Materials Research Express

PAPER

Effects of annealing temperature on structural phase transition and microstructure evolution of hydrothermally synthesized barium titanate nanoparticles

Jongbeom Lee, Haguk Jeong and Seongun Ma

1 Industrial Materials Processing R&D Group, Korea Institute of Industrial Technology, Incheon City, 21999, Republic of Korea
2 EMC R&D part, AMOTECH Co., Ltd, Incheon City, 21629, Republic of Korea
* Author to whom any correspondence should be addressed.

E-mail: ljb01@kitech.re.kr

Keywords: barium titanate, hydrothermal synthesis, annealing process, XRD, DSC, TEM

Abstract

Commercial hydrothermally synthesized BaTiO3 powder with a cubic structure was annealed in a temperature range of 650 °C–900 °C, and the cubic–tetragonal structure transition and microstructure evolution of the powder were investigated in relation to the annealing process. The BaTiO3 powder used had a cubic structure below an annealing temperature of 800 °C and a tetragonal structure above 850 °C. Particle growth occurred under a low activation energy of ~33.2 kJ mol⁻¹ because of the nanocrystalline size effect, while the crystallite size slightly decreased in the powder with the cubic structure and sharply increased in that with the tetragonal structure. This was because the OH group in the powder with the cubic structure influenced the lattice extension on the particle surface. This stabilized the cubic structure and reduced the crystal ordering, which retarded the crystallite size. When the annealing temperature was increased, the crystallite growth reduced the intrinsic strain and enhanced the tetragonality in the powder with the tetragonal structure as a result of the removal of the OH group.

1. Introduction

Barium titanate (BaTiO3) powder has been of interest as a raw material for dielectric devices since the discovery that its tetragonal phase has ferroelectric properties in the 1940s [1, 2]. BaTiO3 powder is used as a basic ferroelectric material in electronic components such as multilayer ceramic capacitors (MLCCs), printed circuit boards (PCBs), dynamic random access memory (DRAM), and positive temperature coefficient of resistance (PTCRs) because of its unique perovskite structure (ABO3) and exceptionally high dielectric constant (2–5 × 10⁵) [3–6]. In recent years, for MLCCs, there has been increasing research to improve the purity and fabrication of BaTiO3 nanoparticles with a high dielectric property because of the growing demand for miniaturization and high-performance applications.

It is well known that the crystal structure and dielectric property of BaTiO3 particles depend on their impurities, defects, shape, size, stoichiometry, and homogeneity. BaTiO3 powders are fabricated using various synthesis methods: solid–solution [7], sol–gel [8, 9], microwave heating [10, 11], microemulsion [12], and hydrothermal [13–15]. Among these methods, hydrothermal synthesis is widely used to fabricate fine BaTiO3 particles because the process makes it possible to prepare highly phase-pure fine BaTiO3 particles with a small particle size from inexpensive and easily accessible precursors in a single step at moderate temperature and pressure by adjusting the synthesis parameters, including the reaction temperature, time, and pH value [16–18]. The structure and morphology of hematite nanoparticles with hierarchical hematite superstructures, nanoparticles, and core–shell nanoplates are reported based on the synthesis conditions [19–22]. In addition, it has the advantage of producing finer particles with a more uniform size because of the chemical reaction of...
Ba(OH)₂ and TiO₂ and avoiding the problems such as poor stoichiometry encountered with the high-temperature processes used in solid–solution reactions due to the easy volatilization of some components [23]. However, the use of aqueous-based chemistry for the synthesis of BaTiO₃ nanoparticles is often impeded by the limited availability due to the presence of OH groups in the surface and outer layer of the crystal [24], which yield pseudo-cubic nanocrystals rather than tetragonal ones [25]. Therefore, post-thermal treatment is required to recover the tetragonal structure and improve the tetragonality of the c/a ratio as a criterion of the dielectric constant. As a result of annealing, the size of BaTiO₃ particles can increase from a few tens of nanometers to a few hundred nanometers via agglomeration; meanwhile, the explosive growth can be suppressed by appropriate functional groups such as hydroxyl (–OH) and nanotubes [26, 27]. In a previous report, the OH group of BaTiO₃ powder was broadly regarded as playing a role in stabilizing the pseudo-cubic structure [28]. However, to date, the phase transition mechanism and microstructure evolution of hydrothermal BaTiO₃ nanoparticles have not been comprehensively studied as a function of the annealing process in relation to the quantity of the OH group. The detailed analysis of the phase transition and grain growth corresponding to the annealing process necessitates the presence of –OH groups in the nanocrystalline BaTiO₃, which may have a tremendous impact on the various potential applications mentioned above.

