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Giant Dielectric Constant of Hexagonal $BaTiO_3$ Crystal Grown by Containerless Processing

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Since the discovery of barium titanate, extensive investigations have been focused on ferroelectric perovskite $BaTiO_3$ (p-$BaTiO_3$) with high permittivity, but only a few studies were performed on polymorphic hexagonal $BaTiO_3$ (h-$BaTiO_3$) with lower permittivity. h-$BaTiO_3$ normally exists above 1703 K[1], can be stabilized as a metastable phase at room temperature (RT), and undergoes successive structural phase transitions at $T_0 = 222$ K and $T_c = 74$ K.[2,3] Electrical measurements using both polycrystal and single crystals that were synthesized by conventional techniques have demonstrated that the stoichiometric h-$BaTiO_3$ has a permittivity of about 200 at RT[4] and that the oxygen-deficient h-$BaTiO_3$ exhibited semiconducting behavior.[5]

In this study, h-$BaTiO_3$ was synthesized with containerless processing using a pressurized electrostatic levitation furnace.[6] The noncontact processing is an attractive technique because it prevents melt contamination, minimizes the heterogeneous nucleation, and permits the synthesis of materials with novel properties by phase selection. Here is reported the successful synthesis of a h-$BaTiO_3$ single crystal that exhibited a giant permittivity of up to 10^5 with a temperature dependence similar to that of $CaCu_3Ti_4O_{12}$.[7−9]

To prepare samples for levitation, high-purity commercial $BaTiO_3$ powder was first compressed at a pressure of 200 MPa into rods and then sintered at 1527 K. Spheroid samples with diameters of ca. 2 mm were made from these rods and levitated by an applied electric field of about 7 kV/cm in a chamber filled with 450 kPa air. Samples were heated and melted using the radiation of a CO_2 laser beam and temperature was measured by pyrometry. Further details about the facility and the levitation procedures can be found elsewhere.[6,10]

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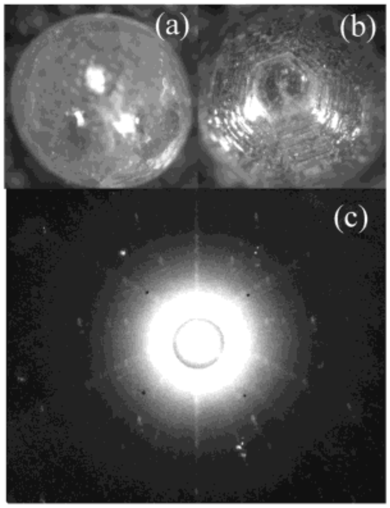

Figure 1. Optical photographs of BTO-A (a) and BTO-B (b), and Laue diffraction spots of (0 0 1) crystal plane of BTO-B (c).

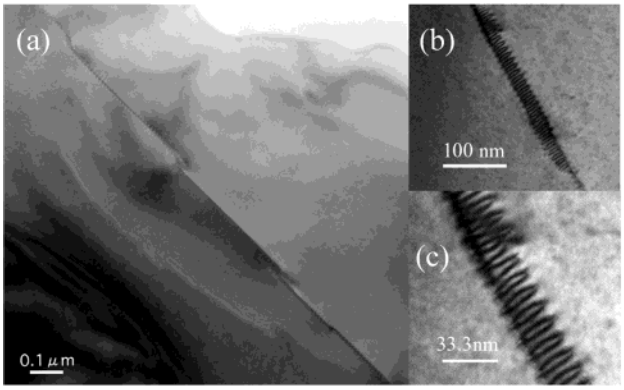

Figure 2. TEM images of BTO-B with different magnifications showing the interfacial boundary consisting of screw dislocations.

