Large electric-field-induced strain in ferroelectric crystals by point-defect-mediated reversible domain switching

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Ferroelectric crystals are characterized by their asymmetric or polar structures. In an electric field, ions undergo asymmetric displacement and result in a small change in crystal dimension, which is proportional to the applied field[1,2]. Such electric-field-induced strain (or piezoelectricity) has found extensive applications in actuators and sensors[2]. However, the effect is generally very small and thus limits its usefulness. Here I show that with a different mechanism, an aged $BaTiO_3$ single crystal can generate a large recoverable nonlinear strain of 0.75% at a low field of 200 V mm^{-1}. At the same field this value is about 40 times higher than piezoelectric Pb(Zr, Ti)O$_3$ (PZT) ceramics and more than 10 times higher than the high-strain Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ (PZN-PT) single crystals[3–5]. This large electro-strain stems from an unusual reversible domain switching (most importantly the switching of non-180° domains) in which the restoring force is provided by a general symmetry-conforming property of point defects. This mechanism provides a general method to achieve large electro-strain effect in a wide range of ferroelectric systems and the effect may lead to novel applications in ultra-large stroke and nonlinear actuators.

A ferroelectric (non-centric) crystal normally exhibits a beautiful pattern of domains as a result of a symmetry-lowering transition from a paraelectric (centrosymmetric) phase[6]. Each domain corresponds to one of several symmetry-allowed equivalent orientation states of the non-centric or polar structure. The polarization direction may differ by 180° or non-180° in different domains, and one domain state can be switched into another state by the electric field. Accompanying non-180° domain switching is a huge strain due to the exchange of non-equal crystallographic axes[7]. Such strain may be one or two orders of magnitude larger than the small linear piezoelectric strain.

Unfortunately, such potentially large electro-strain due to domain switching is an irrecoverable or one-time effect. This is due to the fact that different domain/polarization states are energetically identical; thus there is no driving force to re-establish the initial domain state, and consequently the initial macroscopic shape after the removal of the field. Therefore, this inherent irreversibility in domain switching makes the potentially large electro-strain effect futile. It has been reported that with the use of suitable external 'bias stress' to drive the sample back to its
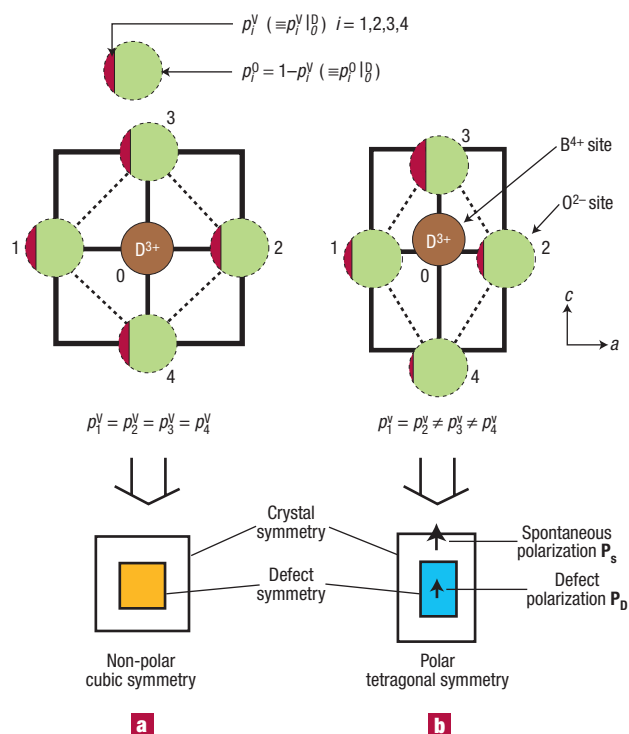

