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Crystal Growth and Dielectric Properties of New Ferroelectric Barium Titanate: $BaTi_2O_5$

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Abstract. Single crystals of the ferroelectric $BaTi_2O_5$ and $BaTiO_3$ were prepared from a solution of 33-mol% BaO and 67-mol% TiO_2 by a rapid cooling method. The dielectric constant (ε') and dielectric loss tangent (tanδ) were measured in a wide temperature range of 10–860 K and in a frequency range of 0.1–3,000 kHz. The ε' along the *b*-axis of the $BaTi_2O_5$ crystal, prepared in air, shows a sharp dielectric anomaly reaching 30,000 at the ferroelectric Curie temperature of $T_C = 752$ K. By contrast, the crystal prepared in a reducing atmosphere shows a diffuse phase transition near $T_C = 703$ K. The values of ε' and tanδ are compared between these three crystals consisting of two kinds of $BaTi_2O_5$ and one $BaTiO_3$.

Keywords: $BaTi_2O_5$, $BaTiO_3$, ferroelectrics, high Curie temperature, high dielectric constant

1. Introduction

A search for Pb-free ferroelectric oxides with a low loss and with a large dielectric constant is important for development of environmentally friendly electric devices. Very recently, we found ferroelectricity in a needlelike crystal of $BaTi_2O_5$; the spontaneous polarization is approximately 7 μC/cm^2 at room temperature and the dielectric constant along the needle direction (the *b*-axis) is very high, reaching 30,000 ($=\varepsilon_{\max}$) at its Curie temperature of $T_C = 703$ K [1]. In comparison with cubic barium titanate ($BaTiO_3$), which is a representative ferroelectric material, $\varepsilon_{\max}$ in $BaTi_2O_5$ is about three times as large and T_C is about 300 K higher.

Statton grew needlelike crystals of $BaTi_2O_5$ from a TiO_2-rich solution of 68.4-mol% in the BaO-TiO_2 system for the first time in the 1950s [2]. Rase and Roy determined the BaO-TiO_2 phase diagram with a stable $BaTi_2O_5$ phase [3]. Harrison disclosed the crystal structure of $BaTi_2O_5$ (the space group is monoclinic-$C_{2/m}$) [4]. According to Jonker and Kwestroo, $BaTi_2O_5$ is a metastable compound formed only through a liquid intermediate [5]. As a consequence, the $BaTi_2O_5$ phase was eliminated from the BaO-TiO_2 equilibrium phase diagram [6, 7]. Contrarily, Ritter et al. reported that the $BaTi_2O_5$ phase exists but it decomposes to $BaTiO_3$ and $Ba_6Ti_{17}O_{40}$ in a temperature range between 1423 K and 1585 K, and proposed another phase diagram [8]. Very recently, Akashi et al. succeeded to prepare the $BaTi_2O_5$ single crystal by a floating zone method [9]. Thus, the thermal stability of $BaTi_2O_5$ is still a controversial problem. Concerning the physical properties of $BaTi_2O_5$, on the other hand, only little information is available.

In this paper, we present experimental results on the dielectric properties of two kinds of single crystals of $BaTi_2O_5$, which were prepared in air and in a reducing atmosphere, and we compare the dielectric properties of $BaTi_2O_5$ with those of $BaTiO_3$ single crystals.

2. Experimental and Results

Fine powders of $BaTiO_3$ (99.98%; Kishida Chemical Co., Ltd.) and TiO_2 (99.9%; Aldrich Chemical Co., Inc.) were used as starting materials. They were mixed in a mole ratio of $0.97BaTiO_3/1.00TiO_2$, which is equal to 67-mol% TiO_2 in the BaO-TiO_2 system and differs slightly from a mole ratio of BaO/2TiO_2 [3, 7, 8]. Then,

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they were placed in a platinum crucible. The crucible was heated to 1,659 K and held for 2 h. Initially it was cooled slowly at a rate of 5 K/h. After that, it was reheated to 1,659 K and then rapidly cooled to room temperature at a rate of 150 K/h. These thermal processes for the crystal growth were performed in a reducing atmosphere and in air; let us call the grown crystals #A and #B, respectively. In the reduced atmosphere, black needlelike crystals with dimensions of approximately 0.5 × 0.5 × 5 mm grew in a glassy matrix. After taking them off the matrix and annealing them at 1,273 K in air for 8 h, they became transparent and colorless ($BaTi_2O_5$, #A). In an air atmosphere, not only the transparent and colorless needlelike crystals ($BaTi_2O_5$, #B), but also yellowish round crystals ($BaTiO_3$) were obtained together. The $BaTi_2O_5$ single crystals appear to grow up larger in a reducing atmosphere than in air.

