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# FERROELECTRIC PHASE TRANSFORMATION AND DENSITY OF HEATED HYDROTHERMAL BARIUM TITANATE.

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Commercially available hydrothermal barium titanate (BT-01) was heated to investigate followings. Density of the powder heated at 500℃ for 2 h was 5.642 $10^3$kgm$^{-3}$. This value was significantly smaller than that of X-ray density, 6.015 $10^3$kgm$^{-3}$. It was evident from these densities that the heated barium titanate has considerable lattice defects. Density of the specimen was increased by heating at higher temperatures. This increase in density was attributed dominantly to the decrease in lattice defects, in place of inter-granular pore related model proposed. A CIPed disk was heated under various conditions to measure its capacitance as a function of temperature up to 220℃. The increase in capacitance which was attributable to the tetragonal-cubic transformation was recorded about a disk heated at 550℃ for 240 h, although it was very difficult via XRD to imagine the presence of the tetragonal phase in this disk.

## 1. INTRODUCTION

There is a steady increase of world market of multilayer ceramic capacitors (MLCC), and Japan shares dominant parts of MLCC [1,2]. State of arts and subjects of MLCC including processing of coming days of 1 μm in layer thickness have been overviewed recently [3]. Accordingly, preparations and properties of fine powder of $BaTiO_3$ are hot topics. Hydrothermal fine powder of $BaTiO_3$ [4] was heated in this study to follow our studies [5-8]. Main subjects of this study are densities of heated powders and the formation of the tetragonal phase at low temperatures.

## 2. EXPERIMENTAL

The raw powder of this study was commercial hydrothermal $BaTiO_3$ (BT-01) [4] of Sakai Chemical Industry Co. Ltd.. TG was performed using a TG-DTA (TAS-100, Rigaku) at a rate of 10 Kmin$^{-1}$; typical mass of its sample was 110 mg. The raw powder was pressed under 4 MPa using a die 16 mm in diameter followed by CIPing under 1 GPa. Those CIPed disks were heated. Density of the heated specimen was measured by a helium densitometer (AccuPyc 1330, Micromeritics).

$BaTiO_3$ specimens were characterized by XRD (Rigaku, RINT2500VHF). Lattice parameters were evaluated by means of a Si internal standard method. Diffractions 111 and 222 were measured by the fixed time mode of 1 s and typically 6 s, respectively, to evaluate crystallite size and lattice strain from an Wilson plot by using a Rigaku application software MJ13028A. The standard material was prepared by cracking a piece of as grow single crystal of $BaTiO_3$ [9].

Pt was spattered on two flat faces of a disk. The capacitance of this Pt-electroded disk was evaluated at room temperature by a meter (4194A, HP). Further, the disk was set in an oven to measure its capacitance from room temperature to 220℃ by a meter works at 1 kHz (2500A, Andeen-Hagerling).

## 3. RESULTS

The TG curve of the raw powder and XRD of 002/200 indices of heated at temperatures for 2 h were extremely identical respectively to those reported [5,6,8] to show here again. However, it is illustrated that the loss in mass of the raw powder from 100℃ to 600℃ is 1.29%.

The raw powder contains very small amount of $BaCO_3$ as an impurity which is marked in Fig. 1. This fact consistent with hydrothermal $BaTiO_3$ having an accurate atomic ratio of Ba/Ti = 1.00 [4,10]. XRD intensity of $BaCO_3$ is trace for the specimen heated at 700℃. Those were not observed for the heated at 800℃; moreover, no other impurities such as BaO or titanium-rich phases were detected via XRD despite of an intensive measurement. However, $BaCO_3$ was detected again after keeping in air even the powder heated at 1200℃ for 2 h. The reformation was accelerated by steam or water.

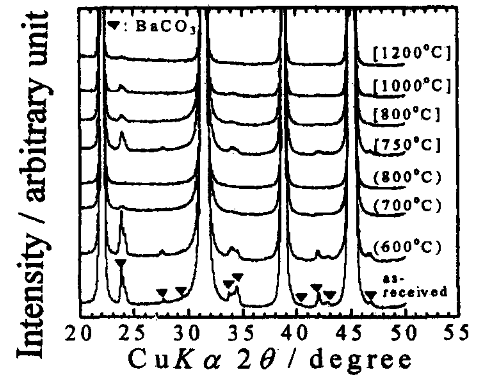

Fig. 1. XRD of $BaTiO_3$ raw powder heated at a given temperature for 2 h. Diffractions of $BaCO_3$ are marked on XRD of the raw powder. The fresh specimen after heating is marked its heating temperature by ( ); the specimen marked by [ ] is one hold-ed in air for about 4 months after heating.

A rough estimation of relative permittivity of a heated disk is shown in Fig. 2. The sharp increase of it at temperatures higher than 700℃ is consistent with the splitting of 002/200 diffractions (Fig. 6).

The lattice strain of the raw powder is as large as 0.203% (Fig. 3). Which reflects considerable inhomogeneity of this powder. The strain value decreased sharp by heating, namely by the dehydration. However, the strain becomes negligible at last by heating so high as at 1300℃. The crystallite size was increased with increasing temperatures. Two crystallite sizes heated at 470℃ and 510℃ for 1440 h are smaller than that heated at 800℃ for 2 h.

