Giant elastic tunability in strained BiFeO$_3$ near an electrically induced phase transition

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Elastic anomalies are signatures of phase transitions in condensed matters and have traditionally been studied using various techniques spanning from neutron scattering to static mechanical testing. Here, using band-excitation elastic/piezoresponse spectroscopy, we probed sub-MHz elastic dynamics of a tip bias-induced rhombohedral – tetragonal phase transition of strained (001)-BiFeO$_3$ (rhombohedral) ferroelectric thin films from $\sim 10^3$ nm$^3$ sample volumes. Near this transition, we observed that the Young's modulus intrinsically softens by over 30% coinciding with two- to three-fold enhancement of local piezoresponse. Coupled with phase-field modelling, we also addressed the influence of polarization switching and mesoscopic structural heterogeneities (for example, domain walls) on the kinetics of this phase transition, thereby providing fresh insights into the morphotropic phase boundary in ferroelectrics. Furthermore, the giant electrically tunable elastic stiffness and corresponding electromechanical properties observed here suggest potential applications of BiFeO$_3$ in next-generation frequency-agile electroacoustic devices, based on the utilization of the soft modes underlying successive ferroelectric phase transitions.
Ferroelectrics underpin a vast spectrum of modern technologies, including ultrasonic transducers, precision actuators, nonvolatile memories, to name a few. Pivotal to the continued development of ferroelectrics is a deep understanding of their structural – dynamics relationship, which is conventionally separated into lattice and domain structure levels. The intrinsic lattice contribution has long been centred on the concept of morphotropic phase boundary (MPB), which describes the degeneracy/coexistence of, classically, rhombohedral (R) and tetragonal (T) phases across structural transitions driven by composition, temperature, applied electric (E-) field, epitaxial strain and pressure. This MPB picture has been substantially refined over last two decades through the discoveries of monoclinic bridge phases12,13 and associated polarization (P) rotation mechanism14. At the domain level, extrinsic structural dynamics takes place via domain wall motions and contribute to many of the ferroelectric properties15,16. Recent studies have also revealed that monoclinic phases can be stabilized under local stress/electric fields generated by complex domain structures in BaTiO3 and KNbO3 (refs 6,17), thus blurring the boundary of such structural hierarchy.

Scattering techniques based on X-ray/neutron and electron probes are capable of resolving subtleties in crystal structure and lattice dynamics near the MPBs and allow in situ tracking of their response to external stimuli; however, these techniques generally fall short of capabilities to correlate structural dynamics with real-space microstructures, especially regarding domain structures. To this end, piezoresponse force microscopy (PFM) has emerged as a primary tool for imaging electromechanical properties of materials with nanoscale resolution, and PFM spectroscopy has also been developed in some forms enabling local probing of polarization switching dynamics. This latter issue has been the subject of extensive PFM studies, yielding significant observations of, for example, low-energy nucleation centres at ferroelastic domain walls. In a limited number of cases, hints of phase transition phenomena have also been reported.

As the most studied multiferroic compound, BiFeO3 (BFO) shows many promising functionalities emerging from its intercoupled polarization, transport, mechanical and magnetic properties. Mixed-R/T phase BFO thin films near a strain-induced MPB (on LaAlO3 substrates) have attracted particular interests for piezoelectric applications due to their large field-induced strains and shape-memory effects. These effects, though being reversible, are hysteretic (that is, the field-induced state has to be annihilated by applying an opposite field) as a consequence of the intricate mixed-phase microstructure and thus are undesirable in applications of, for example, tunable devices. For such purpose, BFO in the stability field of R-phase is to be considered instead.

Here, we employed band-excitation piezoresponse spectroscopy (BEPS) to probe local bias-induced R - T phase transition as well as polarization switching behaviour of strained R-BFO thin films. By deciphering the elastic spectroscopy inherent in BEPS that acts as a nanoscale analogy to macroscopic resonant ultrasound techniques, we examined the sub-MHz elastic dynamics associated with both intrinsic and extrinsic structural activities of the system. This added information channel supported by phase-field modelling allowed us to further explore the kinetic interaction between the polarization switching and heterogeneous domain structures with the R - T transition. Our results highlight giant electrically tunable elastic properties of BFO heretofore largely unappreciated.