A chemical analysis was performed using an electron probe micro-analyzer (EPMA) (JXA-8800M; JEOL); a commercial $BaTiO_3$ crystal was used as a standard material. Ratios of Ti/Ba for the needlelike crystals were estimated to be 1.96 ± 0.05 and 1.99 ± 0.06 for #A and #B, respectively. In addition, XRD patterns of the pulverized single crystals were measured using an X-ray diffractometer (RINT 2000; Rigaku Corp.), and the X-ray results agreed well with those reported previously on $BaTi_2O_5$ [4]. Thus, both of the #A and #B crystals are certainly $BaTi_2O_5$. On the other hand, solid products obtained by a slow cooling method at a rate of 5 K/h were found to consist of very small crystals of $BaTiO_3$ and $Ba_6Ti_{17}O_{40}$, in accordance with the BaO-TiO_2 equilibrium phase diagram reported by Kirby and Wechsler [7].

The crystals were cut perpendicularly to the b-axis in $BaTi_2O_5$ and to the [100] direction in cubic $BaTiO_3$ for measurements of the dielectric constant (ε') and dielectric loss tangent ($\tan\delta$). Silver paste (#7095; DuPont and Co.) was painted on the main faces of the capacitor specimen as electrodes; gold lead wires with a diameter of 25 μm were attached to the faces. The specimen was fired at 773 K to harden the contact. Electrode area and thickness of the capacitors were approximately 0.5 × 0.5 mm and 0.4 mm for $BaTi_2O_5$, and 1.2 × 1.2 mm and 0.8 mm for $BaTiO_3$, respectively. We performed AC impedance measurements in two frequency ranges of 0.1–1,000 kHz and 75–3,000 kHz using two LCR meters (HP 4284A and HP 4285A). Absolute values of the dielectric constant contain about 5–10% errors coming from using these small samples. However, difference of the sample sizes between $BaTi_2O_5$ and $BaTiO_3$ will not intrinsically affect the experimental results in this low frequency rage, judging from our experience in the experiments on many sizes of $BaTiO_3$ single crystals [10, 11]. A closed-cycle cryostat (M310; Iwatani Ind. Gases Corp.) and a hand-made electric furnace were used for temperature ranges of 10–300 K and 300–900 K, respectively. Temperature dependence of the dielectric constant was measured on heating at a rate of 1 K/min.

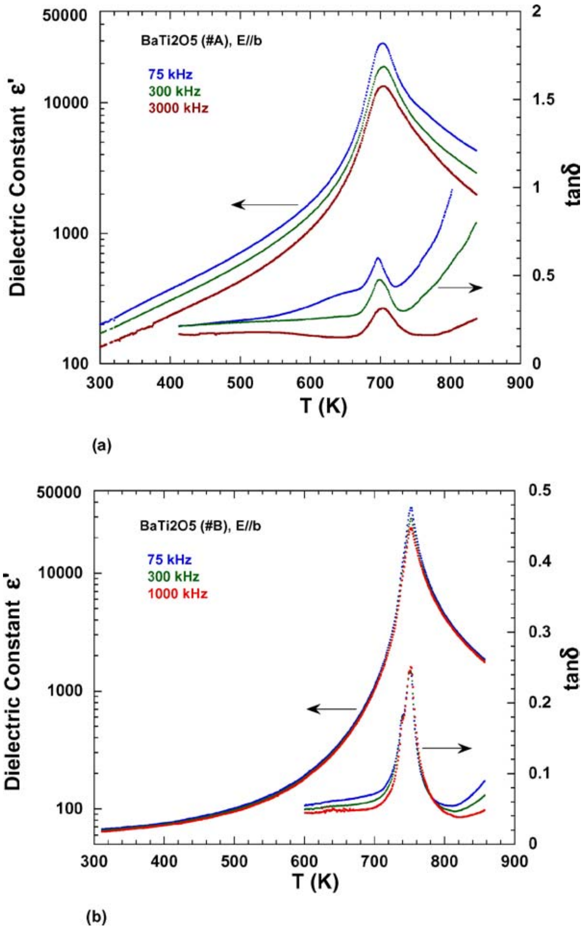

Fig. 1. Temperature dependence of the dielectric constant (ε') and dielectric loss tangent ($\tan\delta$) of two kinds of $BaTi_2O_5$ single crystals: (a) crystal #A grown in a reducing atmosphere, and (b) crystal #B grown in air. Electric field E was applied along the b-axis.

