructural with $BaNiO_3$. The $BaTiS_3$ with the $BaNiO_3$-type structure contains two kinds of chains, the Ba chain and the face-shared $TiS_{6/2}$ octahedron chain, which are along the c axis in a hexagonal system. Both chains have identical periodicity in the c direction. On the other hand, in $BaTiS_3$ with the composite crystal structure, the two kinds of chains have a different periodicity. The lattice parameter in the c axis is, therefore, represented by $c = pc_{TiS_3} = qc_{Ba}$, where p and q are integers, and c_{TiS_3} and c_{Ba} stand for the periodicities of the TiS_3 and Ba chains, respectively. The subcells are shown in Fig. 1. (Generally, the composite crystals are incommensurate, and the word "periodicity" here represents the periodicity of the fundamental structure or average structure (9, 10).)

The composite crystal structure exists at $x = 1.00$–1.05 in previously reported Ba_xTiS_3 (5). As c_{TiS_3} and c_{Ba} vary with Ba content, an infinite number of structures with different periodicities are generated over the composition range of $x = 1.00$–1.05. Most of the structures crystallize in an incommensurate structure. We can call this type of structure an infinitely adaptive structure. The aggregation of the structures can be represented as a single structure with the homogeneity range of Ba when a four-dimensional formalism is employed (5).

The purpose of this paper is to report that the infinitely adaptive structures exist in the sulfur-deficient compositions ($y = 2.70$–3.00 in $BaTis_y$), which is the same for the Ba-rich compositions ($x = 1.00$–1.05 in Ba_xTiS_3) reported in a previous paper (5).

EXPERIMENTAL

The preparation of $BaTiS_y$ was carried out as follows. The starting material, $BaTiO_3$ (purity 99.9%), was dried in an air bath at 100°C for one day to remove the adsorbed water. The starting material in the silica boat was, first, placed in a furnace and heated at 750°C for 3 days in a CS_2 atmosphere. The CS_2 gas was carried by N_2 gas. The obtained sulfide, $BaTiS_{2.93}$, was then annealed at 750°C under various sulfur atmospheres which were developed by mixing H_2 and N_2 (CS_2) at various ratios. The obtained specimens were sealed in evacuated silica tubes and heated at 900°C for 3 days, and then quenched in water. $BaTiS_{2.82}$ was the most deficient in sulfur of the sulfides obtained using this method. The sulfur content of these sulfides was obtained by the difference in weight between the starting oxide and the sulfide produced. Further desulfurization was carried out using Ti metal powder as a sulfur getter. The $BaTiS_{2.93}$ was sealed in an evacuated silica tube with Ti metal powder which was placed in a silica crucible.

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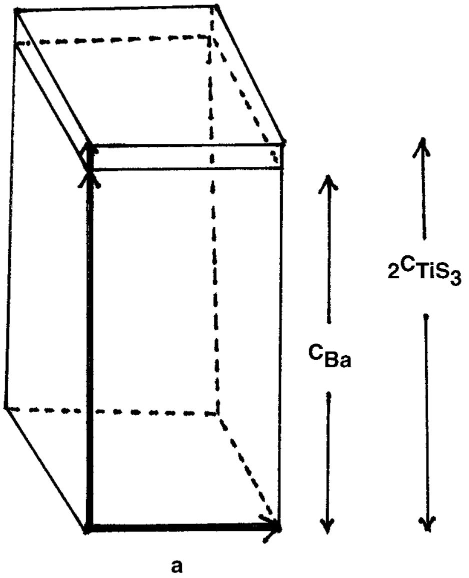

FIG. 1. Schematic subcells.

