Synthesis of BaZrS$_3$ in the presence of excess sulfur

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Abstract

Synthetic reaction of barium zirconium sulfide, BaZrS$_3$, was studied in a large excess amount of sulfur melt at temperatures of 623–723 K and in the presence of a small amount of excess sulfur at temperatures of 623–823 K, respectively. The results showed that BaZrS$_3$ was formed with high yields by heating at temperatures ranging from 723 to 873 K, if a proper amount of excess sulfur and 10 mole% of BaCl$_2$ were added in the starting materials. The compound could be obtained in almost a single phase with only 2–3 mole% ZrO$_2$ impurity after the 8 min water treatment of the products obtained at 873 K. The modified method studied in this paper, i.e. reaction in the medium temperature range of 723–873 K, was shown to be applicable for synthesizing the mixed sulfides of some kinds including BaZrS$_3$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Chemical synthesis; Semiconductors; Crystal structure

1. Introduction

BaZrS$_3$ is a member of perovskite type sulfides which constitute d^0 diamagnetic semiconductors together with hafnium compounds, exhibiting mostly orange–brown to green color [1]. This compound has been synthesized by various methods.

Hahn and Mutschke [2] prepared BaZrS$_3$ by heating the mixture of binary sulfides BaS and ZrS$_2$ in a sealed evacuated quartz tube for several weeks. They found the compound to be dimorphic. The low temperature phase prepared at 1073–1173 K was tetragonal with $a=0.4990$ and $c=0.5088$ nm. The crystal was of distorted perovskite type, brittle and light brown colored. On the other hand, the crystal structure of the light green high temperature phase formed at temperatures 1173–1273 K could not be resolved. According to Aslanov and Kovba [3], the crystal system of the low temperature phase BaZrS$_3$, which was prepared at 1073 K in a similar way as above, is tetragonal, but the cell parameters should be twice as large as the reported ones, i.e. $a=2\times0.4986\pm0.0004$ and $c=2\times0.5049\pm0.0004$ nm.

Synthesis of BaZrS$_3$ has also been carried out by sulfurizing BaZrO$_3$ with CS$_2$ at temperatures 773–1623 K

for periods ranging from several hours to one day [4]. The X-ray diffraction patterns of the products heated at 1223–1473 K were the same, showing that BaZrS$_3$ was formed in a single phase in this temperature range. The compound was concluded to have a distorted perovskite structure with GdFeO$_3$ type [5]. The diffraction peaks were indexed on the basis of the orthorhombic system with $a=0.7037$, $b=0.9983$ and $c=0.7050$ nm.

BaZrS$_3$ has also been prepared by heating the mixture of BaCO$_3$ and ZrO$_2$ in a stream of H$_2$S at temperatures around 1373 K for 7 days [6]. The compound was proved to be isostructural with GdFeO$_3$. Its crystal parameters were refined by neutron powder profile refinement technique [7]. The obtained lattice parameters were $a=0.70599$, $b=0.99813$ and $c=0.70251$ nm, and the space group was *Pnma*, $Z=4$.

As described above, it is thought that BaZrS$_3$ is dimorphic. The change of the crystal structure is possibly associated with sulfur non-stoichiometry related to the preparation conditions. We have been studying a low temperature synthetic method for mixed sulfides in sulfur melt [8–10], which is considered to give the sulfides with fully co-ordinated sulfur. Therefore, it is intriguing to apply the method for the preparation of BaZrS$_3$. In this work, the synthesis of BaZrS$_3$ at temperatures below 873 K was investigated taking two different routes. One was to synthesize BaZrS$_3$ in a large excess of sulfur melt at 623–723 K. Ba$_x$TiS$_y$ [8] and PbTiS$_3$ [9] were successfully

prepared by this low temperature method in our previous work. The other was to synthesize $BaZrS_3$ in the presence of a small excess amount of sulfur at 623–873 K. This is the newly developed method here. As in the case of the syntheses of Ba_xTiS_y and $PbTiS_3$ [8–10], the addition of 10 mole% of $BaCl_2$ exhibited its importance also for the synthesis of $BaZrS_3$ together with (a small amount of) excess sulfur at temperatures 723–873 K. The effect of the addition amount of sulfur, heating temperature, BaX_2 (X= F, Cl, I) addition as well as heating time on the yield of $BaZrS_3$ was investigated.

2. Experimental

2.1. Starting materials

BaS of 99% up, BaI_2 of 99% up and ZrS_2 of 98% purities were obtained from High-Purity Chemicals Laboratory. Guaranteed reagent BaF_2 of 99.9% purity was purchased from Wako Pure Chemicals Industries Ltd. $BaCl_2$ and sublimed sulfur of analytical grade (99.0%) were obtained from Kanto Chemical Co. Inc. Anhydrous $ZrCl_4$ was prepared by the chlorination of Zr powder (99.5%) obtained from Hirano Seizaemon Shoten using Cl_2 gas at 673 K. Analytical grade CS_2 with boiling point of 319–320 K and acetone were purchased from Wako Pure Chemicals Industries Ltd. and used as received.

2.2. Experimental procedures

2.2.1. Preparation of $BaZrS_3$ in a large amount of sulfur melt

Calculated amounts of BaS (and $BaCl_2$) and ZrS_2 (and $ZrCl_4$) were intimately mixed together with a large excess amount of sulfur, namely 50 times of the molar numbers of BaS and ZrS_2. The total 1.8~2.0 g starting materials were mixed in an agate mortar for about 20 min and then sealed in the evacuated Pyrex ampoules of 10 mmϕ and about 10 cm long. The mixing operation involving $ZrCl_4$ was carried out in an N_2 dry box because $ZrCl_4$ is hygroscopic. The ampoules were placed stood in a muffle furnace, and subsequently heated for 7 days. The reaction temperatures studied were 623 and 723 K.

After heating, the ampoules were taken out from the furnace, and they were air-cooled to room temperature. The unreacted excess sulfur was removed from the product by the following two-step treatments immediately after the cooled ampoule was cut-opened.

2.2.1.1. Step 1: filtration of sulfur melt

The filtration separation of sulfur was implemented using a separator of which the details have been described elsewhere [8]. The apparatus is composed of two parts: a vertical resistance tube-furnace with its wall made of Pyrex glass, and a Pyrex glass separator connected to vacuum line. The ampoule was cut near the middle part, and it was set with the open end downward in the separator on the glass filter (G4). The separator was then heated with suction by rotary pump. The filtration was monitored through the glass tube furnace.