Figure 1(a) and 1(b) show experimental results on the #A and #B crystals of $BaTi_2O_5$, respectively; ε' is represented by a logarithmic scale (see the left-side y-axis), but $\tan\delta$ is represented by a linear scale (see the right-side y-axis). As seen in Fig. 1(a) and 1(b), the #A crystal exhibits a diffuse phase transition at temperatures near $T_C = 703$ K. The dielectric anomaly is very

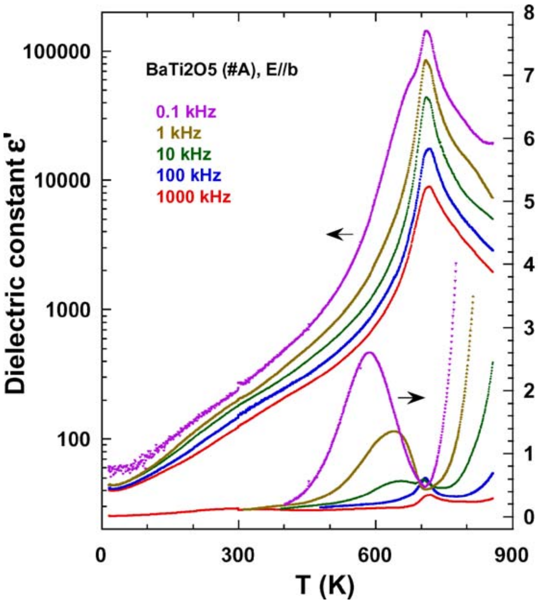

Fig. 2. Temperature dependence of the dielectric constant (ε') and dielectric loss tangent (tanδ) of a $BaTi_2O_5$ single crystal #A, grown in a reducing atmosphere. Electric field E was applied along the b-axis.

broad and dispersive. By contrast, the #B crystal shows a sharp phase transition at $T_C = 752$ K. The ε' for #B reaches about 30,000 at T_C and is somewhat larger than that for #A. As temperature is falling from T_C, ε' for #B decreases rapidly, so that ε' for #A becomes larger than that for #B at temperatures of 300–600 K. In addition, tanδ for #A is considerably larger than that for #B over the whole temperature range: the values of tanδ at 300–600 K are about 0.3 for #A and 0.06 for #B.

We measured the ε' and tanδ at lower frequencies of 0.1–1,000 kHz and at wider temperatures of 10–860 K, to obtain further information about dispersive phenomena of the #A crystal. Three kinds of low frequency dispersion appear in three temperature ranges, as shown in Fig. 2: (1) tanδ increases steeply at temperatures above 700 K, because of increasing ionic conduction; (2) very large dielectric dispersion, which is caused by ferroelectric domain-wall motion, is seen in a temperature range from about 400 K to the transition temperature T_C; and (3) weak dielectric dispersion appears at around 200–300 K, which is due to freezing of the domain-wall motion.

The logε' and tanδ on the (100) plate of the $BaTiO_3$ single crystal are shown in Fig. 3 as a function of temperature. As shown by abrupt jumps in ε', the crystal undergoes successive phase transitions of the first order at $T_1 = 195$ K, $T_2 = 286$ K and $T_C = 405$ K, at which the crystal structure changes as follows: rhombohedral, orthorhombic, tetragonal and cubic. On heating, the dielectric constant ε' increases abruptly at T_C by 8,000 and reaches 10,000; after that, ε' decreases with temperature, in accordance with the Curie-Weiss law [12]. These behaviors near T_C very much resemble those of the crystals grown by a top seeded solution growth method [13, 14]. Furthermore, we can see a glassy phase transition at around 100 K, which is the same one as observed recently in high purity $BaTiO_3$ single crystals prepared for optical devices [11]. The tanδ maintains very low values smaller than 0.02 at temperatures of 200–500 K, but it changes discontinuously at the transition temperatures. On the other hand, at higher temperatures above 500 K, tanδ increases steeply with increasing temperature, reflecting increase of some kinds of electronic or ionic conduction. The temperature of 500 K is too low for oxygen ions to start moving [15]; another mechanism should be constructed to explain the increase of tanδ at around 500 K in $BaTiO_3$.

