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1 **Deterministic optical control of room temperature multiferroicity in BiFeO₃ thin**
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32 **Abstract**

33 Controlling ferroic orders (ferroelectricity, ferromagnetism, and ferroelasticity) by optical
34 methods is a significant challenge due to the large mismatch in energy scales between order
35 parameter coupling strengths and incident photons. Here, we demonstrate an approach to
36 manipulate multiple ferroic orders in epitaxial mixed-phase BiFeO₃ thin film at ambient
37 temperature via laser illumination. Phase-field simulations indicate that a light driven flexoelectric
38 effect allows targeted formation of ordered domains. We also achieve precise sequential laser
39 writing and erasure of different domain patterns, demonstrating deterministic optical control of
40 multiferroicity at room temperature. As ferroic orders directly influence susceptibility and
41 conductivity in complex materials, our results not only shed light on optical control of multiple
42 functionalities but also suggest possible developments for opto-electronics and related applications.

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46 Bismuth ferrite (BiFeO_3 , BFO) is an archetypical room-temperature multiferroic¹ with coupled
47 ferroelectric and antiferromagnetic order parameters, in which the spontaneous strain also
48 accompanies the ferroelectricity. In bulk, the $\langle 111 \rangle$ -oriented ferroelectric polarization directly
49 couples with the G-type antiferromagnetism as well as a weak ferromagnetic moment driven by
50 Dzyaloshinskii–Moriya interaction^{2,3}. Furthermore, the rotation of the ferroelectric polarization in
51 BFO results in corresponding modulation of the (anti)ferromagnetism⁴. The demonstration of robust
52 multiferroic properties in epitaxial BFO thin films, heralded as one of the breakthrough findings of
53 the past decade⁵, has opened several unforeseen device opportunities in oxide electronics
54 technologies⁶. In addition to being sensitive to external stimuli such as stress⁷, magnetic field⁸, or
55 electric field⁵, BFO has tremendous potential in optoelectronic applications^{9,10}. There has been an
56 intense flurry of research activities focusing on electric field control of magnetism (and vice-versa)
57 for BFO¹¹. In contrast, reports on precise optical modulation of phase and structure of BFO, and
58 hence functional responses remain scarce.

59 The deterministic control of electric, magnetic, and elastic orderings by means of light is not
60 trivial. From an energy perspective, the scales for tailoring exchange coupling, spin-spin, and
61 spin-orbital interactions range from few hundreds of μeV to meV ¹²⁻¹⁵, which are always
62 significantly lower than the energy of a single photon in the visible spectrum (few eV). Such a huge
63 energy mismatch typically inhibits precise manipulation of the ferroic orders under external light
64 stimulus. Notwithstanding the above challenge, successful optical modulation of ferroic order
65 parameters has been realized through tuning the complex interactions such as delicate combination
66 of thermal effects, electronic excitation, phase stability, electrical field, and polarity of light¹⁶⁻²². In
67 most cases, this is either done at low temperatures or with illumination by high-intensity pulsed
68 lasers. Nevertheless, all-optical control of multiferroicity in a non-volatile way, especially at
69 ambient temperature, has rarely been reported.

70 When proper in-plane compressive strain is applied to the epitaxial BFO film, it undergoes a
71 phase transition to a mixed-phase system, which is composed of a tetragonal-like (T-BFO) and a

72 rhombohedral-like (R-BFO) BFO phases²³. Mixed-phase BFO shows significant piezoelectricity²⁴
73 and enhanced magnetization²⁵. The barrier for phase transition in this system is relatively low so
74 that it can straddle easily across the R-T boundary under external stimuli²⁴ (typically exploited
75 using either stress or electric field). The light-induced tuning of mixed-phase BFO could lead to the
76 non-volatile optical control of multiferroicity, electromechanical response as well as the correlated
77 magnetism, thus giving unprecedented device opportunities. In this study, we demonstrate distinct
78 non-volatile manipulation of the phase and domain structures that exhibit coupled ferroic orders in
79 mixed-phase BFO by light illumination. We find that the combination of light-induced thermal and
80 flexoelectric effects effectively determines the domain transformation as well as the R-T phase
81 distribution in mixed-phase BFO, enabling the deterministic control of corresponding ferroic orders.

82 **Laser illumination on mixed-phase BFO**

83 As the experimental setup illustrated in Fig. 1a, a 532 nm solid-state continuous wave laser
84 (CW laser) is focused on the sample, where the power density is calibrated to be ~ 16 mW/ μm^2 . Fig.
85 1b and c show the topography of the mixed-phase BFO before and after laser illumination,
86 respectively. The as-grown image shows irregular distribution of flat T-BFO and mixed-phase
87 stripes composed of T-BFO and R-BFO. The light illumination results in the reconstruction of the
88 as-grown mixed-phase feature as evidenced by the noticeable change in the illuminated region. For
89 this region, T-BFO with a flat topography appears within the square region, while mixed-phase
90 stripes form at the edge of illuminated area.

91 Having demonstrated that light-induced change in mixed-phase BFO is indeed possible, we
92 next investigated the ferroelectric polarization as well as corresponding domain patterns after light
93 illumination to reveal the key underpinning physical mechanisms. Note that in the case of the
94 BaTiO₃ (BTO) single crystals, it was found that polarized light induced stress at the domain wall is
95 the main cause behind the ferroelastic domain switching^{21,22}. In the case of epitaxial BFO thin film
96 system, more complexity arises from the additional in-plane polarization degrees of freedom²⁶⁻²⁸.
97 Whilst the in-plane (IP) polarization components of R-BFO lies along the $\langle 110 \rangle_{\text{pc}}$ axis, those of

98 T-BFO can be approximated to be along $\langle 100 \rangle_{\text{pc}}$ directions at room temperature (here the pc refers
99 to pseudo-cubic index). Thus, to simplify the case here, a well-aligned T-BFO domain with majority
100 downward polarization component ($P_z \approx -1.4 \text{ C/m}^2$) and a small in-plane component ($P_{x,y} \approx 0.4$
101 C/m^2), with ordered domain wall orientation lying along the $[110]_{\text{pc}}$ axis is first created using a
102 biased scanning probe. The inset of Fig. 2a shows the in-plane piezoresponse force microscopy (IP
103 PFM) image of the artificially created pure T-BFO background. After light illumination, the PFM
104 images reveal that the direction of out-of-plane (OP) polarization of the light induced R- and T-BFO
105 domains remains unchanged (Fig. 2b).