This study systematically investigated commercially available hydrothermal BaTiO₃ nanoparticles to determine the effects of the further fractional annealing temperature on the cubic–tetragonal structure transition and microstructure evolution for morphology, particle growth and structural transition. X-ray diffactometry (XRD) was used to confirm the change in the crystal structure and impurities, and scanning electron microscopy (SEM)/transmission electron microscopy (TEM) were used to investigate the morphology and lattice distortion. Differential scanning calorimetry (DSC) analysis was used to determine the enthalpy change, and TGA-DTA analysis was used to identify the presence of the OH group in the particles used.

### 2. Material and methods

This study investigated hydrothermally synthesized BaTiO₃ powder (Shandong Sinocera Functional Material Co., Ltd., China) before and after annealing at a temperature range of 650 °C–900 °C for 6 h. The annealing temperature ranges for removing the remnants of –OH groups after hydrothermal synthesis were determined based on the boiling point of barium hydroxide (780 °C). The powders annealed at various temperatures were characterized using x-ray diffractometry (XRD, Smartlab, Rigaku Co. Japan) to determine the lattice parameters and phase transformation (Cu Kᵣ, λ = 1.54059 Å, 25 mA × 40 kV power, in the range of 2θ = 20°–100°, and a step size of 0.02°) at room temperature. An SEM device (Sirion TM, FEI Co, USA) equipped with a field emission gun and TEM (Tecnai G2 F20, FEI Co, USA) at 200 keV were used to observe the morphologies and microstructures of the powders. The surfaces of the powders were coated with a platinum layer for the SEM investigation, and a drop of particles dispersed in ethanol was allowed to dry on a TEM carbon-coated copper grid. The calorimetric measurements were performed using DSC (Q100, TA instruments) in a range of 30 °C–200 °C at 10 °C min⁻¹. The thermal behaviours of the annealed powders were evaluated using a thermogravimetric analysis (SDT Q600, TA instruments) in the range of 50 °C–1200 °C at 10 °C min⁻¹.

The diffraction patterns obtained using the powerful Rietveld refinement method [29] were used to calculate the lattice parameter and lattice strain. Both the crystallite size and intrinsic strain were calculated using the size–strain plot (SSP) method, which considered the XRD peak profile to be a combination of the Lorentzian function and Gaussian function, where the size-broadened XRD profile was labelled as the Lorentz function and the strain-broadened profile was labelled as the Gaussian function [30]. We applied the SSP method to accurately calculate the crystallite size and intrinsic strain based on the study result [31] that the SSP method always provides a better result for isotropic broadening because it gives more importance to low angle reflections, where the accuracy and precision are greater than those at higher angles. Thus, the total broadening of the SSP can be expressed as follows:

$$\beta_{hkl} = \beta_L + \beta_G$$

where $\beta_L$ and $\beta_G$ are the peak broadening values due to the Lorentz and Gaussian functions, respectively. The SSP calculation is performed using the following equation [32]:

$$\left( d_{hkl} \cdot \beta_{hkl} \cdot \cos \theta \right)^2 = \frac{k \lambda}{D} \cdot \left( d_{hkl}^2 \cdot \beta_{hkl} \cdot \cos \theta \right) + \frac{\varepsilon^2}{4}$$

where $\lambda$ is the incident radiation, $D$ is the average crystallite size, and $d_{hkl}$ is the lattice distance between the $(hkl)$ planes for a cubic crystal.
A plot based on equation (2) could be drawn with the \((d_{hkl} \cdot \beta_{hkl} \cdot \cos \theta)\) term on the X axis and \((d_{hkl} \cdot \beta_{hkl} \cdot \cos \theta)^2\) on the Y axis corresponding to each diffraction peak. The slope of the straight line provides the average crystallite size, and the intercept gives the intrinsic strain.

