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Large Electric-Field Induced Strain in $BiFeO_3$ Ceramics

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Large bipolar strain of up to 0.36% (peak-to-peak value) was measured in $BiFeO_3$ ceramics at low frequency (0.1 Hz) and large amplitude (140 kV/cm) of the driving field. This strain is comparable to that achievable in highly efficient morphotropic phase boundary (MPB) Pb-based perovskite ceramics, such as $Pb(Zr,Ti)O_3$ and $Pb(Mg,Nb)O_3$–$PbTiO_3$. The strain showed a strong dependence on the field frequency, and is probably largely associated with domain switching involving predominantly non-180° domain walls. In addition, application of an electric field of low frequency rearranges the defects, which act as pinning centers for the domain walls. The resulting depinning of the domain walls leads to a more efficient switching and, consequently, to an increased response. The large strain reported here suggests that the domain-wall motion in $BiFeO_3$ may be as large as in classical lead-based ferroelectrics. We hope that this finding might further stimulate the search of new lead-free MPB compositions based on $BiFeO_3$.

I. Introduction

Bismuth ferrite ($BiFeO_3$) has recently been a subject of intensive research, driven primarily by its ability to exhibit both ferroelectric and antiferromagnetic ordering.[1,2] Significant efforts have been put particularly in understanding of how to manipulate magnetic ordering by applying electric field (magnetoelectric coupling). As this coupling requires ferroelastic rather than ferroelectric domain reversal,[3] the switching of ferroelectric-ferroelastic 71° and 109° domains in this rhombohedral structure, which is accompanied by strain in the material, has been of particular interest.[4–6] Strain–electric-field relationship in epitaxial $BiFeO_3$ thin films has been recently reported by Zeches *et al.*[7] and Zhang *et al.*[8] Bipolar strain as large as 5% was measured at fields of >1000 kV/cm and was associated with phase transformation (motion of the interphase boundary). On the other hand, maximum strain of 0.2% was reported in a $BiFeO_3$ film prepared using a chemical method.[9] Even smaller strain was found in $BiFeO_3$ ceramics (0.07%), which was, however, measured at 60 kV/cm, i.e., well below the coercive field of 100 kV/cm.[10] Application of large fields in bulk ceramics of $BiFeO_3$ is challenging, especially at low frequencies, due to the high conductivity often observed in this material. As bipolar strain larger than presently reported can be expected in $BiFeO_3$ ceramics, further studies on the strain versus electric-field relationship are needed.

Recently, we have succeeded in obtaining $BiFeO_3$ ceramics with sufficiently low DC conductivity to apply large electric fields at low frequencies.[10] Using the method given in Ref. 11, we estimate the DC conductivity in our samples to be about 10^{-7} to 10^{-8} $(Ohm\text{-}m)^{-1}$. Exploiting this opportunity, herein, we report a large electric-field induced strain in $BiFeO_3$ ceramics. A tentative explanation is proposed for its origin.

II. Experimental Procedure

$BiFeO_3$ ceramics were prepared by sintering a mechanochemically activated Bi_2O_3–Fe_2O_3 powder mixture at 760°C for 6 h. The synthesis procedure is described elsewhere.[10] X-ray diffraction analysis (X'Pert Pro diffractometer; PANalytical B.V., Almelo, the Netherlands) of the ceramics showed phase-pure $BiFeO_3$; however, a small amount of secondary phases, i.e., $Bi_{25}FeO_{39}$ and $Bi_2Fe_4O_9$, was detected using scanning electron microscopy (SEM JSM-7600F; JEOL Ltd., Tokyo, Japan). The concentration of these phases, as estimated from an SEM image,[12] was around 3% (in area fraction). The relative geometrical density of the pellets was 93% and the grain size, which was determined from an SEM image of a thermally etched sample[13] was 1.8 ± 0.9 μm.

For the electrical measurements, the sintered pellets were thinned to approximately 0.2 mm, polished, and electroded with Cr/Au by sputtering. Strain and polarization measurements were done simultaneously using an aixACT TF 2000 analyzer (aixACT Systems GmbH, Aachen, Germany) equipped with a laser interferometer (aixPES). The samples were measured in a "single loop mode", i.e., single period sinusoidal electric-field waveforms of defined frequency and amplitude were applied. At each frequency, the polarization state of the sample was preset by a first cycle (not shown), followed by the second cycle that is shown here. Measurements were made using the autorange function. During the measurements, the samples were immersed in silicone oil. Strain–electric-field curves were plotted by taking the initial strain to be zero.

