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Effects of Oxygen Pressure during Crystal Growth on the Polarization Properties in $Bi_4Ti_3O_{12}$ Single Crystals

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We have investigated the effects of high-oxygen-pressure crystal growth of ferroelectric $Bi_4Ti_3O_{12}$ on the polarization properties along the ***a***(***b***) axis. Domain observations by piezoresponse force microscope demonstrated that a small remanent polarization (P_r) for the crystals grown with 0.02 MPa oxygen pressure is attributed to the clamping of 90° domain walls by oxygen vacancies. The vacancy formation of Bi and O during crystal growth at high temperatures is suppressed at a higher oxygen pressure, leading to a larger P_r of 47 $\mu C/cm^2$ for the crystals grown at 1 MPa oxygen. High-oxygen-pressure sintering is proposed to be effective for obtaining $Bi_4Ti_3O_{12}$-based devices with enhanced polarization properties.

Key words: $Bi_4Ti_3O_{12}$, defect, oxygen vacancy, domain structure, domain pinning

1. INTRODUCTION

Ferroelectric bismuth titanate [$Bi_4Ti_3O_{12}$(BiT)] has been regarded as a promising material for innovative semiconductor-based applications such as nonvolatile memories, electro-optic devices and uncooled infrared detectors because of its high Curie temperature, large spontaneous polarization (P_s), and large electro-optic coefficient. [1-3] The control of polarization states is the underlying basis of these functional devices, and polarization switching is achieved through nucleation of domains and following domain-wall motion by applying an electric field (E). Leakage current arising from defects, however, interferes with the polarization switching of the BiT-based materials. [4-7] In addition, oxygen vacancies are known to act as an obstacle to the polarization switching, [8-10] and a resultant remanent polarization (P_r) is suppressed by the clamping of the domain walls by oxygen vacancies. The leakage current and domain clamping by oxygen vacancies make BiT unsuitable for the practical applications. [11-15] Thus, a guiding principle of defect control is required to be established for obtaining high-quality BiT-based devices with a large P_r as well as a low leakage current.

In this letter, we show that high-oxygen-pressure crystal growth is effective process for obtaining high-quality BiT crystals with a large P_r and low coercive field (E_c) as well as low leakage current. Domain observations by piezoresponse force microscope (PFM) demonstrate that the clamping of 90° domains deteriorates P_r for the crystals grown at 0.02 MPa oxygen, which is suggested to originate from the strong attractive interaction [9,10,16] between 90° domain walls and oxygen vacancies. The vacancy formation of Bi and O during crystal growth at high temperatures is suppressed at a higher oxygen pressure, leading to a larger P_r of 47 $\mu C/cm^2$ and lower E_c of 26 kV/cm for the crystals grown at 1 MPa oxygen.

2. EXPERIMENTAL PROCEDURE

Single crystals of BiT were grown by a self-flux method from the raw powders of Bi_2O_3 (99.9999%) and TiO_2 (99.99%). [15] The crystals were grown in air (Po_2 = 0.02 MPa) and under O_2 gas flow of Po_2 = 0.1 MPa (Po_2 denotes oxygen pressure during crystal growth, hereafter). High oxygen-pressure crystal growth was performed using the pocketed-heat electronic furnace (HPF-1300, Crystal Systems Corp.) at a Po_2 of 1 MPa. The mixed raw materials were soaked at 1200°C for 10 h in Pt crucible, slowly cooled to 1000°C for 40 h, and then furnace cooled to room temperature. Before electrical measurements and domain observations by PFM, the crystals were annealed at 950°C for 10 h in air to reduce strain induced during crystal growth. Synchrotron radiation powder diffraction experiments of the crushed powder of the crystals were performed at 25°C using a large Debye-Scherrer camera with an imaging plate installed at BL02B2 in SPring-8 synchrotron radiation facility. [17] We used high-energy synchrotron radiation (SR) with a wavelength of λ = 0.035639(2) nm (E~35 keV) to reduce absorption by the samples. The BiT crystals under different Po_2 atmosphere had almost the same lattice parameters:

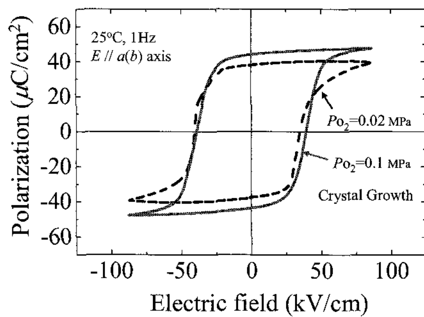


FIG. 1 Polarization hysteresis loops along the ***a*(*b*)**-axis for the BiT crystals grown at a Po_2 of 0.02 and 0.1 MPa.