106 Using vector PFM analysis, the polarization of individual domains could be further revealed
107 (see supplementary information Fig. S1), as labeled by the small colored arrows in Fig. 2a. For
108 comparison, the individual and net polarization directions of untreated regions are also marked in
109 Fig. 2a. Here the light induced T-BFO square created within the illuminated area splits into two
110 triangular segments, each with different net in-plane (IP) polarizations, ie. $[110]_{\text{pc}}$ and $[\bar{1}\bar{1}0]_{\text{pc}}$, as
111 indicated by the blue and red arrows in Fig. 2a. Note that the light induced T-BFO possesses the
112 domain wall parallel to $[\bar{1}\bar{1}0]_{\text{pc}}$ axis and the net IP polarization pointing outward the illumination
113 area (red and blue arrows), which shows a 90° rotation with respect to the net IP polarization of
114 non-illuminated area (green arrow). The PFM and topography images also reveal the new
115 mixed-phase BFO stripes created at the boundaries of the illumination area for minimizing local
116 elastic energy. To sum up our observation, the polarization configurations before and after light
117 illumination are schematically illustrated in Fig. 2c and d.

118 It is noteworthy that a direct interaction between the electric field of the light and the
119 spontaneous polarization is unlikely, given that the electric field of visible light oscillates at a much
120 higher frequency ($\sim 10^{15}$ Hz) as compared to that of a ferroelectric dipole, unless nonlinear effects
121 such as optical rectification are considered. To preclude the nonlinear effect of light, which usually
122 exhibits angle dependent changes, we highlight that similar results could be obtained by using

123 different linearly and circularly polarized light under the same experimental setup (Fig. S2). This
124 observation suggests the direct interaction between ferroelectric polarization and electric field of the
125 incident light due to the non-linear effects has no dominant influence on the light-induced domain
126 patterns. Through ultraviolet-visible and photoluminescence spectroscopies, we also learned that
127 the illumination of a 532 nm laser would not generate significant amount of photo-excited carriers
128 to drive the rotation of the ferroelectric polarization (Fig. S3). The observed light-driven phase and
129 domain evolution of mixed-phase BFO could therefore be attributed to two possible mechanisms,
130 i.e. photostrictive effect^{10,29} or local heating³⁰. However, the light induced photostrictive effect in
131 BFO¹⁰ is too small to provoke such a significant change. As a result, it is thought that the local
132 heating effect might play the key role in driving the domain change.

133 **Raman study during light illumination**

134 To verify the role of local heating effect induced by light illumination, Raman spectroscopy
135 was employed next to gain vital insight into details of (crystallographic) phase variation under light
136 illumination. The power-dependent and temperature-dependent Raman spectra were taken for
137 comparison, as shown in Fig. 3a and b, respectively. Note that the T-BFO exhibits a structure
138 transformation from M_C tetragonal-like to M_A tetragonal-like phase at ~ 150 °C, accompanied by the
139 in-plane rotation of polarization direction from $\langle 100 \rangle_{pc}$ to $\langle 110 \rangle_{pc}$ ²⁶, as illustrated in the inset of
140 Fig. 3c (also refer to Fig. S4). When the phase transformation takes place, the characteristic phonon
141 intensity of M_C phase T-BFO, at ~ 360 cm^{-1} ,³¹ decreases along with increasing temperature. The
142 laser induced heating can thus be calibrated by comparing the power-dependent and
143 temperature-dependent spectra.

144 The strained BFO shows an anomalous change in phonon mode of ~ 360 cm^{-1} when laser
145 power density is increased to the value of ~ 16 $\text{mW}/\mu\text{m}^2$, which is the power density adopted in Fig.
146 1 to drive the light-induced domain transformation. The decrease in intensity of characteristic
147 phonon peak (360 cm^{-1}) with increasing laser power density indicates a gradual phase transition
148 from M_C to M_A during light illumination. By further comparing the power-dependent and

149 temperature-dependent Raman spectra, it can be inferred that the effect of laser illumination is
150 essentially the same as the effect of local heating. This comparison is also in nice agreement with
151 temperature estimation deduced from Stokes–anti-Stokes ratio, as shown in Figure 3d (also refer to
152 Fig. S5 and S6). The estimated local temperature with light illumination of $16 \text{ mW}/\mu\text{m}^2$ is close to
153 $\sim 150 \text{ }^\circ\text{C}$, at which the T-BFO tends to transform from M_C to M_A phase. This suggests the thermal
154 effect is responsible to the presence of light-induced phase change and domain reconstruction in
155 BFO; however, it still can't explain why the induced ferroelectric domains transform in such a
156 highly ordered pattern after illumination.

157 **Role of flexoelectricity and phase-field simulations**

158 To further explore the mechanism of light-induced ferroelectric domain switching in BFO, we
159 carried out phase-field simulation³²⁻³⁵. As illustrated the lattice expansion during light illumination
160 in Fig. 4a, we model the light illumination effect by setting the temperature to a higher value and
161 adding a lattice expansion induced strain in the centered illumination region (see Methods for
162 details). We start from a single M_C phase BFO before light illumination, with P_z along $[00\bar{1}]$ and
163 alternating P_x / P_y along $[\bar{1}00] / [010]$ directions, which forms 45° oriented domain walls (Fig. 4b),
164 in agreement with the experimental characterization (inset of Fig. 2a). Under light illumination, the
165 induced vertical strain in the illumination region is deduced from the lattice expansion along $[001]_{pc}$
166 via x-ray diffraction (see Methods and Fig. S4 for details). Assuming that ϵ_{33} is proportional to the
167 light intensity (Fig. S7), we assume a dome-like distribution of ϵ_{33} and σ_{33} (Fig. S8). The vertical
168 strain induces in-plane strain gradient ($d\epsilon_{33}/dx_{1,2}$) and flexoelectric field ($E_{1,2}^f$) are related via
169 $E_{1,2}^f = f_{12} \left(\frac{d\epsilon_{33}}{dx_{1,2}} \right)$, (also refer to Methods) where $x_{1,2}$ and f_{12} are the in-plane directions and the
170 transverse flexoelectric coupling coefficients. The induced flexoelectric field is oriented in radial
171 direction from the center to the edges of the illumination region (see Fig. S8), while the simulated
172 domain structure under this radial flexoelectric field is shown in Fig. 4c. In the bottom-right of the
173 illumination region, the simulated domain patterns exhibit the exact arrangement with net

174 polarization pointing along $[110]_{pc}$ and $[\bar{1}\bar{1}0]_{pc}$ as what we observed in the experiment; while in the
175 top-left of the illumination region, they remain the same as those in the unilluminated region. The
176 discrepancy exists in the top-left simulated pattern as compared to experimental observation. This is
177 possibly due to the reasons that the flexoelectric field may be slightly asymmetric in experiment
178 because of the light-focusing geometry and local thermal equilibrium, enabling the bottom-right
179 configuration to consume the top-left unchanged area.

