Preparation and investigation of hexagonal-tetragonal BaTiO₃ powders

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Hexagonal-tetragonal co-existing barium titanate powders were prepared by reducing commercial barium titanate powders with their particle size of about 100 nm in a hydrogen atmosphere for 1 h at several temperatures, and the microstructures were observed. It was found that the hexagonal-tetragonal barium titanate powder had a co-existing hexagonal and tetragonal phase in a particle rather than a mixture of two phases in the powder. The hexagonal contents of about 0, 25, 50, 70, 85, and 100 wt % were obtained at temperatures of 1310, 1315, 1320, 1324, 1330, and 1333 °C, respectively. The hexagonal phase was returned to the tetragonal phase by annealing at 1200 °C in air. A model for the mechanism of a complete transformation of barium titanate polymorph from tetragonal/cubic to hexagonal phases is proposed.

Key-words : Barium titanate powder, Co-existing, Hexagonal-tetragonal, Hydrogen atmosphere, HM-EPD

1. Introduction

Barium titanate (BaTiO₃, BT) is a very first manmade piezoelectric material with a perovskite structure. Recently, its friendly nature with the environment has attracted researchers’ interest in the further enhancement of its piezoelectric properties.¹ For randomly oriented BT ceramics with a large grain size of about 20 µm, a piezoelectric constant (d₃₃) of 191 pC/N has been reported.² Many researchers have shown that its piezoelectric response increases with decreasing the grain size and it gets maximized at around 1 µm,³–⁵ which is attributed to an increased 90° domain wall density.⁶ In addition, for BT ceramics with large grains, Wada et al. enhanced its piezoelectric coefficient value up to 788 pC/N using its engineered domain configuration with grain orientation along the (110)-direction.⁷ This result suggests that the piezoelectric properties can be strongly increased by texturing in off-spontaneous polarization directions and it has opened the door for the possibility of enhancement in fine-grained BT ceramics with suitable engineered domain configurations.⁸ Regarding the enhancement of piezoelectric coefficient of the BT ceramics, Kobayashi et al. took (111)-direction of its engineered domain configurations with the hope that one extra equivalent domain along this direction will help for additional enhancement in the piezoelectric coefficient.⁹ For this, they adopted a high-magnetic-field electrophoretic deposition (HM-EPD) method with a hexagonal BT powder which has a larger lattice constant c/a ratio than a tetragonal BT powder to facilitate the magnetic alignment of the particle. Although (111)-oriented BT ceramics were prepared, their piezoelectric properties were not enhanced. They attributed this to (111) twins formed in the BT ceramics at the transformation from the hexagonal phase to the tetragonal phase. In our previous work,¹⁰ we took a BT powder with hexagonal and tetragonal phases instead of a pure hexagonal BT powder for the preparation of (111)-oriented BT ceramics using the HM-EPD technique. The BT powder with the hexagonal and tetragonal phases was prepared by reducing pseudo-cubic BT powders in H₂ atmosphere at different annealing temperatures, and we found that the BT powders with about 70–90 wt% hexagonal content were better for increasing the piezoelectric properties.

Regarding BT powders, Glaister and Kay¹¹ claimed that each BT particle of their BT powder fired at 1330 °C in H₂ was a BT particle containing both hexagonal and tetragonal phases (co-existing). On the other hand, Kirby and Wechsler¹² reported that their BT powder consisted of about equal volume mixture of single-phase hexagonal and tetragonal BT particles after heating at 1445 °C in the air due to a sluggish phase transition from the cubic to hexagonal phases. Such a sluggish phase transition was also reported for BT powders with different particle sizes; that is, single-phase tetragonal BT particles were observed
for BT powders with a diameter of 140 nm and 430 nm, while coexisting tetragonal and hexagonal BT particles were observed for BT powders with a small diameter of 40 nm. They explained that this was due to an increased particle surface area. The unit cell expands around the particle surface and the hexagonal phase with a larger unit cell size is stabilized. In this study, we investigated the microstructures of reduced BT powders to clarify whether the reduced powders were merely a simple mixture of two phases or a co-existing phase in a particle. In addition, we proposed a model for the transformation of BT polymorphs from the tetragonal/cubic to hexagonal phases.

