Mechanochemical Synthesis of $BaTiO_3$ from TiO_2 and $BaCO_3$

KONDO Akira*, SHIMODA Hirofumi**, SATO Kazuyoshi*,
ABE Hiroya*** and NAITO Makio****

Abstract

Mechanochemical synthesis of $BaTiO_3$ from a powder mixture of $BaCO_3$ and TiO_2 was investigated. An attrition type of milling apparatus was used. It was found that the mechanochemical reaction was strongly dependent on the size combination of the respective two materials. By milling a powder mixture of $BaCO_3$ (50nm) and TiO_2 (7nm), the single phase $BaTiO_3$ was synthesized after milling for only 15min. On the other hand, the reaction was not well promoted by the milling of a mixture of $BaCO_3$ (50nm) and TiO_2 (70nm).

KEY WORDS: (nanoparticulates), (barium titanate), (mills/milling), (synthesis)

1. Introduction

Barium titanate ($BaTiO_3$) finds extensive application in electronic industry due to its high relative dielectric constant and low losses. In the conventional solid reaction, difficulty exists due to the growth of grains during calcinations at high temperatures. To prepare fine powders, chemistry-based processing methods[1,2] have been investigated. However, most of these methods are more expensive than the solid state reaction and some of them have significant drawbacks.[3] A satisfactory alternative may be a mechanochemical method.[4]

The mechanochemical method is characterized by the repeated welding, deformation and fracture of the constituent powder materials.[5] Chemical reactions occur at the interfaces of the particles that are continuously re-generated during milling. As a consequence, solid-state reactions can be promoted in the milling apparatus without any need for external heating. Stojanovic et al. reported that the mechanochemical reaction led to the gradual formation of $BaTiO_3$ phase from the powder mixture of BaO and TiO_2.[6] Xue et al. synthesized single phase $BaTiO_3$ from the powder mixture of BaO and TiO_2 under a nitrogen atmosphere.[7] To date, fine $BaTiO_3$ powder has not been obtained from the powder mixture of $BaCO_3$ and TiO_2 by mechanical activation without additional heat treatment.

In this study, mechanochemical synthesis of $BaTiO_3$ from powder mixtures of $BaCO_3$ and TiO_2 was investigated. It was found that the mechanochemical reaction was strongly dependent on nanoscale size combinations of the respective two materials.

2. Experimental

Raw materials were nanocrystalline $BaCO_3$ (BW-KS20, Sakai Kagaku, Japan), TiO_2 (ST-01, Ishihara Sangyo, Japan) and TiO_2 (HT2301, Toho Titanium, Japan). The mean particle sizes calculated from the specific surface area (SSA) were 50nm, 7nm and 70nm for the $BaCO_3$, TiO_2(ST-01) and TiO_2(HT2301), respectively. $BaCO_3$ and TiO_2(ST-01), or $BaCO_3$ and TiO_2(HT2301) were mixed in equimolar ratios, and then the powder mixture of 60g was put into the chamber of an attrition type apparatus.[8] This apparatus was employed for the mechanochemical synthesis of $LaMnO_{3+\delta}$.[8] Its main components are a fixed chamber and a rotor set with a certain clearance against the inside wall of the chamber. Both the chamber and the rotor were made of stainless steel. When the rotor rotates, the powder mixture is compressed into the clearance (1 mm gap) and receives various kinds of mechanical forces such as compression and shearing. No media balls were employed in this milling, and the ambient atmosphere in the chamber was not controlled, i.e., the milling was conducted in air. The rotating speed of the rotor was 4000 rpm in the present experiment. The milled powders were then characterized by X-ray diffraction (XRD; JDX-3530M, JEOL, Japan) using Ni filtered Cu-Kα radiation. SSA of the samples was measured by a nitrogen gas adsorption instrument (micromeritics Flowsorb 2300, Shimadzu, Japan) based on the BET method.

† Received on November 10, 2006
* Designated researcher
** Kurimoto Ltd.
*** Associate Professor
**** Professor
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3. Results and Discussion

Figure 1 shows the XRD patterns of the starting powder mixture ($BaCO_3$ and TiO_2(ST-01)) and the milled powder mixtures that have been milled for various time periods: 0, 15min. Only peaks correspond to $BaCO_3$ and TiO_2 were observed for the powder mixture before the milling. These peak intensities drastically decreased with an increase in milling time at early stages of the milling (<7min). After 15 min, the peaks correspond to $BaCO_3$ and TiO_2 almost disappeared, and only peaks for $BaTiO_3$ were observed. The SSA of the powder mixture milled for 15min was about $5m^2/g$, and its equivalent diameter was calculated as 200nm.

Figure 2 shows the XRD patterns of the starting powder mixture ($BaCO_3$ and TiO_2(HT2301)) and the milled powder mixtures that have been milled for various time periods: 0, 15min. After 15 min, although peaks for $BaTiO_3$ were detected, the peaks correspond to $BaCO_3$ and TiO_2 still strongly existed. Thus, it was found that the mechanochemical reaction was strongly dependent on the size combination of the respective two materials.