180 To offer a more accessible simulation result after light illumination based on real experiment,
181 we set the same flexoelectric field effectively pointing along the $[110]_{pc} / [\bar{1}\bar{1}0]_{pc}$ directions in the
182 illuminated region. The simulated equilibrium domain pattern is shown in Fig. 4d, which is, in a
183 nice agreement with our experimental observation. For comparison, we also applied flexoelectric
184 field along the $[\bar{1}\bar{1}0]_{pc} / [110]_{pc}$ directions in the illuminated region (see Fig. S9a-c). In this scenario,
185 no new super-T phases are formed in the illuminated region. Since the net in-plane component of
186 the initial M_C phase is along $[\bar{1}\bar{1}0]_{pc}$, it is easier to switch to either $[110]_{pc}$ or $[\bar{1}\bar{1}0]_{pc}$ directions by
187 90° (Fig. S9d, e), than to $[1\bar{1}0]_{pc}$ direction by 180° under radiative flexoelectric field. This explains
188 why only certain domain orientations are preferred as observed in real experiments (Fig. 2a).
189 Additionally, reference simulations with smaller flexoelectric field are performed (Fig. S10).
190 Clearly no new T phase domain pattern inside the illumination region is observable. Our phase-field
191 simulation indicates that local heat and flexoelectric effect are both important to the domain/phase
192 reconfiguration during illumination.

193 In order to experimentally examine the existence of flexoelectricity, Kelvin probe force
194 microscopy (KFM) is employed to map the potential energy profile after illumination. As shown in
195 Fig. 4e and f, a ring-shape accumulation of negative charges is observed at the edge of the
196 illuminated area, which indicates a radiative flexoelectric field is built under light illumination. The
197 light induced strain gradient towards the center of the illumination area results in the creation of

198 flexoelectric polarization that is opposite to the strain gradient³⁶, as illustrated in Fig. 4a. As the
199 local region is heated up by light illumination, the generated hot carriers drift from the illuminated
200 region to the boundaries along with the flexoelectric field built up by the strain gradient, resulting in
201 the ring-like charge accumulation.

202 Fig. 4g schematically illustrates the evolution of the optically controlled domain formation.
203 The first step exploits the possible domain variants in T-BFO, where each can occur with sequential
204 rotation of polarization. The light induced phase transformation from M_C to M_A phase rotates the
205 polarization variants of each domain for 45° , creating a metastable state during light illumination. In
206 the meanwhile, the flexoelectric effect takes place and builds up the flexoelectric field at the
207 illuminated area, leaving the polarizations pointing outward. As the light is turned off, the centered
208 BFO domains transform back to M_C tetragonal-like phase. Taking flexoelectric field and boundary
209 conditions of as-grown domains into consideration, the anisotropic build-in electric field results in
210 the perpendicular feature between the induced and original domain walls (Fig. 2d).

211 **Modification of correlated ferroic orders**

212 To investigate the correlated ferroic orders altered by light illumination, photoemission
213 electron microscopy (PEEM) and x-ray absorption spectroscopy (XAS) were performed at
214 BL11.0.1 at the Advanced Light Source, Berkeley Lab and at TPS45A NSRRC-MPI beamline at
215 Taiwan Photon Source (TPS), respectively (see Methods and Fig. S11 for details). Fig. 5a combines
216 the in-plane PFM and the corresponding x-ray linear dichroism (XLD)/x-ray circular dichroism
217 (XMCD) -PEEM images acquired at the same position. Our XLD experiment implemented at TPS
218 reveals the local antiferromagnetic Néel temperature (T_N) of T-BFO is significantly lower than that
219 of the R-BFO (Fig. S11). The spatially resolved XLD-PEEM image in Fig. 5a also shows that the
220 R-BFO among the mixed-phase stripes (shown in black contrast) has significantly stronger linear
221 dichroism contrast (due to antiferromagnetism) than the matrix, T-BFO (shown in gray contrast).
222 The image contrast in PEEM-XMCD is effectively a map of the local ferromagnetic order, in which
223 the areas that have their magnetic moments lying parallel to k-vector of the incident X-ray show red

224 contrast, whereas those that are antiparallel appear in blue contrast. By mapping the local
225 magnetization, no magnetic moment is detectable above noise level in the T-BFO area, while the
226 magnetic contrast could be clearly observed at the stripes created at the boundaries of the
227 illumination area. This observation agrees with previous studies, in which the enhanced
228 magnetization in mixed-phase stripe is attributed to the strained R-like BFO phase²⁵. With these
229 measurements taken as a whole, we can conclude that tuning the BFO domain structures and phase
230 distribution via light stimulus is essentially controlling the correlated ferroelectricity,
231 antiferromagnetism and remnant magnetization simultaneously.

232 Having understood the key factors underpinning light induced changes in BFO, macroscopic
233 domain engineering can be achieved with proper control of the motion of the laser spot. Fig. 5b and
234 c shows the schematic of the tuning feature and experimental demonstration of domain percolation
235 via continually moving the laser spot, respectively. Fig. 5b illustrates the formation of a ‘designer
236 domain architecture’ achieved by moving illumination spot. Moving the illumination spot along the
237 different $\langle 100 \rangle_{pc}$ directions effectively breaks the polarization symmetry. As a result, the
238 orientation of domain pattern at the rear side of the moving illumination trajectory is always
239 preferred, dominating the polarization of resultant domains. The presence of domain
240 symmetry-breaking is similar to the electrical control of polarization in BFO mixed-phase system,
241 enabling the preferred domain pattern determined by the moving tips^{27,37}. In light of the
242 antiferromagnetism and enhanced magnetization in BFO are closely related to the mixed-phase
243 stripes, the light induced designer domain architectures can be seen as different non-volatile
244 memory or function units.

