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Domain switching contribution to piezoelectric response in BaTiO₃ single crystals

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Piezoelectric responses of barium titanate single crystals are investigated along the [720] and [111] directions, respectively, in order to verify the ultrahigh piezoelectric constant (2000 pC/N) reported in a previous study [Appl. Phys. Lett. 86, 012905 (2005)]. The results suggest that electric-field-induced strain can be largely enhanced by the domain switching in barium titanate single crystal along the [720] direction; however, the piezoelectric response under small field measurement has not been enhanced as much as expected because domain switching is a nonlinear and irreversible process. © 2008 American Institute of Physics. [DOI: 10.1063/1.3025842]

Due to their superior piezoelectric response, ferroelectric single crystals have attracted much attention for applications in sensors, actuators, and transducers.1 The origins of the piezoelectric response in these materials are attributed to intrinsic contribution by lattice and extrinsic one, i.e., domain wall movement. Accordingly, excellent properties would be expected by increasing the intrinsic or extrinsic contributions. To enhance intrinsic piezoelectricity, two ways usually are adopted: (1) one way is enhancing the intrinsic piezoelectric response by chemical modification (composition, dopant, etc.). Although many researchers have implemented a lot of experiments, a large enhancement in piezoelectric properties has hitherto not been obtained. (2) The other is making use of the anisotropy of the ferroelectric single crystals as a function of the crystallographic orientation. This method now is widely recognized as the “domain engineering technique.” Piezoelectric properties of many single crystals can be dramatically enhanced, especially for relaxor-based ferroelectric single crystals, such as Pb(Zn₁₋ₓNbₓ)O₃–PbTiO₃ and Pb(Mg₁/₃Nb₂/₃)O₃–PbTiO₃ (PMN-PT) single crystals, whose d₃₃ along the [001] direction is much larger than that along the [111] spontaneous polarization direction.2,3

In domain engineering technique, nevertheless, the enhancement in piezoelectric properties is still restricted by intrinsic piezoelectric response of single domain. That means that we cannot expect a dramatic increase in d₃₃ in barium titanate (BT) single crystals, as in PMN-PT single crystals. On the other hand, in order to replace lead-based piezoelectric materials, equivalent piezoelectric performance of lead-free piezoelectric materials is expected. Consequently, many researchers want to enhance the piezoelectric properties by increasing the extrinsic contributions. Recently, Wada and co-workers reported an enhancement in piezoelectric properties in BT single crystal by decreasing the domain sizes (explained as 90° domain wall contributions to piezoelectric property of BT single crystal).4,5 However, this enhancement was still not enough to fulfill application requirement. At the same time, an ultrahigh piezoelectric constant of about 2000 pC/N was obtained in a [720] oriented BT single crystal.6 Although a tentative model based on the switching of 90° domain wall was proposed by Liu et al.,7 a sufficient explanation is still expected. Thus it seems necessary to identify the ultrahigh piezoelectric response along the [720] direction in BT single crystals and clarify the mechanism governing this phenomenon.

In this letter, commercial BT single crystals were cut into small plates (5 × 5 × 1 mm³), with the main surface (5 × 5 mm²) perpendicular to the [111] and [720] directions, respectively. Silver electrodes were coated fully on the main surface. In the following experiments, samples were poled prior to measurement by the application of 1000 V/mm for 10 min at room temperature (25 °C). Strain versus electric field measurement was implemented combining an optical probe system (MTI-2000 photonic sensor) and a power system amplified by Trek 610D. A triangular electric field up to 1000 V/mm was applied at low frequency (0.1 Hz). The dc bias field dependence of the d₃₃ coefficient was measured by the Berlincourt-type quasistatic method described in detail in Refs. 8 and 9. The amplitude and frequency of the applied force were about 0.5 N and 110 Hz, respectively. An important difference between this and some commercially available instruments is that a dc bias field generated by a high voltage source (SRS 350, Stanford Research System) was applied to the sample and a protective circuit was also placed between the source and lock-in amplifier (7280 DSP, Signal Recovery of Advanced Measurement Technology, Inc.), which was used to measure the generated piezoelectric charge.

Figure 1 shows strain-field loop of BT single crystals along the [720] and [111] directions, respectively. The strain-field loop along the [111] direction is unhysteretic and quite linear in the whole electric field range, while the strain-field loop along the [720] direction is hysteretic, which opens at point A (about zero electric field) and closes at point D (about 850 V/mm). This loop at the high field portion “DE” is linear. The strain along the [720] direction (about 0.148%) is approximately nine times that along the [111] direction (about 0.0178 %) at the same electric field (1000 V/mm). In order to exclude the randomness in this measurement, strain-field loops were repeated at least ten times and still similar results were obtained.