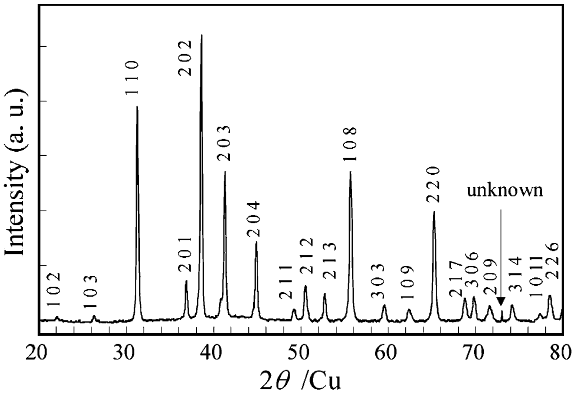

Figure 3. X-ray diffraction pattern of BTO-B crystal showing a hexagonal $BaTiO_3$ structure.

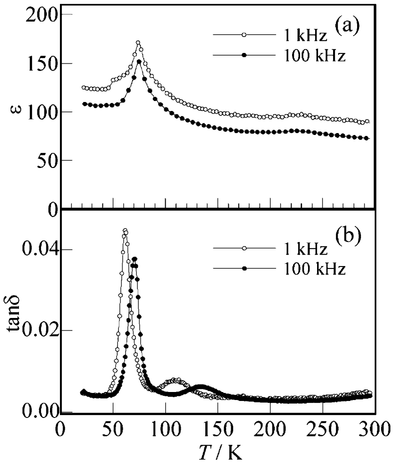

Figure 4. Temperature dependence of dielectric constant ϵ' (a) and loss component tanδ (b) for BTO-A.

The samples were superheated by about 50 K (T_m = 1897 K) for several minutes and then cooled with different rates. The lower cooling rate (ca. 30 K/s) yielded a pale yellow translucent spheroid sample (BTO-A, Figure 1a) whereas the higher cooling rate (ca. 300 K/s) yielded a blue translucent spheroid sample (BTO-B, Figure 1b). The blue color was attributed to oxygen deficiency.[5] Composition analysis was performed by EPMA (CAMECA SX100) using a commercial stoichiometric p-$BaTiO_3$ single crystal as a standard reference. From an average concentration of 10 analyzed spots within an area of about 1 mm^2, BTO-B was determined to be $BaTiO_{2.84}$ with the standard deviations of 0.3, 0.3, and 0.6 for Ba, Ti, and O at. %, respectively. Since no grain boundary was observed by optical microscopy, both translucent samples were measured with a Laue X-ray diffraction meter and confirmed as bulk single crystals. Figure 1c shows a Laue image of (0 0 1) crystal plane of BTO-B, taken from the cross-section parallel to the growth facet at the top surface of the sample (Figure 1b). In addition, TEM images of Figure 2 illustrate that BTO-B is characteristic of interfacial boundary (small angle boundary) consisting of screw dislocations. To identify the form of $BaTiO_3$ present, crystals were mounted on a two-axis moving stage (oscillating ω in the range of 20−30°, rotating ϕ from 0 to 360°) and measured by an X-ray microdiffraction system (D/max RAPID, Rigaku Co.).[11] A two-dimensional X-ray diffraction image was detected by a cylindrical imaging plate and then converted into a powder X-ray diffraction pattern (Figure 3). All peaks in Figure 3, except one, culd be identified by the diffraction of h-$BaTiO_3$ (Ref: ICSD Code 75240). The crystals were further measured precisely by a single-crystal X-ray diffractometer (AFC-6S Rigaku Co.) and then the lattice parameters were refined as $a = 0.5711(3)$ nm and $c = 1.3945(6)$ nm for BTO-A, and $a = 0.5720(3)$ nm and $c = 1.396(5)$ nm for oxygen-deficient BTO-B using a program of PRECELL. The cell parameters increased due to oxygen deficiency, which was consistent with the results of neutron diffraction measurement for oxygen-deficient h-$BaTiO_3$.[5]

The temperature dependence of permittivity was measured with an impedance analyzer (HP-4194A) from 20 to 300 K over a frequency range of 100 Hz to 1 MHz. For initial measurements, the samples were cut into disks of ca. 0.3−0.4 mm thickness and Au was sputtered as electrodes. Figure 4 shows the temperature dependence of permittivity, ϵ', and loss component, tanδ, of BTO-A at 10 kHz and 100 kHz. This figure exhibits a $\epsilon' \approx 100$ and a tan$\delta \approx 0.01$ at RT as well as anomalies at