245 **Reversible optical control at ambient temperature**

246 The optical tunability of the phases and complex domain architectures shown above for
247 mixed-phase BFO (a morphotropic phase boundary (MPB) like piezoelectric material) makes it now
248 possible to demonstrate the deterministic control of correlated phenomena. The MPB in
249 piezoelectric materials is rich with unique physical properties, including large dielectric,

250 conductivity, significant piezoelectricity and enhanced elasto-optic effects^{9,38-40}. Here, reversible
251 modulation of the enhanced piezoelectricity is achieved by erasing and rewriting the T-BFO and
252 MPB by means of light. Fig. 6a shows the AFM images taken at the same area after repeatedly
253 illumination with controlled moving spot. The illumination center was focused on the blue circle as
254 the first step (State 1), moved towards red triangle (State 2) and then returned to the blue circle once
255 again (State 3). It could be seen that the BFO at blue point experiences an evolution from pure
256 T-BFO to mixed-phase, and then back to pure T-BFO morphology after the third step. On the
257 contrary, the red triangle region evolves from mixed-phase to pure T-BFO and back to mixed-phase.
258 The piezoelectric coefficient, d_{33} , which quantifies the volume change of a piezoelectric material
259 under electric field at blue circle and red triangle in each step are recorded accordingly, as plotted
260 the piezoelectric hysteresis loop in Fig. 6b,c. The blue circle region shows an enhancement in d_{33}
261 for 40 % when the T-BFO matrix is switched to mixed-phase state, while the reverse control is
262 demonstrated when the region transforms to T-BFO once again, presenting a low-high-low
263 (80-110-78 pm/V) d_{33} switching. On the other hand, the red triangle region behaves in an opposite
264 trend, showing a high-low-high (112-72-115 pm/V) d_{33} sequence. In the same manner, the
265 reversible optical control of electrical conductivity can also be carried out, taking advantage of the
266 high conductivity occurring at T-R phase boundary in mixed-phase system (see Fig. S12).

267 **Outlook**

268 Our results successfully demonstrate the non-volatile and deterministic optical control of the
269 multiferroic BFO at ambient temperature, a non-contact external control without any aid of applied
270 electrical or magnetic fields. The illumination of laser spot results in well-defined domain patterns,
271 driven by a decent combination of thermal and flexoelectric effects. Taking the advantage of the
272 correlated order parameters, the ferroelectricity, antiferromagnetism and enhanced magnetization in
273 BFO can be tuned simultaneously by means of light. Further symmetry-breaking is fulfilled by the
274 motion of laser spot, giving rise to the artificial domain writing capability on macroscopic scale.
275 The optical control of multiferroicity not only offers an effective approach to tailor the ferroic

276 orders in complex materials, but also a distinct direction towards technologically important
277 applications such as non-volatile random access memories and data storage devices^{6,41,42}.
278

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381

382 **Author contributions**

383 J.C.Y., Y.L.H. and Y.H.C. processed the sample growth. Y.D.L. and Y.Y.C. conducted the laser
384 illumination, Raman spectroscopy and scanning probe microscopy, and analyzed the data. R.T.H
385 and Y.C. conducted the phase-field simulation. Y.C.W and H.J.L processed x-ray reciprocal
386 mapping and resolved the phase transformation at elevated temperature. R.V.C. acquired and
387 analyzed PEEM results. C.Y.K, C.T.C., A.T., C.F.C. and L.H.T measured and analyzed XAS and
388 XLD, and conducted cluster calculation. V.N. analyzed the PFM data and provided guidance on
389 related experiments. Y.C.C. and J.C.Y. conceived the idea, led the project, analyzed data and
390 co-wrote the paper. All authors contributed to the manuscript.

391

392 **Competing Interests**

393 The authors declare no competing interests.

394

395 **Additional Information**

396 Supporting Information is available online.

397 Correspondence and requests for materials should be addressed to Y. C. Chen or J. C. Yang.

398 **Methods**

399 **Sample growth**

400 The mixed-phase BFO film with thickness of 120 nm was deposited on the conductive LaNiO₃
401 (LNO) buffered (001) LaAlO₃ (LAO) substrates via pulsed laser deposition (Mobile Combi-Laser
402 MBE MC-LMBE, Pascal Co, Ltd.). A KrF excimer laser was employed to strike a stoichiometric
403 BFO target at a laser repetition rate of 10 Hz. The growth temperature was fixed at 700°C with an
404 oxygen pressure of 100 mTorr. After the deposition, the films were cooled in 1 atm of oxygen.
405 Reflection high energy electron diffraction was used to *in-situ* monitor the growth.

406 **Illumination setup**

407 The optical modulation process was performed via micro Raman spectroscopy with 532 nm
408 solid-state continuous wave (CW) laser as the excited source. The laser beam was then focused into
409 a spot size with diameter of 2 μm by a 100X objective lens (NA = 0.95). The incident laser power
410 was precisely controlled by an attenuation-adjustable neutral density filter. The
411 Stokes/Anti-Stokes-shifted Raman spectra were collected via confocal backscattering-based
412 detection in ambient environment and then analyzed by spectrometer (iHR550, Horiba Jobin Yvon)
413 with spectra resolution ~0.74 cm⁻¹. A high-precision step-motor stage (Tango desktop,
414 MÄRZHÄUSER WETZLAR) was used to control the motion of the samples.

415 **Scanning probe characterization**

416 The images of surface topography, piezoresponse force microscopy (PFM), surface potential
417 (measured by Kelvin probe force microscopy, KPFM) and conductive atomic force microscopy
418 (C-AFM) were recorded by a commercial scanning probe microscope system (multimode 8, Bruker)
419 using commercial Pt-Ir coated probe with elastic constants about 7 N/m. During the PFM imaging,
420 ac voltage with amplitude of 1 V and frequency of 7 kHz was applied to the probe and the direction
421 of cantilever was parallel to the [010] crystalline axis of the T-BFO matrix.