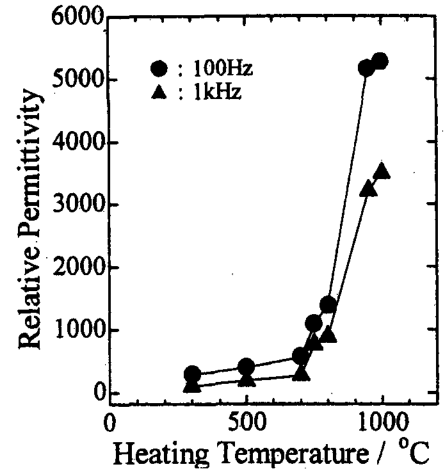

Fig. 2. A roughly estimated relative permittivity of heated a disk for 2 h.

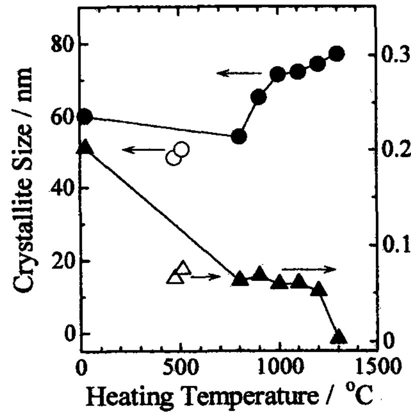

Fig. 3. Crystallite size and lattice strain of $BaTiO_3$ of a heated disk. Solid marks are data heated for 2 h, and open marks are those heated for 1440 h.

The density of the raw powder 5.647 $10^3 kgm^{-3}$ in Fig. 4 is compared very well with a reported 5.65 $10^3 kgm^{-3}$ [11]. Further, the value was 5.744 $10^3 kgm^{-3}$, if the raw powder was hold in a dry oven before measurement. The density increase sharp at a temperature higher than 500℃, and by heating at 1000℃ it almost reach to 6.012 $10^3 kgm^{-3}$ – X-ray density of tetragonal $BaTiO_3$ (JCPDS 5-0626). Figure 5 shows that the theoretical density was obtained by heating at 900℃ for duration longer than 240 h. However, by heating at 770℃ for 720 h, the density looks as if to have reached an equilibrium which is significantly smaller than 6.012 $10^3 kgm^{-3}$.

These splittings of 002/200 diffractions in Fig. 6 of

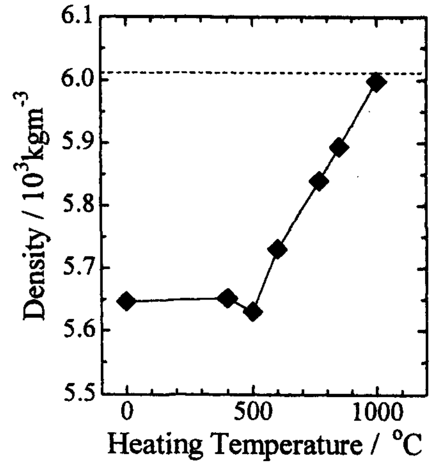

Fig. 4. Density of a heated disk for 2 h.

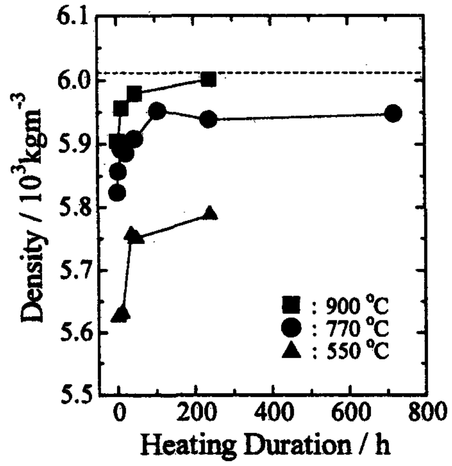

Fig. 5. Density of a heated disk.

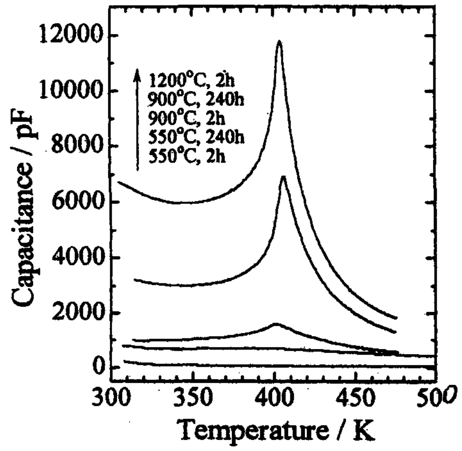

Fig. 6. Selected XRD of 002/200 diffractions to compare Fig.7.

