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Oxygen Diffusion and Nonstoichiometry in $BiFeO_3$

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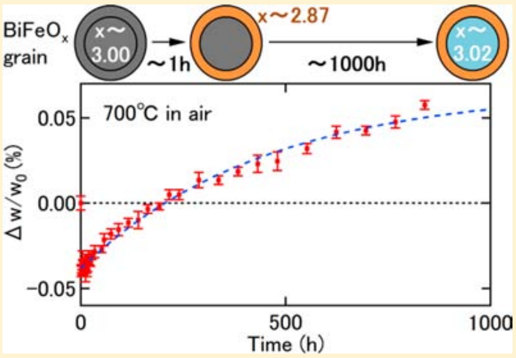
ABSTRACT: Leakage current is a serious problem for the use of ferroelectricity in room-temperature multiferroics $BiFeO_3$, and oxygen nonstoichiometry is considered as one of its principal origins. In order to establish a method to control oxygen content in the compound, we investigated the annealing process of stoichiometric $BiFeO_3$ grains in air and revealed that oxygen diffusion occurs in two steps: (1) the weight of the sample decreases in a short time, which originates from the generation of oxygen deficiency near the surface of the grains; and then (2) it increases gradually and slowly, which originates from oxygen diffusion toward equilibrium in the inner part of the grains, introducing excess oxygen there. Step 1 causes the leakage current, and step 2 tends to cause inhomogeneity of oxygen content as well as the leakage current. Steps 1 and 2 are related to oxygen deficiency and excess oxygen often observed in thin films and bulk crystals, respectively. For the synthesis of homogeneous and highly insulating bulk sample, it is important to avoid these annealing processes, and it is a good way to grow a crystal with stoichiometric oxygen content by the control of atmospheric oxygen partial pressure and taking out its inner part.



I. INTRODUCTION

Although $BiFeO_3$ (BFO) is thought as a promising multiferroic material realized at room temperature, its leakage current has been a serious problem to be solved.[1] BFO has the perovskite structure, and it is well-known that this crystal structure can accommodate both oxygen deficiency and excess oxygen (or cation vacancy), as well-studied for $LaMnO_3$.[2−4] It is believed that such oxygen nonstoichiometry in BFO induces charge carriers and causes the leakage current.[5−8] In thin films, oxygen deficiency is often observed, which is an origin of the leakage current.[7,8] When they are annealed in an oxygen-rich atmosphere, their oxygen content is increased and the leakage current is suppressed.[7,8] In single crystals, on the other hand, excess oxygen is often introduced, which is another origin of the leakage current.[9] When oxygen content in a crystal is decreased by lowering atmospheric oxygen partial pressure during growth, the leakage current is suppressed.[9] The tendency for the oxygen deficiency in the thin films seems to contradict that for the excess oxygen in the bulk crystals.

In order to reduce the leakage current, it is important to understand the oxygen dynamics and to control the oxygen content precisely in BFO. For this purpose the change of the oxygen content by annealing has been studied by various techniques. By thermogravimetry (TG), the composition (weight) change of polycrystalline BFO samples was not detected.[10] By the coulometric titration, oxygen nonstoichiometry was estimated as being $|\Delta x| < 0.01$ for $BiFeO_{3+\Delta x}$ polycrystalline samples.[11] By nuclear resonance backscattering spectrometry, the ratio of oxygen deficiency to stoichiometric oxygen concentrations, $-\Delta x/3$, was estimated as being 11.2% for an as-deposited thin film and as becoming 6.0% after annealing.[12] The values of $|\Delta x|$ for the bulks and the thin films are very different.

In order to provide a clue to the discrepancy in the oxygen nonstoichiometry for the thin films and the bulks, we have studied the weight change of well-characterized samples by annealing, which depends not only on temperature but also on time. Such time-resolved experiments show that oxygen diffusion occurs in two steps, from which the discrepancy between the thin films and the bulks is explained consistently. We will also discuss a procedure to control oxygen content as well as a temperature range in which multiferroic properties are available.

