

# Low Temperature Recycling Process for Barium Titanate Based Waste

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## チタン酸バリウム系廃材の低温リサイクルプロセス

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A recycling process was developed for barium titanate based waste material, which is produced in the large scale industrial production of ceramic capacitors and related devices. Barium titanate powder was first dissolved in a concentrated aqueous HCl solution, followed by dilution with water and heating to 100°C, which resulted in the precipitation of a white crystalline titania powder. The crystalline phase of the prepared titania can be controlled by the preparation conditions, i.e., heating rate, and this process successfully produced pure anatase powder with good photo-catalytic activity. The barium ion, another main component, was also separated as barium sulfate by a simple precipitation process. [Received February 21, 2006; Accepted March 16, 2006]

**Key-words :** Recycle process, Barium titanate, Photocatalyst, Anatase, Rutile

### 1. Introduction

Recently, demand for the development of environmentally friendly materials and processes is significantly increasing, even in the ceramic industry. For example, the toxic lead component of lead titanate is separated by a reaction with sulfuric acid.<sup>1)</sup> Because barium titanate (BT) is one of the essential ceramic materials used for the electronic devices such as ceramic multi-layer capacitors, it is important to recycle BT based waste that results from industrial production. It is also desirable to treat thousands of tons of waste with an environmentally acceptable process of low energy consumption. Precipitation of crystalline titania from pure metal chloride or nitrate has already reported,<sup>2),3)</sup> and some groups are also investigating the low temperature syntheses of crystalline titania from an acidic solution prepared by titanium chloride and titanium alkoxide.<sup>4)-6)</sup> In the present work, a very simple process was proposed to recycle BT powders as crystalline titania and barium sulfate at temperatures below 100°C.

### 2. Experimental section

#### 2.1 Treatment of BT powder

The experimental design is summarized in Fig. 1. A commercial barium titanate powder (2.5 g, Sakai Chemical Co., Ltd., BT01, av. particle size 0.1 μm) was dissolved into a 10 M HCl (15 ml, 35% Kishida Chemical Co., Ltd.) solution by stirring at room temperature for three days, and the nearly transparent prepared solution was centrifuged to remove any particles. Then the solution was diluted with water to 150 ml. Heating of the solutions was performed at two different heating conditions, (a) 15°C/min and (b) 2°C/min. The obtained white precipitates were also separated by ultra-filtration using a polyflon filter (Advantec PF050) under N<sub>2</sub> pressure and washed with water and ethanol, followed by drying at 100°C in air. Figure 2 is a diagram of the model experiment using metal chlorides, TiCl<sub>4</sub> (Kishida Chemical Co., Ltd.) and BaCl<sub>2</sub>·2H<sub>2</sub>O (Katayama Chemical Co., Ltd.), which were used to confirm the effect of a coexisting barium ion. Sulfuric

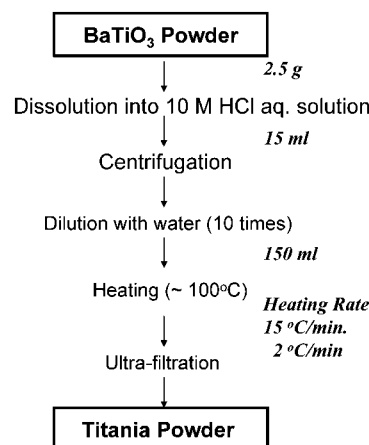


Fig. 1. Recycling Process of BaTiO<sub>3</sub>.

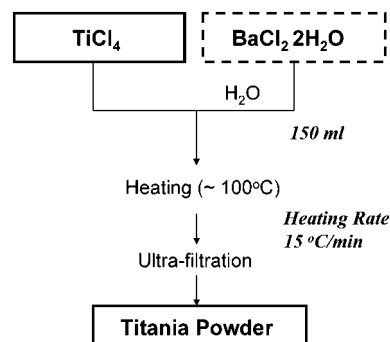


Fig. 2. Model experiment to precipitate crystalline titania.

acid solution (1N, Hayashi Pure Chemical Ind., Ltd.) was also added to improve the process.

