Domain switching in nanometer scale in Bismuth-based relaxor solid solution

Naohiko Yasuda¹, Natsumi Takahashi¹, Nur Hidayah¹, Hidehiro Ohwa¹, Osamu Sakurada² Yoshihito Tachi³, Kazuhiro Fujita⁴, Yohachi Yamashita⁵, Makoto Iwata⁶, Hikaru Terauchi⁷ and Yoshihiro Ishibashi⁸

¹Electrical and Electronic Engineering Department, Gifu University, Gifu 501-1193, Japan
²Material Science and Technology Department, Gifu University, Gifu 501-1193, Japan
³Research Laboratories, JFE MINERAL Company, LTD. Chiba 260-0826, Japan
⁴Electronic and Control Engineering Department, Gifu National College of Technology, Gifu 501-0495, Japan
⁵Corporate R & D Center, Toshiba Corporation, Saiwai-ku, Kawasaki 212-8582, Japan
⁶Department of Engineering Physics, Electronics and Mechanics, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan
⁷Advanced Research Center of Science, School of Science, Kwansei-Gakuin University, Sanda 669-1337, Japan
⁸Department of Physics, Kyushu University, Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan

Corresponding author: yasuda-n@gifu-u.ac.jp

Abstract. Microscopic piezoresponse force microscopy observation in 0.9967(Na₁/₂Bi₁/₂)TiO₃(NBT)-0.0033BaTiO₃(BT) rhombohedral (001) plate reveals two kinds of piezoresponse images, one with domain switching characterized with superior piezoresponsibility and the other without one, whereas macroscopic observation reveals non-switching of domain. Such microscopic remarkable difference of domain switching depends on coercive field caused by localized nucleation of domains with reversed polarization. Such coercive fields depend on relaxor states induced by random fields due to built-in charge disorder resulting from lattice defects at A-site and oxygen vacancies in ABO₃ perovskite. The random fields based on lattice defects on {110} plane lower activation barrier for domain switching, leading to nucleation and growth of domains, while for non-switching of domains, oxygen vacancies on {110} and/or {001} plane play a role as clamping center for restriction of domain switching.

1.Introduction

Experimentally measured value of the ferroelectric coercive field, which indicates the magnitude of an external electric field required to reverse the macroscopic polarization, has been known [1] to be smaller than the intrinsic value predicted by the phenomenological theory. The low extrinsic coercive field observed in ferroelectrics has also been reported [2,3] to be caused by localized nucleation of domains with reversed polarization, which then grow in both the forward and side wide directions by domain wall motion. Relatively little energy has been reported [2,3] to be required to reverse polarization in a small nucleation volume around a defect compared to the energy needed for...
collective polarization reversal of crystal. Lattice defects has been known [3-6] to play an important role in the mechanism for the switching of polarization in ferroelectric properties. The piezoresponse force microscopy (PFM) has been applied to the study of ferroelectric materials on the nanometer scale [7-9]. The advantages of the PFM are a high spatial resolution and a high sensitivity to local polarization [7,10]. In this work, bismuth-based relaxor (Na_{1/2}Bi_{1/2})TiO_3 (NBT)- BaTiO_3 (BT) solid solution single crystals were grown by the Bridgman method [5]. The obtained single crystals had good both optical quality and electrical properties [5]. The domain-switching on the rhombohedral NBT-BT (001) plate was microscopically investigated by using PFM. In this paper, the field-induced strain and the piezoelectric images on the rhombohedral NBT-BT (001) plate are presented, and discussed from the microscopic domain structure induced by random fields based on the lattice defects.

2. Experimental
The concentration of NBT-BT single crystals obtained was determined using an inductive charge plasma (ICP) analysis to be 0.487, 0.435 and 0.0033 for Bi, Na and Ba ions [5]. Single crystals obtained were cut into plates with a (100) orientation, as confirmed by X-ray diffraction method. 0.9967NBT-0.0033BT rhombohedral (001) plates were used. PFM studies were performed using a commercial PFM (SPA300/SP13800N, Seiko Inc, Japan [7,9]. An external voltage was applied to one crystal surface through the Al coated cantilever (SI; DF3-R, f=25 kHz, C=1.4 N) with a tip apex radius of 30 nm as a top electrode. The other surface was electrode by silver paste and glued to the sample holder as a bottom electrode. The PFM images were taken over 3 μm and 300 nm length scales on (001)_cub faces at room temperature. When an ac voltage V_{ac}=V_0 \sin \omega t is applied between the tip top electrode and the bottom one of the sample, the alternating external electric field gives rise to the piezoelectric vibration of the sample or a change in the sample thickness due to the converse piezoelectric effect. In this experiment, an imaging ac voltage with amplitude V_0 between 2 and 50 V and a frequency ω/2 π of 5 kHz was applied [9]. The resolution limit of detected domain nucleus length and radius at applied voltage of 5 V for the tip radius R=30 nm were reported [10] to be about below 1 nm. ITO electrodes were deposited by conventional sputtering. The electrical capacitance and dielectric loss tangent tan δ were measured using an LCR meter at 1, 10 and 100 kHz with the probe field weaker than 10 V/cm at a rate of 1 K/min. The relationship between polarizations P and electric fields E was examined with an improved Sawyer-Tower circuit at 30 Hz.