422 **Phase-field modeling**

423 In the phase-field simulation, polarization vector $P_i = (P_1, P_2, P_3)$ was chosen as the order
424 parameter to describe the ferroelectric state in BiFeO₃ thin film. The temporal evolution of P_i is
425 governed by the time-dependent Landau-Ginzburg-Devonshire (LGD) equations,

$$426 \quad \frac{\partial P_i(\mathbf{x}, t)}{\partial t} = -L \frac{\delta F}{\delta P_i(\mathbf{x}, t)}, (i=1 \sim 3) \quad (1)$$

427 where \mathbf{x} is the spatial position, t is the time, L is the kinetic coefficient related to the domain wall
428 mobility. The total energy of the system (F) is expressed as a volume integral of total free energy
429 density (f), i.e., $F = \int_V f dV$, in which f includes the Landau free energy density (f_{land}), the gradient
430 energy density (f_{grad}), the elastic energy density (f_{elast}), the electrostatic energy density (f_{elec}) and
431 the flexoelectric energy density (f_{flexo}). Detailed expressions of each free energy density can be
432 found in literature^{43,44}. Equation (1) is numerically solved using a semi-implicit spectral method
433 based on a 3D geometry sampled on a $256\Delta x \times 256\Delta x \times 36\Delta x$ system size, with $\Delta x = 1.0$ nm. The
434 thickness of the film, substrate and air are $20\Delta x$, $10\Delta x$ and $2\Delta x$ respectively. The isotropic relative
435 dielectric constant (κ_{ii}) is chosen to be 50. The gradient energy coefficients are set to be
436 $G_{11}/G_{110} = 1.0$, $G_{12}/G_{110} = 0.0$, $G_{44}/G_{110} = 0.5$ while $G_{110} = 1.73 \times 10^{-10} \text{ C}^2 \text{ m}^4 \text{ N}$. The biaxial
437 substrate strain is set to be -4.5% based on the lattice mismatch between the BiFeO₃ film and
438 LaAlO₃ substrate. The Landau energy coefficients, electrostrictive coefficients and elastic
439 compliance constants are collected from literature^{45,46}. In all the Landau energy coefficients (α 's)

440 only α_1 is temperature dependent. Based on the Curie-Weiss law it is written as
 441 $\alpha_1(r)=[T(r)-T_0]/(2\epsilon_0 C)$, in which r is the position, T_0 is the Curie temperature, ϵ_0 is the
 442 dielectric permittivity of vacuum, C is the Curie constant, and $T(r)$ is the position-dependent
 443 temperature. To model the laser illumination on the center area of the BFO thin film, we set $T(r)$
 444 to be,

$$445 \quad T(r) = \begin{cases} T_{\text{illumination}} & (r \leq a) \\ 298\text{K} & (r > a) \end{cases} \quad (2)$$

446 where $r = \sqrt{(x-x_0)^2 + (y-y_0)^2}$ is the distance from the illumination center (x_0, y_0) , and a ($=64\Delta x$)
 447 is the radius of the illuminated region. The light induced vertical strain (ϵ_{33}) is assumed to be in a
 448 dome-like distribution (Fig. S8) according to the measured light intensity profile (Fig. S7), it is
 449 written as,

$$450 \quad \epsilon_{33}(r) = \begin{cases} \epsilon_{33}^{\text{center}} \sqrt{1 - \frac{r^2}{a^2}} & (r \leq a) \\ 0 & (r > a) \end{cases} \quad (3)$$

451 where $\epsilon_{33}^{\text{center}}$ represents the maximum vertical strain in the center of the illumination region. It is
 452 approximated from the lattice expansion along $[001]_{\text{pc}}$ direction, i.e., $\epsilon_{33} = (c_{T2} - c_{T1}) / c_{T1}$, where c_{T1}
 453 and c_{T2} are the experimentally measured lattice constants of the super-T phase before and after the
 454 illumination (supplementary information Fig. S4). In our simulation, the light-induced in-plane
 455 strains (ϵ_{11} , ϵ_{22}) are negligible due to the substrate constraint. The flexoelectric energy density
 456 (f_{flexo}) can be written as a function of polarization (P_i) and its spatial gradient (∇P), as well as
 457 strain (ϵ_{kl}) and its spatial gradient ($\nabla \epsilon_{kl}$),

$$458 \quad f_{\text{flexo}}(P_i, \epsilon_{kl}, \nabla P_i, \nabla \epsilon_{kl}) = \frac{1}{2} f_{ijkl} \left(\frac{\partial P_k}{\partial x_l} \epsilon_{ij} - \frac{\partial \epsilon_{ij}}{\partial x_l} P_k \right) = \frac{1}{2} F_{ijkl} \left(\frac{\partial P_k}{\partial x_l} \sigma_{ij} - \frac{\partial \sigma_{ij}}{\partial x_l} P_k \right) \quad (4)$$

459 in which f_{ijkl} (unit: V) and F_{ijkl} (unit: Vm^2N^{-1}) are the flexoelectric coupling coefficient (FCC)
 460 tensors, which are related through $f_{ijkl} = c_{ijmn} F_{mnl}$. The effect of flexoelectric energy on the
 461 polarization evolution is modeled by minimizing f_{flexo} over P_k ,

$$462 \quad \frac{\delta f_{\text{flexo}}}{\delta P_k} = \frac{\partial f_{\text{flexo}}}{\partial P_k} - \frac{\partial}{\partial x_l} \frac{\partial f_{\text{flexo}}}{\partial P_k / \partial x_l} = -F_{ijkl} \frac{\partial \sigma_{ij}}{\partial x_l} = -E_k^f \quad (5)$$

463 For cubic symmetry the flexoelectric coupling coefficient tensor has three independent components,
 464 i.e., F_{1111} , F_{1122} and F_{1221} .⁴⁷⁻⁴⁹ By using Voigt notation $F_{11} = F_{1111}$, $F_{12} = F_{1122}$ and $F_{44} = 2F_{1221}$,
 465 Eq. (5) can be expanded as,

