

Carbon Dioxide Absorption of Barium Titanate System

Toshihiro ISOBE, Shiomi SAITO, Takumi OSHIMA, Hiroki TANAKA, Kotaro YAMAURA,
Takuya HOSHINA, Daiki ATARASHI and Osamu SAKURAI

(Tokyo Institute of Technology 2-12-1 Ookayama, Meguro-ku, Tokyo, 152-8550)

The CO₂ absorption capability of Ba₂TiO₄/BaTiO₃ composites was evaluated. Samples prepared from BaTiO₃ and BaCO₃ powders had chemical compositions of BaTiO₃, Ba₂TiO₄/BaTiO₃, and Ba₂TiO₄/BaCO₃. Their CO₂ absorption capability was estimated using mass change. The specific surface area of the obtained samples with Ba/Ti ratio of 1, 1.33, 1.67, 2 and 2.33 was, respectively, 1.8, 2.0, 1.7, 0.5 and 1.2 m²·g⁻¹. This difference originates that the grains grew during heat treatment. Although BaTiO₃ showed no CO₂ absorption capability, Ba₂TiO₄/BaTiO₃ and Ba₂TiO₄/BaCO₃ composite powders did. The maximum absorption amounts were calculated from the chemical reaction during. The obtained value was about 10 times larger than that estimated from absorption test. It is regarded that the Ba₂TiO₄ reacted incompletely with CO₂, indicating that the CO₂ absorption capability depends on the powder properties. High CO₂ absorption ability is attributable to balance between high Ba₂TiO₄ loading and specific surface area. The powders after the CO₂ absorption test could reproduce by heating at 1373 K.

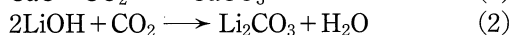
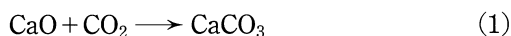
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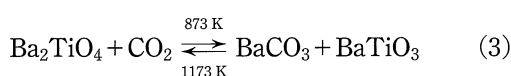
Key words : CO₂ absorption, Dielectric material, Recycle

1 Introduction

As global warming countermeasures, many policies and technologies have been proposed for the reduction of CO₂ emissions. In the field of energy, wider use of fuel cells¹, solar cells², and wind energy³ are intended to limit atmospheric CO₂ levels. Nevertheless, widespread practical use of these technologies will take time. Carbon dioxide capture and storage (CCS) technologies^{4,5} can be used in the near future as important alternatives for CO₂ abatement. Especially, capturing CO₂ is a key technology for CCS. Methods of carbon dioxide scrubbing include adsorption, amine absorption⁶, molecular sieving, and membrane filtering. Recently, chemical reaction methods using CaO⁷ and LiOH⁸ have been reported.



Saito *et al.* reported that Ba₂TiO₄^{9,10} is also available for this technique. For these materials, which have higher reaction velocity, the absorption and desorption temperatures were determined using the following thermodynamic relation.



From the viewpoint of barium element recycling,

Ba₂TiO₄ is an interesting material because large amounts of BaTiO₃ used in electronic applications generates a considerable amount of waste. Consequently, the chemical reaction and thermodynamics of this material as a chemical substance are widely discussed. However, its properties as the material are scarcely reported, leaving a dearth of knowledge of its specific surface area (SSA) and particle size. Such knowledge can support the practical use of CCS using a barium titanate system.

Pfaff reported that the SSA-controlled Ba₂TiO₄ was obtained by heating of Ba₂TiO₂(OH)₃(OOH) at appropriate temperature¹¹. This method is useful to merely synthesis of Ba₂TiO₄. However, another reason to use Ba₂TiO₄ as the CO₂ absorbent is recycling of BaTiO₃ as above. Therefore, it is desirable to prepare the Ba₂TiO₄ from BaTiO₃ as a starting material. It is reported that controlling chemical composition is one of the easiest way to change the SSA. For instance, the SSA of NiO-Al₂O₃ solid solution depended on the NiO loadings¹². The powder of stoichiometry chemical composition (NiAl₂O₄) showed the lowest SSA. Moreover, the metal ions is well known to control the decrease in SSA at high temperature^{13,14}.

These results suggest that the SSA of the Ba₂TiO₄ may be controlled by changing the Ba loading. In contrast, the change the Ba loading can lose the CO₂ absorption ability. Based upon the foregoing, it is

thought that balance of SSA and Ba loading of the absorbent is important.