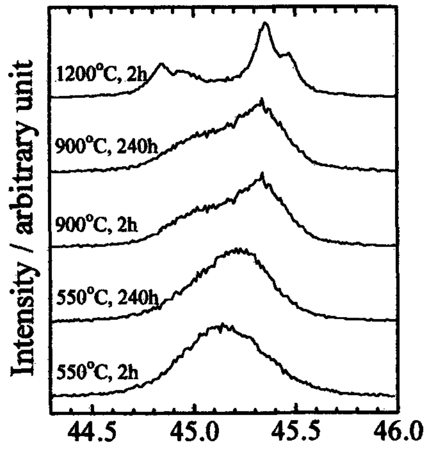

Fig. 7. The cooling trace of capacitance as a function of temperature of a heated disk at a respective condition.

heated disks at 900°C for 2 h and 240 h, and at 1200°C for 2 h are compared reasonably with respective tracings in Fig. 7. That is, the increase in capacitance, which is caused by the tetragonal-cubic transformation, is strong and sharp for the specimen showing clear splitting of 002/200 diffractions. Furthermore, following situations about two disks heated at 900°C are notable. There were certain differences in two XRDs heated for 2 h and 240 h. However, although dimensions of two electrodes and the distance between them were not normalized, this difference in the two tracings in Fig. 7 including capacitances at low temperatures, were furthermore than the differences in XRDs. The inter-granular connectivity may be the key to understand this situation as discussed below.

The diffraction of the disk heated at 550°C for 240 h looks as if there is no tetragonal $BaTiO_3$ in the specimen. However, it is evident from the relation of capacitance v.s. temperature that this specimen contains considerable amount of tetragonal $BaTiO_3$. We are sorry that this relation shown in Fig. 7 is too small to recognize easily the decrease of capacitance with temperature at higher temperatures after the phase transformation. Moreover, it is noted that the tetragonal grains formed by heating at 550°C for 240 h are connected certainly each other among them to connect spacings between the two electrodes so as to compensate polarizations of grains.

The peaks in capacitances which were attributable to the transformation were recorded for heated disks at 550°C-48 h, 510°C-480 h, 510°C-960 h, and 470°C-2160 h, and doubtful for 470°C-1800 h, and not for at 550°C-36 h. It was certain that tetragonal $BaTiO_3$ was formed from this hydrothermal $BaTiO_3$ and further those tetragonal grains have formed inter-granular connections to make compensations of polarization at these low temperatures.

The highest temperature of the peak of capacitance in Fig. 7 is 125℃, which compares well with 126℃, the highest temperature of these measurements. On the other hand, the lowest peak temperature of these measurements was 110℃, which was only 16 ℃ lower than the transformation temperature of normal $BaTiO_3$, 126℃ by this work.

## 4. DISCUSSION

The decomposition products of $BaCO_3$ were not detected by XRD, but it was reformed easily in a humid circumstance at room temperature to make an agglomeration which was detected via XRD. There may be no decomposition products but $BaTiO_3$; moreover, $BaTiO_3$ of this kind is easy to react in air to make $BaCO_3$. Authors wander in thinking the relation of agglomerated $BaCO_3$ and spread its decomposition products. This wandering reminds authors that they know no papers reporting the identification of $BaCO_3$ by TEM observations.

It is reasonable to attribute 1.29%, the loss in mass of the raw powder from 100 ℃ to 600℃, to the dehydration from OH-base. Further, the atomic ratio Ba/Ti = 1.00, accordingly the chemical form of the raw powder is written as $[Ba_{1-6/x}(VBa_{x/6})][Ti_{1-6/x}(VTi_{x/6})]O_{3-x}(OH)_x$, which is a simultaneous formation of barium and titanium vacancies model [11]. From this form and the value of dehydration, 1.29%, $x$ is calculated as 0.320. Then the form is given as $Ba_{0.947}Ti_{0.947}O_{2.68}(OH)_{0.320}$. The X-ray density of this raw powder is given as 5.771 $10^3 kgm^{-3}$ by referring its unit cell volume, 64.37(4) $10^6 pm^3$. The observed densities 5.647 $10^3 kgm^{-3}$ and 5.744 $10^3 kgm^{-3}$ were compared to support this model.

The observed density of the powder heated at 500℃ for 2 h is 5.642 $10^3 kgm^{-3}$. The X-ray density of this powder is given as 6.015 $10^3 kgm^{-3}$ by referring its unit cell volume, 64.35(4) $10^6 pm^3$. This difference in densities must be caused by lattice, which gave $x = 0.372$ according to the form above mentioned. This coincidence of the two independent values $x$, 0.372 and 0.320 was supported the chemical form proposed.

Hennings et al.[11] have made a similar discussion on hydrothermal $BaTiO_3$, and further they attribute the differences between observed and calculated densities to the intra-granular pores and their migrations. Authors were also observed those pores but only in limited numbers. Accordingly, a simple model is proposed here that the increase in density by a heating temperature (Fig. 4 and 5) is caused mainly by the disappearance of lattice defects. This model works well to explain the heat capacity of this powder heated at a temperature [6,7]. Namely, the reason why the cubic $BaTiO_3$ at room temperature is cubic even at 13 K [6,7] is that these lattice defects of the crystal prevent the transformation.

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