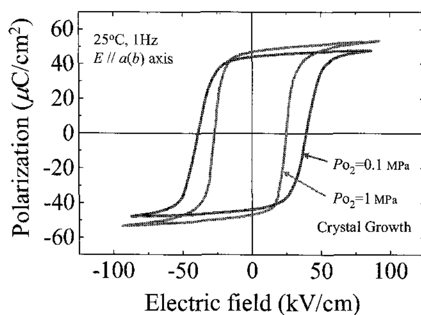


FIG. 2 Polarization hysteresis loops along the ***a*(*b*)**-axis for the BiT crystals grown at a Po_2 of 0.1 and 1 MPa.

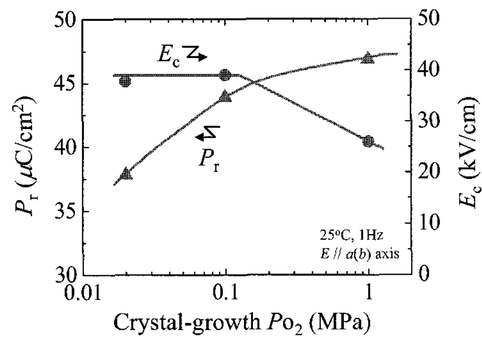


FIG. 3 Remanent polarization (P_r) and coercive field (E_c) as a function of Po_2 during crystal growth (25°C, 1 Hz).

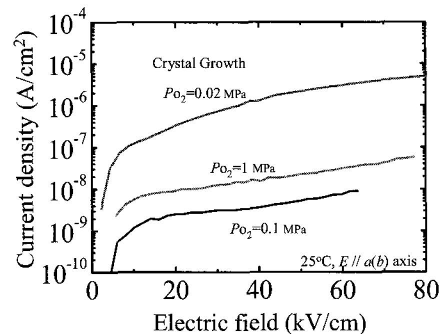


FIG. 4 Leakage current density (J) as a function of E along the ***a*(*b*)**-axis for the BiT crystals (25°C, 1 Hz).

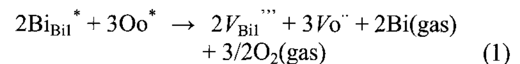
a = 0.54505(5) nm, b = 0.54108(4) nm and c = 3.2834(3) nm. Significant difference in lattice parameters was not detected in our study because the concentration of Bi vacancies and oxygen vacancies is expected to be less than 1%. [13,15] For the domain observations by PFM, the crystals annealed in air were cut along the ***a*(*b*)** axis, and the cut surface (the ***a*(*b*)-*c*** plane) was mechanically polished using alumina powder followed by colloidal silica. Domain structures were observed by a commercial PFM unit (SII SPI3800N). The details are described in Refs. 18 and 19. Since BiT belongs to the monoclinic system with $B1a1$ symmetry, the P_s vector slightly tilts at an angle of ~5° from the ***a*** axis in the ***a-c*** plane. [1,20] Here, we focus our attention on the major P_s component along the ***a*** axis [$P_{s(a)}$] to visualize domain structure because [$P_{s(a)}$] is ten times as large as P_s along the ***c*** axis. [1,18,21]

3. RESULTS AND DISCUSSION

Figure 1 and 2 show the polarization hysteresis loops measured along the ***a*(*b*)** axis (25 °C, 1 Hz). The crystals (Po_2 = 0.02 MPa) exhibited a hysteresis with a P_r of 38 μC/cm² and an E_c of 38 kV/cm. The high-Po_2-grown crystals indicated a larger P_r of 44 μC/cm² (Po_2 = 0.1 MPa) and 47 μC/cm² (Po_2 = 1 MPa). Note that the crystals (Po_2 = 1 MPa) showed a well-saturated polarization hysteresis with an E_c of 26 kV/cm. This E_c value was much lower than those of the other crystals. Figure 3 shows the P_r and E_c as a function of Po_2 during crystal growth. With increasing Po_2, P_r monotonically increased, while the decrease in E_c was marked over Po_2 = 0.1 MPa.