466

$$\begin{aligned}
E_1^f &= F_{11} \frac{\partial \sigma_1}{\partial x_1} + F_{12} \left(\frac{\partial \sigma_2}{\partial x_1} + \frac{\partial \sigma_3}{\partial x_1} \right) + F_{44} \left(\frac{\partial \sigma_5}{\partial x_3} + \frac{\partial \sigma_6}{\partial x_2} \right) \\
E_2^f &= F_{11} \frac{\partial \sigma_2}{\partial x_2} + F_{12} \left(\frac{\partial \sigma_3}{\partial x_2} + \frac{\partial \sigma_1}{\partial x_2} \right) + F_{44} \left(\frac{\partial \sigma_6}{\partial x_1} + \frac{\partial \sigma_4}{\partial x_3} \right) \quad (6) \\
E_3^f &= F_{11} \frac{\partial \sigma_3}{\partial x_3} + F_{12} \left(\frac{\partial \sigma_1}{\partial x_3} + \frac{\partial \sigma_2}{\partial x_3} \right) + F_{44} \left(\frac{\partial \sigma_4}{\partial x_2} + \frac{\partial \sigma_5}{\partial x_1} \right)
\end{aligned}$$

467 We made assumption that the light-induced strain and stress are confined along $[001]_{\text{pc}}$ direction,
468 which gradually decrease from the illumination center to the edges. The variation of strain and
469 stress along the $[001]_{\text{pc}}$ direction are neglected. Based on these assumptions and according to Eq.
470 (6), the vertical stress induces an in-plane stress gradient ($\partial \sigma_3 / x_{1,2}$) and flexoelectric field ($E_{1,2}^f$),
471 i.e., $E_{1,2}^f = F_{12} (\partial \sigma_3 / x_{1,2})$, where $x_{1,2}$ and F_{12} are the in-plane directions and the transverse
472 flexoelectric coupling coefficients. The flexoelectric coupling coefficients are chosen to be
473 $f_{ij} = 10\text{V}$ or $F_{ij} = 1.0 \times 10^{-10} \text{Vm}^2\text{N}^{-1}$. They are estimated from the literature⁵⁰.

474

475 Photoemission electron microscopy

476 X-ray imaging with variable linear and circular polarization at the Fe L edges was performed at
477 the PEEM3 endstation of BL11.0.1 at the Advanced Light Source, Berkeley Lab. The sample is held
478 at an angle of 60 degrees with respect to the surface normal, and was mounted such that the x-rays
479 are incident along the in-plane $[100]_{\text{pc}}$ direction. For all images, the x-ray incidence direction is
480 from the right. The sample was held at a voltage of -18 kV to accelerate the photo-emitted and
481 secondary electrons, proportional to the local x-ray absorption coefficient, through a series of
482 electrostatic lenses towards a phosphor-coated fiber bundle coupled to a Peltier-cooled CCD
483 detector. This allows spatial mapping of the polarization dependent x-ray absorption coefficient
484 with a spatial resolution at or better than 50 nm. To probe antiferromagnetic and ferroelectric axis
485 orientation projections along the x-ray linear polarization axis, linear dichroism images at the Fe L_2
486 A and B edges of 720.6 eV and 722 eV were taken first with x-ray polarization in the plane of the
487 sample parallel to the $[010]$ axis (s polarization), then with polarization nearly out of plane (p
488 polarization). To enhance the ferroic contrast and to minimize topographic and work function
489 contrast, the difference images of the L_2 A and B images were taken, then the ratio between s and p
490 polarization difference images were used in Fig. 5a. For mapping the ferromagnetic domain contrast,
491 the Fe L_3 A and B energies at 707.4 eV and 708.3 eV were used with right and left circular x-ray
492 polarization. The difference between right and left circular polarization at each energy gives the
493 projection of magnetization along the x-ray incidence direction, showing strong contrast for
494 domains along the in-plane $[100]$ and $[\bar{1}00]$ directions, and no sensitivity to magnetization along
495 the in-plane $[010]$ and $[0\bar{1}0]$ directions.

496

497 Data availability

498 The data supporting the findings of this study are available within the article and its
499 supplementary files and available from the authors upon reasonable request.

500

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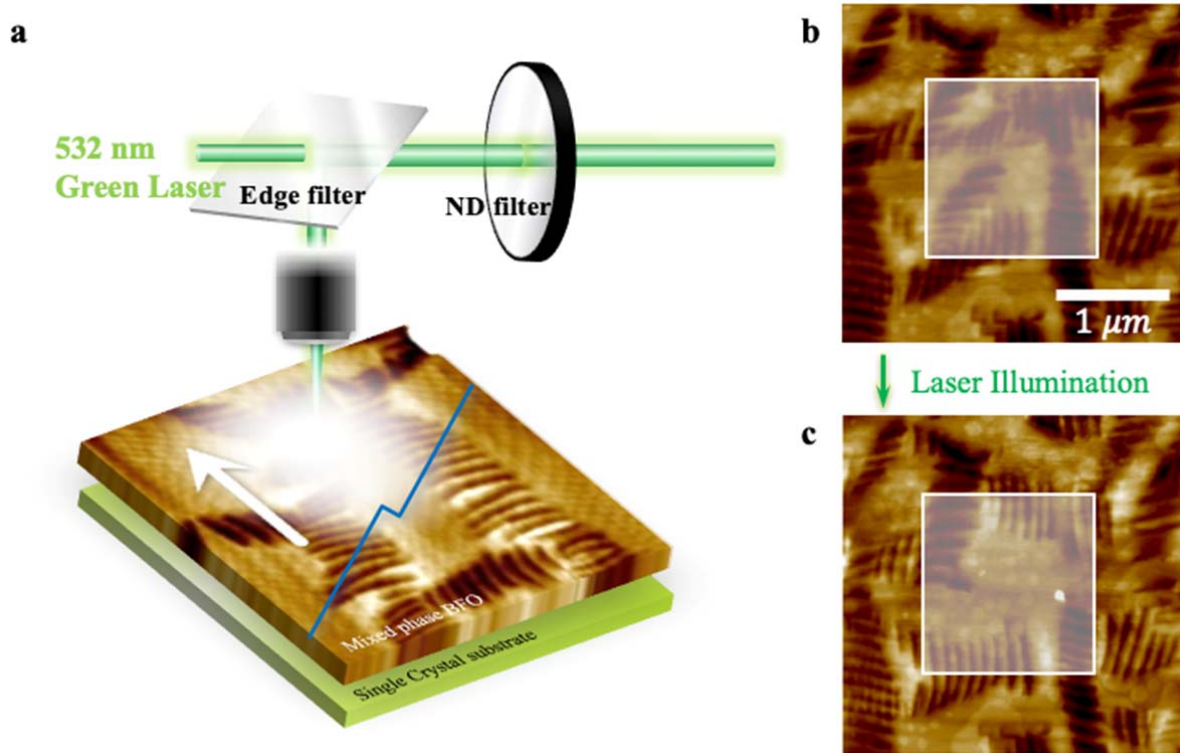
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521 **Figures**