The separation experiment was performed at a temperature of 428±2 K to keep the sulfur low viscosity. To accelerate the filtration, a controlled pressure of N_2 gas was applied to the melt from the inlet of the separator. The solid product was collected on the filter while the sulfur melt was removed by passing through the filter.

2.2.1.2. Step 2: dissolution of the remaining sulfur

A small amount of sulfur was sometimes attached to the product still after the filtration separation. It was dissolved by CS_2 immersion for 2 h. This washing solution CS_2 was discarded by decantation, and then the product was washed with acetone followed by air-drying.

2.2.2. Preparation of $BaZrS_3$ in the presence of a small excess amount of sulfur

Calculated amounts of BaS (and 10 mole% BaF_2, $BaCl_2$ or BaI_2) and ZrS_2 were intimately mixed together with various amounts of sulfur ranging from 0 to 2 times of the molar numbers of BaS and ZrS_2. The starting materials of the total amount 0.4~0.5 g were mixed in an agate mortar for about 20 min and then sealed in evacuated Pyrex (10 mmϕ and about 10 cm long) or quartz (8 mmϕ and about 10 cm long) ampoules. The process involving BaI_2 mixing was carried out in an N_2 dry box to avoid the absorption of moisture by BaI_2. The sealed ampoules were placed stood in a muffle furnace, and subsequently heated for 7 days. The reaction was made at temperatures between 623 and 873 K.

After heating, the ampoules were taken out from the furnace, and they were air-cooled to room temperature. The separation of excess sulfur was not needed in this experiment since sulfur usually deposited at the upper part of the inner wall of the ampoule due to small amount in separation from the mixed sulfide product which was formed at the bottom of the ampoule.

2.2.3. Purification of $BaZrS_3$

Distilled cold water was used to remove the impurities such as BaS_3 and $BaCl_2$ by dissolving them from the $BaZrS_3$ product. The acetone-washing was followed immediately after the water-washing to remove moisture.

2.3. Analysis of $BaZrS_3$

The phase relation and crystal structure analyses of the obtained samples were carried out by means of X-ray powder diffractometry with a Rigaku RAD-IC diffractometer using Cu$K\alpha$ radiation (40 kV, 20 mA) monochromatized by curved pyrolytic graphite. The lattice parameters of

$BaZrS_3$ formed were calculated using the LCR2 program [11].

The molar ratio of barium and zirconium in the product was determined by inductively coupled plasma emission spectroscopy (ICP–ES) using a PERKIN ELMER Optima 3300 XL spectrometer. The sample was dissolved in 4 M HCl, and standard solutions were also diluted by this acid. Since the accuracy of sulfur is low, the sulfur amount in $BaZrS_3$ was determined by subtracting the weights of Ba and Zr from the total weight of the sample. The composition of the mixed sulfide was determined for four $BaZrS_3$ particles by means of EPMA analysis (Hitachi X-560 electron probe microanalyzer).

3. Results and discussion

3.1. Synthesis of $BaZrS_3$ at a temperature range 623–723 K

3.1.1. Reaction in a large amount of sulfur melt

In our preceding papers [8–10], a low temperature method for synthesizing mixed sulfides in sulfur melt was proposed. The method was demonstrated for the syntheses of Ba_xTiS_y and $PbTiS_3$, which are the MTS_3 (M: typical metal and T: transition metal) compounds with different structure types, i.e. $CsNiCl_3$-like chain type structure [1,12] and the layer type structure described as the formula $(MS)_xTS_2$ [13], respectively. So, the preparation of $BaZrS_3$ was studied first by this method in the temperature range 623–723 K.

The starting materials used were as follows:

$$BaS + ZrS_2 + 50S \tag{1}$$

$$0.9BaS + 0.1BaCl_2 + ZrS_2 + 50S \tag{2}$$

$$BaS + 0.9ZrS_2 + 0.1ZrCl_4 + 50S \tag{3}$$
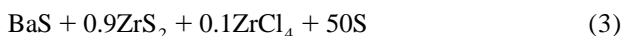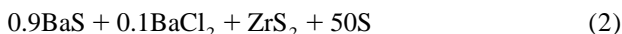
Calculated amounts of BaS and ZrS_2 were let to react with a large excess amount of sulfur in reaction (1), while 10 mole% of $BaCl_2$ was substituted for the same amount of BaS in reaction (2). In reaction (3), 10 mole% of $ZrCl_4$ was substituted for 10 mole% ZrS_2. The starting materials were intimately mixed and heated in the sealed evacuated Pyrex ampoules for 7 days at 623 or 723 K. The result, however, showed that $BaZrS_3$ did not form at all by this method. The product of reactions (1) and (2) heated at 723 K was only a mixture of BaS_3, ZrS_3 and ZrO_2 after the separation of unreacted sulfur. The product of reaction (2) heated at 623 K was a mixture of BaS_3, ZrS_2 and other unknown phases. That of reaction (3) heated at 623 K was a mixture of BaS_3, ZrS_2, $BaCl_2$ and unknown phase(s).

3.1.2. Reaction in a small excess amount of sulfur

As described above, in a large amount of sulfur melt, large amounts of BaS_3 or ZrS_3 were formed. They were

assumed to hinder the formation of $BaZrS_3$. Then, the heating experiment to synthesize $BaZrS_3$ was performed at the same temperatures using the starting materials in which the sulfur amount was much reduced. The starting materials were as follows:

$$BaS + ZrS_2 + \alpha S \tag{4}$$

$$0.9BaS + 0.1BaCl_2 + ZrS_2 + \alpha S \tag{5}$$
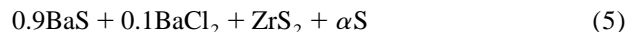
where the amount of sulfur is in a range 0~2.0. It was found that no $BaZrS_3$ was formed by heating the calculated amounts of BaS and ZrS_2 ($\alpha = 0$) in reaction (4) at 723 K if $BaCl_2$ was not added. The product of this reaction was still merely a mixture of BaS_3, BaS_2, ZrS_3, ZrS_2 and ZrO_2 for $\alpha = 1.0$ at 723 K. On the other hand, if the starting materials were those of reaction (5), $BaZrS_3$ could be obtained under certain selected reaction conditions: By heating the starting materials in the presence of a proper amount of excess sulfur at 723 K for 7 days, $BaZrS_3$ was observed to be formed at $\alpha = 0.5 \sim 2.0$. The formation of $BaZrS_3$ appears to be sensitive to the sulfur amount added in the starting materials. As can be seen from Table 1, no $BaZrS_3$ was formed when $\alpha = 0$ and 0.2, and it was formed only in a very small amount when $\alpha = 2.0$. On the contrary, $BaZrS_3$ could be obtained as a main phase in the products if the sulfur amount added was in a range $\alpha = 0.5 \sim 1.5$. The X-ray powder diffraction patterns of the products obtained with these starting materials are shown in Fig. 1. The reaction conditions are 723 K and 7 days. It is seen from the figure that $BaZrS_3$ was synthesized in this case with high yields. The diffraction peaks for $BaZrS_3$ in Fig. 1(a)–(c) are in good agreement with those of $BaZrS_3$ obtained by Lelieveld and Ijdo [6] by heating the mixtures of $BaCO_3$ and ZrO_2 in a stream of H_2S at temperatures around 1373 K for 7 days. The diffraction peaks for $BaZrS_3$ at $\alpha = 0.5$ (Fig. 1(a)) are broad and slightly shifted to the lower angle side (larger lattice parameters) compared with those for $BaZrS_3$ obtained with $\alpha = 1.0$ and 1.5. This difference is assumed to be caused by the sulfur gas pressure during heating in the sealed evacuated ampoules. The sulfur addition amount of $\alpha = 0.5$ seems to be too low to develop the well crystallized compound. On the other hand, the yield of $BaZrS_3$ significantly decreased when α was increased from 1.0 to 1.5 as shown in Fig. 1. The

Table 1
Phases in the products obtained by reaction (5) at 723 K (heating time: 7 days)

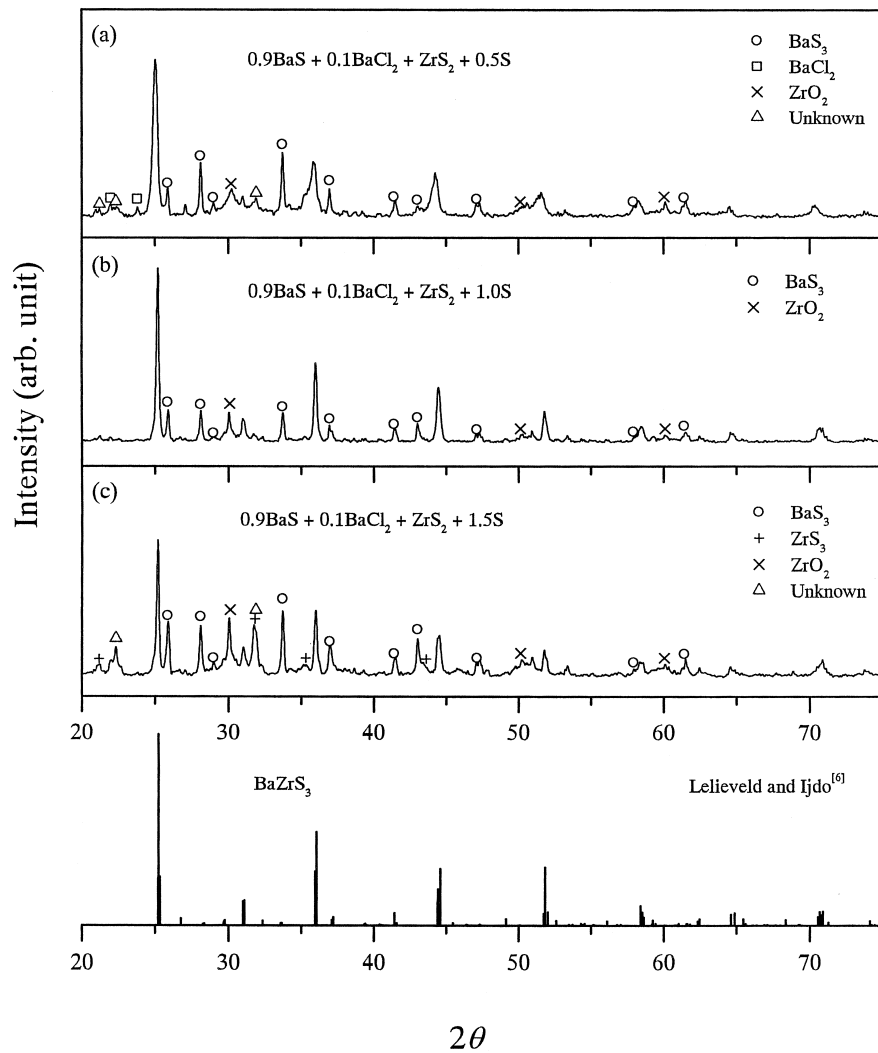| No.	α	Phases in the products
1-1	0	BaS_2, ZrS_2, BaS, ZrO_2, Unknown Phase(s)
1-2	0.2	BaS_2, ZrS_2, ZrO_2, Unknown Phase(s)
1-3	0.5	$BaZrS_3$, BaS_3, ZrO_2, Unknown Phase(s)
1-4	0.8	$BaZrS_3$, BaS_3, ZrO_2
1-5	1.0	$BaZrS_3$, BaS_3, ZrS_3, ZrO_2
1-6	1.5	$BaZrS_3$, BaS_3, ZrS_3, ZrO_2, Unknown Phase(s)
1-7	2.0	BaS_3, ZrS_3, $BaZrS_3$, Unknown Phase(s)

Fig. 1. X-ray powder diffraction patterns of the products obtained at 723 K (heating time: 7 days).

amount of each phase in the product in mole fraction is listed in Table 2. The mole fraction in the table was calculated from the integrated intensity of the strongest X-ray diffraction peak of the corresponding phase. The samples of Fig. 1(a)–(c) are those of sample numbers 2-1, 2-2, and 2-3 in Table 2, respectively. The mole fraction of

Table 2
Phases in the products of reaction (5) and their mole fractions (heating time: 7 days)