Figure 4 shows the leakage current density (J) as a function of E along the ***a*(*b*)** axis (25 °C). The crystals (Po_2 = 0.02 MPa) indicated a high J of the order of 10^{-7} to 10^{-6} A/cm². The increase in Po_2 to 0.1 MPa led to a drastic decrease in J to the order of 10^{-9} A/cm². The crystals (Po_2 = 1 MPa) exhibited a relatively low J of the order of 10^{-8} A/cm².

Here, we consider the defect formation of BiT at high temperatures. *Ab initio* calculations [15,22] within density functional theory have suggested that vacancy formation energy of Bi1 in the perovskite layers is lower by about 2 eV than that of Bi2 in the Bi_2O_2 layers (Fig. 5). This result indicates that the vacancy formation of Bi proceeds preferentially at the Bi1 site rather than at the Bi2 site. The trigger of defect formation of BiT at high temperatures is suggested to be the formation of Bi1 vacancy (V_{Bi1}'''), which is accompanied by the formation of oxygen vacancy ($V_O^{\cdot\cdot}$) adjacent to Bi1. [22] The vacancy formation of BiT at high temperatures is expressed by



$$2Bi_{Bi1}^{*} + 3O_O^{*} \rightarrow 2V_{Bi1}''' + 3V_O^{\cdot\cdot} + 2Bi(gas) + 3/2O_2(gas) \quad (1)$$

where Bi_{Bi1}^{*} is Bi at the Bi1 site and Oo* denotes oxygen at the O site adjacent to Bi1. This reaction of the vacancy formation [Eq. (1)] has been reported to occur above 1000 °C in air. [15]

It is interesting to note that the weight loss caused by the formation of V_{Bi1}''' and $V_O^{\cdot\cdot}$ at high temperatures are reduced under a higher Po_2 atmosphere. [15] The Po_2

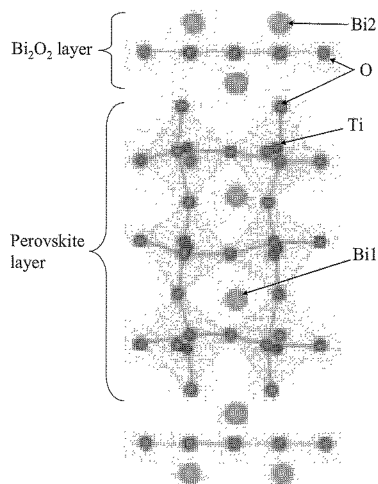
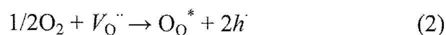


FIG. 5 Crystal structure of BiT crystals.

dependence of weight loss indicates that the limiting factor of the vacancy formation is not diffusion of the vacancies inside the crystals but surface reaction on the crystal surface. The following model of the vacancy formation of BiT is proposed. [22] Two Bi_{Bi1}^* and three O_O^* in the perovskite layers migrate to the surface of BiT crystals but do not react with each other because of the low possibility of Bi_{ad} to meet O_{ad} on the surface due to the low vacancy concentrations, where Bi_{ad} and O_{ad} are adsorbed Bi and O on the surface. At a relatively high Po_2 , Bi_{ad} reacts with O_2 (gas) in the atmosphere promptly and evaporates as Bi_2O_3 (gas). In reducing atmosphere, Bi_{ad} detaches from the surface as Bi (gas). These reactions proceed quickly and do not limit the vacancy formation of Eq. (1). In contrast, O_{ad} has to meet another O_{ad} on the surface to form an O_2 molecule and then diffuses to the atmosphere. The reaction related to O_{ad} that is suppressed at a higher Po_2 is the limiting factor of the vacancy formation. Consequently, a higher-Po_2 atmosphere during crystal growth is effective for synthesizing high-quality BiT crystals with less V_{Bi1}''' and $V_O^{\cdot\cdot}$. [15,22]

During cooling or annealing below 1000°C, in which the vacancy formation does not occur, BiT crystals absorb oxygen from the ambient and the following oxidation reaction produces electron holes ($h^\cdot$)



$$1/2O_2 + V_O^{\cdot\cdot} \rightarrow O_O^* + 2h^\cdot \qquad (2)$$

The carrier of the leakage current at room temperature has been reported to be $h^\cdot$ generated by Eq. (2). [15] As discussed above, the crystals grown under a lower Po_2 have a higher concentration of $V_O^{\cdot\cdot}$, $[V_O^{\cdot\cdot}]$, because the vacancy formation of Eq. (1) is accelerated under a lower Po_2. Thus the crystals (Po_2 = 0.02 MPa) with a higher ($V_O^{\cdot\cdot}$) have a higher ($h^\cdot$), leading to a higher J (see Fig. 4). Although the crystals (Po_2 = 1 MPa) with low $[V_O^{\cdot\cdot}]$ is expected to exhibit a low J, they showed a slightly higher J compared with the crystals (Po_2 = 0.1 MPa). The value of J is determined by two factors: $[V_O^{\cdot\cdot}]$ and the excess oxygen generated by the oxidation reaction [Eq. (2)]. The slightly higher J observed for the crystals (Po_2 = 1 MPa) is probably due to a larger amount of the excess oxygen generated by the annealing

