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Observations of Domain Structure and Ferroelectricity in $Bi(Ni_{0.5}Ti_{0.5})O_3$ Ceramics Fabricated by High-pressure Sintering

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$Bi(Ni_{0.5}Ti_{0.5})O_3$ (BNT) ceramics with a perovskite structure, which were almost impossible to fabricate under atmospheric pressure, were synthesized at a high pressure of 6 GPa using a multianvil-type high-pressure apparatus. It was confirmed that the synthesized samples had a multidomain structure and ferroelectricity on the basis of scanning nonlinear dielectric microscopy (SNDM) and polarization–electric field (*P*–*E*) hysteresis loop measurements.

Recently, the development of lead-free ferroelectric materials[1] as alternatives for high-performance lead-based materials such as lead zirconium titanate, has been intensively studied from the viewpoint of global environmental conservation. Since Bi^{3+} ion has the same $[Xe]4f^{14}5d^{10}6s^2$ electronic configuration as Pb^{2+} ion, we anticipate that the ferroelectricity of compounds with Bi^{3+} partially occupying the A sites of the perovskite structure can be improved by hybridization between Bi $6s^2$ and 2p orbitals of oxygen as in Pb compounds.[2] However, given that Bi^{3+} has a smaller ionic radius than that of Pb^{2+} and possesses no 12-fold coordination structure barring exceptions of $BiFeO_3$ and $Bi_4Ti_3O_{12}$ as high-temperature phase, the synthesis of $Bi(M_1M_2)O_3$ compounds with Bi^{3+} occupying the A site of the perovskite structure under atmospheric pressure is difficult. Although the ferroelectricity of a few synthetic examples, such as $BiFeO_3$ and $BiMnO_3$, has been confirmed, fundamental research on the synthesis and physical properties of other $Bi(M_1M_2)O_3$ compounds is not well advanced. The possibility of $Bi(Ni_{0.5}Ti_{0.5})O_3$ (BNT) being a multiferroic material having both ferroelectric and ferromagnetic properties is expected in $Bi(M_1M_2)O_3$ compounds, whereas there have as yet been no reports on the domain structure and ferroelectricity of BNT, except for the report on structural and dielectric characteristics by Inaguma et al.[3,4] In the present study, BNT ceramics were fabricated by high-pressure sintering and then their domain structure and ferroelectricity were studied.

BNT samples were synthesized by a solid-state reaction using reagent-grade Bi_2O_3, TiO_2, and $NiCO_3{\cdot}2Ni(OH)_2{\cdot}nH_2O$ as starting materials. A mixture of the raw materials was calcined for 4 h at 800 °C in air. The calcined powder was ground at 200 rpm for 3 h using a planetary zirconia ball mill. After sealing the ground powder in a platinum capsule of 5-mm diameter and 4-mm depth, was placed in a $LaCrO_3$ sleeve. They were assembly set in a pyrophyllite cube block ($15 \times 15 \times 15\,mm^3$) with a cylindrical graphite heater. The charged sample was sintered using a cubic multianvil-type high-pressure apparatus (CA1500P, TRY), which was operated at heating and cooling rates of 100 °C/min, the pressure of 6 GPa, and the temperature of 1000 °C for 10 min. The crystalline phase of the synthesized BNT ceramics was identified using an X-ray diffractometer (XRD; RINT2200, Rigaku). The domain structure of these BNT samples was measured using scanning nonlinear dielectric microscopy (SNDM; home-made system)[5] by observing a phase image under an ac voltage of 5 V p–p at room temperature in air. The time dependence of the dc resistivity (ρ) of the BNT samples was investigated for two weeks after fabrication under a constant electric field of $2\,kV\,cm^{-1}$ using an electrometer (617, Keithley). Polarization–electric field (*P*–*E*) hysteresis loop was measured using a ferroelectric test system (RT-66A, Radiant Tech.).

XRD patterns of BNT ceramics synthesized under (a) atmospheric pressure (101 kPa), (b) high pressure (6 GPa, immediate aftermath of the synthesis), and (c) high pressure (6 GPa, 30 days after synthesis) are shown in Figure 1. No perovskite $Bi(Ni_{0.5}Ti_{0.5})O_3$ phase was confirmed for the sample synthesized under atmospheric pressure. We speculate that the formation of energetically stable $Bi_4Ti_3O_{12}$ (BiT) under atmospheric pressure and the precipitation of unreacted NiO and Bi_2O_3 proceeded in accordance with eq 1 and this was also reported in a previous paper.[6]

$$6Bi(Ni_{0.5}Ti_{0.5})O_3 \rightarrow Bi_4Ti_3O_{12} + 3NiO + Bi_2O_3 \qquad (1)$$

On the other hand, for the sample synthesized under high pressure, it was confirmed that an almost single-phase perovskite structure in BNT ceramics was formed due to structural stabilization caused by high pressure. There is a tendency that the

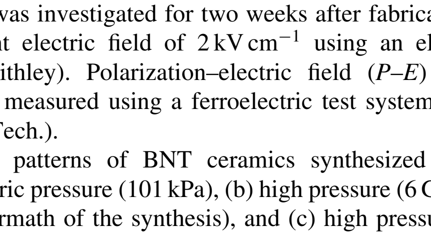

Figure 1. XRD patterns of BNT ceramics synthesized under (a) atmospheric pressure (101 kPa), (b) high pressure (6 GPa, immediate aftermath of the synthesis), and (c) high pressure (6 GPa, 30 days after synthesis).

