

Low temperature synthesis of tetragonal BaTiO₃ by using molten salt

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Tetragonal BaTiO₃ was prepared by reaction of a layered K₂Ti₂O₅ and mixed barium salts (BaCl₂ + Ba(NO₃)₂) at above 700°C. The morphology of the particle was cubic shape and the particle size of the products prepared at 700–1000°C was ~10 μm, and that of the products prepared at higher temperatures (1100–1200°C) was smaller than that of the products prepared at 700–1000°C. From the chemical analysis no potassium atom was detected and the Ba/Ti ratio in the tetragonal BaTiO₃ was 1.00. In the cubic particle of the tetragonal BaTiO₃ surface 90° domain boundaries were observed. Lattice parameters and Curie temperature of the tetragonal BaTiO₃ were $a = 3.995(1)$ and $c = 4.036(1)$ Å and 130°C, respectively.

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1. Introduction

Barium titanate, BaTiO₃ (hereafter BT) is a ferroelectric compound with the perovskite-type structure,¹⁾ and is an important material for dielectric applications. Particularly some multilayer capacitors (MLCs) based on BT exhibit excellent temperature-stable dielectric property. BT has four modifications of rhombohedral, orthorhombic, tetragonal and cubic phases, and the ferroelectric Curie temperature is 132°C at which the tetragonal symmetry changes to the cubic one. Powder sample of BT is easily prepared by high temperature solid state reaction^{2–4)} or hydrothermal reaction,^{5–8)} however, lower temperature solid state reaction or milder hydrothermal condition produces the BT with a cubic symmetry which is a metastable phase stabilized by defects or OH[−] in the crystallite or the presence of a surface layer.^{6–8)} Various synthesis routes for BT powders at low temperatures have been proposed. Mechanochemical reaction with TiO₂ and Ba(OH)₂ in acetone including 4.5 vol % H₂O produced BT powder at room temperature.⁹⁾ Hydrothermal reaction assisted with ball milling process crystallized BT powders at 100°C for 5 h and this condition was milder than that of conventional hydrothermal reaction.¹⁰⁾ Soft chemical reaction with titanate nanosheets produced sheet-like BT powder at 80°C.^{11),12)} Solvothermal reaction formed nano-size BT powder.^{13–15)} Defect- and impurity-free nanosized BT powder were prepared by two-steps thermal decomposition of barium titanyl oxalate, BaTiO(C₂O₄)-4H₂O.^{16),17)} These methods adopted high reactivity routes or more reactive starting materials to accomplish crystallization of BT. Recently Won et al. proposed a unique method for low temperature synthesis of the tetragonal BT by using a precursor powder of BaO₂-TiO₂-C and this method can produce the tetragonal BT above 600°C.¹⁸⁾ We

attempted lower temperature synthesis of BT powder by using a reactive starting compound in molten salt. A layered K₂Ti₂O₅¹⁹⁾ was selected as a starting compound because the arrangement of Ti atoms in K₂Ti₂O₅ was similar to that of the perovskite-type structure and mixed barium salts (BaCl₂ + Ba(NO₃)₂) with the molar ratio of 1:1 was used because of the lower melting point. In this paper we will describe synthesis of the tetragonal BT powder by using molten salt and its properties.

2. Experimental

A starting compound, K₂Ti₂O₅ was prepared by heating the stoichiometric mixture of K₂CO₃ and rutile-type TiO₂ at 700°C for 6 h. The mixture of K₂Ti₂O₅, BaCl₂·6H₂O and Ba(NO₃)₂ with the molar ratio of 1:1:1 was put into an alumina crucible and heated at 500–1200°C for 6 h. The product was washed with distilled water and a dilute acetic acid solution in order to dissolve the potassium and barium salts, and separated by filtration, washed with distilled water and dried at 50°C. The products were identified by X-ray powder diffraction pattern using monochromated Cu Kα radiation. The lattice constants were determined from the X-ray powder diffraction patterns measured in the 2θ range from 20 to 90°. The morphology of the particle was observed by a scanning electron microscopy (SEM). The chemical composition was analyzed as follows. The prepared BT was converted to hydrated titanium oxide in concentrated HNO₃ solution (HNO₃ 10 mL + H₂O 20 mL) under hydrothermal condition at 180°C for 12 h. The product was separated by filtration and the amount of barium and potassium ion in the solution was determined by an induced couple plasma spectroscopy (ICP). The solid was heated at 1000°C for 1 h and the product (rutile-type TiO₂) was weighed. The surface of some samples was etched by 10% HCl and HNO₃ acid solution (50 mL) added 35% HF solution (1 mL) in order to determine whether the prepared particles were a single domain or not. The Curie temperature was measured by DTA curve. Crystal structures were drawn by the computer programs VESTA.²⁰⁾

