

Phase Transformation of Barium Titanate Confirmed by Raman Spectroscopy and Powder X-ray Diffraction

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Powder X-ray diffraction and Raman spectroscopy, equipped with respective temperature control units, were used to identify the phase of fine powders of barium titanate. Those investigated were hydrothermal powder and its heated treated, and another repeatedly cold isostatic pressed (CIPed) powders. The main topics were as follows: (a) Sharp decrease of the diffraction width of the diffused diffraction was evaluated as the conclusive evidence of the tetragonal to cubic transformation. (b) We obtained data to assert that Raman spectrum were not to be used to identify the phase, or at least to identify cubic barium titanate.

Key words: barium titanate, phase transformation, Raman spectrum, size effects, crystallite size

1. INTRODUCTION

Recently, Wada *et al.* published a series of excellent works about the synthesis of nm-ordered barium titanate fine particles and their dielectric properties [1-3]. They have shown that the particles with the size of 17 nm and 40 nm are cubic and tetragonal, respectively; and write that the critical particle size of the ferroelectric transformation from tetragonal to cubic at a room temperature exists between 17 and 40 nm [2]. Moreover, they have evaluated dielectric constants of those fine particles from the measurements of slurries, and have estimated that the particle with a size of 140 nm has the maximum relative dielectric constant of 5000 [3].

Two of the authors of this report [H.I. and M.T.] did some works by another method to investigate the same critical size mentioned above [4-7]. The tetragonal-cubic transformations of the powders used in those studies are investigated in this study by means of high temperature X-ray diffraction and Raman spectroscopy to make it definitely clear the phase at room temperature.

2. MATERIALS and EXPERIMENTAL PROCEDURES

Two commercially available barium titanate powders were used. One was hydrothermal powder of Sakai Chemical Industry Co. Ltd. Sakai Japan (BT-01) [8] having trace of barium carbonate [9] and the other was prepared by a solid-state reaction and then pulverized by KCM Corp. Nagoya Japan (BT-HP9DX). The median diameter of the latter was 0.70 μm , the loss on ignition was 0.32 mass%, and the powder was doped with Sr and Nd according to the product data sheet.

Small pellets of hydrothermal barium titanate were CIPed at room temperature under 1 GPa before heating at temperatures for 24 h up to 1573 K. The heated pellets including a CIPed pellet of as-received powder were polished by using abrasive papers of #1000, #2000, #4000, and/or #8000 for Raman Spectroscopy.

The solid-state reaction powder was heated at 1373 K for 2 h in order to refresh the hydrated surface layer. A lump of the heated powder was CIPed for 5 min under 1.0 GPa and then the pressure was released. This CIPing was repeated up to 100 times. The details of experiments are written elsewhere [4,5]. The specimen was pulverized in an agate mortar and was plunged into a hole of 4 mm in an aluminum plate for the Raman measurement.

Selected X-ray diffraction profiles were measured under air atmosphere in the temperature range between 373 K and 418 K by means of a diffractometer (Rigaku, RINT2500VHF) equipped with a medium and low temperature attachment (Rigaku, 2352A). Temperature stability was within 0.2 K during the measurements, but

we have no data about the deviation of temperature of the specimen of the locations in the holder of Cu plate 15 by 15 mm.

We could obtain the diffraction without delicate vertical setting of the specimen at each temperature using a graded *d*-spacing parabolic multilayer X-ray mirror (Osmic, Max-Flux®). Diffraction intensity was measured by the fixed time mode using Cu $K\alpha$ radiation under a power of 10 kW (50 kV, 200 mA). Sampling times were 1 s for 111, 002/200 and 222 profiles, 6 s for 113/311 profile, or 8 s for 004/400 profile. Scan step was 0.002° for 111, 002/200, and 222 profiles, or 0.01° for 113/311 and 004/400 profiles. The peak fitting and peak separation were carried out by using an application software 'Multi Peak Separation' provided by Rigaku for the measured profiles. The profiles were represented as a linear combination of asymmetric pseudo-Voigt function(s) and a linear base line after smoothing by Savitzky-Golay's method using five measurement points. Profiles of the specimen heated 1573 K were analyzed by estimating two peaks having identical full width of half maximum (FWHM). On the other hand, powders of as-received hydrothermal and CIPed 60 times were analyzed their FWHMs by estimating single peak, respectively.