III. Results and Discussion

Strain–electric-field hysteresis loop of $BiFeO_3$ ceramics obtained by applying a single period of the sinusoidal field of amplitude 140 kV/cm at 0.1 Hz is shown in Fig. 1. Distinct features of a typical "butterfly"-shaped hysteresis loop of a sample with preset polarization can be observed: after an initial decrease, the strain reaches a minimum at the coercive field of around 90 kV/cm, then makes a steep increase until maximum field and, finally, decreases again to a remanent value as the field is released; same trend is repeated for the field cycle of negative polarity. In analogy with other ferroelectric materials, this behavior is commonly linked to switching and movement of domain walls by electric field, particularly of the non-180° domain walls, which may

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involve a significant change in the dimensions of the grains in the ceramics.[14–17] The absence of a more linear part in the strain–field relationship at large electric field of both positive and negative polarity, such as observed, for example, in Pb $(Zr,Ti)O_3$ (PZT),[15,18] suggests that strain is not saturated, and switching is probably not completed even at 140 kV/cm. Experimentally, dielectric breakdown was typically observed above this field.

The most remarkable feature of the hysteresis loop in Fig. 1 is large peak-to-peak strain (difference between maximum and minimum strain), which reaches 0.36%. This value is comparable to the bipolar strain achieved in most known Pb-based perovskite ceramics, such as PZT[15,17–19] and Pb $(Mg,Nb)O_3$–$PbTiO_3$(PMN–PT),[20,21] as well as in lead-free $(Na_{0.5}Bi_{0.5})TiO_3$–$BaTiO_3$–$(K,Na)NbO_3$.[22] In addition, the ratio between peak-to-peak strain and electric-field amplitude in our ceramics (0.36% at 140 kV/cm) is comparable to that obtained in epitaxial $BiFeO_3$ thin films (5% at 1500 kV/cm) reported in Ref. 8. In the following, we limit our discussion to domain reversal as the most probable origin of the measured strain; however, due to large electric field applied, a possibility of electrically driven phase transition, like the one recently demonstrated between tetragonal-like and rhombohedral polymorphs in $BiFeO_3$ epitaxial films,[23] should not be excluded.

It should be stressed that the strain-field curves, similar in the shape and amplitude to the one shown in Fig. 1, were observed on several samples, which were processed in different ways, e.g., directly sintered without calcination or sintered after calcination, and containing different amounts (1–5%) of secondary phases ($Bi_{25}FeO_{39}$ and $Bi_2Fe_4O_9$). Thus, the large strain is little influenced by minor amount of impurity phases, and is probably related intrinsically to $BiFeO_3$.

To explore the origin of the large strain in more detail, the displacement of the sample was measured by applying an electric field of amplitude 120 kV/cm at different frequencies. The strain-field curves measured at 100, 10, 1, and 0.1 Hz are shown in Fig. 2. Strong frequency dependence is evident, both in the magnitude and qualitative aspect of the response. At the driving field of 100 Hz, the sample did not show any measurable displacement up to 100 kV/cm. After an increase of strain to 0.045% above this threshold field, a strong restoring force is observed upon releasing the field, evidenced by zero remanent strain. Note that this behavior is in striking contrast to the response at 0.1 Hz showed in Fig. 1.

At 10 Hz, similar behavior to the one at 100 Hz is observed (Fig. 2); the main difference is the higher peak-to-peak strain, which is 0.08% at 10 Hz compared to 0.05% at 100 Hz. A more opened, but still asymmetric, curve is observed at 1 Hz with larger peak-to-peak strain of 0.16%. Finally, an open and a more symmetric loop is observed at the lowest measuring frequency of 0.1 Hz, which also gave the largest strain (0.21%). We can infer from these results that application of electric field of low frequency enables more efficient switching of domains in $BiFeO_3$ and, consequently, larger strain response. It therefore appears important to prepare $BiFeO_3$ ceramics that may sustain electric field of both large amplitude and low frequency to obtain the large strain response. In the following, based on our experimental results and observations from the literature, a tentative explanation is given for the large strain.

