Synthesis of Ba_xTiS_y in Sulfur Melt*

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Barium titanium sulfide, Ba_xTiS_y with various x and y values, i. e. $x = 0.6 \sim 0.81$ and $y = 2.89 \sim 3.82$, has been synthesized by the reaction of BaS and TiS_2 in sulfur melt at temperatures between 350 and 450 °C. The unreacted solvent sulfur was completely removed by two-step separation method after reaction. The results showed that the x value of Ba_xTiS_y tended to increase with increasing heating temperature and heating time and the maximum x value was around 0.8. The y values were around 3.0 at 400 and 450 °C. The addition of 10 mol % BaCl_2 was found to expedite greatly the yield of reaction to form Ba_xTiS_y especially at higher heating temperature of 450 °C. The BaCl_2 and BaS_3 impurities were removed by treating with water. This treatment was also effected to change some X-ray peak positions of Ba_xTiS_y prepared by the present low temperature method.

KEY WORDS : Barium Titanium Sulfide, Mixed Sulfide, Synthesis, Sulfur Melt, Crystal Structure

1. Introduction

The mixed oxides of perovskite-type structure have been applied as device elements in various fields of advanced technology by virtue of their special electrical and magnetic properties. For example, BaTiO_3 is widely used as dielectrics in electronic industries. The corresponding mixed sulfide, BaTiS_3 , is considered to be an attractive compounds because of the complexity of its crystal structure^{1)–4)} and its semiconductivity⁵⁾. For synthesizing the mixed sulfides, however, more attention is needed to avoid the contamination of oxygen in the compounds. Furthermore, some kinds of mixed sulfides are assumed to be unstable at high temperatures or to change their physico-chemical properties due to sulfur nonstoichiometry and structural modification depending on temperature. For this reason, lower temperature synthesis is required for these sulfides. Two typical methods have been reported to synthesize BaTiS_3 . One method consists of direct reaction of BaS and TiS_2 by heating their mixture in a sealed evacuated quartz tube at a relatively high temperature for several weeks. This method is regarded as the one which is most frequently used¹⁾. The BaTiS_3 compound is usually obtained at temperatures around 800–900 °C. Another method comprises sulfurization of a mixture of various kinds of Ba-bearing and Ti-bearing compounds using CS_2 in N_2 carrier gas. This method stands on the ground of the strong sulfurizing power of CS_2 compared with that of H_2S . Also, it

has been reported that the heating temperatures above 700 °C were required to obtain BaTiS_3 with a satisfactory yield in the latter method^{2)–4)}.

For low temperature synthesis of mixed sulfides, the reaction in sulfur melt is intriguing for this purpose since the reactions are assumed to proceed more rapidly in suitable solvents. The sulfur melt could play a role of solvent as well as reactant. This work was undertaken to study the low temperature synthesis in sulfur melt for the case of BaTiS_3 , which is a corresponding sulfide to BaTiO_3 . The mixture of BaS and TiS_2 were heated in a large amount of sulfur at low temperatures of 350–450 °C. The effect to increase the reaction rate through the reaction of barium ion with TiS_2 and sulfur by way of a dissociable halide, BaCl_2 , added in a small amount, was also studied.

2. Experimental

2.1 Starting materials

BaS used was freshly prepared by heating BaCO_3 in a stream of H_2S at 900 °C for 3 h, since it was easily decomposed by moisture. The X-ray powder diffraction pattern of the product showed the formation of BaS in a single phase. TiS_2 of 99.9 % purity was purchased from High-Purity Chemicals Lab. BaCl_2 and sulfur of analytical grade were obtained from Kanto Chemical Co., Inc. Analytical grade CS_2 having a boiling point of 46–47 °C and acetone were obtained from Wako Pure Chemicals Industries, Ltd., and used as received.

2.2 Experimental procedures

2.2.1 Sample preparation

Calculated amounts of BaS and TiS_2 were intimately mixed together with a large excess of sulfur, which was 50 times of molar numbers of BaS and TiS_2 , by grinding in an agate mortar for about 20 min. The mixture was sealed in evacuated Pyrex

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ampoules, which were then, heated for periods ranging from one to three weeks in a muffle furnace. The reaction temperatures studied were 350, 400 and 450 °C.

2 · 2 · 2 Sulfur separation After heating, the ampoules were taken out from the furnace and air-cooled to room temperature. The unreacted sulfur was removed by the following two-step separation method immediately after the ampoule was opened.