3. Results and Discussions
The electric field-induced strain behavior was microscopically observed using the PFM, based on contact-mode AFM. The two types of examples of strains taken by the surface-displacement detection are shown as a function of tip voltage on the rhombohedral (001) plate in the 0.9967NBT-0.0033BT single crystal as follows. One with domain switching was observed at the point marked with ○ in figure 1(a) as shown in figure 1(b). In figure 1(a) the contrast was reported [8,9,11] to be determined by the out-of-plane component of polarization (P_z), where dark and bright areas correspond to the opposite directions of P_z, (see also figure 2 and figure 3). The other without one was observed at the point marked with ● in figure 1(a), as shown in figure 1(c). The former image reveals the piezoresponse high Z versus a tip voltage V with domain switching, as seen in figure 1(b), where the curve shows the butterfly type hysteresis, corresponding to ferroelectric state. The coercive voltages were estimated to be about 11 V and -9 V as marked with arrows for forward and reverse direction of applied voltage, respectively. The latter one reveals the Z-V curve without domain switching, as seen in figure 1(c), where the curve shows the small hysteresis one characterized with electrostrictive effect, corresponding to relaxor state. The Z-V characteristics with domain switching in the rhombohedral (001) plate with thickness 100 μm to estimate the magnitude in piezoresponse high Z was compared with the poled 0.68PMN-0.32PT rhombohedral (001) plate [12] with thickness of 100 μm with d_{33} ~ 2120 pC/N, as a reference, as shown in figure 1(d).
Figure 1. Planar view of piezoresponse image (a), piezoresponse high Z vs. tip (apex radius of 30 nm) voltage V at point marked with ● (b), that at point marked with ○ (c), and that for poled 0.68PMN-0.32PT single crystal (d). V multiplied by 10 for horizontal axis.

The value of Z=15.0 nm estimated at V=50 V was compared with the Z=10.6 nm at 50 V for poled 0.68PMN-0.32PT (001) plate. The remarkable difference in Z-V curves between switching and non-switching in the 0.9967NBT-0.0033BT rhombohedral (001) plate depends on the ferroic state induced by the random fields based on the lattice defects of Bi, Na and Ba ions and oxygen vacancies [3,5,8]. The substitution of Ba ion for the A-site ion seems to give effect of larger off-center to enhance piezoelectric property [13]. For lattice defects in the case of NBT, the planar defect of Guinier-Preston zones (GPZ’s) was pointed out [14] as follows from the x-ray diffuse scattering study. The asymmetry in the x-ray diffuse scattering intensity was reported [14] to result from the relaxor states induced by random fields based on the planar defects of the GPZ’s characterized with the deformation of the structure around segregation planes in form of monoclinic platelets in random matrix of rhombohedral symmetry. In the case of domain-switching, the planar defects on the {110} plane may contribute to switching sites of domain nucleation, resulting in polarization rotation on the {110} plane, leading to larger piezoresponse high Z [14]. Polar clusters with a reversed polarization within ferroelectric domains seems to be nucleated under applied field in the vicinity of random fields around quenched defects [3]. The random fields was known [3] to lower the activation barrier required for nucleation. Such local random fields due to built-in charge disorder in relaxors were considered as one of the main reasons responsible for the formation of the polar nanoregions [8,11,15].

Figure 2. Piezoresponse images taken over (a) 3 μm and (b) 300 nm length scales on (001)_{cub} faces in imaging ac voltage at 30 V in 0.9967NBT-0.0033BT single crystal at 30 °C.

Figures 2(a) and 2(b) show piezoresponse images taken over 3 μm and 300 nm length scales on (001)_{cub} faces in 0.9967NBT-0.0033BT single crystal in the imaging ac voltage at 30 V by PFM at 30 °C, respectively. The domains are not continuous, some of them disappear or merge, forming labyrinth structures [16], indicating the preferred orientation of domain walls close to the [110] and [100] directions as marked with black dotted line in the figure 2(a). The domain structures
characterized with spherical-like piezoresponse images in some range from about 10 to 100 nm were found as revealed as dark and bright domains in the rhombohedral phase. Micron-sized domains consist of much finer irregular domain structure in nanometer scale. Seemingly dark areas include numerous bright inclusions and vice versa. Appearance of such complex domain structures was known [15] to be a distinctive feature of relaxor crystals, which is associated with the distribution of random electric fields. The random electric fields was reported [15,17] to be Gaussian distributed. The example in the case of 300 nm for the statistical distribution of the domain area inside micron-sized domain at the tip voltage of 5 V is shown in figure 3(a).