The Raman spectra were measured by means of a spectrometer (Kaiser, HoloLab 5000) using SHG of Nd:YAG laser (532 nm, 50 mW). The laser was focused on the sample surface with a spot size of 10 μm , and scattered light was corrected in backscattered geometry using a microscope (Olympus, BX60). Temperature of the sample was controlled from 300 K to 450 K by means of a micro miniature refrigerator (MMR Technologies, R2500-23), which cools the sample by Joule-Thomson expansion of high purity and high pressure nitrogen gas. The stability of temperature was within ± 0.02 K during the measurement.

3. RESULTS

3.1 Temperature dependence of FWHM

Figure 1 shows the 113/311 diffraction of selected temperatures together with respective final fitting curves. Each panel in Fig. 1 shows that the diffraction pattern was fitted well by two peaks to evaluate FWHM. This situation was applicable to all diffractions. The figure shows that the diffractions of 113 and 311 merge into a single diffraction of cubic barium titanate at 412 K and/or 408 K.

Figure 2 shows FWHM of five diffractions as a function of temperature. Three are noted from Fig. 2 as follows: (1) FWHMs of the heating and cooling processes supports to say that the data is reversible. (2) Fitted straight lines of FWHM for 200, 311 and 400 have negative inclinations to temperature, although it is positive

in theory. (3) Limited increases in FWHMs are recognizable for all diffractions except 111. The peak temperatures of FWHM of four diffractions coincide within $401\text{ K} \pm 2\text{ K}$. This is just before the temperature of the transformation by referring 412 K and/or 408 K in Fig. 1 as the first temperature of single 311 peak of cubic

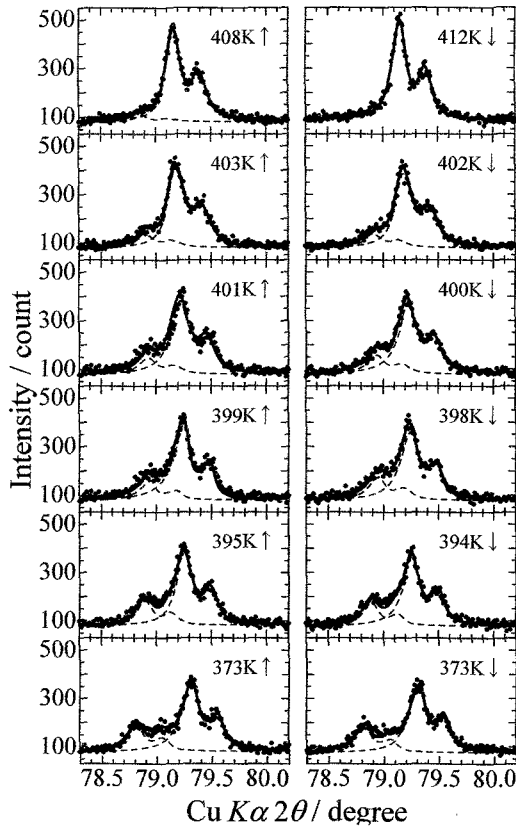


Fig. 1 X-ray diffraction pattern of 113/311 obtained by the FT mode at each temperature for the hydrothermal barium titanate heated at 1573 K for 24 h. The arrow attached the temperature show the measurement on heating or on cooling process. Legend; dot: data, solid line: total fitted curve, two broken lines: two split peaks.

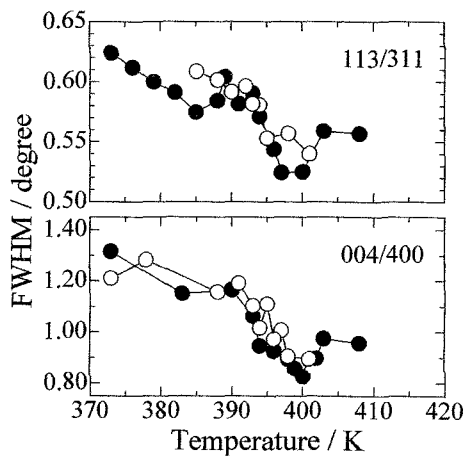


Fig. 3 FWHM of 113/311 and 004/400 diffractions of as-received hydrothermal powder as a function of temperature. The solid and open circles mean data on the heating and on cooling process, respectively.

barium titanate is recorded. This recognition of broadening is discussed later.