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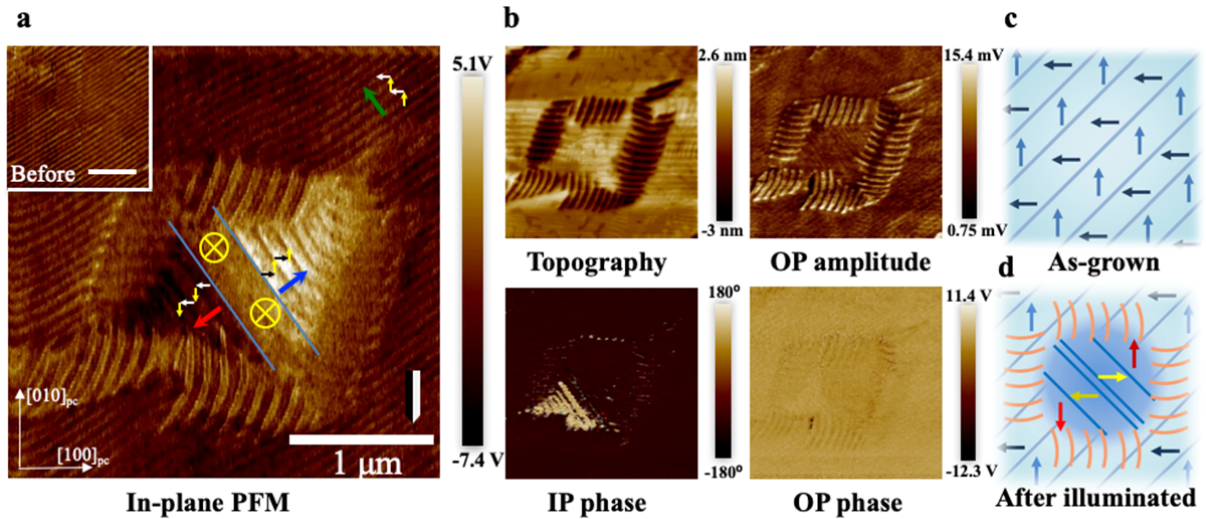
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525 **Fig. 1 Optical modulation of the highly-strained BFO thin film.** **a**, Experiment setup of a
526 double-stage green-laser-based (532 nm) illumination system, in which a attenuation-adjustable
527 neutral density filter (ND filter) is used to offer precise control on the laser intensity. **b**, Topography
528 image of an as-grown mixed-phase BFO thin film. **c**, Topography image of the same area after light
529 illumination, showing a clear phase redistribution of T-like and R-like BFO phases. The white
530 square indicates the illuminated area.

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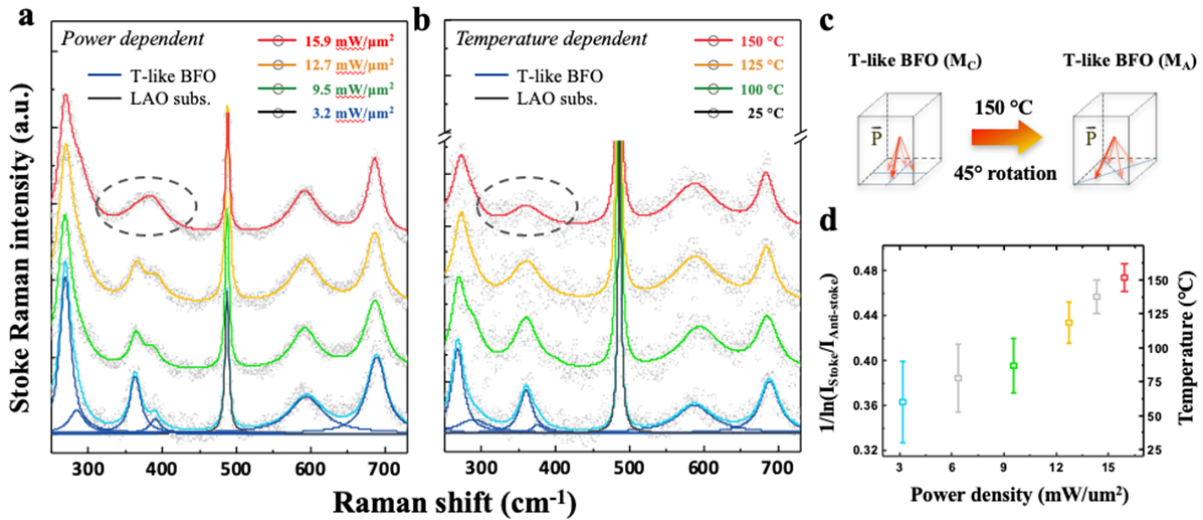
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Fig. 2 The Ferroelectric configuration of a highly-strained BFO thin film after light illumination. **a**, In-plane (IP) PFM image of the light induced domain structure. The directions of the IP polarization of as-grown and induced T-BFO domains are marked by the small colored arrows in the image. The yellow, black and white arrows represent the T-BFO domain with in-plane polarization pointing along $[010]_{pc}/[0\bar{1}0]_{pc}$, $[100]_{pc}$ and $[\bar{1}00]_{pc}$, respectively, as identified by scanning cantilever parallel to $[010]$. The bold arrows (red, blue and green) indicate the net IP polarization directions. The inset shows the IP PFM image of the initial T-BFO domain matrix. **b**, Topography, IP and out-of-plane (OP) PFM taken in the same area. The original downward polarization is presented in OP bright contrast. **c**, Schematics of the domain variation in IP polarizations before and after laser illumination.