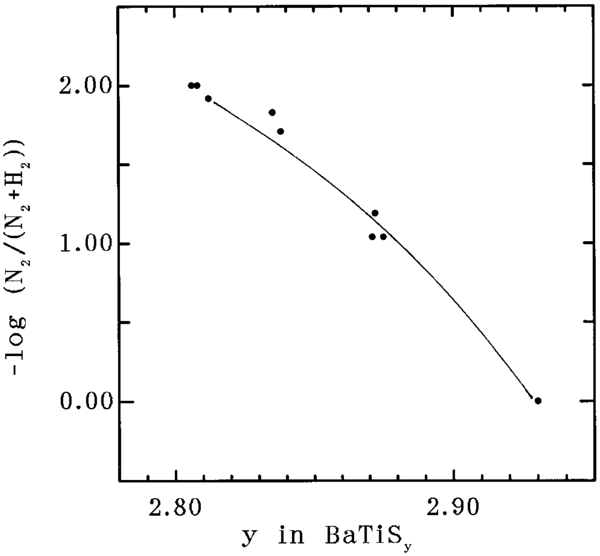

FIG. 2. Atmosphere and sulfur content. H_2 and N_2 stand for the amounts of hydrogen gas and nitrogen gas containing CS_2 vapor.

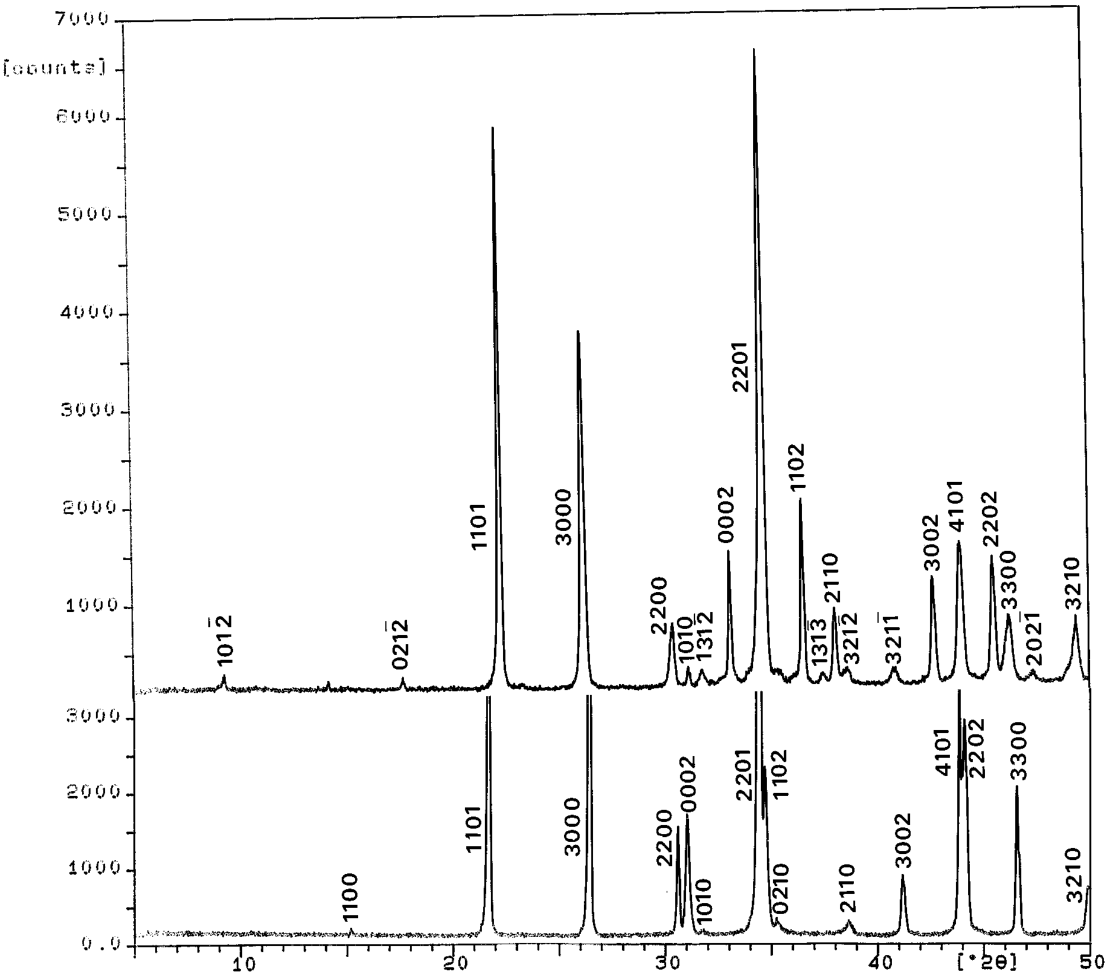

FIG. 3. X-ray powder diffraction patterns of $BaTiS_{2.70}$ (upper) and $BaTiS_{2.93}$ (lower).