Step 1 : Filtration of sulfur melt

The filtration separation was implemented using a specially designed separation system for this study as shown in Fig. 1. The system is composed of two parts ; a vertical resistance tube-furnace with its wall made of Pyrex glass, and a Pyrex glass separator connected to evacuation line. The ampoule with one end cut open was set in the separator with its open-end downward on the glass filter (G4), and then the separator was heated in the furnace during suction by rotary pump. The sulfur separation was checked through the glass-furnace.

The separation experiment was performed at a temperature of 155 ± 2 °C for low viscosity of sulfur. To effect the filtration of sulfur melt, the N_2 gas of a controlled pressure was applied to the mixture of reaction product and sulfur melt from the inlet of the separator. The solid sample was collected on the filter while the sulfur melt was removed by passing through the filter and flowed down to the bottom of the separator.

Step 2 : Dissolution of remaining sulfur in CS_2

To remove the small amount of sulfur still attached to the sample after the filtration process, the solid was immersed in liquid CS_2 to dissolve such sulfur in this solvent. Then, the solid sample was washed by acetone and then air dried.

2 · 2 · 3 Separation of BaS_3 and $BaCl_2$ The impurities of BaS_3 and $BaCl_2$ were dissolved in distilled water. By washing for 10~15 min, BaS_3 and $BaCl_2$ were completely

removed, and Ba_xTiS_y was obtained in a purified form.

2 · 3 Analysis of Ba_xTiS_y

The phase analysis of the product was carried out by means of X-ray powder diffractometry with a Rigaku type RAD-IC diffractometer using $CuK\alpha$ radiation (40 kV, 20 mA), monochromatized by curved pyrolytic graphite.

Barium and titanium were determined by inductively coupled plasma emission spectroscopy (ICP-ES) using a PERKIN ELMER Optima 3300 XL spectrometer. Hydrochloric acid of 6M was used as solvent both for diluting standard solutions and for dissolving samples.

The amounts of BaS_3 , $BaCl_2$ and TiO_2 impurities were estimated by the integrated intensities of BaS_3 , $BaCl_2$ and TiO_2 peaks in X-ray powder diffraction patterns. The x and y values in Ba_xTiS_y were derived from the amounts of barium, total titanium and TiO_2 .

3. Results and Discussion

3 · 1 Synthesis of Ba_xTiS_y

For the synthesis of Ba_xTiS_y , a series of reactions were first carried out by heating the mixture of BaS and TiS_2 in 1 : 1 molar ratio with a large excess of sulfur for one week, i. e.

The heating temperatures studied were 350, 400 and 450 °C.

After sulfur was removed by the process of the liquidization and dissolution, the products were obtained as the mixture of Ba_xTiS_y , BaS_3 and TiO_2 . Table 1 exhibits the reaction conditions and the molar ratios of these compounds in the products. The amount of impurity BaS_3 tends to increase with increasing temperature. Prolonged heating for two or three weeks at 450 °C seems to cause a decrease in the BaS_3 amount to some extent. BaS_3 can completely be removed by the water treatment. The amount of impurity TiO_2 is of the order of a few mol %, the change of which with heating conditions is probably small though obscure because of the scatter of the observed values.

The X-ray diffraction patterns of the products are shown in Fig. 2, where the peaks of impurity BaS_3 are indicated by circles. It can be seen from these patterns that both the peaks of BaS_3 and Ba_xTiS_y grow sharp with the increase of temperature, while the peaks of BaS_3 develop more rapidly than those of Ba_xTiS_y .

The lattice parameters of Ba_xTiS_y were calculated based on the hexagonal system⁶⁾ with space group $P6_3/mmc$. The calculated lattice parameters using the LCR2 program⁷⁾ are $a = 6.756 \pm 0.002$ and $c = 5.806 \pm 0.004$ Å for the sample pre-

Fig. 1 Illustration of sulfur separation system.

Table 1 Compounds in the heated samples after sulfur was removed (Reaction(1)).

Sample No.	Temperature (°C)	Heating time (week)	Compounds (molar ratio)		
			Ba_xTiS_y	BaS_3	TiO_2
1-1	350	1	1	0.14	0.05
1-2	400	1	1	0.27	0.01
1-3	450	1	1	0.39	0.03
1-4	450	2	1	0.14	0.01
1-5	450	3	1	0.22	0.02

Fig. 2 X-ray diffraction patterns showing the effect of heating temperature on the products of reaction (1). Heating time : one week.

pared at 350 °C, while the values are $a = 6.7608 \pm 0.0006$ and $c = 5.8105 \pm 0.0009$ Å at 400 °C. The lattice parameters are $a = 6.7582 \pm 0.0007$ and $c = 5.812 \pm 0.002$ Å for that obtained at 450 °C. Both of the lattice parameters, a and c , are larger when heated at higher temperatures of 400 and 450 °C.