3. Results

Figure 1 shows SEM micrographs of the as-received and annealed BaTiO₃ powders, along with annealing temperature. The particle size of each sample was measured using the software Image-Pro 10, and the particle size histograms determined from the results are presented in figures 2(a)–(e). The histograms were fitted using a log-normal distribution of particle diameters, from which the mean particle diameter \(\langle D \rangle\) and the distribution width \(\delta\) were determined, as shown in figures 2(a)–(e). We observed an increase in the particle diameter and distribution width with increasing annealing temperatures, which is in line with the previous study \([33, 34]\). The particle shape is also a critical factor for nanoparticles, which is why we considered circularity as a shape descriptor. Circularity measures the degree to which a shape differs from a perfect sphere \([19, 20]\). It is usually regarded as the ratio between the area and perimeter of a shape: \(C = 4 \pi \cdot A / P^2\), where \(A\) and \(P\) represent the area and perimeter of the shape, respectively. The mean particle size and the shape distribution of as-received and annealed BaTiO₃ nanoparticles were obtained, in figure 2(f). The mean particle size of the as-received BaTiO₃ powder was approximately 85 nm. It increased with the annealing process until 800 °C and then greatly increased at annealing temperatures greater than 800 °C, finally reaching a mean particle size of approximately 220 nm. The circularity slightly decreased with an increase in annealing temperature; however, the overall shape of the samples was almost circular because the value was greater than 0.95. To determine the crystal systems of the as-received and annealed BaTiO₃ powders, we conducted XRD measurements at room temperature.

As seen in figure 3(a), the XRD patterns of the as-received hydrothermally synthesized BaTiO₃ powder and after annealing between 650 °C and 900 °C showed the characteristic peaks of both the cubic and tetragonal crystal systems of BaTiO₃. The as-received BaTiO₃ powder and powder annealed below 800 °C had a cubic structure within 2θ values of 44°–46°, whereas the powders annealed at temperatures greater than 850 °C exhibited a tetragonal structure in the same range. A commonly applied industrial criterion for the quality assessment of BaTiO₃ powder is the crystallinity. The crystallinity of the powder is defined as \((x-y)/(v-w))\) in figure 3(b). The expression of the crystallinity involves the peak heights and splitting of the ideal cubic (200) XRD peaks.
reflection into two tetragonal (200) and (002) reflections. Thus, it could also be considered the diffuseness during the annealing process at temperatures greater than 850 °C in the present study [35]. The crystallinity values of the BaTiO₃ powders annealed at 850 °C and 900 °C were 5.6% and 23.5%, respectively. Thus, increasing the annealing temperature by 50 °C, from 850 °C to 900 °C, increased the crystallinity value of the hydrothermally synthesized BaTiO₃ powders by up to 4 times. Based on the XRD patterns obtained using the powerful Rietveld refinement method, we calculated the lattice parameters of the a and c axes, tetragonality, crystallite size, and microstrain, as shown in figure 3.

