

## Characterization of Heavily Pressed Barium Titanate Powder

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Barium titanate powder was cold isostatic pressed (CIPed) under 1.0 GPa repeatedly up to 60 times. Crystallite size decreased and lattice strain increased with CIPing times. The specimen was found to belong to the tetragonal phase after CIPing 60 times. The integrated X-ray diffraction intensity of barium titanate was revealed to increase markedly by CIPing. The tweedy and/or squeezed texture was found to comprise collapsed boundary zones and modulated lattice arrays.

Key words: X-ray methods; Electron microscopy; BaTiO<sub>3</sub>; Capacitors; Ferroelectric transformation

### 1. INTRODUCTION

The idea of the foregoing report [1] was given during a search of processes to prepare cubic-phase barium titanate from the tetragonal powder. The decrease in crystallite size and the increase in lattice strain were shown as functions of the pressure of CIPing [1]. Further, a catastrophic decrease in the enthalpy of the tetragonal-cubic transformation was noted — it was 6.7% of that of the starting material after CIPing at 1.0 GPa. In this study, CIPing was repeated up to 60 times. The CIPed specimens were characterized extensively by high-resolution transmission electron microscopy (TEM).

### 2. EXPERIMENTAL

The raw powder was commercially available barium titanate (KCM Corp., Nagoya, Japan, BT-HP9DX). It was prepared by a solid-state reaction and then pulverized. The median diameter was 0.70  $\mu\text{m}$ , the loss on ignition was 0.32 mass%, and the powder was doped with Sr and Nd according to the product data sheet. The as-received powder was heated at 1100°C for 2 h in order to refresh the hydrated surface layer. The heated loose cluster is called the “starting material”.

An agglomeration of the starting material from 5 g to 8 g was put in a decompressed rubber balloon and CIPed for 5 min under 1.0 GPa (Sugino Machine, HPV-150C4) and then pressure was released. This CIPing was repeated up to four times in one batch. The specimen that was CIPed four-times was roughly ground in an agate mortar to prepare it for further CIPing.

Specimens were characterized by XRD (Rigaku, RINT2500VHF) with CuK $\alpha$  radiation, SEM (JEOL, JXA-840A) and TEM. An Si-internal standard method was used to calculate lattice constants. Diffractions 111 and 222 were measured at the fixed time modes of 1 s and 6 s, respectively, to evaluate crystallite size and lattice strain by using the Rigaku application software MJ13028A. Peak separation was carried out using the software MJ13025A. The standard material was prepared by cracking a piece of as-grown single crystal [2].

A thorough mixture containing equal masses of barium titanate and  $\alpha$ -alumina was prepared. Diffractions of 111 of barium titanate and 113 of

$\alpha$ -alumina in the mixture were measured to compare their integrated intensities and rectangular intensities (peak intensity multiplied by full-width at half maximum (FWHM)). After the operation, the sample was mixed again for the next measurement; this handling was repeated four times.

The powder was scooped with carbon-coated micro grids on a copper mesh. Characterization was performed with a TEM (JEOL-3000F) device that made it possible to provide electron probes with an FWHM of around 0.5 nm, and also with sufficiently high current for EDS point analysis.

### 3. RESULTS AND DISCUSSION

The SEM image in Fig. 1 shows that some pulverization occurred after CIPing 20 times. The result is in contrast with the report [1] that no noticeable changes in morphology are seen after CIPing once.

The lattice constants of barium titanate are listed in Table 1. The axial ratio and the cell volume decreased slightly with the increase in CIPing times. This relationship that the decrease in axial ratio occurs together with the decrease in cell volume is consistent with that reported [3]. However, this relationship seems inconsistent with that reporting lattice expansion in nanoparticles [4].