Figure 1 Symmetry-conforming property of point defects. a, Non-polar/centrosymmetric cubic paraelectric state, and **b**, polar tetragonal ferroelectric state. Here, a typical ABO$_3$ (BaTiO$_3$) perovskite structure is considered, which contains an O^{2-} vacancy and an acceptor impurity D^{3+} occupying a B^{4+} site. For simplicity, only the (100) plane of the structure is shown (that is, viewing the structure from the b-axis) and thus the two O^{2-} sites above/below D^{3+} (which are always equivalent to site 1 and 2) are not shown; also A^{2+} ions are not shown. The probability $p_i^V|_0^D$ and $p_i^O|_0^D$ refer to the conditional probability of finding an O^{2-} vacancy and O^{2-} ion at site i (i = 1,2,3,4), respectively, when an impurity ion D^{3+} occupies site O. They are thus related to the short-range order parameter of these point defects. Below each structure is the symbolic representation of its crystal symmetry (large square or rectangle) and equilibrium defect symmetry (small square and rectangle), respectively. In Fig. 1b, the large and small arrows represent respectively the spontaneous polarization **P$_s$** associated with the polar tetragonal crystal symmetry, and the defect polarization **P$_D$** associated with the non-centric distribution of charged point defects.
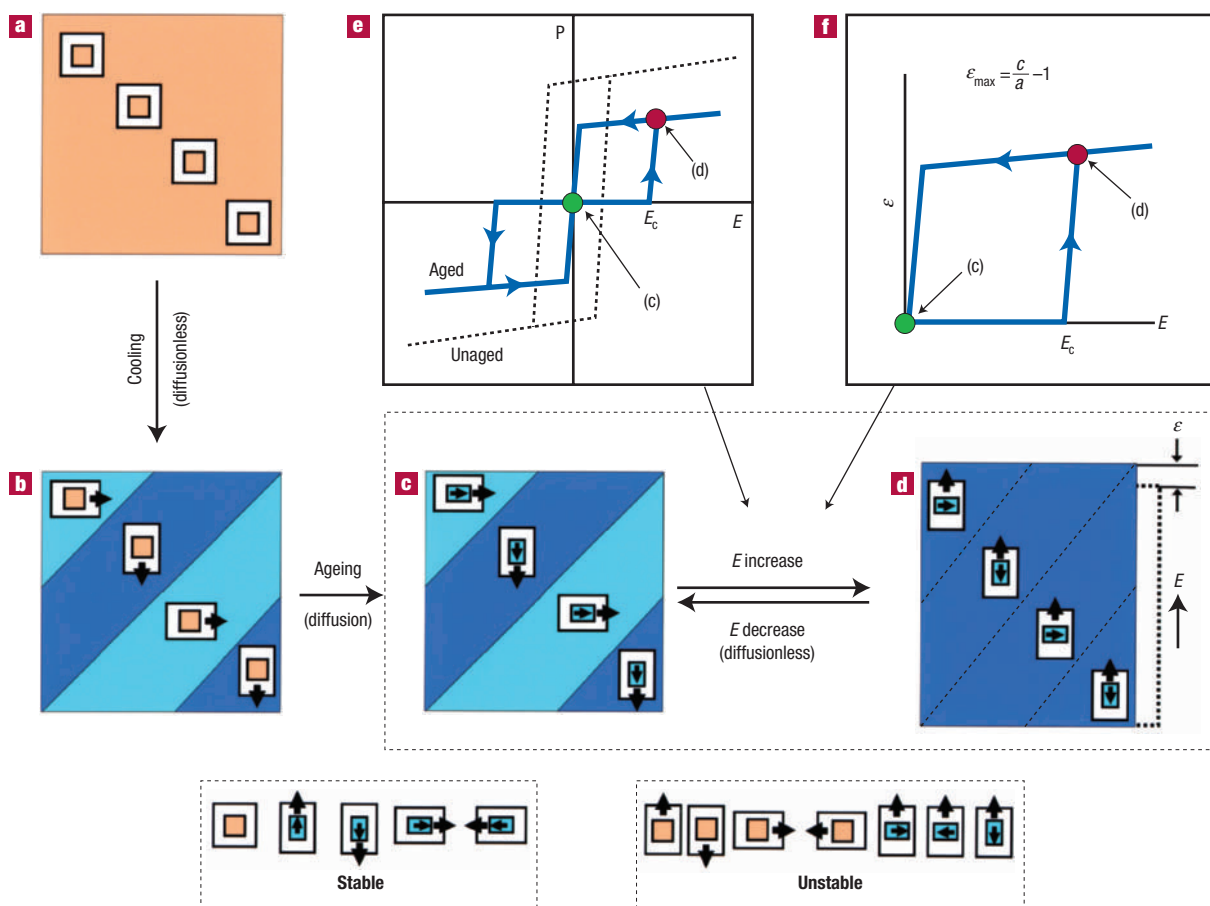
Figure 2 Mechanism of large electro-strain effect by reversible domain switching in aged ferroelectrics due to the symmetry-conforming property of point defects. **a**, Equilibrium cubic paraelectric crystal. **b**, Multi-domain tetragonal ferroelectric crystal immediately after the cubic-to-tetragonal transition, in which defects are unstable. **c**, Stable state after ageing (diffusion) in the ferroelectric state, in which defect symmetry follows crystal symmetry in every domain. **d**, Unstable state after domain switching from **c** by electric field E. **e**, Double hysteresis loop (P–E curve) during reversible domain switching between **c** and **d**, which contrasts the normal hysteresis loop (dotted loop). **f**, Huge recoverable strain (ε–E curve) during reversible domain switching between **c** and **d**. See Fig. 1 for definitions of the squares, rectangles and arrows. Stable states are those where the defect symmetry matches the crystal symmetry; unstable states are those where they do not match.