It is well known that the crystal structure of hydrothermally synthesized BaTiO₃ powder is predominantly cubic, which is generally attributed to the incorporation of hydroxyl ions in the particles. Based on the XRD pattern of figure 4(a), the d-spacing lengths of the a and c axes were the same and consistently decreased until an annealing temperature of 800 °C, indicating that the quantity of hydroxyl ions within the BaTiO₃ powder decreased during the annealing process. This result agreed well with a previous report [36]. Over an annealing temperature of 800 °C, the c-axis parameter suddenly increased, and the tetragonality reached approximately 1.01. The trend of a phase transition from a cubic to tetragonal structure was reported in previous studies [36, 37] on BaTiO₃ powders prepared by hydrothermally synthesis under various experimental conditions, including various OH group contents, Ba/Ti ratios, and synthesis temperatures. Figure 4(c) shows the changes in the crystallite size and intrinsic strain with the annealing temperature of the BaTiO₃ powders obtained from...
the SSP calculations. The crystallite size of the BaTiO$_3$ powder decreased until an annealing temperature of 800 °C and then suddenly increased over this temperature. Meanwhile, the microstrain of the powder showed slight decreases until 750 °C and then significantly decreased when the annealing temperature was greater than 800 °C. It could be inferred that these phenomena were related to the reduction of the OH group contents during the annealing process, which could have been responsible for the changes in the tetragonality, crystallite size, and intrinsic strain. In order to investigate the chemical reaction in the powder as a function of the annealing temperature, we conducted the DSC and TGA-DTA measurements, as shown in figures 5(a) and (b), respectively.

Based on the fact that the crystallinities of the powders prepared at annealing temperatures of 850 °C and 900 °C have different values in figure 3(b), it could be confirmed that the exothermic reaction occurred as a result of crystallization or a phase transition in the BaTiO$_3$ powder with an increase in temperature. As shown in figure 5(a), protruding points for the specific heat capacity ($C_p$) lines of both samples were observed in a range of 120 °C–130 °C. The reaction enthalpy could be obtained from the DSC measurement by integrating the area of the reaction peak and the interpolated baseline between the beginning and end of the reaction. The inset graph of figure 5(a) shows enthalpy values of 0.12 J g$^{-1}$ and 0.55 J g$^{-1}$ for the powders annealed at 850 °C and 900 °C, respectively. Figure 5(b) shows the variation of the weight loss percentage in the BaTiO$_3$ powders before and after being annealed at 700 °C and 900 °C. Between room temperature and 600 °C, the volatilization of the absorbed waste and decomposition of thermally unstable organic compounds in the thermally synthesized BaTiO$_3$ powder were observed. These phenomena disappeared in the annealed BaTiO$_3$ powder in figure 5(b). The increase in weight loss in the temperature range of 700 °C–800 °C occurred as a result of the decomposition
of the OH group contents of the as-received powder and that annealed at 700 °C, but this value decreased with a further increase in the annealing temperature. In the BaTiO3 powder annealed at 900 °C, the weight loss of the OH group contents was not virtually observed within the temperature range. No additional weight loss appeared above 800 °C because of the absence of secondary phases in the XRD patterns of figure 2 in the present study.

To investigate the microstructure evolution of the BaTiO3 powders fabricated by hydrothermal synthesis as a function of the annealing temperature, the TEM technique was utilized, and the results are shown in figure 6. Figures 6(a)–(c) show TEM images of the as-received powder and after annealing at 700 and 900 °C, respectively. Here, these images were obtained by high-resolution TEM for the direct imaging of the atomic structure of the powders, and the white arrows indicate the dark areas induced by the strains from the lattice displacement in the powder particles. The dark areas indicated by the white arrows are observed in figures 6(a) and (b). However, there were no strains in the powder annealed at 900 °C, as shown in figure 6(c). The inset photos show high angle annular dark field–scanning transmission microscopy (HAADF-STEM) images. Using HAADF-STEM made it possible to obtain atomic resolution images, where the contrast of an atomic column was directly related to the atomic number in the sample. In these pictures, no further dark area could be observed in figure 6(c) for the powder annealed at 900 °C, compared to the as-received powder and powder annealed at 700 °C. The HAADF-STEM image of figure 6(c) reveals that there were fewer defects, including the OH group contents, in the powder annealed at 900 °C compared to the powders before and after being annealed at lower temperatures because the atomic number of the powder when incorporating the OH group content was lower than the powder without it. Figure 5 shows a clear trend of decreases in the strain and OH group contents of the BaTiO3 powders prepared by hydrothermal synthesis as a function of the annealing temperature based on observations of the HR-TEM and HAADF-STEM images.