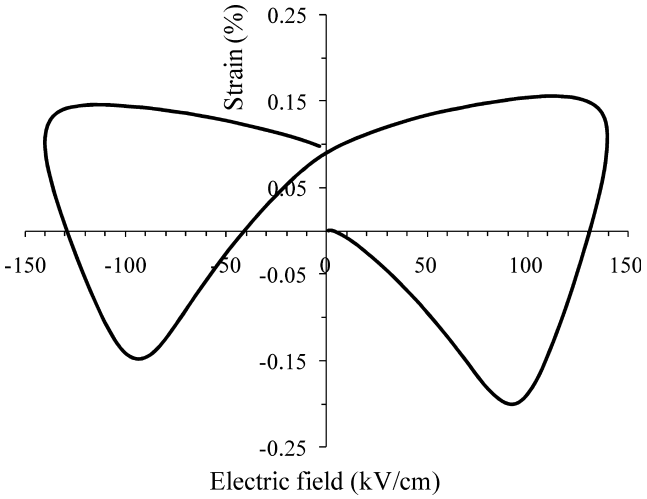

Fig. 1. Strain–electric-field hysteresis loop of $BiFeO_3$ measured at 0.1 Hz and electric field amplitude of 140 kV/cm.

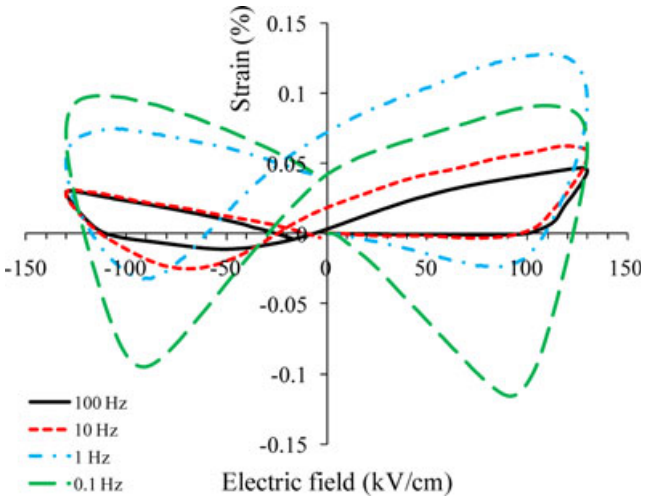

Fig. 2. (Color online) Strain–electric-field hysteresis loops of $BiFeO_3$ measured at different frequencies and electric field amplitude of 130 kV/cm.

Frequency dependence of strain, like the one shown in Fig. 2 for $BiFeO_3$, was also observed in other perovskites, e.g., PZT,[19] PMN–PT,[20] and $Pb(Zn,Nb)O_3$–$PbTiO_3$ (PZN–PT).[24] In PZT ceramics[19] and single crystals of rhombohedral PZN–PT,[24] such frequency dependence was interpreted as being a consequence of a two-stage non-180° domain switching mechanism. A qualitative model was given in Ref. 19 and experimental confirmation in PZN-PT single crystals, using *in-situ* neutron diffraction analysis, is described in Ref. 24. According to this mechanism, polarization reversal occurs via an intermediate state characterized by large amount of non-180° domains, which then switch for a second time to fully reverse the polarization by 180°. Slow movement of these non-180° domain walls was directly related to the strong frequency dependence of macroscopic strain in PZN–PT, i.e., electric field of low frequency kinetically allows a more efficient switching of these low-mobile domain walls, resulting in larger strain.[24] The same mechanism has also been evidenced by other groups in PZT[25] and La-modified PZT ceramics.[26] Slow movement of non-180° domain walls, which is not necessarily related to intermediate switching, has been discussed in Refs. 15 and 27; it was proposed that the frequency dependence has origin in the strain that the material needs to accommodate during ferroelastic reorientation of domains.

Already in 1990, Kubel and Schmid[28] have predicted that 180° polarization reversal in $BiFeO_3$ is energetically less favorable than reversal by 71° and 109°, because the last two reversals require smaller ion displacements. This finding goes in favor with a switching mechanism via non-180° domains, as discussed above. The multistep switching mechanism was also confirmed by Baek *et al.*[6] using phase-field simulation and was recently demonstrated to be the origin of fatigue in $BiFeO_3$ thin fims.[29] Finally, the difficulty of 180° switching

was observed experimentally during poling of a $BiFeO_3$ single crystal.[30] Thus, according to observations in the literature, there is a high probability that the large strain observed here in $BiFeO_3$ ceramics at low frequencies (Fig. 1) and the associated characteristic frequency dependence (Fig. 2) are related to switching of predominantly non-180° domains (71° and 109° in rhombohedral system).