For this study, $\text{Ba}_2\text{TiO}_4/\text{BaTiO}_3$ composites were prepared from BaTiO_3 and BaCO_3 . Then the relation between SSA and chemical composition of the obtained samples was estimated, along with its CO_2 absorption capability.

2 Experimental procedure

High-purity BaCO_3 (Wako Pure Chemical Inds. Ltd., Osaka, Japan) was mixed with BaTiO_3 (BT-01; Sakai Chemical Industry Co., Ltd., Osaka, Japan). The Ba/Ti ratios were 1, 1.33, 1.67, 2, and 2.33. The mixtures were heated at 1373 K for 1 h (heating and cooling rate: 10 K/min). Then CO_2 absorption tests were conducted at 873 K (heating and cooling rate: 10 K/min) for 30 min under a 90% N_2 -10% CO_2 atmosphere (0.3 L/min). After absorption tests, the 2.00 g samples were heated at 1373 K for 1 h for CO_2 desorption tests under air atmosphere. The temperatures were determined using thermodynamic calculation^{9),10)}. Phases formed in the powder were identified using X-ray diffractometry (XRD) with $\text{Cu K}\alpha$ radiation (LabX XRD-6100; Shimadzu Corp., Kyoto, Japan). The powder sample SSA was measured using BET method with nitrogen (Gemini V; Shimadzu Corp., Kyoto, Japan).

3 Results and Discussion

Fig. 1 portrays the XRD patterns of the obtained powders after heating at 1373 K. The sample with a Ba/Ti ratio of 1 consists solely of BaTiO_3 phase. The BaTiO_3 peaks decreased concomitantly with increase of the Ba/Ti ratio. At the Ba/Ti ratio of 2.33, Ba_2TiO_4

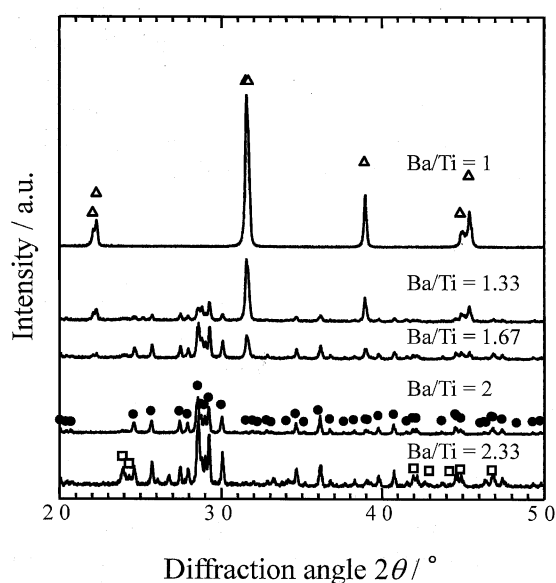


Fig. 1 XRD patterns of samples after heating at 1100 °C for 1 h.

● : Ba_2TiO_4 , △ : BaTiO_3 , □ : BaCO_3

and BaCO_3 were observed because the decomposition temperature of BaCO_3 is about 1723 K. No chart shows any other phase.

The SSAs of the present samples are presented in Table 1. Those of the samples with Ba/Ti ratios of 1, 1.33, and 1.67 were 1.7–2.0 $\text{m}^2\cdot\text{g}^{-1}$. Those of samples with a Ba/Ti ratio of 2 were about 0.5 $\text{m}^2\cdot\text{g}^{-1}$, which is about one-third of those listed above. All values were lower than the SSA of the raw BaTiO_3 powder (12.5 $\text{m}^2\cdot\text{g}^{-1}$). It is considered that the grains grew during heat treatment. The heat treatment of the mixtures was used for the chemical reaction from the mixtures to the objective materials. However, grain growth also occurred. Kwon *et al.* reported that the particle size changes as a function of heating temperature¹⁵⁾. The average size of particles used in their research was about 140 nm. Grain growth was observed at temperatures higher than 1173 K. The average particle size of the sample after heating at 1373 K was about 810 nm. For spherical particles, the relation between the particle size and SSA is described as the relation shown below.