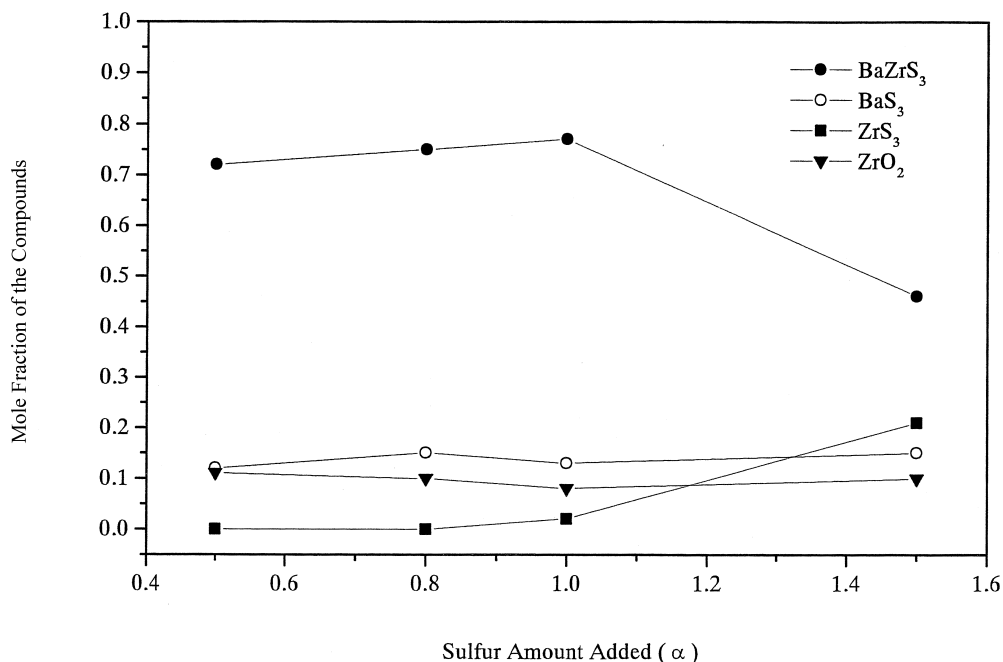| No.	Heating temp. (K)	α	Phases and mole fractions					
			$BaZrS_3$	BaS_3	ZrS_3	ZrO_2	$BaCl_2$	Unknown
2-1	723	0.5	0.72	0.12	–	0.11	0.02	0.03
2-2	723	1.0	0.77	0.13	0.02	0.08	–	–
2-3	723	1.5	0.46	0.15	0.21	0.10	–	0.08
2-4	773	1.0	0.77	0.15	–	0.08	–	–
2-5	773	1.5	0.73	0.20	–	0.07	–	–
2-6	823	0.5	0.64	0.20	–	0.16	–	–
2-7	823	1.0	0.75	0.17	–	0.08	–	–
2-8	823	1.5	0.73	0.20	–	0.07	–	–
2-9	873	0.5	0.69	0.22	–	0.09	–	–
2-10	873	1.0	0.86	–	–	0.04	–	0.10
2-11	873	1.5	0.82	–	–	0.06	–	0.12

Fig. 2. Mole fraction of the products as a function of added sulfur amount α (heating temperature: 723 K, heating time: 7 days).

BaZrS$_3$ for the No. 2-2 sample ($\alpha = 1.0$) is 0.77 which is considerably higher than that for the No. 2-3 sample ($\alpha = 1.5$), i.e. 0.46.

Fig. 2 shows the change of the mole fraction of the phases in the products (723 K heated) as a function of α. When α was increased from 1.0 to 1.5, the yield of BaZrS$_3$ was decreased on account of the mole fraction rise of ZrS$_3$. This result may suggest that the sulfur pressure becomes high at $\alpha = 1.5$ at 723 K and that the ZrS$_3$ compound formed hindered the formation of BaZrS$_3$. The prolonged heating time to 11, 14, 21 days could not contribute to the increase in the BaZrS$_3$ yield. It should be noted also that BaZrS$_3$ could not be formed at all at 723 K if the condition to add 10 mole% BaCl$_2$ and a small amount of sulfur is not satisfied in the starting materials. This experimental fact is in accord with the result of Hahn and Mutschke [2] who reported that BaZrS$_3$ had not been obtained by heating the mixture of BaS and ZrS$_2$ at 873 K for several weeks.

When the same starting materials with $\alpha = 0.5$, 0.8, 1.0

and 1.5 were heated at 623 and 673 K, BaZrS$_3$ did not form. The product was a mixture of various barium and zirconium binary sulfides.

In an effort to produce BaZrS$_3$ with higher yield, a series of experiments were carried out by changing the mixture state for reaction (5) at $\alpha = 1.0$ and 723 K. The results are shown in Table 3, where the No. 3-4 sample is the same as the No. 2-2 sample in Table 2. The No. 3-1 experiment was performed by placing the mixture of the BaS, BaCl$_2$ and ZrS$_2$ on sulfur powder without mixing with the aim to reduce formation of BaS$_3$ and ZrS$_3$. However, the observed yield of BaZrS$_3$ was the least in the series of experiments of Table 3. The No. 3-2 experiment was that which used pelletized mixture. Pellet fragments were heated in an evacuated sealed Pyrex ampoule. The powder particles in the starting materials were thought to be in better contact resulting in the formation of BaZrS$_3$ in a higher mole fraction. The yield was, nevertheless, rather smaller than that of No. 3-4 forming a larger amount of BaS$_3$. The No. 3-3 experiment was carried out to study

Table 3
Effect of reaction conditions on the synthesis of BaZrS$_3$ (reaction (5), $\alpha = 1.0$; heating temperature: 723 K; heating time: 7 days)

No.	Starting materials	Ampoule	Phases and mole fractions				
			BaZrS$_3$	BaS$_3$	ZrS$_3$	ZrO$_2$	BaCl$_2$
3-1	Sulfur was separately added to the mixture powder	Pyrex	0.46	0.36	–	0.17	0.03
3-2	Homogeneous mixture compacted into pellet	Pyrex	0.70	0.22	0.02	0.06	–
3-3	Homogeneous powder mixture	Carbon-coated quartz	0.72	0.19	0.03	0.06	–
3-4	Homogeneous powder mixture	Pyrex	0.77	0.13	0.02	0.08	–

whether it was possible to diminish the amount of ZrO_2 impurity by preventing the starting materials from contact with the wall of the ampoule: The inner wall of the ampoule was coated with carbon. According to Table 3, however, the effect of this treatment is very small if any. The highest yield of 0.77 was obtained for No. 3-4, where only the homogeneously mixed powder was heated.