Domain distribution with polarizations ±Pz as indicated by dark and bright areas in gray tones was shown in figure 3 (a). The average size of fine domains is about 6.5 nanometer in the present scale of 300 nm. The measured piezoresponse signal distribution was reported [11] to be treated as a (001) cut of the three dimensional domain structure existing near the surface because of the rhombohedral symmetry of the 0.9967NBT-0.0033BT (001) plate. The measured piezoresponse signal was reported [11,15] to have only two values of +Pz and −Pz component of polarization, and then the piezoresponse signal in the 0.9967NBT-0.0033BT rhombohedral (001) plate may be considered as an uniaxial relaxor, similar to Sr_{0.61-x}Ce_xBa_{0.39}Nb_2O_6 (SBN61;Ce) [15]. It has been reported [11,15] that the relaxor properties are well described by the random-field Ising Model (RFIM). In the case of a two-dimensional (2D) RFIM model with which the (001) projection of structure is represented, the domain size distribution follows a power law with exponential cutoff [11,15,17];

\[ N_d(S_d) \sim S_d^{-\delta} \exp\left(-\frac{S_d}{S_0}\right) \]  (1),

where \( N_d \) is the number of nanodomains having size \( S_d \). The observed nanodomain size distribution could be fitted with the equation (1) with the parameter, the upper cutoff of nanodomain size, \( S_0 = 94.8 \text{ nm}^2 \) as shown as a solid line in figure 3(b). The fitted value of \( \delta \) is estimated to be 0.7, compared with \( \delta = 0.5 \) for 0.80PMN-0.2PT [11] and \( \delta = 1.5 \) for uniaxial relaxor SBN61;Ce [15]. These values of \( \delta \) in relaxor ferroelectrics correspond to the variation of the number of nanodomains with size. The smaller values was pointed out to correspond to slower variation of number of nanodomain with size [11]. On the other hand, X-ray diffuse scattering patterns for NBT was reported [14] to be asymmetric and characterized with the planar (2D) defect platelet (GPZ’s), whereas those for PMN to be symmetric and isotropic [18]. Such different parameter, \( \delta = 0.7, 0.5 \) and 1.5 for NBT (2D), PMN (isotropic), and SBN61;Ce (1D), respectively, which is closely related to the distribution of random fields, may reflect a different distinctive feature of relaxor single crystals [11,15,17]. On the other hand, in oxide perovskite, it has been reported [19] that increasing numbers of oxygen vacancies in perovskites cause a self-ordering into planar structures, which with increasing vacancy concentrations,
grow from an isolated point defect to a linear chain of oxygen vacancies along [101] in the cubic perovskite, resulting in one-dimensional chains whose lengths increase and above a certain vacancy density, in planes equivalent to the [110] plane. On the other hand, the preferential electromigration of oxygen vacancies into sites in planes parallel to the electrodes has also been reported [19]. Such planes seem to be of {001} ones, because of the sample with the rhombohedral (001) plate as a electrode. The different relaxor states for domain-switching and non-switching induced by such cations as Bi$^{3+}$, Na$^{+}$ and Ba$^{2+}$ which have charge and size differences in the A site and oxygen vacancies significantly influence the domain switching, leading to nucleation or clamping effects on domain switching. On the other hand, macroscopic observation of P-E hysteresis loops on the 0.9967NBT-0.0033BT rhombohedral (001) plate exhibits non-switching polarization as shown in figure 4.

![Figure 4](image)

**Figure 4.** Relationships between P vs. E along [001] direction for rhombohedral 0.9967NBT-0.0033BT single crystal (001) plate at 30 °C.

![Figure 5](image)

**Figure 5.** Temperature dependence of (a) real $\varepsilon_r'$ and (b) imaginary parts $\varepsilon_r''$ of complex relative permittivity and (c) reciprocal temperature dependence of relaxational frequency $f$ at 1,10 and 100 kHz along [001] direction in 0.9967NBT-0.0033BT single crystal.