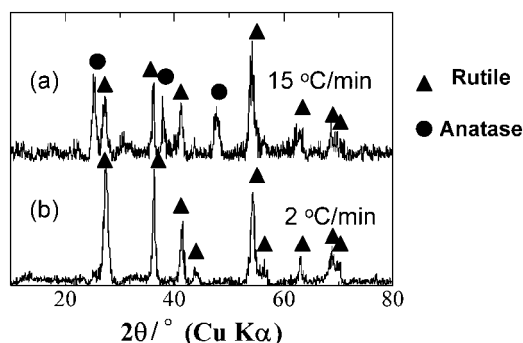


Fig. 3. Effect of heating rate on the resultant phase of the prepared titania powder. (a) Rapid heating, 15°C/min, (b) Slow heating, 2°C/min.

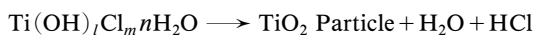
## 2.2 Characterization of the prepared powder

The prepared white powder was examined by X-Ray Diffraction (Rigaku, Rint 2100) and UV-Vis. Spectroscopy (Hitachi, U-3410). Specific surface area and the particle size and shape were also evaluated with chemisorption equipment (Quantachrome Inst., ChemBET-3000) and a TEM (Hitachi, H-800). The photocatalytic activity of prepared powder was compared with a commercially available titania powder (Nippon Aerosil Co., Ltd., Degussa P-25) by a standard measurement process previously described in the literature.<sup>7)</sup>

## 3. Results and discussion

### 3.1 Control of crystalline phase

All of the prepared white precipitates were confirmed to be crystalline titania and the crystalline phase was dependent upon the heating rate as shown in Fig. 3. A pure rutile powder was obtained by slow heating rate (2°C/min), while a mixture of rutile and anatase powders was formed by rapid heating rate (15°C/min). The rate dependence was related to the condensation reaction of titanium species and the resultant crystal structures, although the intermediate state of the formed titanium compound is not yet identified. The rapid heating process led to the meta-stable anatase phase with a smaller density of 3.90 g/cm<sup>3</sup>, which was kinetically formed from the titanium intermediate compound. On the other hand slow heating afforded a preferential condition for the condensation of the titanium species leading to the formation of dense rutile phase with 4.27 g/cm<sup>3</sup>.



So far this process led to approximately 70% recovery of the titanium component from BT, since a certain amount of the titanium species can exist in the acidic solution.

In order to confirm the effect of the coexisting barium ion, a model experiment was performed using two kinds of starting metal chlorides, (1) a barium chloride and titanium chloride solution with the same metal concentration of the dissolved barium titanate solution (each metal concentration,  $7.15 \times 10^{-2} \text{ mol/dm}^3$ ), and (2) a titanium chloride solution with the same titanium concentration of the dissolved barium titanate solution. After heating at a rate of 15°C/min, solution (1) resulted in a mixed powder of rutile and anatase titania at the same percentage as the dissolved barium titanate solution, although the solution (2) resulted in a pure anatase phase. This remarkable effect of the barium ion on the phase development also indicates the possibility of obtaining pure anatase. Based on this result, we improved the recycling

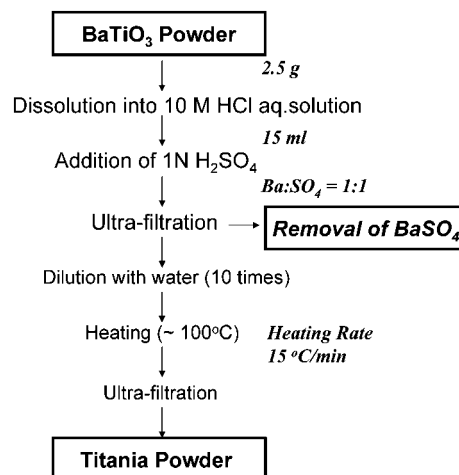


Fig. 4. Improved recycling process of BaTiO<sub>3</sub>.