Explanation of those strain-field loops is based on the schematic shown in Fig. 2. BT single crystal at room temperature is in tetragonal symmetry, and thus the spontaneous

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polarizations are along the [001] direction or equivalent directions. After poling along the [111] direction, domains only along the [100], [010], or [001] direction are kept. Thus domains can rotate among those three equivalent directions when the field is applied along the [111] direction, but the contribution to the strain along the [111] direction is not yet changed. Therefore the electric-field-induced strain is essentially intrinsic in nature for BT single crystal along the [111] direction, resulting in the linearity of the S-E loop, which is a typical characteristic of the engineering domain configuration.\textsuperscript{7} In contrast, the case along the [720] direction is totally different from that along the [111] direction. In Fig. 2(b), we only consider the domains along the [100] and [010] directions since the domain along [001] have splitted into the [100] or [010] direction after poling. Both domains A and B exist to minimize the depolarization energy at zero electric field, as analyzed by Liu et al.\textsuperscript{7} Due to the different angles between the domain and field, domain B could be transferred into domain A in order to minimize the electrical energy when the field is applied along the [720] direction. This transfer indeed is a 90° domain switching corresponding to the hysteresis response portion between points A and D in Fig. 1. Usually domain switching results in a hysteresis behavior. When the electric field is large enough, all of domain B would transfer into domain A. In this case, further increase in the electric field would only enhance the strain by the intrinsic piezoelectric response through domain A, as depicted by \( DE \) in Fig. 1.

In order to verify whether domain wall movements or domain switching can enhance the piezoelectric response as much as electric-field-induced strain or not, dc bias field dependences of piezoelectric constant \( d_{33} \) along the [720] and [111] directions were determined, respectively. In Fig. 3, compared with the calculated result in Ref. 7 (\( d_{33} \) was larger than 700 pC/N), a quite small piezoelectric constant is observed upon any bias field. With increasing the bias field, \( d_{33} \) along the [111] direction increased by almost 10%, while \( d_{33} \) along the [720] direction was suppressed drastically from 230 to 155 pC/N, followed by an evident hysteresis loop. In order to understand this phenomenon we resort to the phenomenological theory. According to the Landau theory, domains with spontaneous polarizations of the [100] and [010] directions are two minimum states of free energy and there is a barrier between them, which means that a small electric field cannot immediately switch the polarization.\textsuperscript{10} From theoretical calculation, as shown in Fig. 4, it is clear that the barrier is reduced by increasing the field along the [720] direction but does not vanish until the field approaches a certain level (1.8 kV/mm theoretically). Therefore, domain switching cannot contribute to piezoelectric response, as discussed in Ref. 7, where domain switching was analyzed only from minimizing the total free energy (competition between external electric field and internal depolarization field) but not considering the barrier between these two minimum states.

Admittedly, the actual process of domain switching cannot be entirely described by the Landau theory since domain switching is actually a nucleation and growth process. Ignoring strain energy, the conditions described in Ref. 7 and analyzed by the Landau theory are two limiting cases. The former one does not consider the barrier, whereas the latter one maximizes the effect of the barrier. Domain switching can enhance the piezoelectric response even at small test signal although not as large as discussed in Ref. 7. There are two evidences: (1) it is shown in Fig. 3 that the piezoelectric coefficient \( d_{33} \) along the [720] direction is larger than that along the [111] direction at zero electric field, which can be attributed to domain switching, since intrinsic piezoelectric constant \( d_{33} \) along the [111] direction is larger than that along the [720] direction no matter whether the single domain is with spontaneous polarization of the [100], [001], or [010]
(2) $d_{33}$ along the [720] direction is decreased by increasing bias field, which suggests that there are some extrinsic contributions (domain wall movements or domain switching) at zero bias field and these domain wall movements and domain switching are clamped by increasing the bias field. Compared with section “BC” in Fig. 1, however, this contribution is very small. Because domain switching is an irreversible and nonlinear process, it is responsible for section BC. Note that $d_{33}$ along the [111] direction is increased slightly by increasing the bias field, since the intrinsc piezoelectric response along the [111] direction is increased with increasing bias field (upon bias field from 0 to 3 kV/mm theoretically) and the poling effect can enhance the piezoelectric response through increasing the bias field. Because even the poling field is strong enough, there are still some $180^\circ$ domains to reduce the free energy and those $180^\circ$ domains will be reversed under bias field.

As demonstrated above, domain switching can largely enhance the electric-field-induced strain without using an external force or internal point defects. However, the piezoelectric response under small field measurement is not enhanced by domain switching as much as Ref. 7 analyzed. We believe that the ultrahigh piezoelectric response recently reported in a [720] cut BT single crystal cannot be attributed to domain switching. Also, this ultrahigh response cannot be considered as a general characteristic of BT single crystal along the [720] direction. On the other hand, as shown in Figs. 1 and 3, domain switching enlarges the nonlinear behavior of piezoelectric response although it indeed enhances the piezoelectric response.

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