4. Discussion

The present study was designed to determine the effects of the annealing temperature on the phase transition and microstructure evolution of commercial BaTiO3 powder fabricated by hydrothermal synthesis in terms of the particle morphology, crystallite size, intrinsic strain, and enthalpy change. Based on the XRD pattern (figure 3), the BaTiO3 powder exhibited a cubic crystal structure without impurities and defects like secondary phases at room temperature. After annealing at a temperature above 850 °C for 6 h, it showed a sharpening of the BaTiO3 peak at a 2θ value of approximately 45°, which may have corresponded to a transformation from the cubic to the tetragonal phase. In accordance with the present results, previous study [18] has demonstrated that hydrothermally synthesized BaTiO3 powders subjected to post thermal treatments above 1200 °C were transformed from a cubic to a tetragonal structure. Comparing the temperature of this phase transition to those in previous studies, the temperature (850 °C) in the current study was much lower because of differences in the annealing period (6 h versus 1–2 h) and particle size (nanoparticles versus micro/submicroparticles).

The particle size of the BaTiO3 powder with the cubic structure gradually increased as a function of the annealing temperature, with a sharp increase above the phase transition temperature. These results were in line with those of previous studies [37, 38]. The nanoparticle growth process in a free-standing nanocrystalline powder is explained by the concept of hard aggregates [39]. During the annealing process for such a free standing powder, the increase in the particle size is mainly attributed to the elimination of the boundaries between the nanocrystallites within the hard aggregates. Consequently, the mean nanoparticle size is likely to approach the mean size of the hard aggregates. According to this study, agglomeration likely occurs because of the removal of
the –OH group (figure 3) of the BaTiO$_3$ matrix that separates nanoparticles in close proximity during annealing over 800 °C, enabling direct contact between nanoparticles. Evidence of agglomeration growth due to the removal of thin parts of the silica matrix using nanoparticles can be found in the literature [33, 34]. To calculate the activation energy ($Q$, kJ mol$^{-1}$) for the nanoparticle growth in the BaTiO$_3$ powders annealed at various temperature, it was assumed that the nanoparticle growth in these powders, as a thermally activated process, was dependent on the annealing temperature, as follows [40]:

$$\ln D_f = \ln D_0 - \frac{Q}{RT}$$

where $D_0$ and $D_f$ are the initial and final nanoparticle sizes, respectively; $R$ is the gas constant (kJ K$^{-1}$ mol$^{-1}$); and $T$ is the annealing temperature (K). When the initial nanoparticle size, $D_0$, is significantly smaller than the mean nanoparticle size, at some later time, then $D_0$ can be neglected, and the nanoparticle growth equation can be written in the following form:

$$\ln D_f = \frac{Q}{R} \left( \frac{1}{T} \right)$$

The activation energy of the nanoparticle growth for annealing at 700–900 °C can be obtained from the mean slope of the graphs in figure 7, and is calculated to be 33.2 ± 7.9 kJ mol$^{-1}$. For the growth of submicro/micro-crystalline BaTiO$_3$, it has been reported to be 470–800 kJ mol$^{-1}$ [41–43], which is much larger than that found in this study. These results agree with the findings of other studies, in which a very low activation energy of $\sim$13 kJ mol$^{-1}$ has been observed for the grain growth in nanocrystalline 3 yttria-stabilized zirconia (3YSZ) powder relative to that ($\sim$580 kJ mol$^{-1}$) exhibited by submicro/micrometer-sized 3YSZ [40, 44]. The author [40] concluded that it could be attributed to the possible presence of a large oxygen-ion vacancy concentration, leading to a much lower activation energy in nanocrystallite powders. In this study, it should also be noted that the reduction of the OH group with an increase in the annealing temperature seen in the TGA results could be associated with an increase in the vacancy concentration, which would cause the BaTiO$_3$ powder to exhibit a much lower activation energy.

