Thermogravimetric Study for the Reaction of $BaTiO_3$ with CS_2 by Using Quartz Spring-Type Thermobalance

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ABSTRACT

The sulfurization behavior of $BaTiO_3$ fine particles was studied by thermogravimetry (TG) using CS_2. The sulfurization process of the fine particles was carried out at a heating rate of 1 °C min^{-1} by using a quartz spring-type thermo balance in a CS_2/N_2 gas flow. The obtained TG curve showed that the sulfurization of $BaTiO_3$ fine particles started at around 380°C, which was considerably low compared with those found for two commercial $BaTiO_3$ powders. The sulfurization occurred up to approximately 730°C with a maximun weight gain of 19.2% forming $BaTiS_3$. At further elevated temperatures, the $BaTiS_3$ lost a small amount of sulfur to give $BaTiS_{3-x}$ as a final product at 1000°C.

Keywords: Barium titanate, thermogravimetry, sulfurization, barium titanium sulfide, nanoparticles, carbon disulfide.

1 INTRODUCTION

$BaTiO_3$ is one of the dielectric materials with high dielectric constant and ferroelectric properties, and is thus widely used for industrial applications such as thermistors, ceramic capacitors, electro-optic devices, and gas sensors. The traditional method for the preparation of this kind of perovskite compounds is sintering the mixture of $BaCO_3$ and TiO_2 at elevated temperatures. Nevertheless, the obtained powders have been characterized as chemically and structurally heterogeneous particles with a large particle size and a wide size distribution. Many studies have been made to overcome those problems, the chemical route or "wet" method being a new alternative for processing of $BaTiO_3$. Among them, Sugimoto *et al.* /1/ developed the gel–sol method to obtain mono-dispersed fine particles at relatively low temperatures, where the as-obtained particles were well-crystallized and chemically homogenous particles with a well-defined morphology.

On the other hand, it is well known that the reduction of particle size originates variations in some properties that were observed in single crystals or larger particles. Thus, recently, $BaTiO_3$ nanoparticles were found active for photocatalytic reactions. Virtually, $BaTiO_3$ shows not only electric properties but also catalytic activity used as supported material of other catalysts for CO_2 reforming or partial oxidation of CH_4 at elevated temperatures /2,3/ or as catalyst for processing of hazard pollutants by non-thermal plasma reactors /4/. However, its photocatalytic activity has not been extensively investigated because of its high band gap energy, approximately 3.0 to 3.7 eV /5/, which is only activated by UV light irradiation.

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Owing to the good stability of this oxide, it is essential to synthesize $BaTiO_3$ with a higher solar spectrum absorption by reducing its band gap energy. In this regard, partial sulfurization could be an alternative because replacement of S by O would produce a modification in its optical properties. Some studies have been carried out for the partial sulfurization of TiO_2 and the results reported the enhancement of its photo electrochemical property /6/ and its catalytic activity /7/.

Therefore, it is necessary to investigate the sulfurization behavior of $BaTiO_3$ nanoparticles, since in the literature survey it was not possible to find similar works that permit selecting the adequate temperature for a partial sulfurization of $BaTiO_3$ nanoparticles. Thermogravimetrt (TG) was done in order to evaluate the sulfurization behavior of $BaTiO_3$ nanoparticles as well as $BaTiO_3$ powders with larger size.

2. EXPERIMENTAL

2.1 Preparation of $BaTiO_3$ fine particles

$BaTiO_3$ was prepared according to Sugimoto *et al.* /1/ as follows. 14.429 g of tetra-isopropyl orthotitanate (TCI) was mixed with 14.949 g triethanolamine (TCI) (molar ratio of 1:2) and kept at room temperature overnight in Ar atmosphere to form a stable Ti complex in order to avoid the uncontrolled hydrolysis. Stock solution was obtained by adding of de-carbonated water to this mixture to make a total volume of 100 ml. 6.31 g of $Ba(OH)_2.8H_2O$ (Wako) was dissolved in 10 ml of de-carbonated water and to this solution 10 ml of stock solution was added and maintained in agitation for 1 hour. The resulting gel was heated in an autoclave at 250°C for 3 hours. The fine particles were recovered by centrifugal separation, washed with water under ultrasonication for three times, and finally the fine particles were dried at room temperature for 24 hours. As-prepared $BaTiO_3$ nanoparticles were named as BT01. Another two kinds of $BaTiO_3$ powders with rather larger sizes were used for controls; they are named BT02 (99.9 %, High Purity Chemicals) and BT03 (99 %, Wako).

2.2 Thermogravimetry

Thermogravimetric analyses of $BaTiO_3$ in argon gas atmosphere were performed from room temperature to 1000°C with a heating rate of 5°C min^{-1} by using a Rigaku Thermoplus TG8120 analyzer. Al_2O_3 powder was used as a reference.