II. EXPERIMENTAL PROCEDURE

Single crystals of BFO were grown by the laser-diode-heated floating zone (LDFZ) method.[13] The oxygen partial pressure was kept at 10 Pa during the growth in the flow of oxygen gas diluted with argon gas. Obtained crystals were almost single-phase with less than 1% of $Bi_{25}FeO_{40}$ (Figure 1a). Their cation and oxygen compositions were nearly stoichiometric, judging from inductively coupled plasma atomic emission spectroscopy (ICP-AES)[9] and the Seebeck coefficient described later in section IVB. After being cleaned carefully, they were pulverized into powder whose grain size was 5−50 μm, in order to make oxygen diffusion fast. When (after) annealed in air where oxygen partial pressure was 20 kPa, the powder was weighed using two methods described below as a function of temperature and time.

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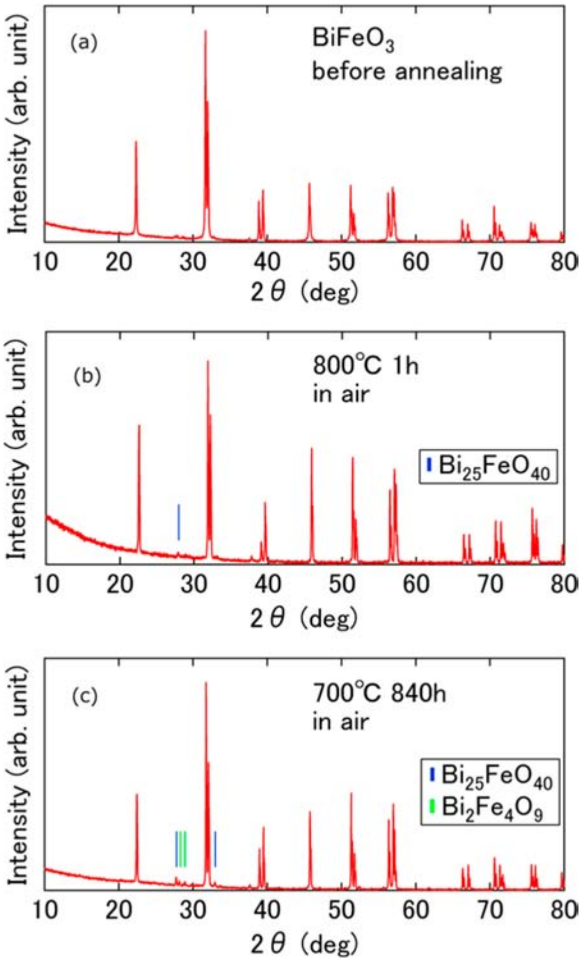

Figure 1. Powder X-ray diffraction patterns of pulverized BiFeO$_3$ crystals (a) before annealing, (b) after annealing at 800 °C for an hour in air, and (c) after annealing at 700 °C for 840 h in air. The impurity phases are highlighted by the colored lines.

A. Method 1. TG. BFO powder (~70 mg) was set on a Pt pan (~200 mg). Alumina powder (~70 mg) set on another Pt pan (~200 mg) was used as a reference. The weight change of the powder sample was measured using TG with temperature sweep at the rate of 10 °C/min. Since the stability of TG was not enough for our purpose, we used this method to confirm the result obtained by method 2. The results obtained by both methods were consistent.

B. Method 2. Quenching Method. BFO powder (~100 mg) on a Pt pan (~150 mg) was set in an alumina crucible with an alumina lid. The crucible with the sample was put in a furnace whose temperature had been stabilized in advance, and the sample was annealed in air. After being kept at predefined temperature for specified time, the sample was quenched to room temperature, and the weight of the sample with the Pt pan was read with an accuracy of 1 μg. The reading was repeated 5 times and averaged. Its error was determined from the maximum and minimum readings. The weight of the sample, w, was obtained by subtracting the weight of the Pt pan from the measured value. Using the weight of the sample before annealing, w_o, we evaluated the weight change $\Delta w = w - w_o$ as well as the weight change ratio $\Delta w/w_o$. Prior to the experiments, we annealed the Pt pan enough in air at 800 °C and confirmed no change in its weight, in order to avoid the increase of its weight by the oxidization of its surface.

Powder X-ray diffraction (XRD) was measured before and after annealing to check the amount of impurity phases. A rotor with a Cu target was used as X-ray source at the output of 40 kV and 100 mA. A linear detector was used.