The activation energy of the nanoparticle growth for annealing at 700–900 °C can be obtained from the mean slope of the graphs in figure 7, and is calculated to be 33.2 ± 7.9 kJ mol$^{-1}$. For the growth of submicro/micro-crystalline BaTiO$_3$, it has been reported to be 470–800 kJ mol$^{-1}$ [41–43], which is much larger than that found in this study. These results agree with the findings of other studies, in which a very low activation energy of $\sim$13 kJ mol$^{-1}$ has been observed for the grain growth in nanocrystalline 3 yttria-stabilized zirconia (3YSZ) powder relative to that ($\sim$580 kJ mol$^{-1}$) exhibited by submicro/micrometer-sized 3YSZ [40, 44]. The author [40] concluded that it could be attributed to the possible presence of a large oxygen-ion vacancy concentration, leading to a much lower activation energy in nanocrystallite powders. In this study, it should also be noted that the reduction of the OH group with an increase in the annealing temperature seen in the TGA results could be associated with an increase in the vacancy concentration, which would cause the BaTiO$_3$ powder to exhibit a much lower activation energy.

The quantity of the OH group in the hydrothermally synthesized nanoparticle BaTiO$_3$ powders gradually decreased during the annealing process, until it was roughly zero at an annealing temperature of 900 °C. Therefore, based on the experimental results, it is probable that the OH group in the cubic structure was more stable than that in the tetragonal structure of the BaTiO$_3$ nanoparticle powders. This confirmed previous findings in the literature [38] that the impurity of BaTiO$_3$ powder could stabilize the metastable cubic form. It is also extended based on a composite structure model of BaTiO$_3$ nanoparticles consisting of (i) an inner tetragonal core, (ii) a gradient lattice strain layer (GLSL), and (iii) a surface cubic layer [36]. This model was designed to incorporate the lattice relaxation [45, 46] between the inner tetragonal core and the surface cubic layer, and the lattice parameters and atomic positions were changed continuously in the GLSL. Using this model, the values calculated by summing up the crystal structure factors of the unit cells over an entire particle could be fitted with the XRD profiles around the (002) and (200) diffraction intensities. The results using the model suggested that a
lattice expansion occurred on the surfaces of the BaTiO$_3$ nanoparticles because the particle size dependence of the $c/a$ ratio should be interpreted as a change in the volume fraction of the surface cubic layer. In the present study, the OH group on the surface of a BaTiO$_3$ powder particle was attributed to the lattice expansion of the a axis because the d-spacing length of the a axis in the powder with a tetragonal structure was lower than that in the powder with a cubic structure as a result of the absence of the OH group. Based on the model, we can infer that the volume fraction of the surface cubic layer decreased with an increase in the annealing temperature by suppressing lattice expansion for the a axis with a decrease in the OH group and steep increase in the tetragonality.

The crystallite size decreased in the BaTiO$_3$ powder with a cubic structure and increased in that with a tetragonal structure (figure 4). In addition, the intrinsic strain in the powder with a cubic structure was higher than that with a tetragonal structure as a function of the annealing temperature. This trend during the annealing process could be attributed to the change in the quantity of the OH group in the BaTiO$_3$ powder. The TGA-DTA results and microstructure evolution (figure 5) provide further evidence for this interpretation of the variation in the intrinsic strain of the powders. As is well known, a powder or particle is composed of individual crystallites, and the crystallite size is related to the crystal ordering inside the powder. Based on the results of the present study, the reduction and movement of the OH group with the annealing temperature could have induced a decrease in the crystallite size, with high distortion inducing low crystal ordering in the nanoparticle powders. However, the removal of the OH group occurred with a marked increase in the crystallite size and lower distortion in the BaTiO$_3$ nanoparticle powder. The evidence from this study implied that it was difficult for crystallite growth to occur in the hydrothermally synthesized BaTiO$_3$ powder during the annealing process because of the change in the OH group until the crystalline powder was transformed from a cubic structure to a tetragonal structure.

One interesting finding is that the tetragonality of the $c/a$ ratio was correlated with the enthalpy of the phase transition if the powder had a tetragonal structure. Tetragonality is usually used as an index to filter high-grade BaTiO$_3$ particles in the MLCC industry [47]. It is also known that the enthalpy of transition ($\Delta H$) is proportional to the polarization ($P$) [38]:

$$\Delta H = 2\pi P^2 T_c / C$$

where $T_c$ is the transition temperature, and $C$ the Curie-Weiss constant. It can be seen that an increase in $\Delta H$ will lead to an increase in $P$. The increase in $\Delta H$ with a higher annealing temperature could be explained by the decrease in the intrinsic strain of the BaTiO$_3$ powder because lattice defects and intrinsic strains could force the structure to become cubic and extend the surface layer [48, 49].