Profiles of 111 and 222 were analyzed using the integral width method of Wilson [5] to obtain data plotted in Fig. 2. The results of runs 1 and 2 are similar to each other. The crystallite size of the starting material is 84 nm (run 1) or 96 nm (run 2); they decrease sharply by CIPing once to 64 nm (run 1) or 67 nm (run 2). Then

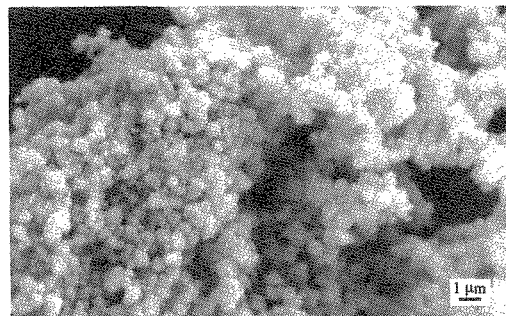


Fig. 1 SEM image of the specimen after CIPing 20 times under 1.0 GPa.

Table 1 Lattice constants of barium titanate before CIPing and after repeated CIPing under 1.0 GPa\*<sup>1</sup>

| Specimen          | $a_0$ / nm | $c_0$ / nm  | $c_0/a_0$ | $V_0 / 10^{-2}\text{nm}^3$ |
|-------------------|------------|-------------|-----------|----------------------------|
| Starting material | 0.39937(1) | 0.40368(2)  | 1.0108    | 6.4386(4)                  |
| CIPed once        | 0.39944(6) | 0.40346(10) | 1.0101    | 6.437(2)                   |
| CIPed 8 times     | 0.39940(7) | 0.40308(9)  | 1.0092    | 6.430(2)                   |
| CIPed 40 times    | 0.39941(7) | 0.40288(10) | 1.0087    | 6.427(2)                   |
| CIPed 60 times    | 0.39941(6) | 0.40280(9)  | 1.0085    | 6.426(2)                   |

\*<sup>1</sup>: estimated standard deviation is enclosed in parentheses.

the crystallite size decreases gradually with further increase in CIPing times. The lattice strain of the starting material is negligible [1]; it increases with CIPing times in a manner opposite to that of the decrease in crystallite size.

The separations of 002/200 and 202/220 diffractions of CIPed specimens into two or three peaks were performed. The latter "three peaks" refers to the coexistence of tetragonal/cubic phases. Fig. 3 shows the results of only one specimen. The diffraction intensity ratios between 002/200 of (a) and 202/220 of (c) are rational respectively. However, those intensity ratios of (b) and (d) are not as rational as (a) and (c), further, the intensity ratios of cubic/tetragonal phases of (b) and (d) are inconsistent. Accordingly, it is concluded that the specimen consists of only the tetragonal phase by referring to the intensity ratios of 002/200 and 202/220, and the intensities of the cubic phase. This conclusion of the single tetragonal phase was also made for all CIPed specimens.

The intensity ratio of 111 of barium titanate to 113 of  $\alpha$ -alumina is listed in Table 2. These values indicate that the intensity of barium titanate increased dramatically on the first CIPing; and this high intensity was maintained throughout the 8 CIPing times. This increase in intensities could not be attributed to the increase in the amount of barium titanate. We hypothesize that the diffraction of the starting material has a considerable effect on the dynamic diffraction of a perfect crystal.

The mosaic structure of the powder CIPed once was shown in reference 1. However, Figs. 4 (a) and (b) show a tweedy and/or squeezed texture. There was a trace of barium carbonate, which was confirmed by EDS. It is

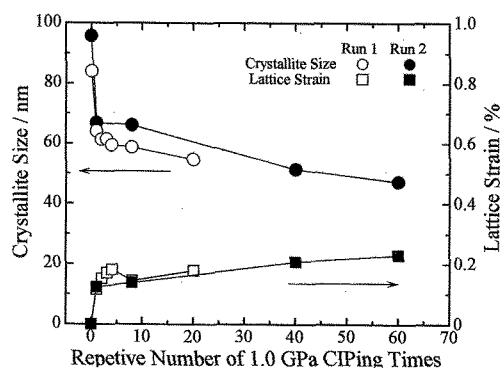


Fig. 2 Crystallite size and lattice strain vs. number of CIPing times.