III. RESULTS

A. Weight Change at Room Temperature. We checked the weight change of the pulverized BFO powder kept at room temperature in air using the same balance as that for the quenching method (method 2). Two-day exposure to the air did not cause weight change, revealing neither the change in oxygen content nor the absorption of moisture or molecules in air.

B. Short-Time Weight Change at High Temperatures. The weight change of the pulverized BFO powder was measured using the quenching method (method 2) after 1-h annealing in air at several temperatures that were increased step by step (Figure 2a). The identical powder sample was used repeatedly throughout this experiment. With increasing the annealing temperature, the weight loss began to appear at 200 °C, increased up to 400 °C, and was nearly saturated at ~0.04% above that temperature. Slight decrease of the weight loss above 600 °C may be due to the long-time weight increase, as will be described in section IIIC.

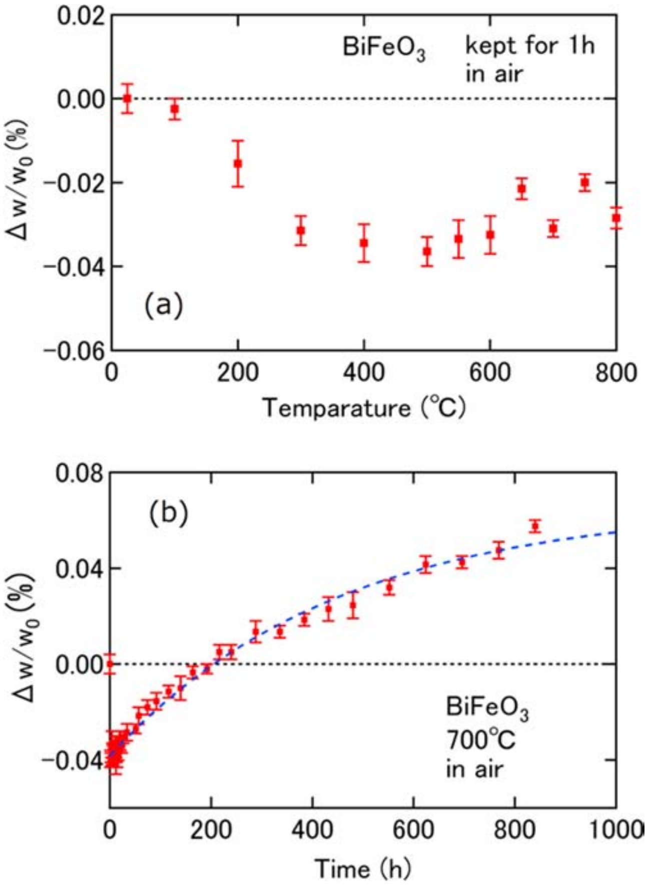

Figure 2. Weight change of pulverized BiFeO$_3$ crystals (a) as a function of temperature, at each of which the sample was kept for an hour in air, and (b) as a function of time, during which the sample was kept at 700 °C in air. The fitted exponential functional form after an hour is plotted by the blue dashed line in part b.

After the annealing no reaction of the sample with the Pt pan was observed, and the sample was still in powder form. The XRD pattern after the annealing at the highest temperature of 800 °C is shown in Figure 1b. The peak of $Bi_{25}FeO_{40}$ that is 2% in intensity is discernible, revealing almost no decomposition during the annealing at 800 °C for 1 h.

For comparison, the weight change of an as-grown BFO bulk crystal with sanded surface was measured using the quenching method (method 2). It was annealed in air at 700 °C for 1 or 3 h. There was no change in its weight in the accuracy of our measurements for each annealing time. After the annealing, its surface became more conducting compared to that before the annealing. From our experiences, annealing in air at a temperature as low as 200 °C makes the surface of the crystals more conducting. If we removed its surface by sanding, it became less conducting again, revealing that the conduction occurs only near the surface.