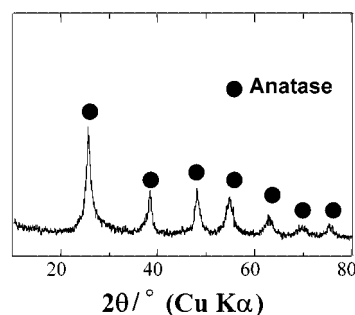


Fig. 5. XRD profile of the titania powder prepared from the solution treated with sulfuric acid (Heating rate: 15°C/min).

process of BT powder by removing the co-existing barium ion as BaSO<sub>4</sub> as in Fig. 4. 1N H<sub>2</sub>SO<sub>4</sub> solution was added to the dissolved BT solution at room temperature with the same amount of Ba<sup>2+</sup>, then the formed powder was removed before heating. XRD analysis revealed that the precipitate was pure BaSO<sub>4</sub> and the recovery was more than 95%. By precipitation with a rapid heating process, removal of the barium ion also resulted in a white suspension of titania. It was identified as pure anatase by XRD as shown in Fig. 5, which also reveals that titania is quite small and caused broadening of the diffraction lines. Figure 6 is the TEM photograph of the prepared powder, showing its crystallite size around 15 nm and the absence of other phases. The specific surface areas of these prepared powders are summarized in Table 1. The titania powder prepared by removing the barium ion has a large surface area of 120 m<sup>2</sup>/g.

Thus, BT based waste powder, including alkali earth elements and transition metal elements, can be successfully recycled to anatase titania and barium sulfate through this process.

### 3.2 Optical and photo-catalytic property

The diffuse reflectance spectra of the prepared samples were recorded by the UV-Vis. spectroscopy. The band gaps determined of the prepared anatase and rutile powders are shown in Table 2, revealing the same trend as those of commercial titania powder. Small differences in band gap could be derived from their size and poor crystallinity due to the low synthesis temperature. Photo-catalytic activity of the powder was con-

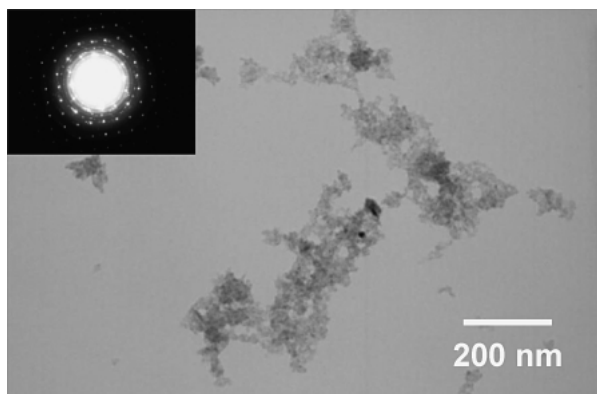


Fig. 6. TEM photograph of prepared titania powder (Anatase Phase).

Table 1. Specific Surface Area of Precipitated Powders

Sample	BET Surface Area
Starting BaTiO <sub>3</sub> powder	12 m <sup>2</sup> /g
Titania powder prepared by direct precipitation	73 m <sup>2</sup> /g
Titania powder prepared by removing Ba ion	120 m <sup>2</sup> /g

Table 2. Band Gap of Prepared Titania

Sample	Band Gap (eV)
Commercial Anatase	3.23
Prepared Powder (Anatase)	3.10
Prepared Powder (Rutile)	3.00
Commercial Rutile	3.02

Table 3. Photocatalytic Activity of Prepared Titania

Sample	Decomposed MB*
Prepared Titania	93 %
Degussa P-25	95 %

Irradiation Time : 60 min.

\*MB: Methylene blue

firmed by the decomposition behavior of the methylene blue aqueous solution based on the standard experiment. The photo-catalytic activity of the prepared powder shown in **Table 3** is almost comparable with that of Degussa P-25, a known useful titania photo-catalyst.

#### 4. Conclusions

This research suggested a new recycling process for barium titanate based waste materials which can be performed at temperatures below 100°C. Although the recovery of the titanium component is over 70%, it might be improved by considering its equilibrium and adjusting precipitation conditions. Barium ion in solution is also recovered as stable barium sulfate, one of the main natural resources of this element.

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