shown in (b) with shapes like thorn on the trunk of barium titanate. A markedly similar thorn like shapes of barium carbonate and its decomposition on hydrothermal barium titanate is first identified by Nakano *et al.* [6]. Figure 5 shows the structure images of the starting material and those CIPed specimens. The normal clear image of (a) is compared with the partially collapsed structures of (b) and (c). No ferroelectric twin structures have been identified in these powders. The

Table 2 X-ray diffraction intensity ratio of 111 of barium titanate to 113 of  $\alpha$ -alumina\*<sup>2</sup>

| Specimen          | Integ. Int. | Rect. Int.* <sup>3</sup> |
|-------------------|-------------|--------------------------|
| Starting material | 1.78(10)    | 0.91(14)                 |
| CIPed once        | 2.31(34)    | 2.25(7)                  |
| CIPed 2 times     | 2.08(29)    | 2.37(19)                 |
| CIPed 8 times     | 2.18(35)    | 2.45(17)                 |

\*<sup>2</sup>: standard deviation for four measurements.

\*<sup>3</sup>: peak intensity multiplied by FWHM.

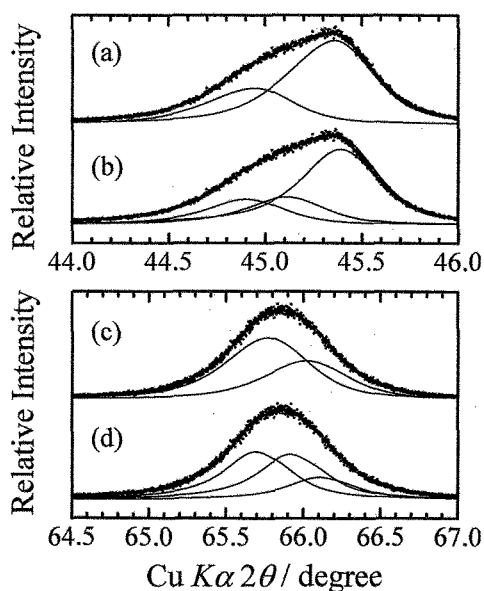


Fig. 3 Separations of 002/200 ((a)/(b)) and 202/220 ((c)/(d)) diffractions of the specimen CIPed 60 times. (a)/(c) and (b)/(d) are separated into two peaks and three peaks, respectively.