The silica tube was heated at 700°C for 7 days and then quenched in water. The sulfides whose sulfur content was $BaTiS_{2.93}$–$BaTiS_{2.82}$ were annealed at 900°C, but the sulfide whose sulfur content was $BaTiS_{2.70}$ was annealed at 700°C because the powder X-ray diffraction peaks were broad when annealed at 900°C. The sulfur content of these sulfides was obtained from the increase in weight of the Ti metal.

The chemical analysis of the obtained sulfide was carried out in order to confirm that the Ba and Ti contents remain unchanged during the desulfurization process. The determination of the Ba and Ti contents was as follows. About 150 mg of the sulfide was placed in a Pt crucible, and heated in the air until the specimen looked white in color for the oxidation. The oxidized specimen was fused in $K_2S_2O_7$ and was filtered after adding HCl and H_2O_2. The Ba content was determined from the weight of the $BaSO_4$ precipitate. The Ti content was obtained from back-titration by Zn-standard solution after adding extra EDTA. Then the sulfur content was determined as follows. About 100 mg of the sulfide was added in a solution consisting of 50 wt% NaOH and 30 wt% H_2O_2. After heating at 120°C for 16 h in a sealed vessel to solve for Ti, $BaCl_2$ was added to form $BaSO_4$ precipitate. The sulfur content was obtained from the weight of the $BaSO_4$.

The chemical analysis was performed for $BaTiS_{2.872}$ which is the calculated composition. The sulfur content in the calculated composition was obtained from the difference in weight of the starting material and the sulfide produced. The Ba and Ti contents in the calculated composition were obtained from the starting materials. For $BaTiS_{2.872}$, the experimental Ba content was 49.04, 49.14, and 49.30 wt% for the calculated value of 49.52 wt%; the experimental Ti content was 17.35, 17.32, and 17.34 wt% for the calculated value of 17.27 wt%; the sulfur content was 33.7, 33.6, and 33.3 wt% for the calculated value of 33.21 wt%. The experimental chemical composition is in excellent agreement with the calculated composition. It can be, therefore, concluded that Ba and Ti do not evaporate during the desulfurization process, and it is confirmed that the S content obtained from the weight difference is correct.

X-ray powder diffraction data were collected using a step-scan procedure on a Philips PW 1800 diffractometer using an automatic divergence slit and counter-side monochromatized Cu*Kα* radiation. Electron diffraction patterns were obtained for crushed particles using a 100 kV electron microscope (Hitachi 500-type).

The density of the specimen was obtained by measuring its 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.

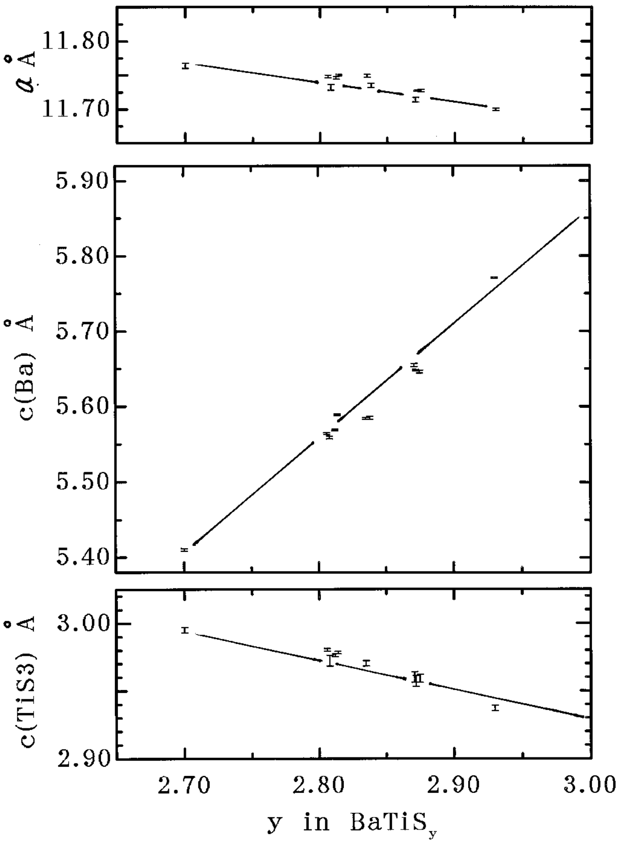

FIG. 4. Lattice parameters and sulfur content.