C. Long-Time Weight Change at High Temperatures. In order to make clear the time scale of the weight change, the long-time weight change of the pulverized BFO powder was measured using the quenching method (method 2) at several temperatures. By the annealing below 600 °C the weight change was very slow after the initial (short-time) weight decrease shown in the section IIIB. By the annealing above 800 °C the weight continued to decrease after the initial weight loss, owing to the evaporation of Bi_2O_3, as will be discussed in section IVA. In addition, by annealing above 850 °C the powder reacted with the Pt pan. In order to make the weight change as fast as possible and to suppress the evaporation of Bi_2O_3 and the reaction with the Pt pan, the detailed study was performed by annealing at 700 °C for various time intervals (Figure 2b). The identical powder sample was used repeatedly throughout this experiment. The weight decreased by ~0.04% within 1 h and then increased gradually and slowly. Even after 800-h annealing, it was not saturated.

After the long-time annealing no notable reaction of the sample with the Pt pan was observed, although the surface of the Pt pan became slightly black. The grains in the powder sample were weakly stuck to each other, which could be easily separated by almost forceless pulverization. There seemed to be no visible change in the grain size, compared with that before the annealing. The XRD pattern after the annealing for 840 h is shown in Figure 1c. The peaks of $Bi_{25}FeO_{40}$ and $Bi_2Fe_4O_9$ that are 4% and 2% in intensity, respectively, are discernible, revealing that the powder was decomposed slightly during the annealing.

IV. DISCUSSION

A. Origin of Weight Change. The two-step weight change was observed, namely, the weight loss within 1 h and then the gradual weight gain persisting for longer than 800 h. We will discuss four possible origins for such successive weight change. (1) The first is evaporation of Bi_2O_3. The weight continues to decrease above 800 °C, which is attributed to the evaporation of Bi_2O_3. It is well-known that Bi_2O_3 evaporates severely above ~800 °C,[14] as is observed during the crystal growth of BFO. In the long-time weight gain at 700 °C, there is no tendency of weight loss even after the annealing for 800 h, and therefore, the effect of the evaporation of Bi_2O_3 seems negligible. The short-time weight loss is not likely due to the evaporation of Bi_2O_3, since it terminates within 1 h and occurs at temperatures as low as 200 °C. (2) The second origin is evaporation or combustion of contaminant. Since the crystals were cleaned before the pulverization and there was almost no impurity phase in the as-grown crystals from the XRD pattern, no effect of contaminant is expected. Since the weight of the pulverized powder did not change at room temperature, there was no absorption of moisture or molecules. Thus, contaminant is not an origin. (3) The third origin is decomposition of the sample. A small amount of impurity phases were created by decomposition during annealing. However, the intensity of their peaks in the XRD pattern is less than 4% of the maximum intensity of BFO peaks, which would not explain the weight change ratio $\Delta w/w_o$ of as large as ~0.1%. The detail of the numerical evaluation will be discussed later in section IVB. (4) The fourth origin is absorption and desorption of oxygen. As many papers report the absorption and the desorption of oxygen by annealing BFO thin films,[7,8,12] the weight change for the pulverized BFO powder is most likely due to the same reason. It is natural to assume that two types of oxygen diffusion occur successively, judging from the two-step weight change.

We speculate that the first step weight loss is due to the desorption of oxygen near the surface of the grains, since it occurs at temperatures as low as 200 °C and is completed in a very short time, less than an hour. Such a process near the surface is very likely, since the annealing conditions for the thin films, e.g., annealing at 390 °C for an hour,[8,15] are close to that for the first step weight loss. More conducting behavior only near the surface of the bulk crystal after annealing and less conducting behavior after sanding its surface also support our speculation. Since the surface area of the bulk crystal is much smaller than that of a powder sample with the same weight, the weight change of the former would be undetectable. We note that the existence of an oxygen deficient layer is reported near the surface of thin films as well.[16] From these results, it is indicated that the surface state of BFO stable at high temperatures is oxygen-deficient.

The exponential time dependence of the weight change as in the second step is often observed for the oxygen diffusion in oxide samples,[17,18] whose detail will be discussed in the section IVB. We speculate that oxygen absorption into the inner bulk part of the grains occurs, since the time scale of this step is much longer than that of the first one. By annealing in the air (at the oxygen partial pressure of 20 kPa), the stoichiometric crystals grown at the oxygen partial pressure of 10 Pa would absorb oxygen toward equilibrium, which would be observed as weight gain.