Figure 3 shows the FWHM of two diffractions of as-received hydrothermal powder analyzed by estimating single peak. FWHM of this specimen is about four times larger than respective those of Fig. 2. FWHMs of the two

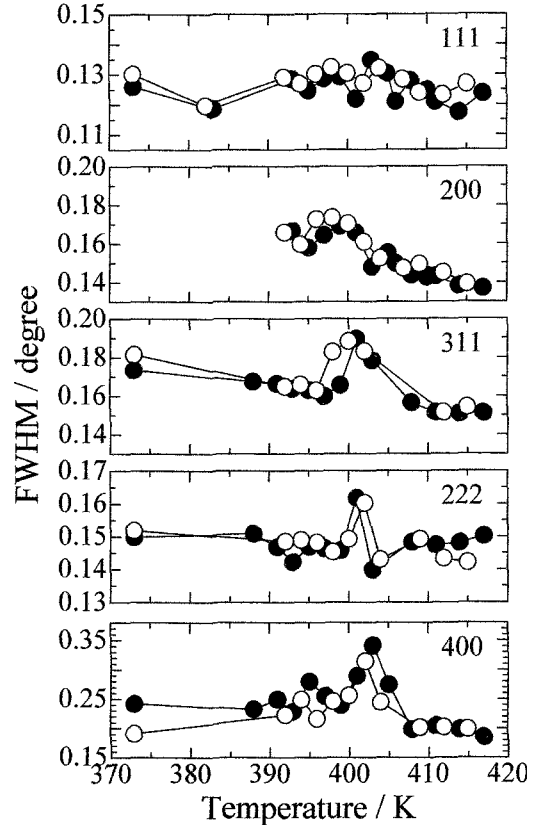


Fig. 2 FWHM of five diffractions of the hydrothermal powder heated at 1573 K for 24 h as a function of temperature. The solid and open circles mean data on heating and on cooling process, respectively.

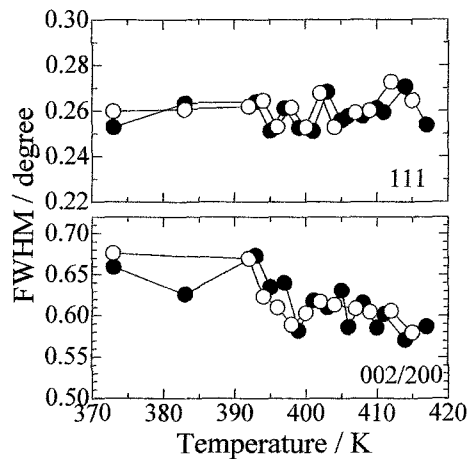


Fig. 4 FWHM of 111 and 002/200 diffractions of the powder CIPed 60 times as a function of temperature. The solid and open circles mean data on heating and on cooling process, respectively.

diffractions have clear tendencies to decrease with temperature to values almost independent temperatures higher than about 396 K; further these decrease and increase are almost reversible. It is reasonable to conclude from Fig. 3 that the specimen is tetragonal at room temperature and is cubic after the sharp decrease in FWHM from 390 K to 396 K. The tetragonal-cubic transformation of this specimen has been confirmed conclusively by this study. The change in FWHM with temperature is sensitive to the phase transformation of barium titanate than the thermal analysis. Namely, it is referred that no abnormal signs of heat capacity corresponding to phase transformations of this specimen have been detected from 310 K to 13 K [4, 5].

The FWHM of 111 of Fig. 4 is independent of temperature, while that of 002/200 has significant dependence on it. Accordingly, the powder CIPed 60 times is tetragonal at room temperature and is cubic after the sharp decrease in FWHM from 392 K to 398 K. The crystallite size and lattice strain of the specimen has been analyzed as 47 nm and 0.23%, respectively based on the profile analysis of 111 and 222 diffractions [7]. Moreover, the specimen has been analyzed tetragonal by separations of diffractions, although the tweedy and/or squeezed texture has been observed throughout the crystal [6,7].