2. Experimental procedure

BT powder (BT01, particle size ~100 nm, Sakai Chemical Industry Co., Ltd.) was reduced under the hydrogen atmosphere for 1 h at temperatures between 1310 and 1370 °C with a constant flow rate of hydrogen gas at 60 ml/min and the rising and falling temperature rates of 5 °C/min. The hydrogen gas was supplied along with the rising temperature and the supply was stopped when the temperature was lower than 600 °C on the cooling. Then, nitrogen gas was purged into the furnace until the furnace temperature reached 100 °C and the powder was taken out from the furnace at room temperature. For each batch, 43 g of BT powder was taken for reduction. The color of the reduced powders was slightly gray or bluish which was quite achievable. The annealing temperature of the unreduced BT particle (before reduction) was measured by XRD (Ultima IV, Rigaku) with Cu-Kα radiation. The microstructures of the powders were observed by transmission electron microscope (TEM; JEM-2100F).

3. Results and discussion

The XRD patterns of the BT powders reduced in the hydrogen atmosphere for 1 h at different temperatures are shown in Fig. 1. The crystal structures were either a tetragonal phase, a mixture of tetragonal and hexagonal phases, or a hexagonal phase depending on the annealing temperatures. The hexagonal contents of about 0, 25, 50, 70, 85, and 100 wt% were obtained at the annealing temperatures of 1310, 1315, 1320, 1324, 1330, and 1333 °C, respectively. Figures 1(b) and 1(c) are magnified versions of hexagonal (103) peaks and tetragonal (202) peaks, respectively. It was observed that at 1310 °C there was no hexagonal phase i.e. the BT powder contained a 100% tetragonal phase. With increasing the annealing temperature, the content of the hexagonal phase was continuously increased and achieved a 100% hexagonal phase at 1333 °C. The complete transformation to the hexagonal phase has been reported at 1460 °C in air and 1330 °C in H2, as reported by Kirby and Wechsler and Glaister and Kay, respectively. The annealing temperature of the 100% hexagonal sample was very close to the latter reported value. We also reduced the powder at different temperatures above 1333 °C up to 1370 °C and found the 100% hexagonal phase. Here, the hexagonal content was determined from the calibration curve which is shown in Fig. 2(a) and also the variation of hexagonal contents with the annealing temperature is plotted in Fig. 2(b). Controlling the hexagonal-tetragonal ratio near the transition temperature (1333 °C) was difficult. However, below this transition temperature the ratio with the uncertainty of ±5% was quite achievable.

The microstructures and crystal structures of the BT powders were investigated. Figure 3 show the TEM image and corresponding selected area diffraction patterns of an unreduced BT particle (before reduction) as a reference and the BT particle reduced at 1370 °C. Note that the reduced particle (powder) was annealed at 1000 °C for 1 h in the air for the oxidation and the particle size of the unreduced BT powders was 100 ± 40 nm and that of the reduced powder at 1370 °C was 3 ± 2 μm. The selected area diffraction patterns of the unreduced and reduced BT particles confirmed pseudo-cubic and hexagonal phases, respectively. The tightly placed diffraction spots along the [001] direction for the reduced, hexagonal BT powder.
were attributed to the longer hexagonal lattice constant \( c_h \) than the hexagonal lattice constant \( a_h \).

Figure 4(a) shows the TEM image of the BT particle reduced at 1320 °C. A boundary was observed in the particle. Magnified TEM images around the boundary are shown in Figs. 4(b) and 4(c), and the selected area diffraction patterns of the left-hand side and right-hand side areas of Fig. 4(b) are shown in Figs. 4(d) and 4(e), respectively. It was confirmed that the hexagonal and tetragonal phases were co-existed in the particle, rather than a mixture of tetragonal and hexagonal phases. A selected area diffraction pattern around the boundary is shown in Fig. 4(f). It can be seen that the two phases were attached with the epitaxial relation that the hexagonal \([001]_h\) direction and the tetragonal \([111]_t\) direction were parallel. This suggests that the hexagonal phase was grown from the tetragonal phase with the epitaxial relation by annealing in the reducing atmosphere. This was consistent with the fact that \([001]_h\)-oriented BT green compacts were changed to \([111]_t\)-oriented BT ceramics by sintering in the air.\(^{14}\) Figures 4(g)–4(l) are the TEM images and selected area diffraction patterns of the BT particle reduced at 1324 °C. Almost the same results were observed, except that the tetragonal area became smaller. Thus, the calculated hexagonal-tetragonal ratios were the average value of the hexagonal-tetragonal portion of the co-existing particles. Although Glaister and Kay\(^{11}\) reported that only the tetragonal phase exists after heating below 1330 °C in the hydrogen atmosphere, we found co-existing hexagonal-tetragonal phases for the powder annealed below this

Fig. 2. (a) Calibration curve for the determination of hexagonal and tetragonal ratio of the hexagonal-tetragonal BaTiO\(_3\) powders. (b) Variation of hexagonal contents of the reduced BaTiO\(_3\) powders with the annealing temperatures.