3.2. Synthesis of $BaZrS_3$ at a temperature range 723– 873 K

The reaction to form $BaZrS_3$ was studied at higher temperatures between 723 and 873 K for reaction (5) with $\alpha = 0.5$, 1.0 and 1.5. The phases in the products (723, 773, 823 and 873 K) and their mole fractions detected and measured by X-ray diffractometry are listed in Table 2. The change of the mole fraction of $BaZrS_3$ with heating temperature is plotted in Fig. 3.

Fig. 3 shows that the mole fraction of $BaZrS_3$ for $\alpha = 1.5$ markedly increased from 0.46 to 0.73 as the heating temperature increased from 723 to 773 K although it remained almost unchanged when the heating temperature was raised from 773 to 823 K. The mole fraction, for $\alpha = 1.5$, again increased from 0.73 to 0.82 with increasing heating temperature from 823 to 873 K. The increase in the range of 823–873 K is considered to be mainly due to the disappearance of the BaS_3 phase above 873 K, whose decomposition temperature is reported to be 827 K [14]. The increase of the yield with increasing temperature in the range 723–773 K would be associated with vanishing of ZrS_3.

For $\alpha = 1.0$ in Fig. 3, the mole fraction of $BaZrS_3$ did not increase as the heating temperature increased from 723 to 823 K. That is to say, the mole fraction of $BaZrS_3$ was already high at 723 K. Since the sulfur amount added was smaller, this result is considered to be brought about by the formation of a very small amount of ZrS_3 at 723 K, i.e. 0.02 as is seen in Table 2. When the heating temperature was raised to 873 K, the mole fraction of $BaZrS_3$ again increased because BaS_3 did not form. This is the same as in the case of $\alpha = 1.5$.

If the sulfur amount was as small as $\alpha = 0.5$, the mole fraction of $BaZrS_3$ evidently decreased from 0.72 to 0.64 as the heating temperature was raised from 723 to 823 K, while it turned into increase from 0.64 to 0.69 (Fig. 3) if the heating temperature was increased from 823 to 873 K. This change was assumed to be due to the sulfur vapor pressure which was not high enough for the formation of $BaZrS_3$. Only the BaS_3 amount was heightened. At 873 K, the sulfur liberated from the decomposed BaS_3 would have caused to increase the mole fraction of $BaZrS_3$.

The X-ray diffraction patterns of the products obtained at 873 K are shown in Fig. 4. Clearly, all the diffraction patterns of $BaZrS_3$ obtained are in good agreement with that of Lelieveld and Ijdo [6]. For $\alpha = 0.5$, a slight peak shift is seen to occur as has been observed for the sample with the same α at 723 K. The pattern of Fig. 4(d) is for $\alpha = 1.0$ without the addition of $BaCl_2$. The amount of BaS_3 is here larger similar to Fig. 4(a).

$BaZrS_3$ could be obtained in almost a single phase with a small amount (2–3 mole%) of ZrO_2 impurity after the water treatment for 8 min on No. 2-10 and No. 4-6
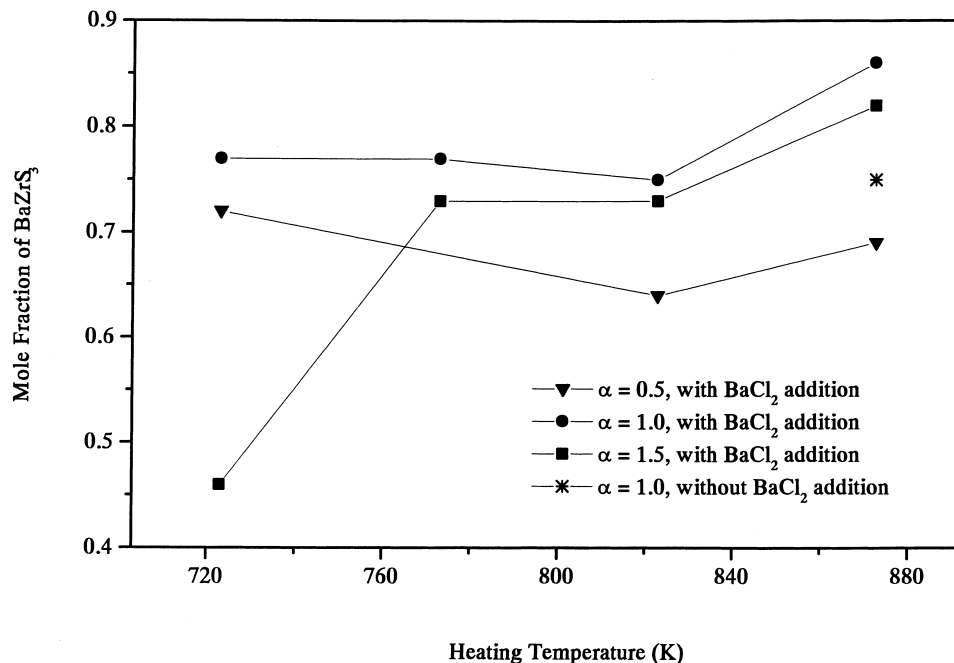