Before measuring the density of the specimen, the density of the fine powder silicon was measured to examine the accuracy of this method. It resulted in 2.31 and 2.32 g/cm^3 (two measurements) compared to the value of 2.33 g/cm^3 from the literature.

RESULTS

The $BaTiS_{2.93}$ was annealed in the atmospheres with various sulfur partial pressures to prepare the sulfides with various sulfur content. Figure 2 reveals the relation of the atmosphere and the sulfur content. The $BaTiS_{2.93}$, $BaTiS_{2.82}$, and $BaTiS_{2.70}$ were obtained in a CS_2 atmosphere, a hydrogen gas atmosphere, and in an atmosphere with the Ti metal as a sulfur getter, respectively. The X-ray powder diffraction patterns could not be indexed because of the large periodicity. The diffraction peaks were, however, indexable with simple periodicities of a, c_{TiS_3}, and c_{Ba} when four-dimensional formalism was employed. How to index was described in detail in a previous

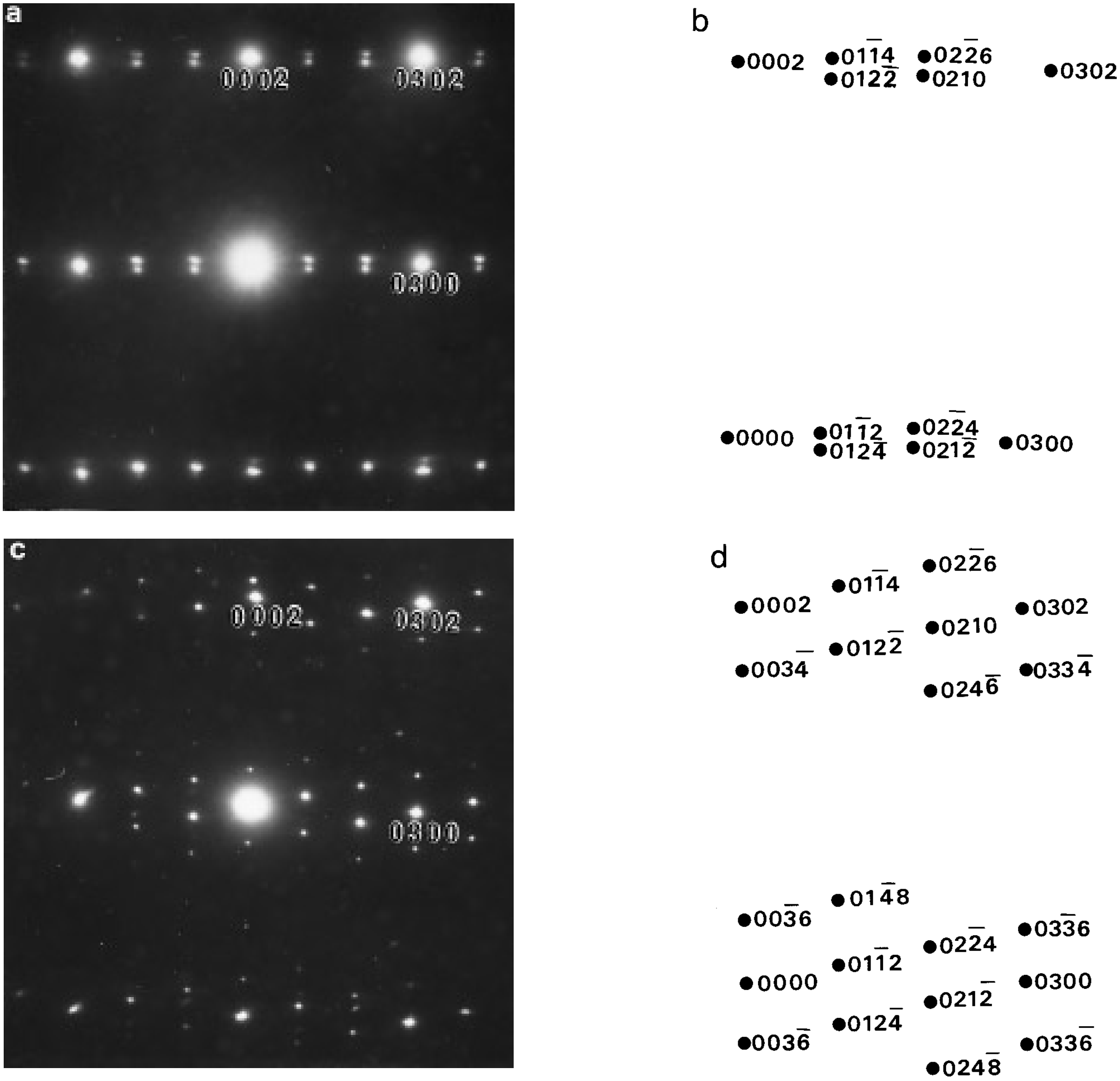

FIG. 5. (a) Electron diffraction patterns of $BaTiS_{2.93}$, (b) schematic drawing of (a), (c) electron diffraction pattern of $BaTiS_{2.82}$, and (d) schematic drawing of (c).

paper (5). The diffraction peaks of the sulfides richer in sulfur than $BaTiS_{2.70}$ could be indexed on the basis of a hexagonal setting (trigonal system) in four-dimensional formalism, but the sulfide poorer in sulfur than $BaTiS_{2.65}$ gave a structure with lower symmetry, and further desulfurization by Ti metal results in the isolation of BaS.

Figure 3 shows the X-ray powder diffraction patterns of $BaTiS_{2.93}$ (a = 11.7135 (8) Å, c_{TiS_3} = 2.937 (2) Å, and c_{Ba} = 5.771 (1) Å) and $BaTiS_{2.70}$ (a = 11.764 (4) Å, c_{TiS_3} = 2.995 (2) Å, and c_{Ba} = 5.410(2) Å). 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 $c_2^* = 1/c_2$.

Figure 4 shows the relationship of the lattice parameters and the sulfur content. The lattice parameters of a and c_{TiS_3} increase with decreasing the sulfur content, while the c_{Ba} decreases.