Fig. 3. TEM images of BaTiO\(_3\) particles (a) 100% pseudo cubic (unreduced), (b) selected area diffraction pattern of (a), (c) 100% hexagonal, and (d) selected area diffraction pattern of (c).
temperature in the hydrogen atmosphere, and it was not an abrupt change in the phases. Kirby and Wechsler’s\(^{12}\) reported that this transition as sluggish transformation, with a mixture of the cubic (at that firing temperature) and hexagonal phases. However, we thought that the transformation is sluggish but with the co-existing hexagonal-tetragonal phase.

To check the reconversion of the tetragonal phase from the hexagonal phase, we annealed these reduced powders at 1200 °C for 5 h in air with a heating rate of 1 °C/min. The XRD patterns of BT powders with about 50, 75, and 100 % hexagonal content after subjecting to the annealing at 1200 °C in air are shown in Fig. 5 as a representative graph. All peaks were assigned to the tetragonal phase.
phase which confirmed the complete transformation of the hexagonal to tetragonal phases at 1200 °C. These patterns confirmed that this annealing temperature was sufficient for the complete transformation of the hexagonal-tetragonal powder to the tetragonal phase.

Based on above results, we propose a mechanism for the complete transformation of the BT polymorph from the tetragonal/cubic to hexagonal phases. Above 1310 °C, all BT particles start growing as co-existing hexagonal-tetragonal particles and the hexagonal portion in the particle increases as the temperature increases. All particles become hexagonal above the transition temperature of 1333 °C, which is depicted in Fig. 6. Watanabe et al. explained this transformation due to the twinning of the cubic crystal at the (111) plane. On the basis of that, here, cubic BT (below 1310 °C) has a stacking sequence of -ABCABC- along \( \{111\} \) as 3C-type BT. Further, as temperature increases, the crystal growth starts slowly and, in some part of it, the stacking sequence also starts to change to -ABCABC- as 6H-type BT along \( \{001\} \) due to cubic crystal accepting twin accompanied by \( \{111\} \) mirror planes. Finally, as the temperature reaches about 1333 °C, all part of the crystal becomes 6H-type BT and this hexagonal phase is attributed to the metastable state of BT polymorph. Thus, the reduced powder is either a mixture of co-existing hexagonal-cubic particles (or hexagonal-tetragonal particles at room temperature) and hexagonal particles or completely hexagonal particles. Furthermore, this hexagonal stacking sequence of -ABCABC- changes completely to cubic/tetragonal stacking sequence of -ABCABC- by reciprocal gliding of the B and C layers at an annealing temperature of about 1200 °C in air. These structural transformations and the retention of the hexagonal phase of BT at room temperature can be found elsewhere for more details. The starting BT powders with co-existing hexagonal and tetragonal phases that we have described in this study shows a high possibility of being used in HM-EPD method to prepare \( \{111\} \) textured BT ceramics with enhanced piezoelectric performance. From this study, one can notice that the large portion of tetragonal phase in the particle will limit the orientation during the HM-EPD process. In our previous work, we noticed that the use of starting BT powders with hexagonal content of above 80% showed a sharp decreasing trend of the piezoelectric coefficient, which was attributed to the possible higher twin density in the BT ceramics. Thus, one can use this co-existing hexagonal-tetragonal BT powders with smaller portion of tetragonal phase in the particles to limit the twin effect and large orientation in \( \{111\} \)-oriented BT ceramics to enhance its piezoelectric properties.

### 4. Conclusions

We successfully controlled the formation of co-existing hexagonal-tetragonal phases in BT particles by reducing it in the hydrogen environment at different temperatures. We prepared different ratios of the co-existing phases and estimated that within ± 5% of uncertainty, which one can...
easily reproduce the ratio at the particular temperature. Further, it was also checked the reconversion temperature of the tetragonal phase from the hexagonal phase. It is also concluded from the different TEM images and proposed that the reduced powders have co-existing particles or both co-existing and hexagonal particles or hexagonal particles but not tetragonal particles. This study adds one more step to understand the hexagonal and tetragonal phases in the reduced BT powders and open the avenues for future applications.

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