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3. Results and discussion

Figure 1 shows the X-ray powder diffraction patterns for the starting compound, $\text{K}_2\text{Ti}_2\text{O}_5$ and the products prepared at the reaction temperature of 500–1200°C. The X-ray powder diffraction patterns for the samples before washing with distilled water and a dilute acetic acid solution showed coexistence of KCl. The tetragonal BT appeared at 600°C in spite of the coexistence of a small amount of the intermediate phase which was obtained at 500°C. Interestingly, no appearance of a cubic phase was observed at the lower temperature than the tetragonal BT appeared. The intermediate phase with low crystallinity was thought to have a different structure from the starting compound and BT. The diffraction lines of 200 and 002 are clearly separated as shown in the superimpose figure of Fig. 1 and each diffraction line indicates $\text{K}\alpha_1$ line. This result implies that the BT prepared at 700°C is the tetragonal phase with high crystallinity. The morphology of the tetragonal BT was cubic shape as shown in **Fig. 2**. The morphology of the particle was cubic shape and the particle size of the products prepared at 700–1000°C was $\sim 10\ \mu\text{m}$, and that of the products prepared at higher temperatures (1100–1200°C) was smaller than that of the products prepared at 700–1000°C. The particle size for any reaction temperature was

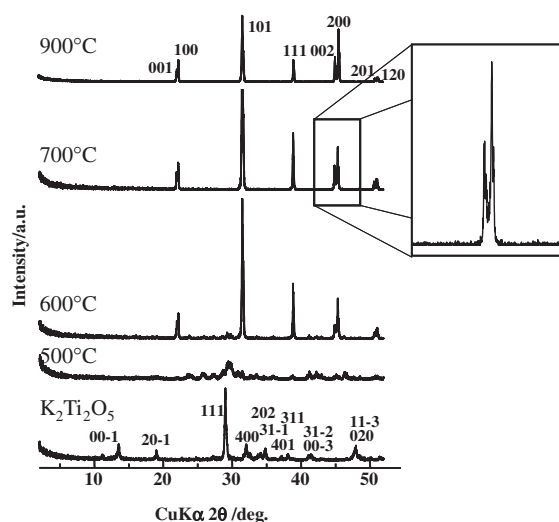


Fig. 1. X-ray powder diffraction patterns of starting compound, $\text{K}_2\text{Ti}_2\text{O}_5$ and the products prepared at 500°C, 600°C, 700°C and 900°C.

not uniform. We could not obtain fine BT particles unlike that prepared by hydrothermal reaction, but prepare tetragonal BT particles with high crystallinity at low temperature. The surface of the etched sample showed the step pattern characterized by domain structure as well as etch pit (**Fig. 3**). This pattern is very similar to that of 90° domain boundaries in BT surface observed by AFM.^{21),22)}

The lattice parameters of the BT prepared at 700°C were $a = 3.995(1)$ and $c = 4.036(1)\text{Å}$ and the c/a ratio was 1.010. The lattice parameters of the samples prepared by the other reaction temperatures were very similar each other ($a = 3.994(1)$ – $3.995(1)\text{Å}$ and $c = 4.035(1)$ – $4.036(1)\text{Å}$). The lattice parameters of BT depended strongly on the Ba/Ti ratio, the lattice defects and the particle size etc. It was reported that the lattice parameters for $\sim 30\ \mu\text{m}$ size single crystal were $a = 3.9998(8)$ and $c = 4.0180(8)\text{Å}$ ($c/a = 1.0046$) which were determined by single crystal X-ray diffraction data.²³⁾ Those for 430 nm size BT fine powder prepared from $\text{BaTiO}(\text{C}_2\text{O}_4) \cdot 4\text{H}_2\text{O}$ were $a = 3.99900(8)$ and $c = 4.03265(9)\text{Å}$ ($c/a = 1.00842$) which were determined by high resolution powder neutron diffraction data.²⁴⁾ The lattice parameters for BT powder obtained by this work were good agreement with those ($a = 3.9940(3)$ and $c = 4.0357(5)\text{Å}$ ($c/a = 1.0104$)) for 500 nm size BT powder prepared by hydrothermal reaction.⁸⁾ From the chemical analysis no potassium atom was detected and the Ba/Ti ratio in the tetragonal BaTiO_3 was 1.00. As shown in **Fig. 4** the endothermic peak in the DTA curve is observed at 130°C for every sample prepared at $\geq 700^\circ\text{C}$. The T_C was somewhat lower than the published value (132°C),²⁴⁾ and this value agreed well with that for 500 nm size BT powder prepared by hydrothermal reaction.⁸⁾

It was reported that mixed salt (50 + 50) of BaCl_2 and $\text{Ba}(\text{NO}_3)_2$ melted at about 500°C.²⁵⁾ SEM observation indicated

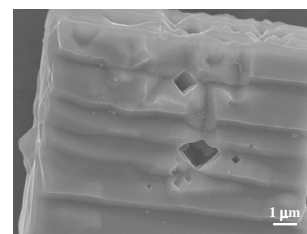


Fig. 3. SEM micrographs of the etched sample prepared at 700°C.