In order to determine the sulfurization behavior, TG curves in CS_2 atmosphere were obtained by means of a quartz spring-type thermobalance, which consists of a vertical resistance tube furnace and a quartz spring with the sensitivity of 6.7 mg mm^{-1}. The change of the quartz spring length was recorded with a levelmeter (Mitsutoyo) with an accuracy of 0.001 mm. Before the measurement, the reaction tube was evacuated to approximately 100 Pa for 30 min and then refilled with N_2 up to ambient pressure. CS_2 in N_2 carrier gas obtained by passing N_2 gas flow through a bubbler containing liquid CS_2 was then introduced. The N_2 gas flow rate was measured using a digital mass flow meter (Kofloc Model DPM-2A) and a CS_2/N_2 flow rate was 5/50 ml min^{-1}. The sample was heated at a heating rate of 1°C min^{-1} from room temperature to 1000°C. Analytical grade of CS_2 (Wako, maximum water content of 0.02%) was used as-received. Argon and nitrogen gases of 99.99% purity (Nippon Sanso) were used as received.

2.3 Characterization

The products were identified by X-ray diffraction analysis using a Rigaku Type RAD-IC diffractometer with a Ni filtered Cu Kα irradiation (40 kV and 20 mA) equipped with a curved pyrolitic carbon. Transmission electron microscopy (TEM) images were taken by a JEOL JEM 2000EX Electron Microscope operating at 200 KV. The specific surface area of BT01 was measured by using a Micromeritics ASAP 2010 equipment.

3. RESULTS AND DISCUSSION

The transmission electron micrographs of the synthesized $BaTiO_3$ (BT01) and both commercial powders (BT02 and BT03) were shown in Fig. 1 (a), (b) and (c), respectively. TEM micrograph for the BT01

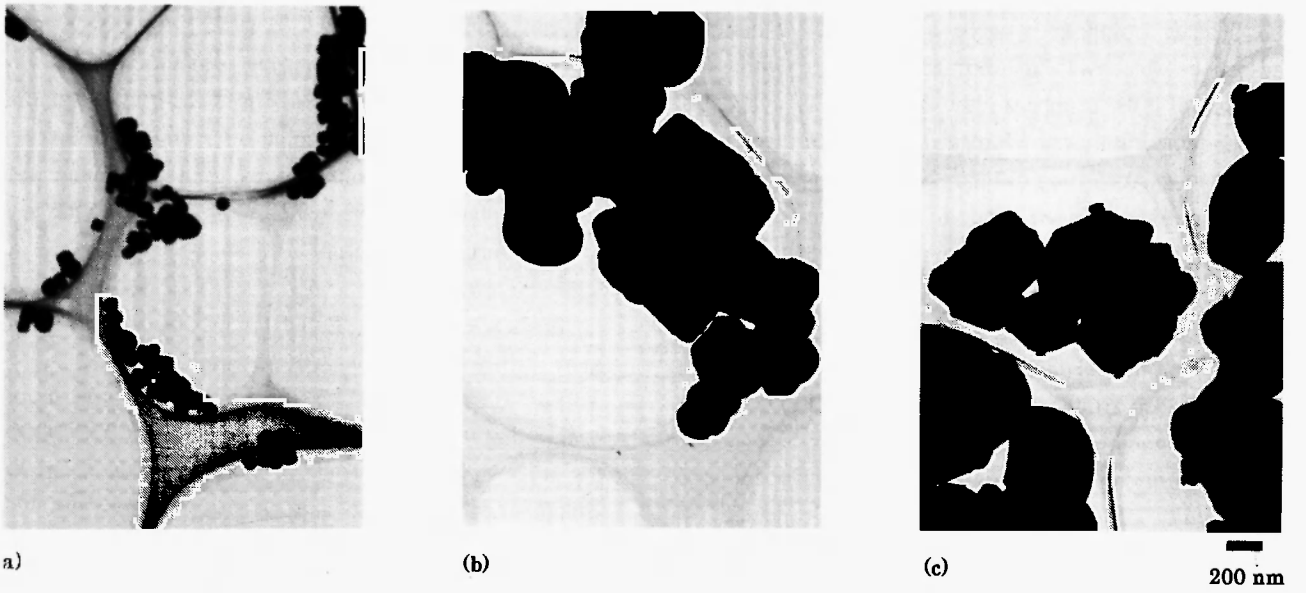

Fig. 1: TEM micrographs of $BaTiO_3$ powders before sulfurizing. (a) BT01, (b) BT02 and (c) BT03.

sample (Fig. (a)) shows it to have the smallest particles compared with those of commercial powders (Fig. (b) and (c)). It was seen that the particles of BT01 were well crystallized and had a cubic morphology. The average particle size was estimated to be 95 nm with a specific area of 12.42 mg m^{-2}. On the other hand, virtually large particle size was observed in commercial powders, BT02 and BT03, whose average sizes are approximately the same, ca. 1μm.