Fig. 3. Change of mole fraction of $BaZrS_3$ in the product with heating temperature (heating time: 7 days).
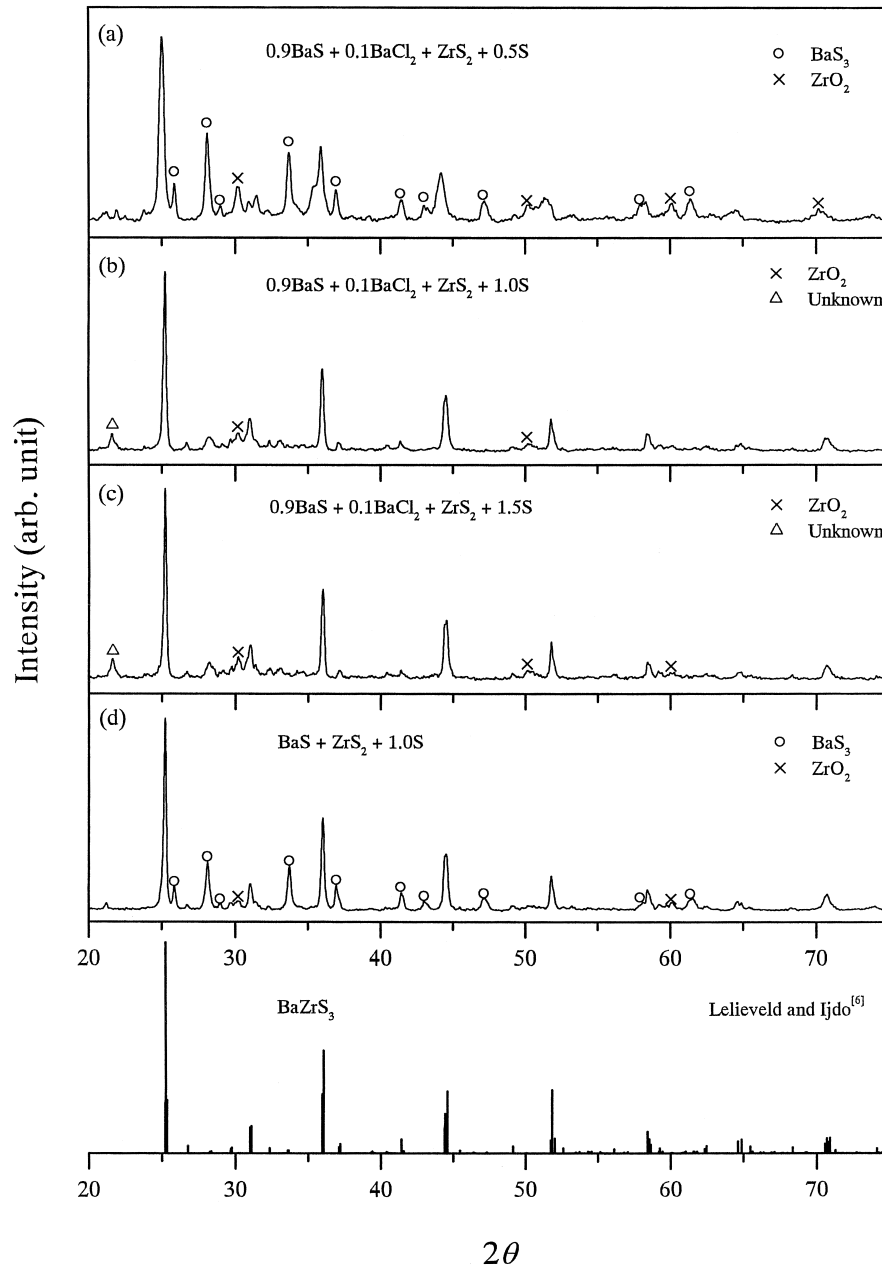
Fig. 4. X-ray powder diffraction patterns of the product obtained at 873 K (heating time: 7 days).

samples. The changes of the X-ray patterns by water treatment for the No. 2-10 and No. 4-6 samples are shown in Figs. 4 and 5. Fig. 4(b) and (d) show the patterns before the treatment. Fig. 5(a) and (b) show those after water treatment. The obtained powder of $BaZrS_3$ was dark-brown or nearly black. In Fig. 5(a) and (b), the impurities except for ZrO_2 are seen to have been removed.

The amounts of barium and zirconium in the No. 2-10 sample after water treatment were determined by ICP–ES method. The sulfur amount was calculated by subtracting the weights of barium and zirconium from the total weight of the sample. In this way, the composition was obtained

as given in Table 4, which gives the molar ratio of Ba:Zr:S as 0.99:1:3.09; very close to the stoichiometric ratio of 1:1:3 for $BaZrS_3$. The composition of the $BaZrS_3$ particles was determined by EPMA. The result was shown in Table 4. Since the error in the measured value of sulfur was relatively large, the weight percent of sulfur in Table 4 was obtained by subtracting the weight percents of barium and zirconium from the total weight. As can be seen from the table, although the standard deviations are relatively large, these values are close to the theoretical wt% of Ba:Zr:S = 42.29:28.09:29.62 for $BaZrS_3$. In molar ratio, Ba:Zr:S becomes 0.98:1:3.06. This ratio is in good agreement with
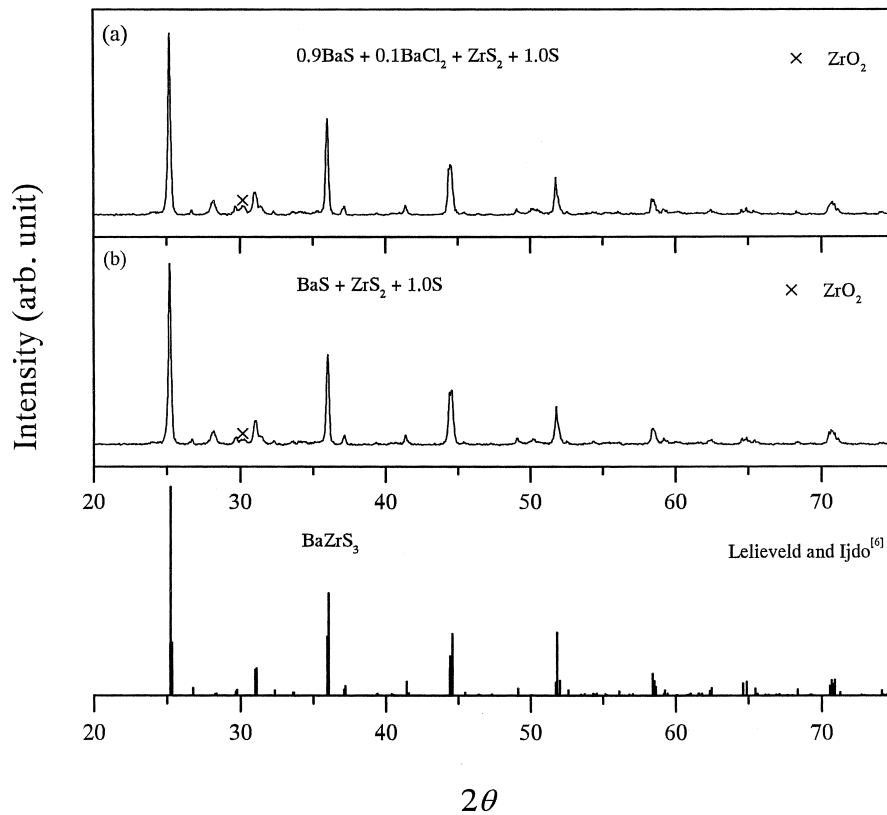
Fig. 5. X-ray powder diffraction patterns of water treated samples after the reaction at 873 K (heating time: 7 days).

that determined by ICP–ES method. It may be assumed that the other specimens also have nearly stoichiometric compositions.