**Results**

**Bipolar BEPS loops.** In this study, we focus on a 50 nm BiFeO3 thin film with a bottom layer of La0.7Sr0.3MnO3 grown on (001)-SrTiO3 (STO) substrates (cubic indices are used in this article). The as-grown BFO film comprises four essentially equally populated, upwards-polarized twin variants due to ~1.5% epitaxial strains imposed by STO and certain electrical boundary conditions. X-ray reciprocal space mapping confirms a distorted R (or monoclinic Mα (ref. 13); Fig. 1a) average symmetry of the film with c/a axis ratio = 1.043. Figure 1b,c illustrate the surface morphology and corresponding vertical/lateral PFM images showing mutually orthogonal surface domain patterns in widths of ~100 nm and separated by largely straight boundaries. Figure 1d–h presents a typical set of single-point (out-of-plane) BEPS results acquired at the domain interior. As is readily seen from the amplitude spectrographs (Fig. 1d), the on-field response shows strong shifts in contact resonance frequency (fc,r) during all the switching cycles, in striking contrast with the off-field response. Further details can be extracted from the derived loops: on the off-field fc,r shifts downwards with bias in both polarities and for large bias windows, it saturates (and slightly recovers) before the maximum bias is followed by a second drop when decreasing the bias thus forming characteristic hysteresis (see the branch A–C in Fig. 1f); for the off-field fc,r loops, only weak anomalies can be found near ± 3 V where the domain switching events occur. Similar patterns are also followed by the quality (Q)-factor loops with relatively larger variation in the off-field state (Fig. 1b).

The off-field piezoresponse loops have the canonical square shape gradually saturating under positive tip biases and in particular, a ‘head’-like hysteretic feature forms in the positive half-cycle. Along with the fc,r anomalies, this feature is well reproducible in BEPS mapping across the film on average leading to two- to threefold enhancement (versus zero-bias) of piezoresponse, and its propensity appears to be weaker for the negative bias side where the applied E-field is parallel to the pristine P direction (Fig. 1i). Note that the measured on-field piezoresponse in these cases is truly dominated by electromechanical response over weak or no contributions from the parasitic electrostatic and conduction current effects (Supplementary Note 1 and Supplementary Figs 1,2). This loop shape is also distinct from those peculiar backswitching loops mediated by charge injection, since it occurs only on-field and without any self-crossings.

In BEPS, systematic and reproducible changes in fc,r are due to alteration of the elastic properties of samples, as is indeed the case here. Through cantilever dynamics and contact mechanics calculations (see details in Supplementary Note 2 and Supplementary Table 1), we find that the Young’s modulus (Y) of the BFO film changes from ~204 GPa in the pristine state to, for example ~141 GPa at 12 V shown in Fig. 1f, where the Δfc,r peaks at ~4.7 kHz, amounting to a remarkable ~30% elastic softening. This softening behaviour can be instantaneously switched on/off by bias within the probed millisecond timescale, and remains basically unchanged when the contact resonance is driven by external mechanical excitation. Similar softening effects are also observed in the lateral/torsional BEPS mode, where in-plane polarization is detected and torsional fc,r reflects the shear modulus (G) of samples. Overall, the lateral piezoresponse loops of this BFO film are not well-defined in the low-bias region compared with their simultaneously acquired out-of-plane counterparts, presumably due to its complex in-plane switching behaviour; however, there is a recurring feature manifest in all the in-plane loops: as illustrated in Fig. 1j,k, the on-field piezoresponse is enhanced along with the elastic softening up to a threshold bias and then drops quickly. All these observed BEPS characteristics imply an intrinsic dynamic process taking place, reminiscent of
the R–T phase transition of the system. The measured Y variations of the BFO/STO film are also found to be bounded by the elastic moduli of different R- or T-phase BFO samples probed at GHz frequencies by Doig et al. Note that similar frequency response and piezoresponse enhancement were also observed in (001)-BFO thin films under different epitaxial strains (for example, BFO/DyScO$_3$, strain approximately −0.5%; Supplementary Note 3 and Supplementary Fig. 3).

Phase-field modelling of a single domain. Phase-field modelling offers direct visualization of the evolution of ferroelectric