The surface of the grains in our experiments, which was originally the inner part of the bulk crystal and newly appeared after the pulverization, is considered as being stoichiometric and different from the surface stable at high temperatures with the oxygen deficiency. In other words, reliable experiments became possible using such stoichiometric and homogeneous powder. A powder sample prepared by the reaction at high temperature contains oxygen deficiency near the surface of the grains from the beginning and does not show the short-time weight loss.

B. Semiquantitative Estimation of Oxygen Content. We semiquantitatively estimate the distribution of the oxygen content in the grains to understand the oxygen dynamics, although thus obtained numerical values may not be so accurate due to the lack of precise knowledge on the variation of the grain size in the powder sample and the mechanism of the oxygen diffusion.

The weight gain in the second step for longer than an hour is well-approximated by an exponential function

$$\Delta w/w_0 = 0.066 \pm 0.005 - (0.105 \pm 0.005) \exp[-t/(450 \pm 40)]\ (\%)$$

where t is the annealing time in hours. This functional form is plotted by blue dashed curve in Figure 2b. From this form we can evaluate the amount of the weight change for each step. For the first step, the weight loss, which occurs in an hour, is evaluated from the initial value of the weight gain in the second step and calculated to be

$$|\Delta w/w_0|_{t=0} = |(0.066 \pm 0.005) - (0.105 \pm 0.005)| = 0.039 \pm 0.007\ (\%)$$

which is consistent with the weight loss shown in Figure 1a. For the second step the weight gain is

$$0.105 \pm 0.005(\%)$$

The time constant of the second step, τ, is 450 ± 40 h, and therefore, a few thousands of hours are necessary to diffuse oxygen deep into the grains homogeneously. The exponential weight change as in the second step is often observed in other oxides accompanied by oxygen diffusion.[17,18] Although it is difficult to evaluate the diffusion constant D precisely in our case because of the wide distribution of the grain size, a rough estimate shows

$$D \sim L^2/\tau \sim 10^{-12}\ (\mathrm{cm}^2/\mathrm{s})$$

where L is the dimension of the grains. We took it as 10 μm, because the majority of the grains have the dimension of 5−20 μm and the contribution of the larger grains (up to 50 μm) to the weight change is small due to the longer diffusion time. This diffusion constant is 5−6 orders of magnitude smaller than that of cuprates,[17,18] and therefore, we need very long time for annealing BFO.

Here we evaluate the oxygen content of the inner part of the grains after the second step annealing. The absolute value of the room temperature Seebeck coefficient of the crystals grown at the oxygen partial pressure of 10 Pa is as large as ~1000 μV/K, and its sign changes from sample to sample, indicating their low carrier density and good oxygen stoichiometry. Therefore, we assume that the oxygen content x of the as-grown BiFeO_x crystals is 3.00. Although we have not accomplished the second step annealing, we assume that the exponential functional form is valid until the weight change is saturated. After the saturation it is natural to assume that the oxygen content is homogeneous in the inner part of the grains. The weight gain of 0.105% in the second step corresponds to the increase of the oxygen content $\Delta x = 0.02$ and the final x of 3.02. Thus, the obtained Δx is comparable to $|\Delta x| < 0.01$ determined by the coulometric titration.[11] This evaluation indicates that the BFO crystals grown in air also have the oxygen content x of 3.02. Such nonstoichiometry in the oxygen content would be one of the reasons why the leakage current is serious in the bulk samples synthesized in air. Thus, the obtained x in the inner part of the grains is not affected within the hundredth digit by the oxygen deficiency near the surface, which will be estimated in the next paragraph. An impurity phase $\mathrm{Bi}_{25}\mathrm{FeO}_{40}$ (~4% in intensity), which is created after the long-time annealing and has excess oxygen, does not affect the evaluation of x within the same accuracy, either. Another impurity phase $\mathrm{Bi}_2\mathrm{Fe}_4\mathrm{O}_9$ is stoichiometric, which does not affect the evaluation above at all. We may need a small correction of Δx by considering the effect of small amount of the larger grains with larger diffusion time constants, which will not be considered here.