original shape, a single crystal of $BaTiO_3$ can generate an essentially recoverable electro-strain up to 0.7–0.8% under bipolar field cycling conditions[8]. Although this method shows potential for certain specific applications, it may be restricted by its requirement for suitable bias stress and for bipolar power sources.

Here I report a mechanism that generates an 'intrinsic' restoring force to make domain switching reversible, and consequently large recoverable electro-strain can be achieved without using external force and a bipolar electric field. This method comes from a mechanism[9,10] to realize reversible domain switching in another class of physically parallel material system, the ferroelastics or martensites, which also have switchable domains (by stress) but without involving a spontaneous polarization as ferroelectrics do. It has been known for decades that after ageing, ferroelastics/martensites exhibit a curious rubber-like elasticity[11–14] in the otherwise plastic ferroelastic state. A unified theory has been proposed[9,10] based on a symmetry-conforming property of point defects. As this property is general[10], we expect it also applies to ferroelectrics and provide a mechanism to realize reversible domain switching.

Figure 1 explains the symmetry property of point defects (dopant/impurity ions and vacancies) in ferroelectrics, exemplified in a typical perovskite ABO_3 ($BaTiO_3$) structure; but the picture will be qualitatively the same for other ferroelectrics because only the symmetry is of concern here. Assume that the crystal contains O^{2-} vacancies and D^{3+} acceptor impurity ions occupying B^{4+} sites, as such a combination of defects satisfies the requirement for charge neutrality. Now we consider the symmetry of the statistical distribution of O^{2-} vacancies around a defect ion D^{3+}. In the cubic paraelectric phase (Fig. 1a), there is an equal probability of finding an O^{2-} vacancy in the neighbouring sites (1,2,3,4) of the defect D^{3+} because these sites are equivalent to the defect D^{3+} at site 0. Thus the symmetry of the defect probability about D^{3+} is cubic, following the cubic crystal symmetry of the paraelectric phase. In the ferroelectric phase (Fig. 1b), the polar tetragonal symmetry makes the sites 1,2,3,4 no longer equivalent with respect to the defect D^{3+} (site 1 and 2 are equivalent but 3 and 4 are not). It is natural that equivalent sites should have the same defect probability (O^{2-} vacancy) and non-equivalent sites should have unequal defect probability; thus it follows that the defect probabilities (see Fig. 1 for definition) should be $p_1^V = p_2^V \neq p_3^V \neq p_4^V$, following the polar tetragonal symmetry of the lattice when in equilibrium. Therefore, the symmetry of short-range order distribution of point defects tends to follow the crystal symmetry when in equilibrium. This is the symmetry-
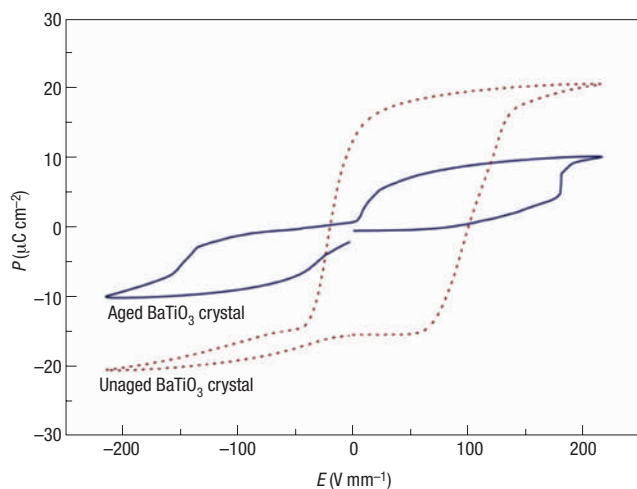
Figure 3 Double hysteresis loop (*P–E* curve) of an aged BaTiO₃ single crystal, in comparison with the normal bistable hysteresis loop (dotted line) of the unaged crystal of the same sample. Hysteresis loop measurement was done at room temperature along the [001] pseudo-cubic direction with a 10 ms period for both cases.