5. Conclusion

BaTiO$_3$ nanoparticle powder fabricated by hydrothermal synthesis was subjected to an annealing process in the temperature range of 650 °C–900 °C for 6 h, and the effects of the annealing temperature on the phase transformation and microstructure evolution were investigated using XRD analysis, SEM/TEM observations, and DSC-TGA measurements. The BaTiO$_3$ powder used exhibited a phase transition from a cubic to a tetragonal structure at an annealing temperature of 850 °C, and the particle size increased with the annealing temperature regardless of the phase transition. The activation energy for particle growth in the powder used was $\sim$33.2 kJ mol$^{-1}$, which was relatively much lower than that of previous reports because of the nanoparticle size effect. The quantity of the OH group in the powder sharply decreased at the cubic–tetragonal structure transition, and its presence could induce a lattice extension on the surface of the powder as a result of a high intrinsic strain, which contributed to the stabilization of the cubic structure. In addition, the change in the quantity of the OH group suppressed the crystallite growth by reducing the crystal ordering in the microstructure of the powder. However, in the powder with a tetragonal structure, the crystallite size rapidly increased because the removal of the OH group influenced the lattice distortion and strain. With a further increase in the annealing temperature, the tetragonality of the $c/a$ ratio and enthalpy of the phase transition were enhanced for the BaTiO$_3$ nanoparticle powder with the tetragonal structure as a result of steep decreases in the intrinsic strain and volume fraction of the OH group on the surface layer of the powder.

Acknowledgments

The authors thank Mr U.Y. Lee (AMOTECH Co., Ltd.) for specimen preparation. This work was supported by materials & components technology development program funded by the Ministry of Trade, Industry & Energy (MOTIE) (No. 20016519, Development of Ultra Wide Band communication MLCC for UWB and 5G).
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Jongbeom Lee  © https://orcid.org/0000-0003-0995-6511