Figure 1 | Bipolar BEPS switching loops of 50 nm BFO/STO. (a) Reciprocal space map near the STO 332 reflection showing three-fold splitting indicative of a $\mathbf{M}_\text{A}$ structure of BFO. Scale bar, 1/3.905 Å$^{-1}$. (b,c) Morphology (b) and corresponding lateral PFM (c) images; Inset in c shows the corresponding vertical PFM image after the center square area was poled with 10 V tip bias. The cantilever alignment adopted in all BEPS measurements is shown in b. Scale bar, 1 μm. (d–h) Single-point BEPS performed under ascending bias windows as shown in d, which also illustrates the measured piezoresponse amplitude spectrographs; total time length = 2.3 s. e is a schematic representation for the chirp-type BE waveform and on/off-field d.c. switching sequences. f–h are the fitted frequency (f), piezoresponse (g) and Q factor (h) loops with their sense marked by arrows and colour coded by the bias windows shown in d. (i) Histogram of the on-field piezoresponse loops acquired from 50 × 50 points over a 1 × 1 μm$^2$ region. (j,k) Single-point in-plane BEPS frequency (j) and piezoresponse (k) loops acquired in the lateral mode with the sense marked by arrows. a.u., arbitrary unit.
polarization during BEPS measurements. We start from a single [111]_B-domain BFO/STO model as illustrated in Fig. 2a. Here the lateral tip potential spreading is modelled as a flat-top Lorentz function, \[ \phi(x,y) = \phi_0 \left( \frac{(r-a)^2}{r} \right), \] where \( r \) is the distance from the tip and \( a \) is the half width at half maximum of applied bias, \( \phi_0 \) given the presence of strong tip indentation, the center area with radius \( a \) obtained self-consistently from the contact mechanics calculations, is set equipotential. Figure 2b shows the calculated depth profiles of normal and shear stresses under the tip loading force. Both types of stresses are concentrated within \( \approx 10 \text{ nm} \) length scale, indicating the size of sample volume where local elasticity is effectively probed, approximately commensurate with that for piezoresponse. Figure 2c shows the calculated local \( P \) values underneath the tip following increasing sequences of tip bias. For both bias polarities, there are sudden jumps in \( P \) occurring within \( 6-10 \text{ V} \), after which its \( Z \) component, \( P_Z \) increases to \( \approx 2.7 P_0 \) and the \( P_X/P_Y \) components reduce to zero. Such jumps signify the \( R-T \) phase transition and the calculated \( P_Z \) faithfully reproduces the experimental \( P \) value (\( \approx 1.5 \text{ C m}^{-2} \)) of T-BFO. The fact that this transition occurs earlier by \( \approx 2 \text{ V} \) along the antiparallel E-field direction (positive bias) is somewhat counterintuitive, as one may assume that the \( M_a = T \) polarization rotation path would be ‘shorter’ in the parallel E-field condition. This points to a competing interaction between the polarization switching and rotation processes, as the domain phase configuration results from minimization of the system free energy with respect to the driving force, electrostatic energy \(-\Phi\). The stabilized domain configurations under \( \pm 10 \text{ V} \) are presented, for example, in Fig. 2d-f. Noticeable in-plane switching (IPS) activities can be seen for both polarities (for positive tip biases, the IPS also involves out-of-plane switching) due to the lateral components of tip E-fields (Supplementary Fig. 4 and Supplementary Note 4), leading to \( \approx 20 \text{ nm} \) domain clusters with four \( R \)-phase twins encasing a \( T \)-phase domain underneath the tip (Fig. 2d,e). In the case of \( 10 \text{ V} \), the \( T \)-phase extends \( \approx 4 \text{ nm} \) into the film assuming a wedge-shape depth profile and around it, a thin (1 or 2 nm) transition layer with higher \( P \) than that of \( R \)-BFO is also visible (Fig. 2f), which could be an indicator of the \( R/T \) phase boundary thickness. Furthermore, we considered the influence of substrate strain on the \( R-T \) transition as well as IPS of the \( R \)-phase. Here the IPS threshold bias is defined as the voltage at which nascent domains are visually detected on the surface, since they do not nucleate right below the tip (see an illustration on Fig. 2d). Within the strain range from \( -0.5 \% \) to \(-2.5 \%\), the \( R-T \) threshold bias decreases monotonically as expected, while that of IPS appears almost independent of substrate strain (Fig. 2g).

In light of these modelling results, we attribute the observed BEPS features to the occurrence of the \( T \)-phase. Note that \( T-BFO \) is not soft per se, neither in terms of elasticity nor piezoelectricity. Therefore, the softening behaviour has to be explained by the \( R/T \) phase coexistence (that is, MPB) or more naturally, the \( R-T \) phase instability. Elastic softening occurs near phase transitions following specific patterns as determined by their transition characters, for example, order parameter type. In our case, it is more complicated because the transition is locally and non-uniformly driven; therefore, the measured dynamics is a convolution of the lattice dynamics and the growth kinetics of the emergent phase. For instance, when a \( T \)-phase nucleus grows outwards under higher biases, the inner region recovers as it passes through the instability field but the surrounding lattice enters that and softens overall, probably...
maintaining the softening trend for the probe volume. This renders it not straightforward to assign an exact $R - T$ transition point to the measured elastic or piezoresponse spectra, albeit their peak softening biases compare favourably with the calculated threshold biases. In this regard, the lateral piezoresponse may be more informative, since in principle it changes most drastically during the $R - T$ transition.