Figure 4 Large recoverable electric field induced strain (*ε*) in an aged BaTiO₃ single crystal along the [001] pseudo-cubic direction, in comparison with the piezoelectric effect of soft PZT ceramics and PZN-PT single crystals. The displacement measurement set-up is shown in the inset; which used an optical displacement sensor (non-contact) to measure the strain from the free upper electrode in order to exclude the possible constraint/clamping effect. The mono-polar measurement was done at room temperature with a 10 ms period and repeated several times.

conforming property of point defects, being the same as the ferroelastic/martensite case[9,10]. Nevertheless, as the ferroelectric phase has polar crystal symmetry, the equilibrium defect symmetry is also non-centric ($p_3^V \neq p_4^V$) as shown in Fig. 1b. This non-centric distribution of charged defects (the O^{2-} vacancy has positive effective charge and D^{3+} has negative effective charge) forms a defect dipole moment $\mathbf{P}_D$ along the polarization direction $\mathbf{P}_s$, as shown in Fig. 1b. The equilibrium defect dipole moment is so arranged because between the two asymmetrical sites 3 and 4, the positively charged O^{2-} vacancy tends to occupy site 3, as it is closer to the negatively charged D^{3+} impurity. It can be proved that similar defect symmetry and the associated defect dipole moment can also be formed with other defect combinations involving vacancies and hetero-valence impurities/dopants on either an A-site or B-site if equilibrium can be attained; thus it is a general property of ferroelectric crystals containing point defects. The symmetry-conforming property of point defects can be simply represented by the symbolic representation below each structure in Fig. 1. In the following we shall use the symbolic representations to discuss the defect-mediated electro-strain effect. It should be noted here that electron paramagnetic resonance (EPR) experiments[15,16] and theoretical modelling[17,18] suggest that defect dipoles tend to align along the spontaneous polarization direction (as shown in Fig. 1b), being consistent with the symmetry-conforming property of point defects.

Now I show that it is this symmetry-conforming property of point defects and associated defect dipole moment that provide a restoring force for reversible domain switching and consequently a large recoverable electro-strain. Consider a macroscopic crystal of equilibrium cubic paraelectric phase (Fig. 2a), which has a cubic symmetry of point-defect distribution (defect symmetry in short) everywhere according to the symmetry-conforming property. When cooled down below Curie temperature T_c, it transforms into a multi-domain tetragonal ferroelectric phase (Fig. 2b). This abrupt lowering of crystal symmetry, however, does not alter defect configuration, as the transition is diffusionless and does not involve any exchange of ions. As the result, the polar tetragonal ferroelectric phase inherits a cubic defect-symmetry immediately after the transition, as shown in Fig. 2b.
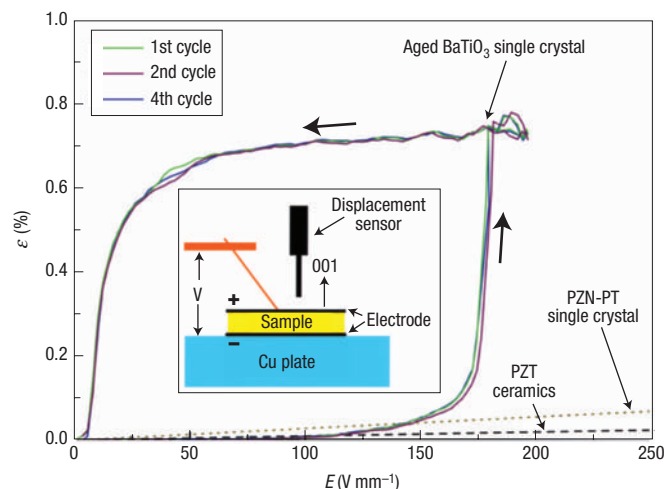
However, the fresh or 'unaged' ferroelectric phase (Fig. 2b) is not a stable state, because the defect symmetry (cubic) does not match the crystal symmetry (polar tetragonal). If defect/vacancy migration is allowed, cubic defect symmetry will be corrected into a polar tetragonal one, which follows the crystal symmetry (Fig. 2c). Such a process involves a short-range migration of ions/vacancies (in the present case the migration of O^{2-} vacancy from site 4 to site 3 in Fig. 1b), and thus requires some time (called ageing) to complete. After ageing, the defect symmetry in each domain follows the polar tetragonal crystal symmetry, and exhibits a defect dipole moment following the polarization direction of the residing domain, as shown in Fig. 2c. Now every domain is in its stable state. When such stable domains are switched by an electric field, domain switching occurs abruptly (without diffusion) with spontaneous polarization following the field direction, and in the meantime the 90° switching of domains generates a large strain (Fig. 2d). However, the defect symmetry and defect dipole moment cannot be rotated in such a diffusionless process. Therefore, this unswitchable defect symmetry, and the associated defect dipole moment, provide a restoring force or a reverse internal field favouring a reverse domain switching when electric field is removed (Fig. 2d to Fig. 2c). As a consequence, the original domain pattern is restored so that the defect symmetry and dipole moment follow those of the crystal symmetry in every domain. Two important macroscopic effects are expected to accompany this reversible domain switching. First, a double hysteresis loop in the polarization–electric field (*P–E*) relation for aged samples (Fig. 2e), as a result of the restoration of the initial multi-domain pattern (which has zero macroscopic/averaged polarization) when the electric field is back to zero. Such an effect contrasts with the normal bistable hysteresis loop (dotted loop) for the unaged sample. Besides, as the aged state (Fig. 2c) is a stable state compared with the unaged state (Fig. 2b), it is more resistive to the change of domain state; thus has higher coercive field E_c, as shown in Fig. 2e.