References

[1] Wal B 1945 Nature 156 480
[2] von Hippel A 1950 Rev. Mod. Phys. 22 221
[3] Zhu W, Akbar S A, Asieh R and Dutta P K 1997 Jpn. J. Appl. Phys. 36 214
[4] Kiss K, Magder J, Vokosovitch M S and Lockhart R J 1966 J. Am. Ceram. Soc. 49 291
[5] Bruno S A, Swanson D K and Burn I 1996 J. Am. Ceram. Soc. 79 1233
[6] Burn I and Maher G H 1975 J. Mater. Sci. 10 633
[7] Yu F, Wang X and Cui B 2007 Scr. Mater. 57 623
[8] Hwang U Y, Park H S and Koo K K 2004 J. Am. Ceram. Soc. 87 2168
[9] Demydov D and Klabunde K J 2004 J. Non-Cryst. Solids 350 165
[10] Malighe Y S, Gurjar A V and Dharwadkar S R 2004 Bull. Mater. Sci. 27 217
[11] Newalkar B L, Komarneni S and Katsuki H 2001 Mater. Res. Bull. 36 2347
[12] Herrig H and Hempelmann R 1997 Nanostruct. Mater. 9 241
[13] Moon J, Suvaci E, Morrone A, Costantino S and Adair J H 2003 J. Eur. Ceram. Soc. 23 2153
[14] Nakano H, Urabe K, Oikawa T and Ikawa H 2004 J. Am. Ceram. Soc. 87 1594
[15] Gersten B L, Lencka M M and Riman R E 2004 J. Am. Ceram. Soc. 87 2025
[16] Pinceloup P, Courtois C, Leriche A and Thierry B 1999 J. Am. Ceram. Soc. 82 3049
[17] Inada M, Enomoto N, Hayashi K, Hojo K and Komarneni S 2015 Ceram. Int. 41 5581
[18] Shi E W, Xia C Y, Zhong W Z, Wang B G and Feng C D 1997 J. Am. Ceram. Soc. 80 1567
[19] Tadic M, Trpkov D, Kopanja L, Vojnovic S and Panjan M 2019 J. Alloys Compd. 792 599
[20] Tadic M, Kopanja L, Panjan M, Lazovic J, Tadic B V, Stanojevic B and Motte L 2021 Mater. Res. Bull. 133 111055
[21] Trpkov D, Panjan M, Kopanja L and Tadic M 2018 Appl. Surf. Sci. 457 427
[22] Tadic M, Kopanja L, Panjan M, Kralj S, Nikodinovic-Runic J and Stojanovic Z 2017 Appl. Surf. Sci. 403 628
[23] Gao J, Shi H, Dong H, Zhang R and Chen D 2015 J. Nanopart. Res. 174 286
[24] Petkov V, Gateshki M, Niederberger M and Ren Y 2006 Chem. Mater. 18 814
[25] Yan T, Shen Z G, Zhang W W and Chen F 2006 Mater. Chem. Phys. 98 450
[26] Ashourifar H, Sebt S A, Mojtahedzadeh Larijani M and Arabi H 2014 Superlattices Microstruct. 72 296
[27] Ashourifar H, Mikali Agah K, Behzadi Pour G, Akbari A and Sebt S A 2019 Journal of Superconductivity and Novel Magnetism 32 3339
[28] Hoshina T, Wada S, Kuroiwa Y and Tsurumi T 2008 Appl. Phys. Lett. 93 192914
[29] Evans I S O and Evans I R 2021 J. Chem. Educ. 98 495
[30] Baltzar D and Ledbetter H 1993 Journal of Applied Crystallography 26 97
[31] Nata D, Singh F and Das R 2020 Mater. Chem. Phys. 239 122021
[32] Mote V D, Purushotham Y and Dole B N 2012 Journal of Theoretical and Applied Physics 6 6
[33] Nikolic D, Panjan M, Blake G R and Tadic M 2015 J. Eur. Ceram. Soc. 35 3643
[34] Tadic M, Milosevic I, Kralj S, Hanzel D, Barудzija T, Motte L and Makove D 2020 Acta Mater. 188 16
[35] Su C Y, Otsuka Y, Huang C Y, Hennings D F, Pithan C, Shiao F T and Vasera R 2013 Ceram. Int. 39 6673
[36] Hongo K, Kurata S, Jomphoak A, Inada M, Hayashi K and Maezono R 2018 Inorg. Chem. 57 5413
[37] Sasirekha N, Rajesh B and Chen Y W 2008 Ind. Eng. Chem. Res. 47 1868
[38] Asieh R, Zhu W, Akbar S A and Dutta P K 1996 Chem. Mater. 8 226
[39] Mayo M J 1996 Int. Mater. Rev. 41 85
[40] Shukla S, Seal S, Vij R and Bandyopadhyay S 2003 Nano Lett. 3 397
[41] Beauchesne S and Poirier J P 1989 Phys. Earth Planet. Inter. 55 187
[42] Carry C and Mucelin A 1986 J. Am. Ceram. Soc. 69 c–213
[43] Park E T 1999 J. Mater. Sci. Lett. 18 163
[44] Nieh T and Wadsworth J J 1990 Acta Metall. Mater. 38 1121
[45] Ishikawa K and Uemori T 1999 Physical Review B 60 11841
[46] Jiang B and Bursill L A 1999 Physical Review B 60 9978
[47] Tsurumi T, Sekine T, Kakenoto H, Hoshina T, Narn S M, Yasuno H and Wada S 2006 J. Am. Ceram. Soc. 89 1337
[48] Nishizawa H, Yamazaki N, Matsuoka K and Mitsuhashi H 1982 J. Am. Ceram. Soc. 65 343
[49] Uchino K, Sadanaga E and Hirose T 1989 J. Am. Ceram. Soc. 72 1555