Another reaction studied to synthesize Ba_xTiS_y is that with the following starting materials :

In this reaction, 10 mol % BaCl_2 was substituted for BaS instead of 1 : 1 molar ratio of BaS and TiS_2 in reaction (1). For reaction (2), BaS , BaCl_2 and TiS_2 were intimately mixed in a proportion of 0.9 : 0.1 : 1 together with a large excess amount of sulfur (50 times in molar ratio), which was the same as that in reaction (1). Then, the mixture was heated at the intended temperature. The reaction temperatures studied were 350, 400 and 450 °C.

There are no reported data about the solubility of solid BaCl_2 (m. p. = 962 °C) in a molten sulfur in the temperature range of this study. But in the alkali-metal chloride melts, the component metal and chlorine are known to exist as the charged ions of +1 and -1, respectively⁸⁾. Therefore, if BaCl_2 is dissolved in sulfur melt, even only to a low concentration, its barium possibly dissociates as Ba^{2+} and reacts with TiS_2 resulting in formation of Ba_xTiS_y in combination with the corresponding amount of S^{2-} . The consumed barium is assumed to be supplied by the dissolution of the remaining BaCl_2 or BaS . The dissociation of BaS in the melt could be enhanced in the presence of Cl^- ion by the following equations (3) and (4) :

Table 2 Compounds in the heated samples after sulfur was removed (Reaction(2)).

Sample No.	Temperature (°C)	Heating time (week)	Ba_xTiS_y	Compounds (molar ratio)		
				BaS_3	BaCl_2	TiO_2
2-1	350	1	1	0.18	0.04	0.03
2-2	400	1	1	0.20	0.04	0.01
2-3	450	1	1	0.07	0.03	0.02
2-4	450	2	1	0.03	0.06	0.02
2-5	450	3	1	0.01	0.02	0.04

However, there remains another possibility that the concentration of BaS in sulfur melt is simply increased by the presence of BaCl_2 . In this case also the reactivity to form Ba_xTiS_y is expected to increase. For the resolution of the reaction enhancement mechanism of BaCl_2 , further studies are needed.

The results of the heating experiments on the basis of reaction (2) are listed in Table 2. At 350 and 400 °C, the molar ratio of BaS_3 in the product is about 0.18~0.20. At 450 °C, however, the molar ratio decreased to 0.07 after one week heating. This amount decreased much more with longer heating time, and it became 0.01 after heating for three weeks.

It is noteworthy that the molar ratio of BaCl_2 was diminished from 0.10 of initial ratio to 0.04 after heating at 350 or 400 °C, and it changed between 0.02 and 0.06 with the change of heating time at 450 °C. The decrease of the BaCl_2 amount is considered to be associated with the formation of sulfur chlorides⁹⁾ such as S_2Cl_2 and SCl_2 . The fluctuation of the BaCl_2 molar ratio at 450 °C can be regarded as due to the error in measuring the BaCl_2 amount. The averaged value is 0.04 which is in agreement with the molar ratio at 350 and 400 °C, suggesting that the solubility of BaCl_2 in sulfur melt to be around this molar ratio without significant change with heating temperature in the range of 350~450 °C. It is assumed therefore that BaS reacts with TiS_2 by way of BaCl_2 resulting in formation of Ba_xTiS_y . Another possibility is a catalytic effect of BaCl_2 in the reaction. It is difficult to verify clearly the contribution of BaCl_2 in reaction (2) at present.

The TiO_2 impurity produced during reaction (2) is in the amount of the same order of magnitude as that produced during reaction (1). The formation of TiO_2 may basically be unaffected by the present reaction conditions. The oxygen of this compound is assumed to be taken from SiO_2 constituting the Pyrex ampoules.

The X-ray diffraction patterns of the products obtained by reaction (2) are shown in Fig. 3, where the peaks of BaS_3 and BaCl_2 are marked out by circles and crosses, respectively. Different from the products of reaction (1), the peak intensities of BaS_3 in Fig. 3 decreased while those of Ba_xTiS_y increased as the heating temperature is increased from 350 to 450 °C. At the highest temperature of 450 °C, the peak intensities of BaS_3 did not change with heating time from one week to two or three weeks. The amount of BaS_3 impurity already attained 7 mol % after one week heating. The lattice parameters of Ba_xTiS_y were $a = 6.757 \pm 0.002$ and $c = 5.809 \pm 0.003$ Å for the 350 °C sample. On the other hand, the lattice parameters were $a = 6.7594 \pm 0.0005$ and $c = 5.814 \pm 0.001$ Å, and $a =$

Fig. 3 X-ray diffraction patterns showing the effect of heating temperature on the products of reaction (2). Heating time : one week.