As the most important consequence of the reversible domain switching, a large recoverable nonlinear strain is expected in aged

samples (Fig. 2f) even under monopolar field cycles, primarily due to the reversible switching of 90° domains. The nonlinearity and hysteresis in strain–electric field (ε–E) curve is due to the nonlinear and hysteretic (that is, requiring nucleation) nature of domain switching. The maximum possible strain can be easily calculated to be (c/a)–1 (where c and a are the length of c and a axes, respectively, of the tetragonal ferroelectric phase) for a complete switching from the a-domain to c-domain state for tetragonal ferroelectrics. An ideal value is about 1% for BaTiO$_3$ and about 6% for PbTiO$_3$ at room temperature.

As a test of the above predictions, we performed experiments on a single crystal of BaTiO$_3$, which naturally contains a small amount of Fe^{3+} impurities (0.02 at%) and O^{2-} vacancies (through charge compensation). The sample was cooled through the Curie temperature (128 °C) to form a fine pattern of 90° and 180° domains, and then aged at 80 °C (ferroelectric state) for five days to make the defect symmetry follow crystal symmetry (Fig. 2c). After ageing, the P–E hysteresis loop shows an interesting double hysteresis (Fig. 3), contrasting the normal hysteresis loop (dotted loop) for the unaged state of the same sample. Besides, the coercive field is much higher than that of the unaged sample and increases with increasing ageing time (Supplementary Information, see Fig. S1), as expected in Fig. 2e. In situ optical microscopy observations on an aged sample showed that there was no perceptible change in the domain pattern after a P–E measurement cycle; this suggests the initial domain pattern is recovered, as expected in Fig. 2c, d.

Most interestingly, besides the double hysteresis, the aged BaTiO$_3$ shows a huge recoverable electro-strain of 0.75% at a low field of 200 V mm^{-1} even under mono-polar cycles (Fig. 4) and without any external recovering bias force, as expected in Fig. 2f. This nonlinear recoverable strain, originating from defect-mediated reversible domain switching shown in Fig. 2c,d, is more than 40 times larger than the best PZT ceramics and over 10 times higher than the high-strain PZN-PT single crystal[3], when compared at the same field. Compared with the linear piezoelectric response, the electro-strain effect due to domain switching is highly nonlinear and hysteretic, and shows a digit-like jump in strain at a critical field. Such a nonlinear on/off feature may be ideal for certain applications that require large displacement at a threshold voltage. Further work should be done on the stability of the effect against load and cycling, although Fig. 4 shows perfect recovery in a few cycles.

Over the past decades there have been quite a number of reports on strange double hysteresis in doped or irradiated ferroelectrics after ageing[19–21]. Such a phenomenon has been considered to relate to certain point defects or defect dipoles[19–21], but a general microscopic mechanism is still lacking. The symmetry-conforming property of point defects shown in Figs 1 and 2 provides a simple and general microscopic explanation to such curious phenomena. More importantly, it unifies the explanation for ageing and reversible domain-switching effect in both ferroelectrics and physically parallel ferroelastics/martensites[14].