**Unipolar BEPS and strain loops.** To further find links between the softening behaviour and the IPS and $R - T$ transition of the BFO film, we performed unipolar BEPS in the parallel E-field condition; to fulfil this, a pre-poling cycle was adopted in the BFO film, we performed unipolar BEPS in the parallel E-field Unipolar BEPS and strain loops

Single-point strain curves (the in-plane switching (IPS) and $R - T$ transition regions, respectively. Dashed lines in $f$ denote the second harmonics response signal noise floor. ($g$,$h$) Single-point strain curves ($g$) and its derivative (that is, static $d_{33}$) loops versus corresponding on-field piezoresponse loops ($h$). (i) Histogram of the static $d_{33}$ loops calculated from $40 \times 40$ strain curves acquired over a $1 \times 1 \mu m^2$ region, via a 6th-order polynomial fitting to the measured data as illustrated in $g$. a.u., arbitrary unit.
mapping data set of strain curves based on their polynomial fits (for the noise reduction purpose; Fig. 3g). The peak $d_{33}$ of these loops distributes over 100 – 130 pC/N, apparently comparable to that attained in mixed-phase BFO films.

**Effects of the complex domain structure.** We have shown that the kinetic interaction between polarization switching and the R – T transition, well within the domain interior, causes characteristic asymmetry and hysteresis in the elastic softening patterns of the BFO. Next, we examine the effects of the heterogeneous domain structure. Figure 4a is a simulated multi-patterns of the BFO. Next, we examine the effects of the characteristic asymmetry and hysteresis in the elastic softening patterns. Negative tip biases were applied on a number of surface positions, and the resultant P-V curves for selected points are shown in Fig. 4b. As can be seen, the R – T transition starts earlier on domain walls or junctions than in the domain interior with up to $\sim 2$ V difference, and consequently, at the same bias the nascent T-phase is more visible on the resultant domain configuration for those ‘easier’ regions (not shown). Examination of the pristine strain state (Fig. 4c) reveals that those ‘easiest’ regions (for example, $p_6$ and $p_7$) are associated with larger local in-plane compressive strains (than $-1.5\%$, the homogeneous value) as well as larger out-of-plane tensile strains; that is, they are closer to the T-phase originally. Across these walls, the polarization vector aligns tail-to-tail leading to an accumulation of bound charge, in agreement with an earlier microscopic observation of T-like structure near the charged domain walls in R-BFO.

Note also that the R – T transition is slightly easier even on the domain walls with reduced in-plane strains (c.f. $p_3$ and $p_1$) suggesting additional roles of domain walls in promoting the T-phase growth kinetics.

To confirm these modelling results experimentally, high-resolution BEPS mapping was performed over a typical domain junction, as shown in Fig. 4d, where the domain wall orientations are inferred from the measured PFM images based on the established domain geometry rules. This junction may well correspond to the $p_6$ region in Fig. 4a, and here a narrow stripe of downwards polarized domain running parallel to the (100)-domain wall is observed to have formed to partially compensate the high-density negative polarization charge nearby. Around such locally stress/charge-concentrated domain walls, the higher measured peak softening $\Delta f_{cr}$ (Fig. 4e) implies faster T-phase growth kinetics than that of the remaining region, consistent with the modelling results. The peak on-field piezoresponse also shows similar contrast in correlation with the elastic softening effect (Fig. 4e); however, this contrast is not fully disclosed in the zero-bias piezoresponse (not shown) as equivalently obtained in static PFM imaging.