3.2 Raman spectroscopy

Selected Raman spectrograms are shown in Fig. 5 (a), (b), (c), and (d). The spectra at 300 K in Fig. 5 (a) is

identical with those reported [10-13] including a sharp dip near 185 cm⁻¹ which has been recorded only for ceramic bulk [11,12]. Three are noted from Fig. 5 (a) as follows: (4) The spectrum can be regarded as reversible strictly by comparing data at 300 K, 396 K, and 398 K on the heating process with respective 397 K, 396 K, and 300 K on the cooling. (5) The sharp decreases in spectrum intensities about 185 cm⁻¹, 308 cm⁻¹, and 720 cm⁻¹ and broadening of those three spectra and the spectrum about 515 cm⁻¹ must be related to the tetragonal to cubic transformation. (6) The cubic phase shows, accordingly, only broad two spectra at around 250 cm⁻¹ and 520 cm⁻¹. These observations agree well with the reports [11-13].

The spectra of pulverized specimen (Fig. 5 (b)) are different considerably from those of the bulk (Fig. 5 (a)). The sharp dip near 185 cm⁻¹ can not found in Fig. 5 (b), and all the sharp changes mentioned above in (5) become dull changes. We can also see, as the results, weak spectra at about 308 cm⁻¹ and 720 cm⁻¹ for the cubic phase by measuring on powder. Those differences in thermo-Raman spectra between the bulk and powder have been reported [11], although our explanation is quite different as discussed later.

There are significant differences between the spectra at 300 K in Fig. 5 (b) and Fig. 5 (c). However, all the above descriptions of Fig. 5 (b) are applied to Fig. 5 (c).

The spectra measured at temperatures in Fig. 5 (d) are very similar one another. That is, we cannot find easily any considerable changes in spectra which are attributable

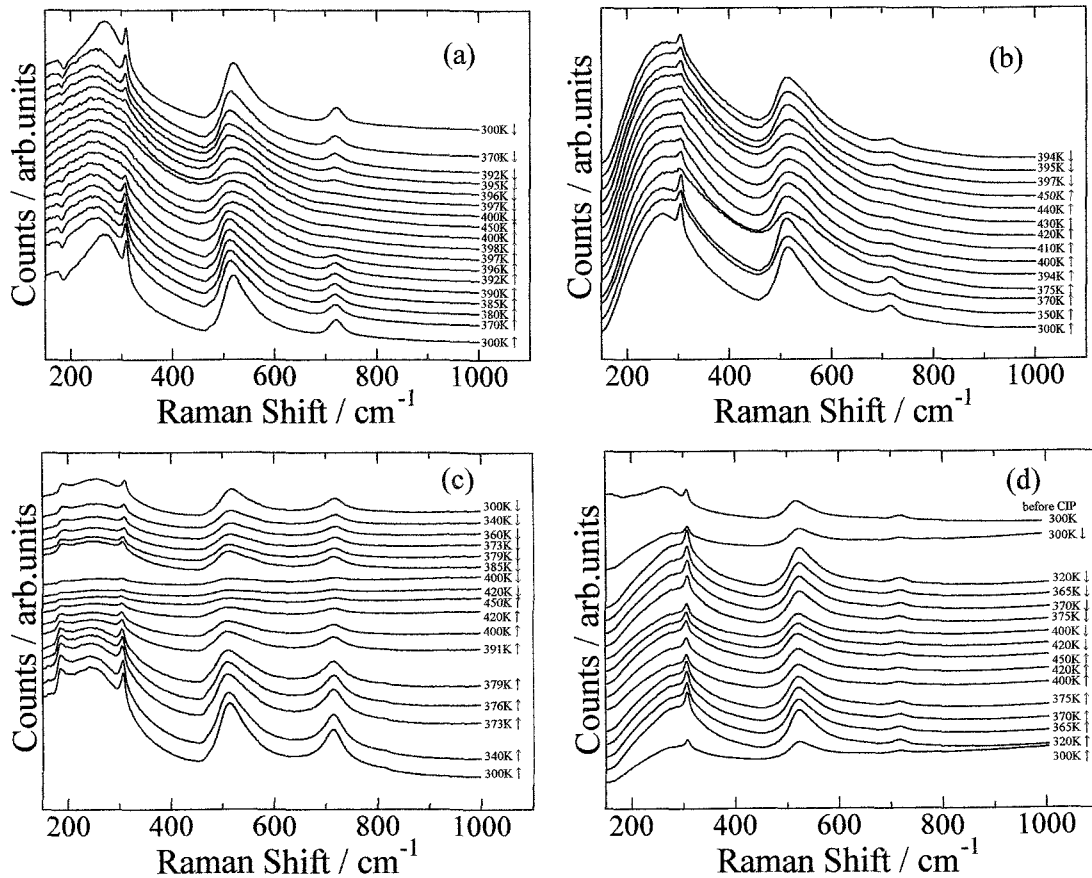


Fig. 5 Temperature dependent Raman spectra of barium titanate. The raw material of all the specimens except that of (d) is hydrothermal powder. The arrow attached the temperature show the measurement on heating or on cooling process. (a): bulk specimen heated at 1573 K for 24 h. (b): pulverized specimen of the bulk specimen of (a). (c): unheated pressed specimen. (d): powder specimen CIPed 60 times.