$$d = \frac{6}{\rho \cdot A} \quad (4)$$

Therein, d , ρ , and A respectively represent the particle size, particle density, and SSA. The respective particle sizes of BaTiO_3 samples (Ba/Ti ratio of 1) before and after heating estimated from this equation are ca. 80 and 555 nm. These show fair agreement with Kwon's report¹⁵⁾. Slight differences originate from the fact that the particles are not perfectly spherical. Large decrease of the SSA of Ba_2TiO_4 samples (Ba/Ti ratio of 2) was observed. Results show that Ba_2TiO_4 has high sinterability. Samples with a Ba/Ti ratio of 1.33 and 1.67 have slightly higher SSA. It is inferred that they have two phases, each of which impedes their grain growth. Moreover, samples including more contents of Ba_2TiO_4 , of which grains grow easily, showed low SSA. At the Ba/Ti ratio of 2.33, BaCO_3 apparently restrains Ba_2TiO_4 particle growth.

The CO_2 absorption capability of the obtained samples was evaluated. The phase change of Ba_2TiO_4 after CO_2 absorption and desorption testing is presented in Fig. 2. The BaCO_3 phase was assigned in samples after the CO_2 absorption test. However, the sample consists mainly of Ba_2TiO_4 , which suggests that Ba_2TiO_4 was not completely reacted with CO_2 . After desorption tests, the BaCO_3 reacted with BaTiO_3 and

Table 1 The specific surface area of the obtained samples.

Ba/Ti ratio	1	1.33	1.67	2	2.33	Raw material (BaTiO_3)
Specific surface area/ $\text{m}^2\cdot\text{g}^{-1}$	1.8	2.0	1.7	0.5	1.2	12.5

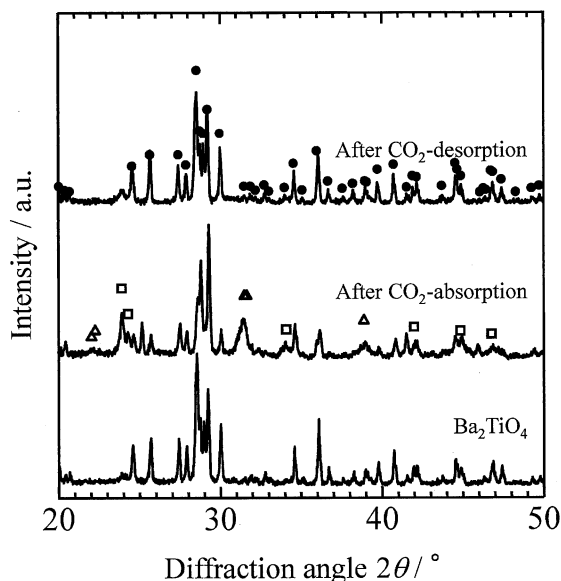


Fig. 2 XRD pattern of the samples with Ba/Ti=2 after absorption and desorption tests.

● : Ba_2TiO_4 , △ : BaTiO_3 , □ : BaCO_3

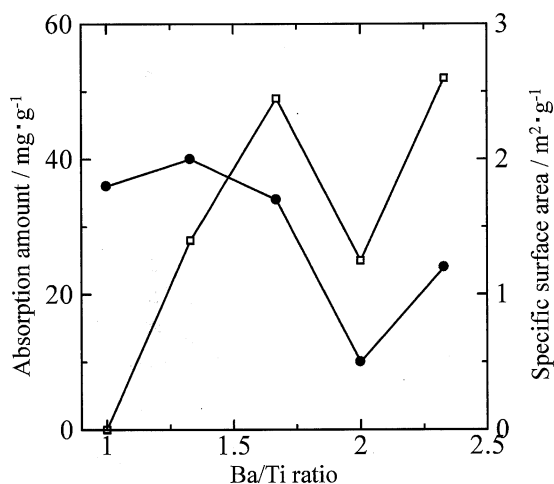


Fig. 3 CO_2 absorption amount and SSA as a function of Ba_2TiO_4 loading in the samples.

● : SSA, □ : CO_2 absorption

the Ba_2TiO_4 was synthesized again. The CO_2 absorption amount is shown in Fig. 3. The SSAs of the samples were also illustrated in Fig. 3. BaTiO_3 has only slight absorption capability. Samples with a Ba/Ti ratio of greater than 1.33 showed CO_2 absorption (about $28 \text{ mg} \cdot \text{g}^{-1}$).