We estimate the oxygen content and the thickness of the outer part (surface layer) of the grains where the oxygen deficiency appears after the short-time annealing. We assume that both of the oxygen diffusion time constants for the outer and the inner parts of the grains are the same and that the oxygen deficiency in the outer part is homogeneous. According to the diffusion equation, the diffusion time is proportional to the square of the sample dimension.[17] Using this proportionality relation and assuming that the diameter of the grains is 10 μm and the diffusion time of the inner part is 2000 h, we roughly estimate that the thickness of the surface layer is ~0.1 μm from the diffusion time of less than 1 h near the surface. From these dimensions, the volume ratio of the inner to the outer parts is ~17. Since the weight loss in the first step is 0.039%, the decrease of the oxygen content in the outer part is estimated as $\Delta x \sim -0.13$, and the oxygen content there is $x \sim 2.87$. The amount of the oxygen deficiency of the surface layer is comparable to that of the oxygen-deficient thin films.[12] The estimated thickness of the surface layer is also comparable to that of the oxygen-deficient surface layer of thin films (~100 nm).[16] The two-step process on the absorption and the desorption of oxygen discussed above is schematically summarized in Figure 3.

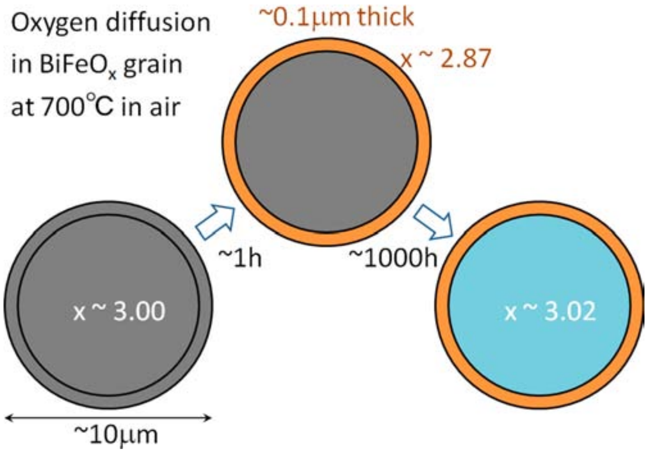

Figure 3. Schematic of the oxygen diffusion in a BiFeO_3 grain of the size of ~10 μm kept at 700 °C in air. The two-step desorption and absorption of oxygen are shown.

From the two-step oxygen diffusion, the tendencies that the oxygen deficiency appears in the thin films and that the excess oxygen does in the bulk samples are understandable. In the former, the film thickness is typically less than 1 μm, and the contribution of the outer part is large; therefore, the effect of the oxygen deficiency is dominant. In the latter, on the other hand, the volume ratio of the inner to the outer parts is large, and the effect of the excess oxygen is dominant.

C. Conditions for Synthesis, Crystal Growth, Annealing, and Usage of BFO. Although annealing is necessary to reduce the excess oxygen and the leakage current in the inner part, the oxygen diffusion is very slow, and it takes thousands of hours even for the 10-μm grains. Therefore, the annealing of the powder samples is not realistic, and the annealing of the single crystals with much larger dimensions is almost impossible. Incomplete annealing causes inhomogeneous nonstoichiometry and leakage current. Even if we could anneal the inner part of the grains in the powder samples homogeneously and suppress the leakage current there, the outer part is oxygen-deficient, which is another origin of the leakage current. Hence, the annealing of the powder sample at any conditions is not effective to reduce the leakage current so much. In order not to use the annealing procedure, the growth of the crystals with stoichiometric oxygen content in well-controlled oxygen partial pressure[9] is reasonable. When we take out the inner part of the crystal boule, it is homogeneous and stoichiometric.

Judging from the physical properties of BFO, i.e., the ferroelectric and the antiferromagnetic transition temperatures of 830 and 370 °C, respectively,[1] one may expect the usage of the multiferroic properties of BFO to be equal to or below 370 °C. However, the leakage current hinders the usage above 200 °C due to the oxygen deficiency created near the surface of the samples. We have to limit the usage temperature of BFO below 200 °C.

V. CONCLUSIONS

In order to investigate oxygen dynamics in BFO crystals, we annealed stoichiometric and homogeneous $BiFeO_x$ ($x \sim 3.00$) grains of the size of ~10 μm in air and measured their weight change accompanying the absorption and the desorption of oxygen. We have succeeded in separating the oxygen dynamics in the outer and the inner parts of the grains. In the outer part (surface layer) with the thickness of ~0.1 μm, oxygen deficiency of $\Delta x \sim -0.13$ in average is stabilized within an hour, which seems similar to the oxygen deficiency in the thin films. In the inner part, on the other hand, excess oxygen of $\Delta x \sim 0.02$ is induced after thousands of hours, which corresponds to the excess oxygen observed in the bulk samples.