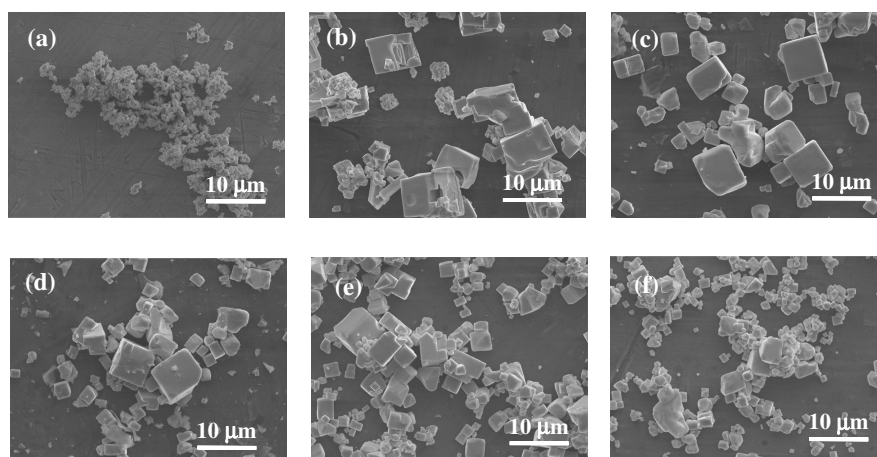


Fig. 2. SEM micrographs of starting compound, $\text{K}_2\text{Ti}_2\text{O}_5$ (a) and the products prepared at 700°C (b), 900°C (c), 1000°C (d), 1100°C (e) and 1200°C (f).

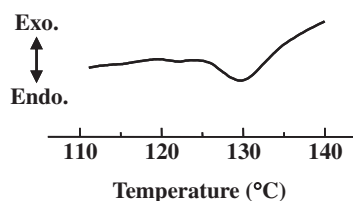
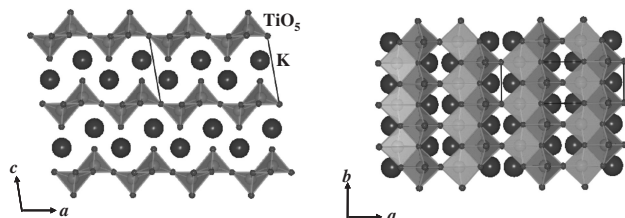
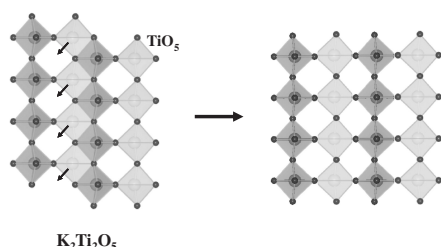


Fig. 4. DTA curve of the sample prepared at 700°C.

Fig. 5. Crystal structure of K₂Ti₂O₅.Fig. 6. Structural change of Ti₂O₅ layer of K₂Ti₂O₅ to the perovskite-type polyhedral arrangement.

that the morphology of the starting compound did not hold and cubic shape particles were formed during this method. The X-ray powder diffraction patterns indicated that the crystallinity of the products was very high. These facts suggest that tetragonal BT particles were crystallized by dissolution–precipitation mechanism at $\geq 700^\circ\text{C}$. The K⁺ ion in the starting compound was replaced completely with Ba²⁺ ion by this method. This complete replacement was considered to be caused by the difference of the ionic size between K⁺ and Ba²⁺ ions; the ionic radius (1.61 Å) of Ba²⁺ ion was smaller than that (1.64 Å) of K⁺ ion and replacement of smaller Ba²⁺ ion was stimulated. The ionic radii of both ions were referred by Shanon's ionic radius with 12 coordination number.²⁶⁾ Also the direct crystallization of the BT may be correlated to the crystal structure of the starting compound, K₂Ti₂O₅. The crystal structure of K₂Ti₂O₅¹⁸⁾ is described as the layered structure formed by edge- and corner-sharing of TiO₅ pyramids and K⁺ ion is located in the interlayer as shown in Fig. 5. Displacement of Ti atoms of edge-shared TiO₅ pyramid array in this Ti₂O₅ layer can form the perovskite-type polyhedral arrangement as shown in Fig. 6. This structural similarity and molten salt may enhance to crystallize the BT with little lattice deficiencies at low temperature, $\sim 700^\circ\text{C}$. As a result of yielding the BT with little lattice deficiencies the tetragonal phase can be obtained. Similar crystallization accompanying replacement of cations was found in calcium manganates, CaMn₂O₄ and CaMn₃O₆, which were prepared by using Na_{0.44}MnO₂ in molten salt CaCl₂.²⁷⁾ The ionic radius (1.34 Å) of Ca²⁺ ion in the products was smaller than that (1.39 Å) of Na⁺ ion in the starting compound like this work. These results imply that the size of the cation which does not form the framework is an important factor for crystallization in molten salt.

4. Conclusion

Reaction of a layered potassium titanate, K₂Ti₂O₅ with mixed molten salt (BaCl₂ + Ba(NO₃)₂) yielded a tetragonal BaTiO₃ with a cubic shape ($\sim 10\ \mu\text{m}$) at above 700°C . The Ba/Ti ratio of the tetragonal BaTiO₃ was 1.00 and its surface had 90° domain boundaries. The formation of the tetragonal BaTiO₃ with a cubic shape was deduced to be dissolution–precipitation mechanism in molten salt.

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