The XRD analyses for those powders (Fig. 2) showed a tetragonal $BaTiO_3$ phase for BT02 and BT03 samples. However, BT01 sample took a cubic structure with a slightly smaller lattice since the peak positions shift to higher angles compared with the reference data (JCPDS 31-174). This kind of structure is called pseudo cubic structure, which is produced by OH defects in the structure of $BaTiO_3$ /8/. Furthermore, the crystalline size of BT01 is the finest judging from peak broadening.

Figure 3 showed the thermal behavior of starting materials in argon atmosphere when the heating rate was 5°C min^{-1}. In the case of the BT01 sample, it decomposed in two steps caused by the removal of adsorbed water, from room temperature up to 200°C, and the dehydration from 200 to 500 °C. Namely, as the gases liberated during the heating were analyzed by gas chromatograph mass spectrometer (TG-GC-MS QP5050 Rigaku) only the removal of water was confirmed but

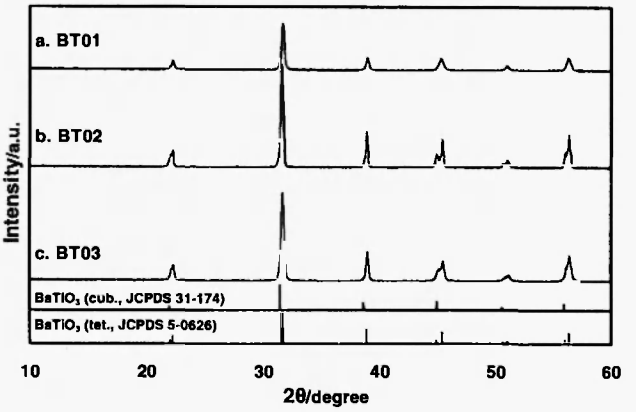

Fig. 2: XRD patterns of $BaTiO_3$ powders before sulfurizing.

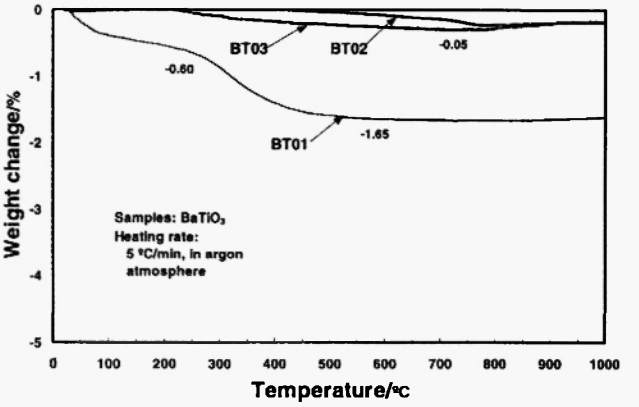

Fig. 3: TG curves for $BaTiO_3$ powders in argon atmosphere at a heating rate of 5 °C min^{-1}.

no organic compounds were found. The amount of adsorbed water was determined as 0.5%, while the content of OH groups in the sample was 1.1%. At higher temperatures no change occurs since there is no weight loss. According to the result of TG-MS analyses, we did not have any evidence of the carbonates or such as $BaCO_3$ during the heating and considered that BT01 only contained water as impurity. The total amount of decomposition of the sample was evaluated as 1.6%. In the cases of the BT02 and BT03 samples, these showed a weight loss around 0.04 %; there are practically no weight changes.

The purity, uniformity in particle size and shape, and crystallinity of these fine particles was expected; in contrast with other chemical routes in which it is necessary to calcinate at low temperature to reach a good crystallization and in many cases decompose the remaining organic materials and carbonates /9/.

TG curves for the sulfurization of $BaTiO_3$ powders are shown in Fig. 4. In the case of the BT01 sample, it liberated the adsorbed water up to 280 °C. Above this temperature the curve became flat. It is probable that in this region CS_2 was absorbed on the surface by means of OH groups since the total amount of weight loss in Fig. 3 was 1.6%, which would be in good agreement with our previous study on TiO_2 /10/. Above 380 °C, the sulfurization of the bulk proceeded slowly, accompanied by weight increase, and at around 450°C the conversion of oxide to sulfide progressed rapidly until 730°C according to Eq. (1). There was a marked weight increase in this range of temperatures reaching the maximum value of 19.7 % at 730 °C. Considering the loss of water, this value coincided with the theoretical value of 20.7 %. The XRD pattern at this temperature showed a complete conversion of $BaTiO_3$ to $BaTiS_3$. At higher temperatures, the weight decreased in a percentage of 0.8 %, which was assigned to the loss of sulfur forming $BaTiS_{3-x}$.