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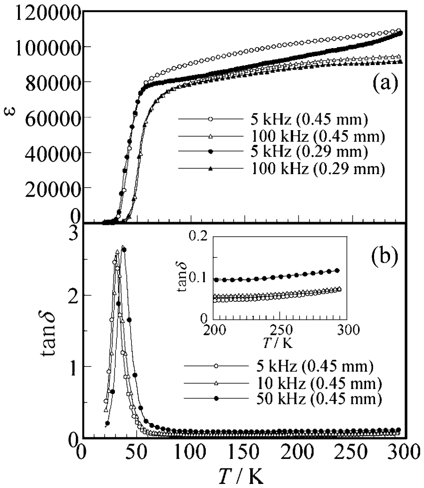

Figure 5. Temperature dependence of dielectric constant ϵ' (a) and loss component tanδ (b) for BTO-B with different thicknesses.

the phase transition temperatures of 74 and 220 K. The dielectric characteristic of BTO-A was consistent with that reported in the literature for stoichiometric h-BaTiO$_3$.[2-4] However, oxygen-deficient BTO-B showed a quite different dielectric behavior, displaying a gigantic $\epsilon' \approx 10^5$ at RT. Since an apparent high ϵ' could be induced by a Shottky barrier effect between Au electrodes and semiconducting BaTiO$_3$, it was necessary to use electrodes with different work functions to clarify that the origin of the gigantic ϵ' was attributed to the contact layers. Although an In−Ga alloy is generally utilized as electrodes for measuring the electrical properties of semiconductor, a good contact between liquid In−Ga and the BaTiO$_3$ single crystal could not be achieved in our experiments. Instead, Ag with a lower work function than Au was sputtered as electrodes. To further check the electrode contributions, we also varied the thickness of the BTO-B sample by polishing it and by taking the measurements again. Figure 5a shows the temperature dependence of ϵ' at 5 and 100 kHz for BTO-B with thicknesses of 0.45 and 0.29 mm. The permittivity measured with Ag electrodes also showed a giant magnitude of 10^5 at 5 kHz at RT, gradually decreasing to 80 000 as the temperature decreased to about 70 K, and then sharply dropping by more than 2 orders of magnitude. This dielectric behavior was very similar to that of CaCu$_3$Ti$_4$O$_{12}$.[7-9] If the high apparent permittivity was dominated by the constant contact capacitance, ϵ' would diminish by about $^1/_3$ if the thickness of the sample was reduced from 0.45 to 0.29 mm since ϵ' is calculated by dividing the capacitance C by the empty capacitance C_0, which is smaller for the thicker sample. However, only a slight decrease of ϵ' was observed at RT, despite the thickness of the sample being reduced by $^1/_3$. This indicated that the origin of the giant ϵ' could not be attributed mainly by the effect of contact contribution. Figure 5b shows the temperature dependence of tanδ for BTO-B at 5, 10, and 50 kHz, exhibiting low values (<0.1) around RT (insert of Figure 5b).

The origin of the high apparent permittivity for materials without ferroelectric phase transition can be interpreted by the Maxwell−Wagner effect contributed from grain boundaries in polycrystal, from interfacial boundaries in single crystal, or from the depletion layer between electrode and sample interface. In this study, the high ϵ' of BTO-B can be interpreted as arising mainly from the Maxwell−Wagner effect contributed by the interfacial boundaries consisting of crystal defects (Figure 3). Our impedance spectroscopy data also revealed that the interfacial boundary layer exhibited a capacitance about 10 nF cm^{-1} ($\epsilon' \approx 1.1 \times 10^5$) at RT.[12]

Bulk crystal of oxygen-deficient h-BaTiO$_3$ was synthesized successfully by noncontact processing. The resulting material exhibited a ϵ' of $\sim 10^5$ with tan δ of $\sim$0.01at RT. Therefore, it could become an attractive candidate for ultra-large-scale integration of the dynamic random access memory.

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