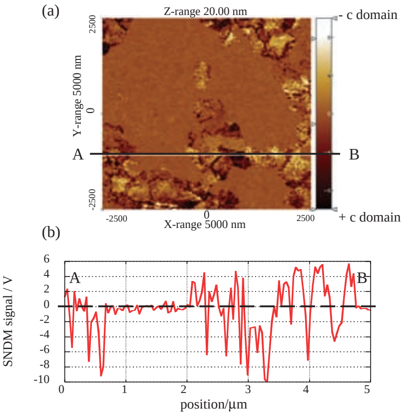

Figure 2. Measurement results of the 180° c–c domain in an as-grown BNT ceramic by SNDM. (a) $A \cos\phi$ image and (b) line profile of A–B.

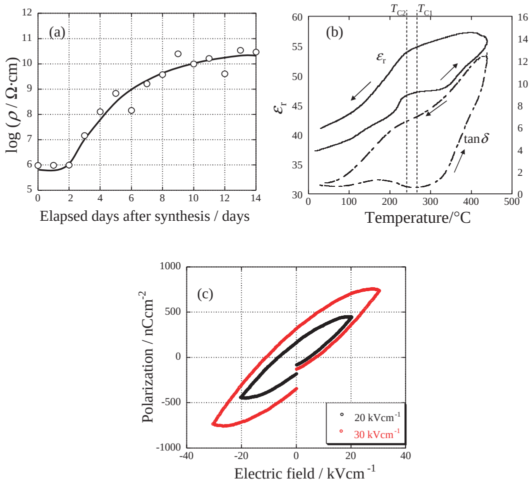

Figure 3. Time dependence of the dc resistivity for BNT ceramics (a), temperature dependence of relative permittivity (ε_r) and dielectric loss (tan δ) (b), and P–E hysteresis loop of a BNT ceramic 30 days after synthesis (c).

coordination number of constituent ions under high pressure becomes larger than that under atmospheric pressure due to an increase in r_c/r_a (r_c: cation radius, r_a: anion radius) ratio, producing stabilization of the structure.[7] For this reason, it can be reasonably expected that Bi^{3+}, which has an 8-fold coordination structure under atmospheric pressure, will have a 12-fold coordination structure under high pressure, occupying the A site in the perovskite structure. Based on the XRD result that the 30-days elapsed sample after synthesis showed an almost single-phase perovskite structure, it was proven that it maintained the perovskite structure in a high resistivity state. Figures 2a and 2b show a phase ($A \cos\phi$) image and the line profile of the polarization component (180° c–c domain) on the surface of an as-synthesized BNT ceramic obtained from three-dimensional nonlinear dielectric constant by SNDM, respectively. Here, A and ϕ indicate the amplitude and phase signals, respectively. The polarity of the domain is positive when the direction of the spontaneous polarization is upward. It was also confirmed that the positive domain indicated a dark area in the present SNDM image. Consequently, the bright and dark areas in Figure 2a correspond to the negative and positive domains, respectively. The areas exhibiting no phase signals of polarization suggest the existence of none-ferroelectric phase and/or an a–b domain in which spontaneous polarizations are located in-plane. Based on the fact that the multidomain BNT structure is observed as indicated in the figure, the present sample was demonstrated to have ferroelectric nature. In addition, the SNDM image visually demonstrates that the high-pressure sintering process enables the synthesis of frozen perovskite BNT ceramics with a multidomain structure. The time dependence of ρ changed significantly 48 h after synthesis (see Figure 3a). The resistivity hardly changed up to 48 h after synthesis, while it increased exponentially from 9.6×10^5 (2 days) to 2.9×10^{10} Ω·cm (2 weeks). This may be explained by assuming that the relaxation of perovskite structure frozen by high-pressure sintering occurred gradually with passage of time, producing an improvement in ρ due to the slight formation of a BiT phase as unidentified in Figure 1c. Figure 3b shows the temperature dependence of the relative permittvity (ε_r) and dielectric loss (tan δ) at 1 MHz. A thermal hysteresis suggests that the present sample has an apparent dielectric anomaly in the vicinity of 245 °C and it is a ferroelectric with the first-order phase transition. The P–E hysteresis loop of the 30-days elapsed BNT ceramics after synthesis is shown in Figure 3c. From Figures 3b and 3c, it is apparent that this material is a ferroelectric with a remanent polarization of $2P_r$ ($=660\,\mathrm{nC\,cm^{-2}}$) and a coercive field of $2E_c$ ($=18.2\,\mathrm{kV\,cm^{-1}}$) at $30\,\mathrm{kV\,cm^{-1}}$. These results lead us to conclude that as-synthesized BNT ceramics are ferroelectrics with a multidomain structure, producing a convincing P–E hysteresis loop.

In conclusion, BNT ceramics with a perovskite structure, which were almost impossible to fabricate under atmospheric pressure, were synthesized at a high pressure of 6 GPa using a multianvil-type high-pressure apparatus. It was confirmed that the synthesized samples had a multidomain structure and ferroelectricity on the basis of SNDM and P–E hysteresis loop measurements. If the present material retains its ferromagnetism, it can greatly be expected as a multiferroic material for multiple-valued logic and optical isolator applications.

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