to the phase transformation, although we have detected the decrease in FWHM of this specimen (Fig. 4). The top spectrum in Fig. 5 (d) was measured about the powder before CIPing. There are considerable changes of spectra only in the range from 150 cm^{-1} to 310 cm^{-1} between two powders before and after CIPing 60 times.

4. DISCUSSIONS

4.1 Effectiveness of FWHM to identify the phase

This study has shown conclusive evidence about the phase transformation of fine powders of barium titanate (Figs. 3 and 4). The hydrothermal powder (BT-01) and the powder CIPed 60times, namely, are tetragonal at room temperature and transform to the cubic phase at around 395 K. This conclusion is derived from the sharp decrease in FWHM of diffractions, the tetragonal splitting of them are difficult to detect because of the broadening of the diffractions. Further, this conclusion talks about the dominant part of the specimen, and does not exclude the idea that the specimen contains small amounts of the cubic phase at room temperature.

Thermal analysis is generally effective to detect the phase transformation. However, we have failed to detect them [4-6] because the transformation enthalpy of barium titanate decreases catastrophically by lattice defects and/or strains [5, 6]. Furthermore, it is uncertain to identify this transformation by Raman, as discussed later.

4.2 Concerning the increase in FWHM of Fig. 2

We have to hesitate to say affirmatively that the broadening of FWHM of the diffraction in Fig. 2 relates to the physical change of the specimen at that temperature. The broadening of FWHM might be brought from the method of analysis as discussed next, although this can not be applied to explain the broadening of 222. That is, the observed data was analyzed by estimating two peaks of the tetragonal phase (Fig. 1); the co-existence of the tetragonal and the cubic phases was not estimated. It is reasonable to point out that the intensities ratio of 113 to 311 is 1 to 2 for the tetragonal phase, accordingly, very large intensity ratios in Fig. 1 at higher temperatures are unacceptable. We propose here to think in a different way about the transition state on the basis of results that all the fittings were made quite well by two peaks method (Fig. 1). Specifically, we think that the barium titanate is at an abnormal state on the phase transformation; accordingly, the intensity ratio of the normal state can not necessarily be applicable to the abnormal state — phase transformation.

This observation has problems as mentioned above, however, the broadening — decrease in crystallite size and/or increase in strain — remind us following phenomena relating to delicate state at the ferroelectric transformation. Wada et al. have observed the formation of many new domains at the transformation and discuss about origin of the strain [14]. Kwei et al. have analyzed three structures of barium titanate powder by means of neutron diffraction to find the decrease of extinction coefficients at the transformations, and have discussed on the decreases of the mosaic size at the transformations [15]. Further, Prof. T. Tsurumi has gave us a private communication that if the broadening is true it reminded him a possible existence of polar nano region in barium titanate, which is the key mechanism to understand relaxor dielectrics [16].

4.3 Suspicion against Raman to identify the phase

On the basis of this study we assert that Raman spectrum is not to be used to identify the phase, or at least to identify cubic barium titanate. There are many Raman spectroscopic studies on ferroelectric perovskite [10-14,

17-19]. Those studies contribute many, however, some of them make serious miss identification of cubic barium titanate, and/or make complicated estimations about spectra at 308 cm^{-1} and 720 cm^{-1} for the cubic phase. Hoshina et al. have revealed not the presence but the sharp increase in damping factor of Raman spectra are used to detect the phase transformation [3]. The results shown in Figs. 5 (a), (b), and (c) support their analyses, however, the spectra of the cubic phase are almost identical with that of the tetragonal in Fig. 5 (d).

If it is possible, let us supplement here that the bulk of Fig. 5 (a) was kept in water for 30 days to detect insignificant changes in Raman spectra. This study now in progress will be reported elsewhere.

It is confirmed that the phase concerns the static state, on the other hand Raman detects dynamic signals. Dynamic signals consist with static data as a general rule, however, this consistency is not supported by the theory.

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