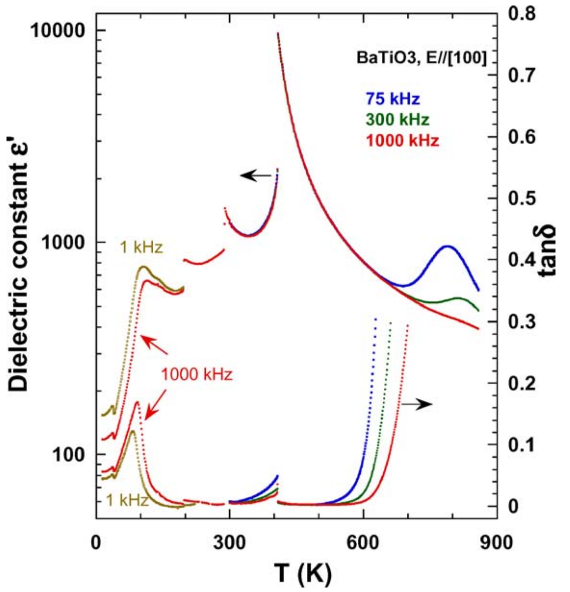

Fig. 3. Temperature dependence of the dielectric constant (ε') and dielectric loss tangent (tanδ) of a $BaTiO_3$ single crystal grown in air. Electric field E was applied along the cubic [100] direction.

3. Discussion

First, let us compare dielectric properties of the #A and #B crystals in $BaTi_2O_5$. The #A crystals were grown in a reducing atmosphere; the black grown crystals contain considerable oxygen vacancies. Even if they were subjected to sufficient oxidization, some amounts of oxygen vacancies remain in the crystals. These oxygen vacancies operate to activate ionic conduction of oxygen ions. The experimental results, that tanδ in #A is much larger than that in #B and it increases rapidly at temperatures above 700 K (see Figs 1(a) and 2), suggest that the ionic conduction of oxygen takes place easily in #A than in #B, because #A crystal is considered to contain much more oxygen vacancies than #B. This explanation due to oxygen vacancies agrees well with the thermogravimetric behavior on oxidization of reduced perovskite-type ABO_X compounds; that is, the weight of the compounds begins to change at temperatures of 700–900 K on heating in air [16]. Moreover, existence of these mobile oxygen vacancies (or mobile oxygen) appears to induce a decrease of T_C and broadening of the phase transition, as observed in K-modified PLZT [17]; in addition, it appears to enlarge the low frequency dielectric dispersion associated with domain wall motion at temperatures just below T_C, as seen in Fig. 2.

Next, let us compare dielectric properties of $BaTi_2O_5$ (#B) and $BaTiO_3$ (see Fig. 1(b) and Fig. 3). They were grown at the same time in air. The $BaTiO_3$ has a large ε' (larger than 1,000) and low tanδ (smaller than 0.02) in the temperature range of 300–500 K, so that it is widely used as electric devices such as a ceramic condenser. Unfortunately, at temperatures above 500 K, tanδ in $BaTiO_3$ increases steeply with temperature. Therefore, in the high temperature range of 600–900 K, $BaTi_2O_5$ is very promising for electric devices instead of $BaTiO_3$, because $BaTi_2O_5$ has high ε' and low tanδ in comparison with $BaTiO_3$.

Finally, let us consider about origin of the increase of tanδ above 500 K in $BaTiO_3$. According to Raevski et al., in the temperature range below approximately 600 K, charge carrier concentrations in titanates are changed as the result of changes in the degree of the ionization of defects, but not the result of charges in the total concentrations of the defects. As the possible defects in non-doped $BaTiO_3$, we can consider oxygen vacancies (V_O), cationic vacancies (V_{Ba} and V_{Ti}) and acceptor-type background impurities. Since the present $BaTiO_3$ crystal was prepared from a TiO_2-rich solution in air, it may contain a relatively large amount of Ba-vacancies (V_{Ba}), in comparison with the other defects. In addition, it is well known that the non-doped and well-oxidized $BaTiO_3$ shows p-type conduction at high temperatures [18]. Therefore, we consider that an electronic conduction due to thermally activated holes from acceptors associated with V_{Ba} takes place above 500 K in $BaTiO_3$.

4. Conclusions

We prepared two kinds of ferroelectric $BaTi_2O_5$ single crystals (#A and #B, grown in a reducing atmosphere and in air, respectively) by a rapid cooling method. The dielectric properties along the b-axis of the crystals were measured in a wide temperature range of 10–860 K and in a frequency range of 0.1–3,000 kHz. The #A crystal shows a broad and dispersive dielectric anomaly near $T_C = 703$ K, and shows three kinds of dielectric dispersions: an oxygen ionic conduction (above 700 K), ferroelectric domain-wall motion (400–700 K), and freezing of the domain-wall motion (200–300 K). We discussed these diffusive behaviors as a result induced by mobile oxygen vacancies. By contrast, ε' on the #B crystal shows a sharp peak reaching 30,000 at $T_C = 752$ K. These values of ε' and tanδ were compared between three crystals of $BaTi_2O_5$ (#A), $BaTi_2O_5$(#B), and $BaTiO_3$.

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