In summary, the reversible domain-switching mechanism proposed here provides a general method to realize a large electro-strain effect in a wide range of ferroelectrics with non-180° domains, and the aged BaTiO$_3$ reported here is just one example. Figure S2 of the Supplementary Information shows the large electro-strain effect is also achieved in K-doped BaTiO$_3$. Such a large nonlinear electro-strain effect may lead to applications in novel actuators. Also importantly, this effect is realized in a Pb-free ferroelectric (BaTiO$_3$); which has the implication that this method may generate a wide range of environmentally friendly materials with high electro-strain effect.

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Competing financial interests
The author declares that he has no competing financial interests.

Here additional experimental data on large and reversible electro-strain effect in BaTiO$_3$ single crystals are presented. These data will provide additional information about the effect and its generality.

Fig. S1 shows the aging time dependence of the electro-strain behavior for BaTiO$_3$ (naturally doped with 0.02at%Fe, the same sample as in Fig. 3 and 4). It is clear the behavior is strongly dependent on aging time (but saturates at long aging time). For unaged sample there is no shape recovery after removing electric field. Shape recovery becomes more and more complete with increasing aging time. The coercive field (marked by arrows) also increases with increasing aging time, suggesting the increase of domain stabilization with prolonged aging. The point-defect mediated reversible domain-switching mechanism shown in Fig.2 of the paper expects that reversible domain switching

can be achieved only after aging in ferroelectric state (Fig.2c). Consequently, it is natural to expect that there is an aging-time dependence of the electro-strain behavior. Fig. S1 confirms such dependence. The aging time dependence stems from the short-range diffusion/migration of vacancies to follow the crystal symmetry. This behavior is also similar to the aging behavior of metallic martensite, suggesting the existence of a common governing mechanism (Ref.14).

Fig. S2 shows the point-defect mediated recoverable electro-strain effect is also found in a lightly K-doped BaTiO$_3$ single crystal after room-temperature ageing for 2 months. The fact that large recoverable electro-strain is achieved in a different sample (K-doped BaTiO$_3$) indicates the effect is a general one and such effect is expected to exist in a wide range of ferroelectrics.
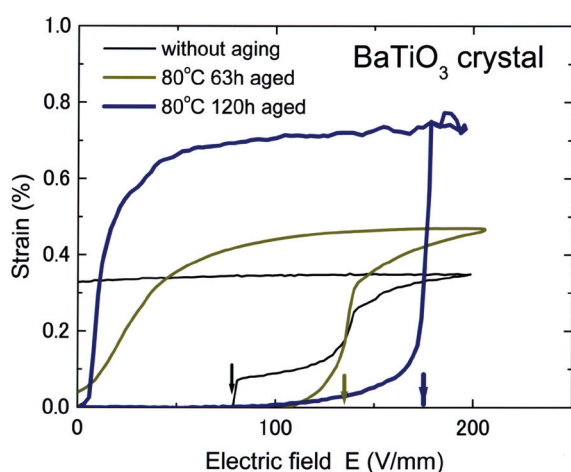

Fig. S1
Aging time dependence of electro-strain behavior of a BaTiO$_3$ single crystal. Note the increase of critical field with aging time and improvement of electro-strain recoverability.
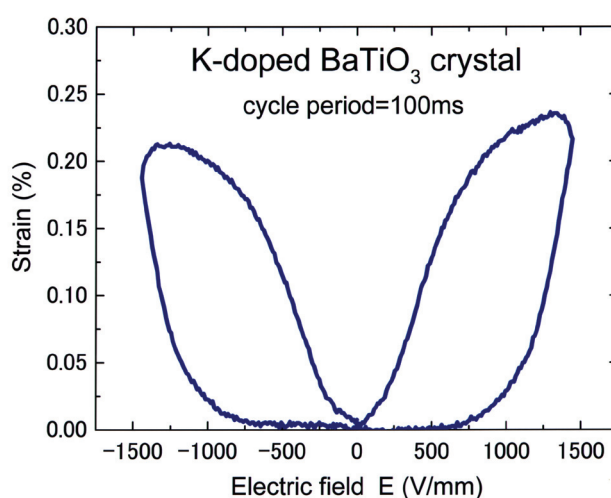

Fig. S2
Recoverable large electro-strain for a lightly K-doped BaTiO$_3$ single crystal after room-temperature ageing for 2 months.