Figure 5 shows the electron diffraction patterns of $BaTiS_{2.93}$ and $BaTiS_{2.82}$. All the spots could be indexed by the four-dimensional formalism. These lattice parameters agreed with those obtained from the X-ray powder diffraction.

As was shown above, the X-ray powder diffraction patterns of $BaTiS_{2.93}$–$BaTiS_{2.70}$ was indexable when four-dimensional formalism is employed. That is to say, in four dimensional formalism, the structure can be represented as a single structure which has a homogeneity range of $BaTiS_{2.93}$–$BaTiS_{2.70}$. On the other hand, from the view point of three-dimensional formalism, the unit cell consists of the two subcells shown in Fig. 1. The lattice parameter a in the hexagonal setting is common for both subcells and the lattice parameters in the c direction have different values, c_{TiS_3} and c_{Ba}. The c_{TiS_3} elongates with decreasing sulfur content while c_{Ba} shrinks. Since the lattice parameter c of the unit cell is represented by $c = pc_{TiS_3} = qc_{Ba}$ where p and q are integers, a slight difference in the sulfur content leads to a different structure with a different c axis. Therefore, an infinite number of structures exists in the composition range of $BaTiS_{2.70}$–$BaTiS_{3.00}$, i.e., an infinitely adaptive structure. This type of structure was observed in the composition range of $x = 1.00$–1.05 in Ba_xTiS_3 as reported in a previous paper (5). The $BaTiS_3$ has an infinitely adaptive structure on both sides, i.e., Ba excess and sulfur deficient regions.

In this type of composite crystal structure, the chemical composition can be determined from the ratio of the lattice parameters in incommensurate direction. In the present case, the composition, Ba/TiS_3, should be given by the ratio of c_{TiS_3} and c_{Ba}, i.e., $Ba/TiS_3 = 2c_{TiS_3}/c_{Ba}$. In the equation, $2c_{TiS_3}$ not c_{TiS_3} was adopted, because the TiS_3 cell contains three TiS_3 molecules in the unit cell while the Ba cell contains six Ba atoms. The a_1 and a_2 are common to both cells.