The absorption amount of the sample with Ba/Ti of 1.67 was about $49 \text{ mg} \cdot \text{g}^{-1}$. It is considered that this increase originates to increase of Ba_2TiO_4 . However, the absorption amount of pure Ba_2TiO_4 was lower than that of the samples with Ba/Ti of 1.33 and 1.67 (about $25 \text{ mg} \cdot \text{g}^{-1}$). The chemical reaction of CO_2 absorption, described by eq. (3), can be used to calculate the maximum obtainable amounts from this

chemical reaction. The value of $114 \text{ mg} \cdot \text{g}^{-1}$ was obtained, which is much higher than the measured value. For the Ba_2TiO_4 phase, which is regarded as indispensable for CO_2 absorption, the chemical reaction occurs only at the particle surface. In contrast, the sample with Ba/Ti ratio of 2.33 showed the highest CO_2 absorption. This samples includes BaCO_3 other than Ba_2TiO_4 . However, the SSA of the sample is more than twice as high as that of the pure Ba_2TiO_4 .

These results suggested that both SSA and chemical composition are important for CO_2 absorbance. Moreover, it indicates that SSA of absorbance should increase at the cost of amount of Ba_2TiO_4 phase in some cases.

4 Summary

The $\text{Ba}_2\text{TiO}_4/\text{BaTiO}_3$ and $\text{Ba}_2\text{TiO}_4/\text{BaCO}_3$ composite powders were prepared by solid-state reaction of BaTiO_3 and BaCO_3 powders. Their CO_2 absorption capability was estimated. We conclude that Ba_2TiO_4 loading and SSA affected the barium titanate system's CO_2 absorption capability. To improve CO_2 absorption, the Ba/Ti ratio should be set as greater than 2, and particles should be small.

The following results were obtained:

- 1) The crystalline phase of the powder with a Ba/Ti ratio of 1 was BaTiO_3 phase. It showed no CO_2 absorption capability.
- 2) The $\text{Ba}_2\text{TiO}_4/\text{BaTiO}_3$ composite powders (Ba/Ti ratio of 1.33 and 1.67) have CO_2 absorption capability. The CO_2 absorption amount increased with increasing the Ba_2TiO_4 loading. However, the Ba_2TiO_4 reacted incompletely with CO_2 .
- 3) The sample with a Ba/Ti ratio of 2 consists solely of Ba_2TiO_4 phase with SSA of $0.5 \text{ m}^2 \cdot \text{g}^{-1}$. It showed lower CO_2 absorption capability than the above composites. It is considered that the low CO_2 absorption capability originates to the low specific surface area of the sample.
- 4) The $\text{Ba}_2\text{TiO}_4/\text{BaCO}_3$ composite powder (Ba/Ti ratio of 2.33) also has CO_2 absorption capability. It is regard that it has higher specific surface area than Ba_2TiO_4 .

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チタン酸バリウム系材料による二酸化炭素の吸収

磯部 敏宏・斉藤 潮美・大嶋 拓実・田中 宏樹・山浦考太郎・
保科 拓也・新 大軌・櫻井 修
(東京工業大学)

$Ba_2TiO_4/BaTiO_3$ 複合材の CO_2 吸収能を評価した。 $BaTiO_3$ と $BaCO_3$ 粉末から作製したサンプルの化学組成は $BaTiO_3$, $Ba_2TiO_4/BaTiO_3$ と $Ba_2TiO_4/BaCO_3$ であった。これらの CO_2 吸収能は、重量変化で求めた。 Ba/Ti 比が 1, 1.33, 1.67, 2, 2.33 のサンプルの比表面積は、それぞれ、1.8, 2.0, 1.7, 0.5, 1.2 $m^2 \cdot g^{-1}$ であった。この違いは熱処理中の粒成長によるものである。 $BaTiO_3$ は CO_2 吸収能を示さなかったが、 $Ba_2TiO_4/BaTiO_3$ と $Ba_2TiO_4/BaCO_3$ 複合材は CO_2 吸収能を示した。化学反応式から最大 CO_2 吸収量を計算したところ、実験で得られた値の約 10 倍だった。これのため Ba_2TiO_4 が CO_2 と完全には反応しておらず、 CO_2 吸収能が単に化学反応だけでなく、粉末の特性に依存したと考えられる。また、高い CO_2 吸収能は Ba_2TiO_4 量と高比表面積のバランスによると示唆された。また、 CO_2 吸収した後の複合材は、1373 K で加熱することで再生することができた。