The following steps are indicated for the powder combination of $BaCO_3$ and TiO_2(ST-01):
(1) amorphization of the raw material in the early stage of the milling (<7min), and (2) solid state reaction, which led to the formation of crystalline $BaTiO_3$ phase.
Any structural defects and disorder together with a degree of amorphization will favor diffusion and atomic rearrangement at a reduced temperature.[9] Localized heating and pressure at regions of contact between the reactant grains may be a contributing factor for the phase formation in the activated matrix.[10] Our results indicated that the considerable activation of the nanocrystalline powder mixture and the phase formation between nanosized grains occurred for $BaCO_3$ and TiO_2(ST-01, 7nm). On the other hand, the reaction would not proceed efficiently for $BaCO_3$ and TiO_2(HT2301, 70nm). The influence of the size combination on the mechanochemical reaction of $BaTiO_3$ will be explained in detail in the future.

4. Conclusions

When milling a powder mixture of $BaCO_3$ (50nm) and TiO_2 (7nm), the single phase $BaTiO_3$ was synthesized after milling for only 15min. The SSA of the powder mixture milled in 15min was about $5m^2/g$, and its equivalent diameter was calculated as 200nm. On the other hand, the peaks correspond to $BaCO_3$ and TiO_2 strongly existed after the same milling time for $BaCO_3$ (50nm) and TiO_2 (70nm). The size combination of the respective materials therefore plays an important role in the mechanochemical formation of $BaTiO_3$.

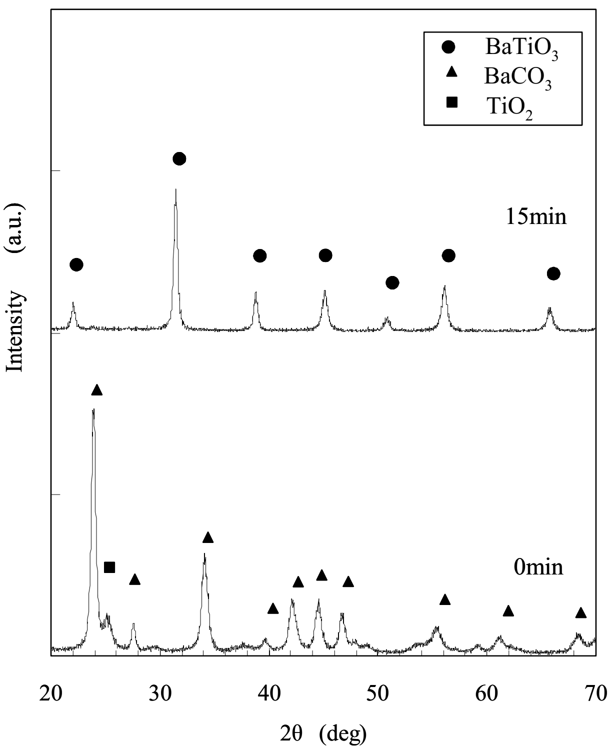

Figure 1. XRD patterns of the starting and the milled powder mixtures. ($BaCO_3$(50nm) and TiO_2(7nm))

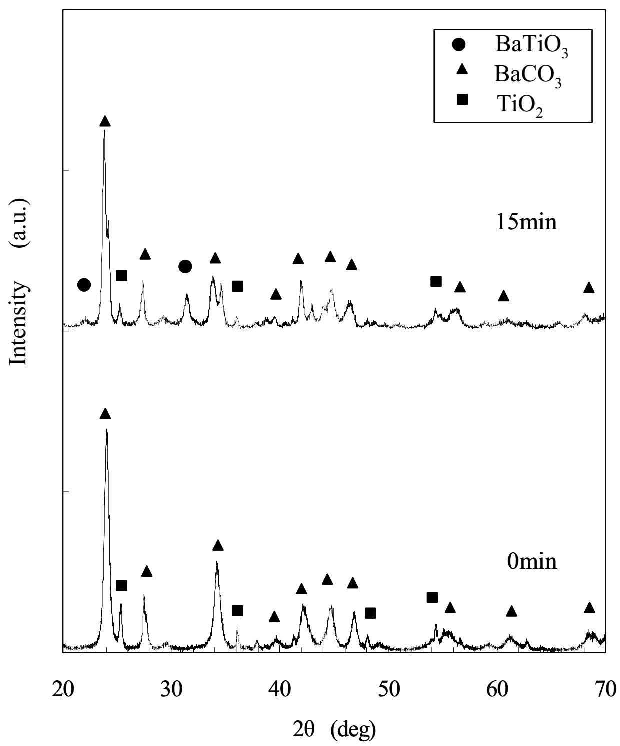

Figure 2. XRD patterns of the starting and the milled powder mixtures. ($BaCO_3$(50nm) and TiO_2(70nm))

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