As for the domain walls observed along the [110] and [001] direction at 30 °C, the [110] type domain walls disappeared with heating on going to $T_n$, while the [100] type ones remained in the rhombohedral phase [5]. The [110] type domain walls was reported [6] to vary sensitively with the variation of oxygen pressure at a high oxygen pressure crystal growth, and also the switched spontaneous polarization to increase with increasing oxygen pressure. The temperature dependence of the real $\varepsilon_r'$ and imaginary parts $\varepsilon_r''$ of complex relative permittivity in the 0.9967NBT-0.0033BT (001) plate for different frequencies are shown in figure 5 (a) and 5 (b), respectively.
Dielectric dispersion in audio frequency range appeared clearly at temperatures below the $T_n$ and then its dielectric dispersion disappeared at temperatures above $T_n$. Such dielectric dispersion below $T_n$ in the 0.9967NBT-0.0033BT single crystal was described with Vogel-Fulcher [13] type one with $f=f_0 \exp\{-E_a/(k(T_m-T_f))\}$, where the Boltzmann constant $k$, the Debye frequency $f_0=2.2 \times 10^{10}$ Hz, activation energy $E_a=92$ meV, freezing temperature $T_f=320$ K, as shown in figure 5 (c). Such dielectric dispersion is considered to origin from the domain wall movement based on hierarchical domain structures from μm to nanometer scale. Judging from such phenomena, the isotropization appeared at temperatures above $T_n$ [5] is considered to be due to the domain breaking from macroscopic domain to polar region in nanometer scale due to random fields. Thus, there are little defects in this NBT-BT single crystal [5] relative to other single crystals grown by Bridgman method reported previously [4].

5. Conclusions
Superior piezoresponce image on the 0.9967NBT-0.0033BT rhombohedral (001) plate was observed as well as the poled 0.68PMN-0.32PT rhombohedral (001) plate. This origin is considered to be the random field due to Bi, Na and Ba lattice defects at A-site and oxygen vacancies in ABO$_3$ perovskite. Preferential planes of lattice defects such as {001} and {110} ones play an important role for domain switching mechanisms. The {110} planar defects may play a role as a nucleation sites to lower the activation barrier for domain switching, leading to the polarization rotation from the [111] direction in the rhombohedral phase to the [001] one in the tetragonal phase through the [110] one in the intermediate monoclinic plane under electric fields applied along the [001] direction, whereas oxygen vacancies of planar defects on the {001} and/or {110} plane have the clamping effect of pinning domain wall movement, leading to non-switching polarization.

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References
[1] Gerra G, Tagantsev A K, and Setter N 2005 Phys. Rev. Lett. 94 107602
[2] Bratkovsky A M and Levanyuk A P 2000 Phys. Rev. Lett. 85 4614
[3] Viehland D and Chen Y H 2000 J. Appl. Phys. 88 6696
[4] Ge W, Liu H, Xiangyong Z, Bijun F, Xiaobing L, Feifei W, Di L, and Haosu L 2008 J. Phys. D : Appl. Phys. 41 115403.
[5] Yasuda N, Hashimoto S, Ohwa H, Sakurada O, Fujita K, Yamashita Y, Iwata M, and Ishibashi Y 2009 Jpn. J. Appl. Phys. 48 09KC06
[6] Yamamoto K, Suzuki M, Noguchi Y, and Miyayama M 2008 Jpn. J. Appl. Phys. 47, 7623.
[7] Tanaka K, Kushida K, Torii K, and Miki H 1994 Jpn. J. Appl. Phys. 33 3193
[8] Bdikin I K, Shvartsman V V, and Khoklin A L 2003 Appl. Phys. Lett. 83 4232
[9] Rahman Md M and Yasuda N 2009 Solid State Commun. 149 630
[10] Molotskii M I and Shvebelman M M 2005 Phil. Mag. 85 1637
[11] Shvartsman V V and Khoklin A L 2004 Phys. Rev. B69 014102
[12] Matsushita M, Tachi Y and Ebchizenya K 2001 Abstract American Ceramic Society, 103rd Annual Meeting p.247
[13] Samara G A 2003 J. Phys. Condens. Matt. 15 R367
[14] Kreisel J, Bouvier P, Dkhil B, Thomas P A, Glazer A M, Welberry T R, Chaabane B, and Mezouar M 2003 Phys. Rev. B 68 014113
[15] Kleemann W 2006 J. Mater. Sci., 41 129
[16] Bai F, Li J, and D. Viehland 2005 J. Appl. Phys. 97 054103
[17] Esser J, Nowak U, and Usadel K D 1997 Phys. Rev. B55 5866
[18] Kreisel K, Bouvier P, Dkhil B, Chaabane B, Glazer A M, Thomas P A, and Welberry T R 2004 Ferroelectrics 302 293
[19] Scott J F and Dawber M 2000 Appl. Phys. Lett. 76 3801