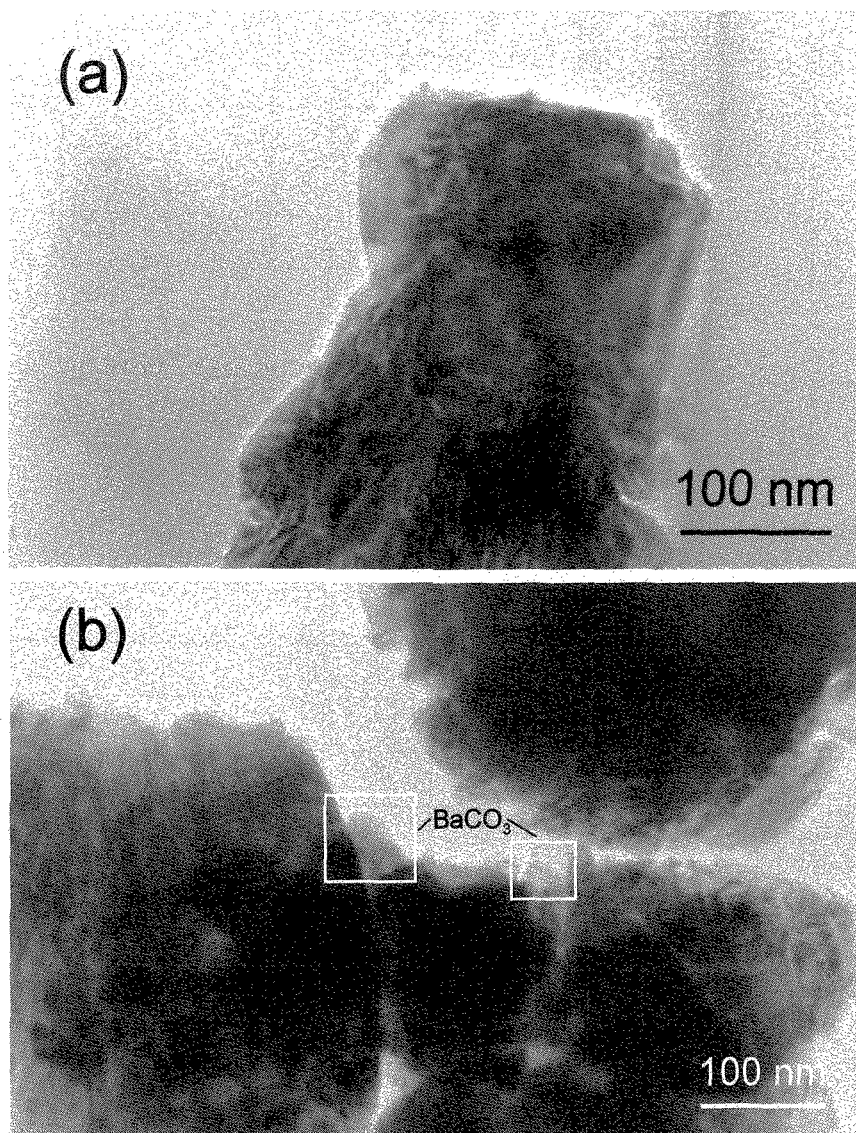


Fig. 4 TEM images of the specimen CIPed 60 times.

collapsed belts appear as if they were the slipping planes under pressure. Moreover, some collapsed belts are almost parallel to each other. Figures 6(a) and (b) are structure images showing the coexistence of various lattice modulations. There are many dislocations, wavy lattices arrays, and various modulations of periodicities. Those modulations occur in circles or in belts with different widths. However, we did not find amorphous zones. It is certain these modulations are products of plastic deformation by CIPing. Accordingly, these structure images share many common features with a shock-consolidated compact [7]. There are many wavy contrast zones in Figs. 6(a) and (b), which have different shapes, sizes, and periodicities; however, their appearances are similar to those of tricalcium silicate [8].

The enthalpy for the tetragonal-cubic transformation of the specimen CIPed once is only 6.7% of that of the starting material [1]. The collapsed belts are found in the

powder (Figs. 5(b) and (c)). However, most parts of the structure images appear similar to those of the normal crystal; namely, it is very difficult to imagine the catastrophic decrease in the transformation enthalpy from their structure images. In contrast to the blunt changes in the structure images, these distinct changes by the first CIPing are recorded; those are crystallite size and lattice strain (Fig. 2), the intensity of X-ray diffraction (Table 2), axial ratio ( $c_0/a_0$ ), and cell volume (Table 1).