3.3. Crystallinity and lattice parameters of BaZrS₃

As has been shown in Figs. 1 and 4, the crystallinity of $BaZrS_3$ obtained was good giving sharp and clear X-ray diffraction peaks when the sulfur amounts α were 1.0 and 1.5. On the other hand, relatively broad X-ray diffraction patterns of $BaZrS_3$ were obtained when the addition amount of sulfur was $\alpha = 0.5$. No clear effect of heating temperature on the crystallinity of $BaZrS_3$ was observed in this experiment.

Fig. 6(a) shows the X-ray diffraction pattern for the water treated sample (treatment time: 10 min) after heated

Table 4
Composition of $BaZrS_3$ determined by ICP–ES and EPMA

Element	Ba (wt%)	Zr (wt%)	S (wt%)
Measured (ICP–ES)	41.85	27.88	30.27
Measured (EPMA)	41.5 (0.7)[a]	28.2 (2.3)[a]	30.3 (3.0)[a]
Theoretical ($BaZrS_3$)	42.29	28.09	29.62

[a] Values in parentheses are standard deviations.

at 723 K. It indicates that the $BaZrS_3$ crystal, which was formed at 723 K by reaction (5) with $\alpha = 0.5$, was damaged to a large degree by the water treatment. It is supposed that the compound was hydrolyzed into an amorphous hydrate. The X-ray peaks remained were mainly those of ZrO_2 [15]. On the other hand, $BaZrS_3$ formed at the same heating temperature by reaction (5) with increased sulfur amount $\alpha = 1.0$ showed good crystallinity even after 15 min of water treatment, although an increase in the ZrO_2 amount caused by water treatment was observed [Fig. 6(b)].

Unlike the $BaZrS_3$ sample formed at 723 K, $BaZrS_3$ formed at 873 K by reaction (5) with $\alpha = 0.5$ was not so attacked by the water treatment for 10 min. The X-ray peaks were broadened and slightly shifted but they showed $BaZrS_3$ still to be the main phase in the water treated sample. The water treatment removes BaS_3, but it causes a relative increase of the amount of ZrO_2 which is not removed at all. Also, if not short time, the water treatment appears to produce some other oxide impurities. However, $BaZrS_3$ formed at 873 K with either reaction (5) [Fig. 4(b)] or reaction (4) [Fig. 4(d)] with $\alpha = 1.0$ exhibits an excellent crystallinity after 8 min water treatment as shown in Fig. 5(a) and (b). Here, no increase in the relative amount of ZrO_2 was resulted from the water treatment. It was found that increasing the heating temperature effects
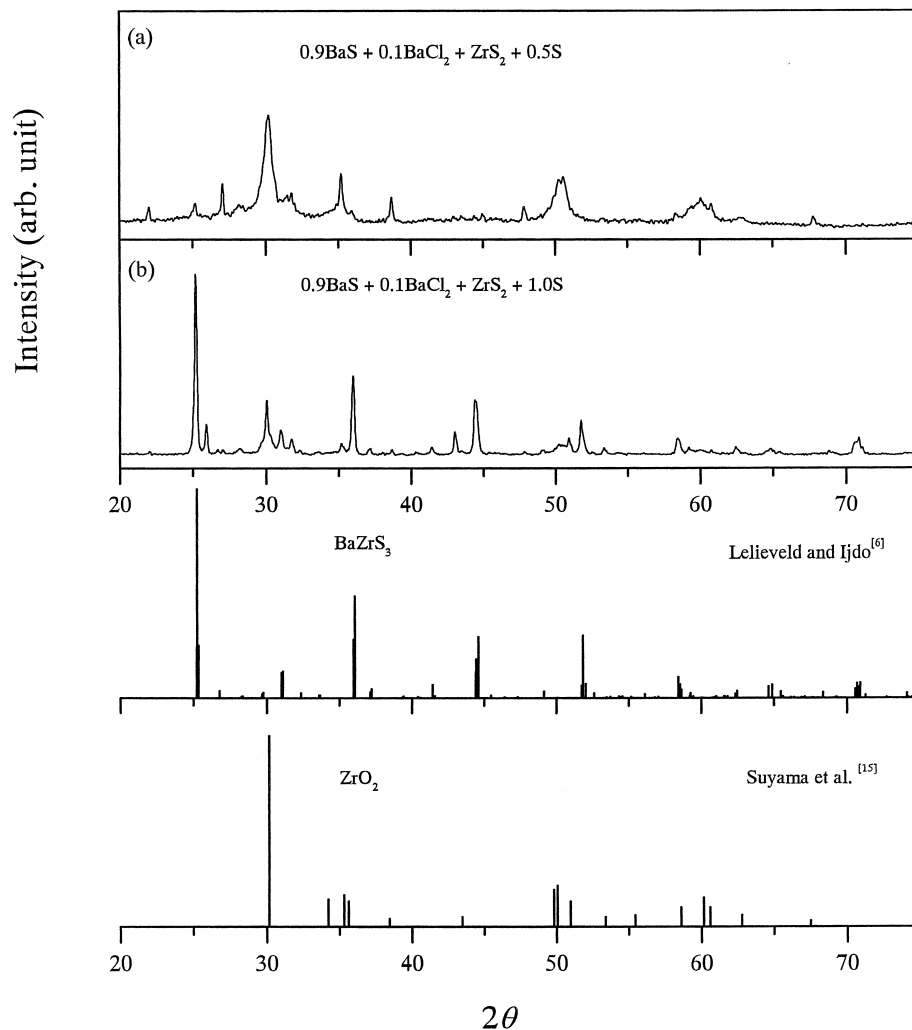
Fig. 6. X-ray powder diffraction patterns of water treated samples after the reaction at 723 K (heating time: 7 days).

to stabilize the $BaZrS_3$ crystal that has already formed in the proper gas pressure supplied by the excess sulfur.