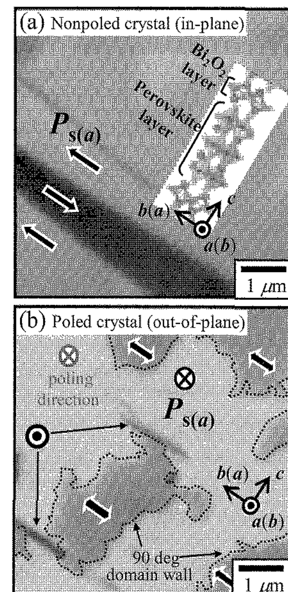


FIG. 6 PFM images of the ***a***(***b***)-***c*** surface of the BiT crystals grown in air (Po_2 =0.02 MPa); (a) in-plane image of the nonpoled (as-annealed) crystal, and (b) out-of-plane image of the poled crystal. The poling was conducted by applying an E of 100 kV/cm along the ***a***(***b***)-axis at 25°C.

at 950°C in air before measurements. The concentration of $h^\cdot$ in crystals (Po_2 = 1 MPa) is slightly larger than in crystals (Po_2 = 0.1 MPa) while $[V_o]$ is smaller than that of $h^\cdot$.

Here, we discuss the mechanism of the domain clamping during the polarization switching along the ***a***(***b***) axis. Figure 6 shows the PFM images observed on the ***a***(***b***)-***c*** surface of the crystals (Po_2 = 0.02 MPa). The in-plane PFM image of the as-annealed crystals (nonpoled crystals) [Fig. 6(a)] exhibits 180° domain walls (DWs) parallel to the ***a***-***b*** plane. After an E of 100 kV/cm was applied along the ***a***(***b***) axis at 25°C, the out-of-plane PFM image of the poled crystals was observed [Fig. 6(b)]. A single domain state was not established for the poled crystals even though the applied E (100 kV/cm) is much higher than the E_c value (38 kV/cm). The domains with $P_{s(a)}$ parallel to the poling direction were found. This experimental fact is a direct evidence that 90° domain switching is achieved by applying an E of 100 kV/cm. Note that unswitched regions, i.e., 90° domains with $P_{s(a)}$ normal to the poling direction remained, and 90° DWs with irregular structure appeared. The irregular-shaped 90° DWs (Ref. 19) have been reported to originate from the attractive interaction [9,10,16] between $V_O^{\cdot\cdot}$ and the electric field established near the 90° DWs due to the discontinuity of the P_s component normal to the DWs. In the domains with $P_{s(a)}$ parallel to the poling direction, a small number of 180° domains with $P_{s(a)}$ antiparallel to the poling direction were observed. These 180° domains are a result of the domain backswitching due to depolarization field. Our PFM observations lead to the conclusion that the clamping of 90° DWs plays a detrimental role in the $P_{s(a)}$ polarization switching in the BiT crystals. The vacancy formation at high temperatures is suppressed under a higher-Po_2 atmosphere, and then $[V_O^{\cdot\cdot}]$ becomes

lower for the crystals grown at a higher Po_2. [15,22] The larger P_r observed for the crystals (Po_2 = 1 MPa) is found to originate from suppressed 90° domain clamping because of a lower [$Vo^{\cdot\cdot}$].

4. CONCLUSION

The effects of Po_2 during crystal growth of BiT on the domain switching behaviors have been investigated through polarization measurements and domain observations by PFM. The crystals grown at a high Po_2 of 1 MPa showed a large P_r of 47 μC/cm^2 and low E_c of 26 kV/cm. PFM observations demonstrate that the clamping of 90° DWs plays a detrimental role in polarization switching, leading to a low P_r. High-Po_2 sintering is proposed to be effective process for suppressing the formation of the vacancies of Bi and O, leading to high-quality BiT-based devices with enhanced polarization-switching properties as well as low leakage current.

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