$$BaTiO_3 + 3/2CS_2 \rightarrow BaTiS_3 + 3/2CO_2 \quad (1)$$

For BT02 and BT03 samples, the sulfurization occurred at temperatures ranges appearing at 430-780°C for BT02 and 450-750°C for BT03, accompanied by weight increase of 20.6 and 18.8 %, respectively. The product obtained from BT02 sample would be almost pure $BaTiS_3$ since the weight increase (20.6%) is in good agreement with the theoretical value. At elevated temperatures, the obtained $BaTiS_3$ lost sulfur to give $BaTiS_{3-x}$ as a final product. The temperatures of sulfurization were slightly higher than BT01 that would be caused by the larger sizes and absence of OH groups in those samples. The conversion of $BaTiO_3$ to $BaTiS_3$ seemed to be slower when the particle size increases.

The amounts of sulfur loss were estimated in 0.8, 0.4 and 0.5 % for BT01, BT02 and BT03 respectively, which could be associated with the particle size as shown in Fig. 1.

XRD analyses for sulfurized products of those samples after sulfurizing at 1000 °C were seen in Fig. 5. The XRD patterns revealed that the peak positions do not coincide with the JCPDS card No 49-1573 for hexagonal $Ba_{1.04}TiS_{2.93}$ compound. Saeki *et al.* /11,12/

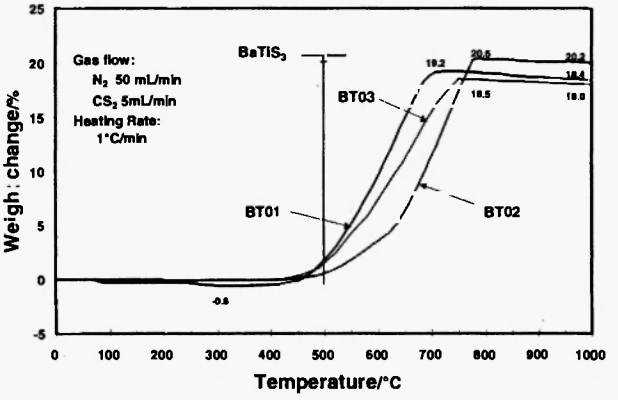

Fig. 4: TG curves for the sulfurization of $BaTiO_3$ powders in CS_2/N_2 atmosphere at a heating rate of 1 °C min^{-1}.

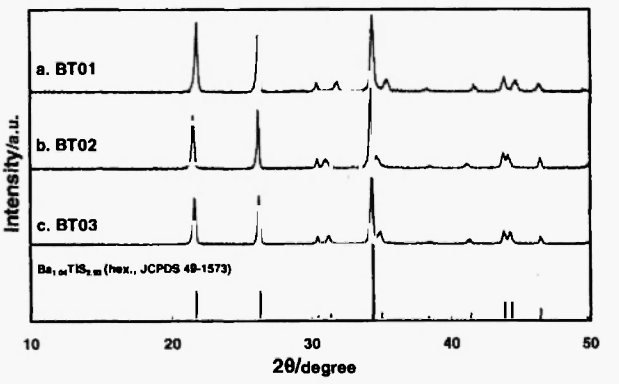

Fig. 5: XRD patterns for $BaTiO_3$ samples sulfurized at 1000 °C in CS_2/N_2 atmosphere.

stated that at elevated temperatures $BaTiS_3$ structure consists of two interpenetrating cell, i.e. Ba and TiS_3 cells, with a common parameter *a* and different parameter *c* and that the sulfur loss produces a variation in those lattice parameters.

CONCLUSION

Well-crystallized and homogeneous nanoparticles were sulfurized at a heating rate of 1 °C/min^{-1} and a CS_2/N_2 flow rate of 5/50 ml min^{-1}. The sulfurization behavior was determined to occur in different stages: 1) removal of water, 2) adsorption of CS_2, 3) sulfurization and 4) decomposition of $BaTiS_3$.

The reduction of particle size modified the sulfurization behavior of $BaTiO_3$ powders so we could see that the starting temperature of sulfurization and decomposition decreased with decreasing particle size, the rate of conversion from oxide to sulfide was slightly higher in nanoparticles and the amount of sulfur loss was higher in nanoparticles than in large particles.

In accordance with the results obtained on TiO_2, the starting temperature of sulfurization would be favored by the presence of OH groups on the surface of $BaTiO_3$ nanoparticles.

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