Another aspect of the strain response of $BiFeO_3$, which behaves as a "hard" ferroelectric material,[10] is the interaction of domain walls with defects. Movement and switching of domain walls in "hard" ferroelectrics, which are strongly restricted due to pinning of the walls by defects, can be facilitated by exposing the material to, e.g., continuous electric-field cycling.[31] We presented evidence of such a depinning mechanism in $BiFeO_3$ ceramics in our previous study, where it was shown that the mobility of the domain walls can be increased considerably by electric-field cycling, during which the charged defects rearrange, effectively releasing domain walls.[10] Cycling experiments in that study were performed at 50 Hz; however, it is reasonable to assume that a more efficient depinning could result in application of a lower frequency field. To verify this hypothesis, we compare two polarization–electric-field hysteresis loops taken at 100 Hz and 120 kV/cm: (i) before (full-line curve in Fig. 3) and (ii) after (dashed-line curve in Fig. 3) applying to the $BiFeO_3$ sample, three single sinusoidal waveforms with the frequency of 10, 1, and 0.1 Hz (in sequence) and amplitude of 120 kV/cm. The pinched-like shape and internal bias of the loop in Fig. 3 (full-line curve) are macroscopic manifestations of the domain-wall pinning by defects.[10] After first experiencing a field of lower frequency, the sample exhibited larger maximum polarization and more than two times larger remanent polarization (dashed-line curve in Fig. 3); the hysteresis loop is now depinched and more open. In agreement with the polarization data, a larger response was also observed in the strain (not shown). The results from Fig. 3 are therefore consistent with the assumption of a domain-wall depinning effect upon application of low-frequency field. Similar depinning by repeated switching was also observed in $BiFeO_3$ thin films.[32]

We note that polarization loops taken at frequencies of 10, 1, and 0.1 Hz showed substantial "lossy" behavior and were not analyzed further. From this point of view, in electrically lossy materials strain–electric-field measurements can give more information on the switching process than polarization loop measurements.

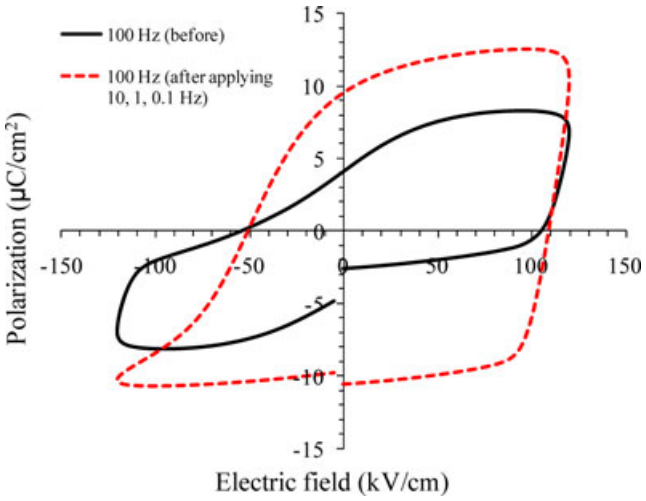

Fig. 3. (Color online) Polarization–electric-field hysteresis loops of $BiFeO_3$ measured at 100 Hz and electric field amplitude of 120 kV/cm: (i) before (full-line curve) and (ii) after applying sinusoidal waveforms of the same amplitude, but lower frequency, i.e., 10, 1, and 0.1 Hz (dashed-line curve).

IV. Summary

In summary, large strain induced by electric field was measured in $BiFeO_3$ ceramics at low frequency (0.1 Hz) and large field amplitude (140 kV/cm). Considerable dependence of the strain on the frequency of the applied field and remanent strain suggest a possible role of non-180° domain switching mechanism. In addition, domain-wall depinning, realized by applying low field frequency, leads to a more efficient switching of domains and therefore to an increased response. The measured strain, which is comparable to that achieved in Pb-based ceramics with MPB compositions, demonstrates that the contribution of domain-wall movement to the electromechanical response of $BiFeO_3$ may indeed be large. We believe that this finding might be useful in the current search of new lead-free piezoelectric compositions, as it suggests that large extrinsic contributions to the electromechanical response might also be expected in $BiFeO_3$-based MPB systems.

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