The lattice parameters of $BaTiS_{3.0}$ can be estimated from the extrapolation in Fig. 4, since $BaTiS_{3.0}$ could not be prepared because of its high sulfur activity (or high equilibrium sulfur partial pressure in the atmosphere). According to the extrapolation in Fig. 4, c_{Ba} and $2c_{TiS_3}$ have identical values at $BaTiS_{3.0}$ ($2c_{TiS_3}/c_{Ba} = (2 \times 2.93)/5.86 = 1$). However, as the composition is poorer in sulfur than $BaTiS_3$, the chemical composition is not estimated from the lattice parameters.

DISCUSSION

A question arises as to the defect structure of the sulfur deficient $BaTiS_y$ (y = 2.93–2.70). The periodicity of the Ba chain reduces with decreasing sulfur content, while the periodicity of the TiS_3 chain enlarges. This means that the number of Ba sites is larger than that of Ti sites for the composition poorer in sulfur than $BaTiS_3$, despite the equimolar Ba and Ti, and despite the fact that the metal ratio remains equimolar during the desulfurization of $BaTiS_{2.93}$. Three models are considered to explain the inconsistency between the metal ratio and the metal site ratio. They are (1) the Ba vacancy model, (2) the interstitial Ti model, and (3) the substitution model in which some Ba sites are substituted with Ti atoms. The density was measured for the sulfides with various sulfur contents, in order to compare with the calculated densities which are given by $M/2V_1$ for the Ba vacancy model, M/V_2 for the interstitial Ti model, and $M(2V_1 + V_2)/4V_1V_2$ for the substitution model, where M is the molecular weight contained in the subcell, V_1 is the cell volume of the TiS_3 subcell, and V_2 is the cell volume of the Ba subcell. These calculated densities were, therefore, obtained from the experimental lattice parameters and the experimental sulfur contents. Figure 6 gives the relation of the densities and sulfur content. As is seen in Fig. 6, the experimental density suggests the substitution model and rejects both the Ba vacancy model and the interstitial Ti model. The density is, however, poor evidence to prove the substitution model. A better way to confirm the correct model is to compare the experimental and calculated intensities of the X-ray powder diffraction. It is, however, considered to be difficult to calculate the intensity because of the modulated structure.

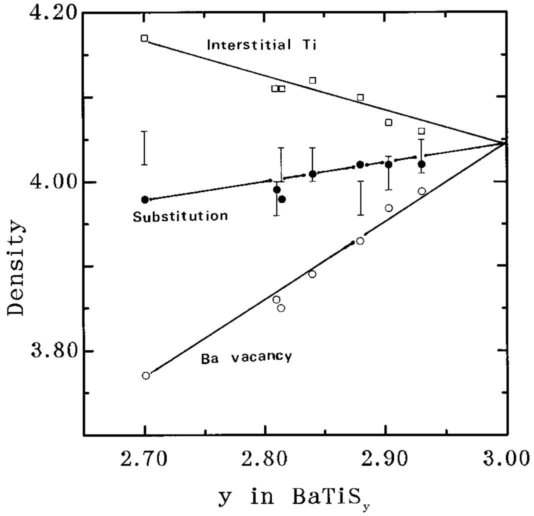

FIG. 6. Density and sulfur content. Calculated density for the Ba vacancy model is represented by open circles, the interstitial Ti model by open squares, and the substitution model by solid circles. The experimental density is given by a vertical bar which contains the experimental error.

CONCLUSIONS

A previous paper reported that Ba_xTiS_3 is a composite crystal with an infinitely adaptive structure for a composition richer in Ba than $BaTiS_3$. In addition, this paper described that $BaTiS_3$ also has an infinitely adaptive structure for a composition poorer in sulfur than $BaTiS_3$. The chemical composition cannot be estimated from the lattice parameters for the sulfur-deficient composition $BaTiS_y$ ($y < 3.00$).

For the defect structure of sulfur-deficient $BaTiS_y$, the simple models for a Ba vacancy and interstitial Ti are rejected by the density measurements.

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