**Discussion**

For our BEPS measurement geometry, the vertical and torsional contact mode involves the $Y$ and $G$ moduli, respectively, of the (001)-BFO thin film, corresponding to its elastic compliance or stiffness tensors $Y_{ijkl}$ and $G_{ijkl}$, $Y_{ijkl} = \frac{1}{2}[(c_{ij} + c_{kl}) + (c_{kl} + c_{ij})]$ and $G = c_{ij} - c_{kl}/2$. Thus, their concomitant anomalies under E-fields appear most likely to be.
driven by $(c_{11} - c_{12})$. Softening of this elastic constant has been known to signify lattice instabilities against tetragonal shear strains (that is, pointing to the $R \rightarrow T$ transition here), common for many displacive ferroic systems as exemplified by Pb-based perovskite relaxors. For instance, an entire softened acoustic phonon branch propagating along [110] (with [1–10] transverse polarization), controlled by the $(c_{11} - c_{12})$ mode, was observed in near-MPB $R$-phase Pb(Zn$_{1/3}$Nb$_{2/3}$)$_2$O$_3$–4.5%PbTiO$_3$ coinciding with its colossal piezoelectricity. Enhanced thermal diffuse scattering as a clue for $T$-point phonon softening was also observed in $R$-field approaching to an $E$-field-driven $R$–$T$ transition. It is noteworthy that structurally the $T$-BFO stabilized on LaAlO$_3$ exhibits a large distortion of the oxygen octahedron and loss of its rotation pattern in $R$-BFO$_{65,64}$ implying that this transition involves multiple lattice instabilities at the $R$/M-points. These zone-boundary antiferrodistortive modes, in fact, have been argued based on first-principles calculations to be the primary order parameter, as opposed to the $T$-point polar mode, for the $R$–$T$ transition of strained BFO, posing it as a (pseudo-)proper ferroelastic transition. All these complex transition characters clearly have effects on the strain-coupling mechanism and elastic softening dynamics of BFO. Given a dearth of experimental lattice dynamics studies of the system thus far, we leave this as an inconclusive account of the detailed microscopic picture behind our observations; nevertheless, these results per se are clearly a direct measure of soft acoustic modes of BFO in the long wavelength limit.

This giant elastic softening effect of BFO coupled with non-hysteretic and reasonably low-loss characteristics suggests its usefulness in tunable microwave electroacoustic devices. Currently, the prevailing materials for these applications are based on paraelectric-phase (Ba,Sr)TiO$_3$ with incipient polar instability (that is, soft optic modes), while materials set in polar phases are less often considered due to unfavourable domain switching related hysteresis and loss. In both cases, frequency tunability is underlain by the soft optic phonons (and/or switching related hysteresis and loss). The latter two quantities encode near-surface elastic information of the sample; thereby contact resonance plays another important role in BEPS besides signal enhancement. BEPS mapping was performed on grids of points evenly spaced on predefined scan regions. Conduction current was monitored with a current amplifier (DLPCA-200, Femto).

**Phase-field modelling.** Temporal, three-dimensional spatial evolution of the ferroelectric polarization of the BFO films is modelled by numerically solving the time-dependent Landau–Ginzburg–Devonshire (LCD) equations:

$$\frac{\partial P_i(x,t)}{\partial t} = -L \frac{\partial F}{\partial P_i(x,t)} , \quad i = 1, 2, 3,$$

(1)

in which $P_i$ is the polarization vector, $x$ is the spatial position, $t$ is the time, $L$ is the kinetic coefficient related to the domain wall mobility, $F$ is the total free energy,

$$F = \int \sum_{i} f_{\text{mag}}(P_i) + f_{\text{elas}}(P_i) + f_{\text{Pie}}(P_i, E) \, dV$$

(2)

in which $f_{\text{mag}}(P_i)$, $f_{\text{elas}}(P_i)$, $f_{\text{Pie}}(P_i, E)$ and $f_{\text{elas}}(P_i, E)$ represent the LJD free-energy density, gradient-energy density, elastic-energy density and electrostatic-energy density, respectively. Detailed description and analytic expressions for these energy terms can be found in literature. In particular, here we adopted an eighth-order LJD free energy expansion for BFO. Isotropic gradient energy coefficients $g_3 = 0.3$ and relative dielectric constant $\varepsilon_r = 50$ were assumed. All the energy coefficients of BFO and detailed model parameters are provided in Supplementary Table 2. Equation 1 was solved by a semi-implicit spectral method using a realistic three-dimensional geometry sampled on a fine grid mesh of $128\times 128\times 64\times 64$, where the grid size $\Delta = 1.0$ nm. The film and substrate thickness are $50\times 10$ and $16\times 10$, respectively. Periodic boundary conditions were applied for the in-plane directions ($x$ and $y$); the top film surface is assumed to be stress-free, while the bottom surface of BFO is coherently strained by the substrate. Electric biases were incrementally applied via the tip function described in the text.

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Author contributions
Q.L. conceived the study, performed PFM, analysed the results and wrote the article. Y.C. designed and performed phase-field modelling with input from L.Q.C and F.X. derived the LGD energy coefficients. P.Y. provided the materials. N.L. performed XRD. A.T. performed cantilever dynamics calculation. R.K.V., N.L. and P.M. discussed the results. N.B. and S.V.K. supervised the study and co-wrote the article. All authors commented on the manuscript.

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