6.758 ± 0.001 and $c = 5.818 \pm 0.002$ Å for the samples of 400 and 450 °C, respectively. The lattice parameter, c , was larger when the heating temperature was high, i. e. 400 and 450 °C, whereas the a parameter remains almost unchanged. The c parameters of Ba_xTiS_y of reaction (2) are larger (by ~ 0.005 Å) than those of Ba_xTiS_y of reaction (1). In contrast, there are no marked differences in the a parameters of reactions (1) and (2).

3 · 2 Composition of mixed sulfide Ba_xTiS_y

The x and y values in Ba_xTiS_y were calculated from the Ba and Ti amounts determined by ICP-ES in combination with X-ray diffractometry after BaS_3 and $BaCl_2$ were removed from the samples by the water treatment. Since TiO_2 was found to dissolve together with Ba_xTiS_y in 6M HCl solution used for the ICP-ES analysis, the Ti amount of Ba_xTiS_y was obtained by subtracting the Ti amount of TiO_2 (Tables 1 and 2) from the total Ti amount determined by ICP-ES. The sulfur amount (y value) was obtained by subtracting the weights of Ba and Ti from the total weight. The x and y values worked out are summarized in Table 3.

Fig. 4 shows the effect of heating temperature on the x and y values for the samples of one week heating time. The x value of Ba_xTiS_y obtained by reaction (2) increased with increasing temperature in a similar manner with that of Ba_xTiS_y obtained by reaction (1) : The enhancement of the x value was large in a range between 350 and 400 °C, though the curves are levelling off between 400 and 450 °C. The x values of reaction (2) are larger than those of reaction (1) at all temperatures studied by 0.10~0.15. As for y value, its change with temperature is not straightforward. At 350 °C, the y value of reaction (1) is exceedingly large ($y = 3.82$) although it is

Table 3 Determination of x and y values in Ba_xTiS_y .

Sample No.	Sample Weight ($\times 0.05$ mg)	Ba Weight ($\times 0.05$ mg)	Ti Weight(as sulfide) ($\times 0.05$ mg)	x	y
1-1	24.2	7.79	4.50	0.60	3.82
1-2	26.2	10.20	5.28	0.67	3.01
1-3	56.4	22.40	11.21	0.70	2.96
1-4	55.8	23.50	10.30	0.80	3.16
1-5	45.8	19.40	8.72	0.78	2.98
2-1	37.8	15.70	7.41	0.74	2.89
2-2	47.4	20.50	8.93	0.80	2.98
2-3	71.1	30.48	13.15	0.81	3.07
2-4	58.2	24.95	10.91	0.80	3.02
2-5	45.0	18.10	8.70	0.73	3.02

Fig. 4 Change of the composition of Ba_xTiS_y with heating temperature: (a) : x value, (b) : y value.

rather small ($y = 2.89$) when Ba_xTiS_y was obtained by reaction (2). At 400 and 450 °C, the y values of Ba_xTiS_y are around 3.0 for both reactions (1) and (2). Considering the errors in the determination of these y values, the mixed sulfide synthesized at 400 and 450 °C can be regarded as sulfur stoichiometric Ba_xTiS_3 .

Fig. 5 shows the effect of heating time on x and y values for the samples heated at 450 °C. For reaction (1), the x value increased from 0.70 to 0.80 when the heating time was prolonged from one week to two weeks. The x value then slightly turned to decrease to 0.78 when the sample was heated for three weeks. For reaction (2), the x value remained unchanged at about 0.80 in both cases of one week and two weeks. However, the x value significantly decreased to 0.73 when the sample was heated for longer time of three weeks. From Figs. 4(a) and 5(a), the maximum and minimum x values in reaction (1) are after all around 0.80 and 0.60, respectively, of which the difference is fairly large. For reaction (2), the difference is smaller : The x values are 0.82 and 0.73. The obtained y values, on the other hand, are around 3.0 excluding the case of heating at 350 °C for one week for both reactions (1) and (2) as seen in Figs. 4(b) and 5(b).