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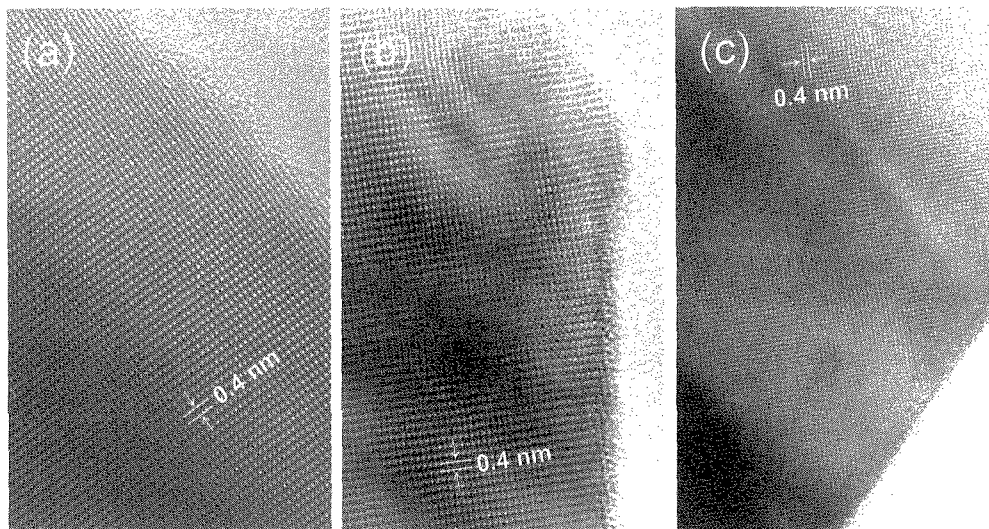


Fig. 5 High-resolution structure images. (a) the starting material, normal to  $[110]$ , (b) the specimen CIPed once, normal to  $[110]$ , (c) the specimen CIPed 20 times, normal to  $[100]$ .

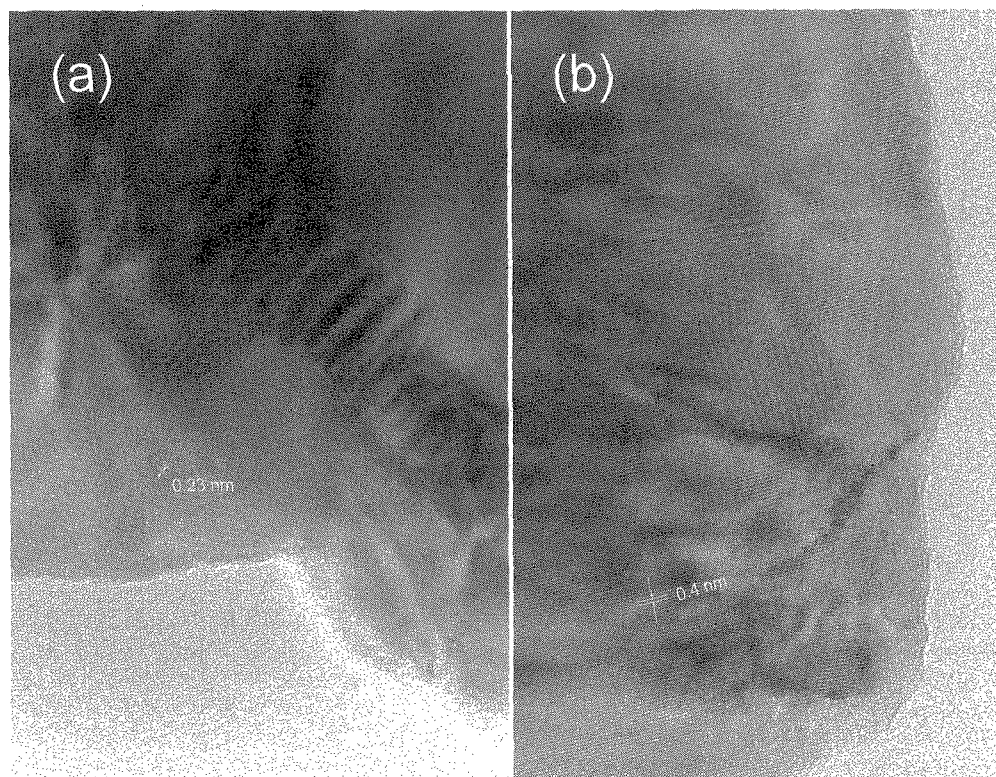


Fig. 6 High-resolution structure images of the specimen CIPed 60 times. (a) normal to  $[111]$ , (b) normal to  $[110]$ .

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