As has been stated in Sections 3.1 and 3.2, the X-ray diffraction patterns of $BaZrS_3$ obtained in this work were in good agreement with that of Lelieveld and Ijdo [6],

showing that the crystal structure is the same. The lattice parameters of $BaZrS_3$ obtained were calculated based on the orthorhombic system with space group *Pnma*. The results are given in Table 5. The lattice parameters of $BaZrS_3$ obtained by adding sulfur with $\alpha = 1.0$ and 1.5 are

Table 5
Lattice parameters of $BaZrS_3$

| No.	Heating temp. (K)	α	Lattice parameters of $BaZrS_3$ ($\times 10$ nm)		
			a	b	c
2-1	723	0.5	7.0799 ± 0.0059	10.0207 ± 0.0081	7.0313 ± 0.0067
2-2	823	0.5	7.0884 ± 0.0063	10.0211 ± 0.0050	7.0456 ± 0.0035
2-3	873	0.5	7.0828 ± 0.0067	10.0204 ± 0.0040	7.0294 ± 0.0033
2-4	723	1.0	7.0628 ± 0.0025	9.9828 ± 0.0023	7.0236 ± 0.0033
2-5	773	1.0	7.0659 ± 0.0025	9.9809 ± 0.0028	7.0231 ± 0.0026
2-6	823	1.0	7.0652 ± 0.0022	9.9812 ± 0.0024	7.0223 ± 0.0023
2-7	873	1.0	7.0659 ± 0.0019	9.9842 ± 0.0019	7.0240 ± 0.0018
2-8	723	1.5	7.0641 ± 0.0028	9.9816 ± 0.0030	7.0237 ± 0.0021
2-9	773	1.5	7.0675 ± 0.0021	9.9841 ± 0.0023	7.0217 ± 0.0021
2-10	823	1.5	7.0675 ± 0.0033	9.9826 ± 0.0027	7.0265 ± 0.0024
2-11	873	1.5	7.0651 ± 0.0022	9.9796 ± 0.0019	7.0227 ± 0.0020

Table 6
Effect of BaX$_2$ addition on the synthesis of BaZrS$_3$ (heating time: 7 days)

No.	Reaction No.	BaX$_2$ added	α	Heating temp. (K)	Phases and mole fractions						
					BaZrS$_3$	BaS$_3$	BaS$_2$	ZrS$_3$	ZrS$_2$	ZrO$_2$	Unknown
6-1	(4)	None	1.0	723	–	0.54	0.10	0.15	0.10	0.11	–
6-2	(6)	BaF$_2$	1.0	723	0.64	0.28	–	0.02	–	0.06	–
6-3	(6)	BaCl$_2$	1.0	723	0.77	0.13	–	0.02	–	0.08	–
6-4	(6)	BaI$_2$	1.0	723	0.60	–	0.08	0.02	–	0.15	0.15
6-5	(4)	None	1.0	873	0.75	0.22	–	–	–	0.03	–
6-6	(6)	BaCl$_2$	1.0	873	0.86	–	–	–	–	0.04	0.10

almost the same. They are $a=0.70655\pm0.00009$, $b=0.99821\pm0.00009$ and $c=0.70235\pm0.00008$ nm in average. These lattice parameters are close to those of Lelieveld and Ijdo [6] ($a=0.70599$, $b=0.99813$ and $c=0.70251$ nm). The lattice parameters of BaZrS$_3$ obtained for $\alpha=0.5$ are, however, a little larger than the lattice parameters above, i.e. $a=0.70837\pm0.00036$, $b=1.00207\pm0.00034$ and $c=0.70354\pm0.00027$ nm in average. From the observed data, there seemed to be no significant correlation between the heating temperature and the lattice parameters. The water treatment also did not seem to cause any change in the lattice parameters of BaZrS$_3$.

3.4. Effect of BaX$_2$ addition on the synthesis of BaZrS$_3$

The effect of the addition of barium halides on the synthesis of BaZrS$_3$ was investigated by substituting 10 mole% of BaX$_2$ (X=F, Cl, I) for the same amount of BaS in the starting materials. The reaction studied was:

$$0.9BaS + 0.1BaX_2 + ZrS_2 + \alpha S \qquad (6)$$
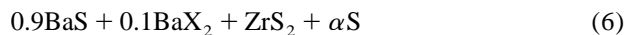
In the above reaction, study was made for the α value of 0.5 and 1.0. The heating temperature was 723 K and the heating time was 7 days. It was found that BaZrS$_3$ could not be obtained by heating the mixture of starting materials without BaX$_2$ (X=F, Cl, I) [reaction (4)] at 723 K for both $\alpha=0.5$ and 1.0. This result is in contrast to the result of reaction (6), BaZrS$_3$ was formed as a main phase in the product at both 723 and 873 K for $\alpha=1.0$. If the amount of added sulfur was $\alpha=0.5$, BaZrS$_3$ was formed as the main phase in the product only when BaCl$_2$ was used. In the case of BaI$_2$, BaZrS$_3$ was obtained as a minor phase. It did not form at all if BaF$_2$ was added.

The phases and their mole fractions in the products obtained by reactions (4) and (6) with $\alpha=1.0$ at 723 K are shown in Table 6. BaZrS$_3$ was not produced without the addition of BaX$_2$ (No. 6-1). However, if 10 mole% of BaX$_2$ was added in the starting materials, it formed giving the mole fractions 0.60–0.77. In the three halides, BaCl$_2$ appeared to be the most effective. The addition of BaI$_2$ exhibited no large effect to promote the formation of BaZrS$_3$ although it had been effective in synthesizing Ba$_x$TiS$_y$ [10]. This difference is probably due to the formation of the unknown impurity.

4. Conclusion

1. BaZrS$_3$ was synthesized with high yields by heating at temperatures of 723–873 K, if a proper amount of excess sulfur and 10 mole% of BaCl$_2$ were added and mixed in the starting materials.
2. The compound could be obtained in almost a single phase with only 2–3 mole% ZrO$_2$ impurity after the 8 min water treatment of the products obtained at 873 K.
3. The excess sulfur added is thought to give a certain sulfur pressure in the sealed ampoule rendering an accelerating effect on the formation and crystallization of BaZrS$_3$ at relatively low temperatures.
4. The addition of a small amount (10 mole%) of BaX$_2$, especially BaCl$_2$, was essential for the formation of BaZrS$_3$ in the closed system reaction at the heating temperature range studied.

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