3 · 3 Crystallinity of Ba_xTiS_y

The broadening of X-ray diffraction peaks is known to be

Fig. 5 Change of the composition of Ba_xTiS_y with heating time. (a) : x value, (b) : y value.

caused by the small particle size of the crystallites and the lattice deformation in the crystallites. There have been a large number of studies in which these effects are separately analyzed from the observed X-ray peaks. They may be classified into the integrated peak width method⁽¹⁰⁾⁽¹¹⁾, the variance method⁽¹²⁾⁽¹³⁾ and the Fourier transform method⁽¹⁴⁾. The lattice deformation is supposed to raise an important problem with regard to the low temperature synthesis of the compounds as in the present case, since the crystals are not fully developed on reactions at low temperatures. In this work, efforts are focused to the possibility of synthesis of a mixed sulfide, Ba_xTiS_y , at low temperatures, so that the close analysis of the crystallinity is out of the scope. Here, the peak broadening is shown for the (200) and (002) peaks at 30.0~31.5 °. Fig. 6 shows the peak profiles of the reaction products before water treatment. Obviously, the peaks become sharp as the heating temperature is increased and the heating time is elongated for both reactions of (1) and (2).

Another point worthy to be noted is the effect of water treatment on the crystallinity of Ba_xTiS_y . Most peak positions of Ba_xTiS_y obtained by heating at lower temperatures of 350 and 400 °C shift to higher reflection angles comparing with the data of Clearfield⁽²⁾. However, such a shift was not seen after 10~15 min of water treatment. Also, the peaks were sharper giving better resolution. The (200) and (002) reflections are shown as an example in Fig. 7. Thus, in addition to remove BaS_3 and BaCl_2 by dissolution, the water treatment is found to play an important role in accelerating the crystal development yielding the lattice parameters closer to those of Ba_xTiS_y formed by the usual method at high temperatures. Too long period of the water treatment, however, does not seem to be suited for having Ba_xTiS_y of good crystallinity because of hydrolysis.

Fig. 6 Effect of heating temperature and time on the X-ray peak intensity and resolution of (200) and (002) doublet. Samples are not water treated. (a) : products of reaction (1), (b) : products of reaction (2).

Fig. 7 Change of the intensity and resolution of X-ray peaks shown for (200) and (002) doublet as an example (Reaction (1), 400 °C). (a) : before water treatment, (b) : after water treatment.

4. Conclusion

A new route for synthesizing mixed sulfides at lower temperatures in sulfur melt was proposed. This method was

applied for the synthesis of Ba_xTiS_y using barium and titanium bearing materials in a sulfur melt. It was found that Ba_xTiS_y was synthesized by heating the mixture of BaS and TiS_2 in a large excess amount of sulfur melt at a relatively low temperature of 350–450 °C. The compound was obtained in a purified form by two-step separation of excess sulfur and water treatment for impurities such as BaS_3 and BaCl_2 . The x value of Ba_xTiS_y tended to increase with increasing heating temperature for one week heating time. At 450 °C, the value did not change on elongated heating of two and three weeks at its maximum value of around 0.8. On the other hand, the y value was close to a stoichiometric one i. e. 3.0 when the heating temperature was set at 400 and 450 °C. Addition of a small amount ($\sim 10\%$) of BaCl_2 was proved to be effective for promoting the yield of Ba_xTiS_y especially at a higher heating temperature of 450 °C. The water treatment was found to be not only effective for removal of BaS_3 and BaCl_2 impurities but also for having Ba_xTiS_y of good crystallinity.

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溶融硫黄を用いる Ba_xTiS_y の合成

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溶融硫黄中 BaS と TiS_2 を 350 から 450 °C において反応させることにより、バリウムチタン硫化物、 Ba_xTiS_y ($x = 0.6 \sim 0.81$, $y = 2.89 \sim 3.82$) を合成した。未反応の硫黄溶媒は反応後に二段階分離法により完全に除去した。 Ba_xTiS_y の x 値は加熱温度および時間の増加とともに増加し、最大値は 0.8 となった。 y 値は加熱温度 400 および 450 °C においてほぼ 3 であった。10 mol % の BaCl_2 を添加すると、特に高温 (450 °C) において Ba_xTiS_y の生成を大きく促進させることが分かった。 BaCl_2 や BaS_3 のよ

うな不純物は水洗により除去できた。また、この処理により本研究において低温合成された Ba_xTiS_y の X 線回析のピーク位置をシフトさせる効果が見られた。

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キーワード：バリウムチタン硫化物、複硫化物、合成、溶融硫黄、結晶構造