Polycrystalline samples are not appropriate for the use of ferroelectricity in BFO, since the oxygen deficiency and the leakage current are induced near the surface of the grains by the synthesis or the annealing. Instead, the usage of the inner part of single crystal boule grown at the atmospheric oxygen partial pressure of 10 Pa without annealing is reasonable. The usage of the multiferroic properties is limited below 200 °C.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Catalan, G.; Scott, J. F. *Adv. Mater.* **2009**, *21*, 2463.

(2) Töpfer, J.; Goodenough, J. B. *J. Solid State Chem.* **1997**, *130*, 117.

(3) Kuo, J. H.; Anderson, H. U.; Sparlin, D. M. *J. Solid State Chem.* **1989**, *83*, 52.

(4) Mizusaki, J.; Mori, N.; Takai, H.; Yonemura, Y.; Minamiue, H.; Tagawa, H.; Dokiya, M.; Inaba, H.; Naraya, K.; Sasamoto, T.; Hashimoto, T. *Solid State Ionics* **2000**, *129*, 163.

(5) Wang, Y. P.; Zhou, L.; Zhang, M. F.; Chen, X. Y.; Liu, J.-M.; Liu, Z. G. *Appl. Phys. Lett.* **2004**, *84*, 1731.

(6) Chen, F.; Zhang, Q. F.; Li, J. H.; Qi, Y. J.; Lu, C. J.; Chen, X. B.; Ren, X. M.; Zhao, Y. *Appl. Phys. Lett.* **2006**, *89*, 092910.

(7) Go, H.; Wakiya, N.; Funakubo, H.; Satoh, K.; Kondo, M.; Cross, J. S.; Maruyama, K.; Mizutani, N.; Shinozaki, K. *Jpn. J. Appl. Phys.* **2007**, *46*, 3491.

(8) Yang, H.; Jain, M.; Suvorova, N. A.; Zhou, H.; Luo, H. M.; Feldmann, D. M.; Dowden, P. C.; DePaula, R. F.; Foltyn, S. R.; Jia, Q. X. *Appl. Phys. Lett.* **2007**, *91*, 072911.

(9) Ito, T.; Ushiyama, T.; Yanagisawa, Y.; Kumai, R.; Tomioka, Y. *Cryst. Growth Des.* **2011**, *11*, 5139.

(10) Lebeugle, D.; Colson, D.; Forget, A.; Viret, M.; Bonville, P.; Marucco, J. F.; Fusil, S. *Phys. Rev. B* **2007**, *76*, 024116.

(11) Li, M.; MacManus-Driscoll, J. L. *Appl. Phys. Lett.* **2005**, *87*, 252510.

(12) Yang, H.; Wang, Y. Q.; Wang, H.; Jia, Q. X. *Appl. Phys. Lett.* **2010**, *96*, 012909.

(13) Ito, T.; Ushiyama, T.; Yanagisawa, Y.; Tomioka, Y.; Shindo, I.; Yanase, A. *J. Cryst. Growth* **2012**, *363*, 264.

(14) Ilin, V. K. *Zh. Neorg. Khim.* **1976**, *21*, 1645.

(15) Wang, J.; Neaton, J. B.; Zheng, H.; Nagarajan, V.; Ogale, S. B.; Liu, B.; Viehland, D.; Vaithyanathan, V.; Schlom, D. G.; Waghmare, U. V.; Spaldin, N. A.; Rabe, K. M.; Wuttig, M.; Ramesh, R. *Science* **2003**, *299*, 1719.

(16) Yuan, G. L.; Martin, L. W.; Ramesh, R.; Uedono, A. *Appl. Phys. Lett.* **2009**, *95*, 012904.

(17) Kishio, K.; Suzuki, K.; Hasegawa, T.; Yamamoto, T.; Kitazawa, K. *J. Solid State Chem.* **1989**, *82*, 192.

(18) Idemoto, Y.; Fueki, K.; Sugiyama, M. *J. Solid State Chem.* **1991**, *92*, 489.