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556 **Fig. 3 Raman scattering study on the illuminated area. a,b,** Power-dependent (a) and

557 temperature-dependent (b) Raman spectra of mixed-phase BFO film. The weakened and broaden

558 feature of phonon mode $\sim 364 \text{ cm}^{-1}$ of T-BFO is observed in both spectra due to structure phase

559 transition, which corresponds the power density of $15.9 \text{ mW}/\mu\text{m}^2$ to local heating temperature of

560 $\sim 150^\circ\text{C}$. Detailed analysis of peak evolution during phase transition is provided in supporting

561 information (Fig. S5). c, Schematic of T-BFO phase transition at 150°C , at which the monoclinic M_C

562 phase transforms to M_A phase, accompanying a 45 degree rotation of polarization. d, Local heating

563 temperature estimated by Stokes/Anti-stokes ratio of 689 cm^{-1} Raman band of T-BFO. The error bar

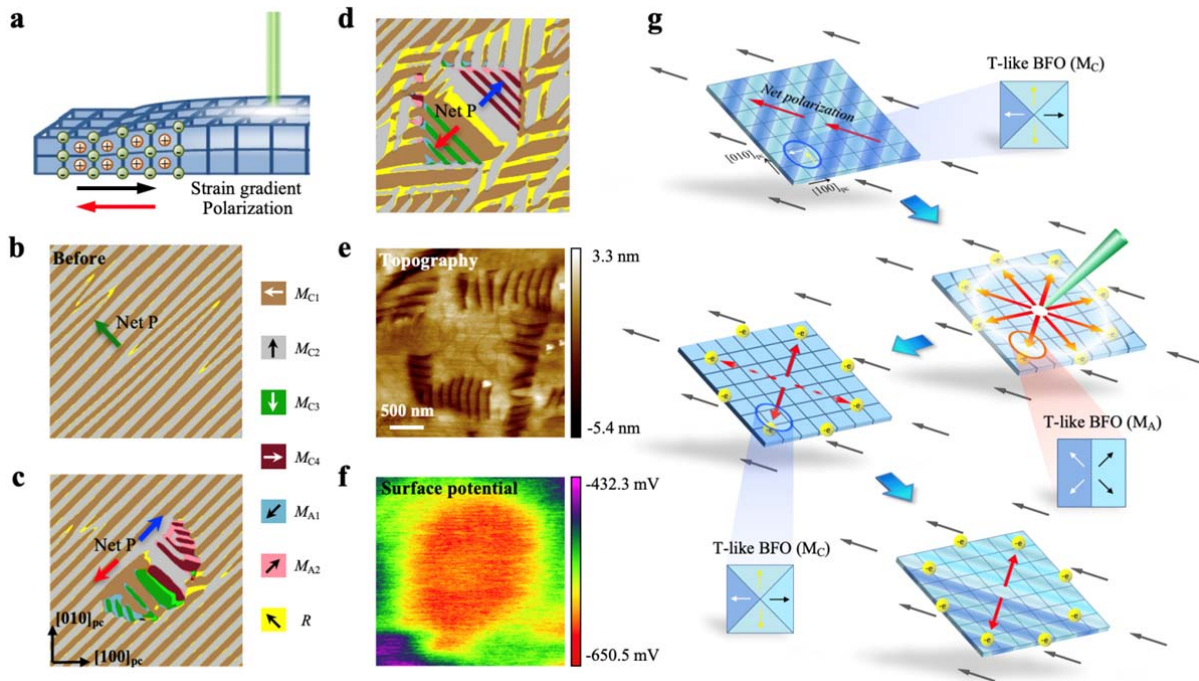
564 is calculated by considering the signal-to-noise ratio based on different illumination condition. The

565 detailed information related to the temperature estimation is described in supporting information

566 (Fig. S6)

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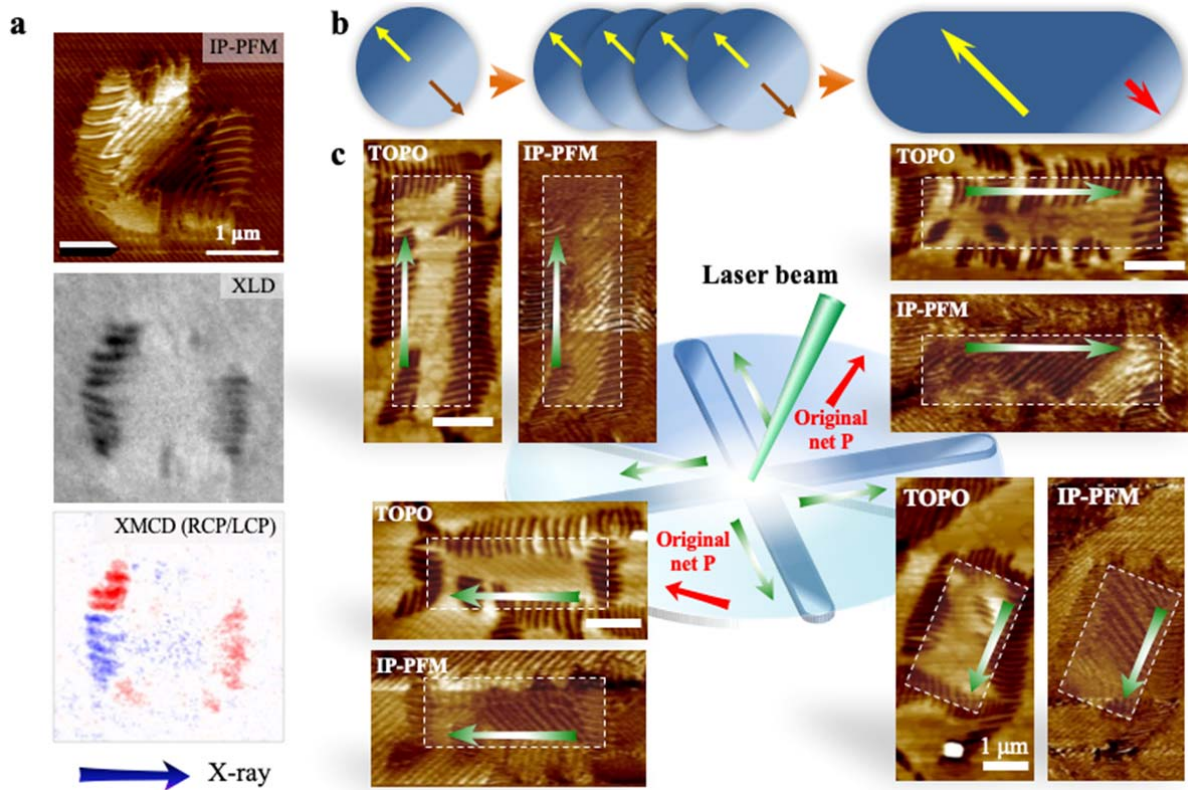


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570 **Fig. 4 Phase-field simulations and flexoelectric effect under illumination.** **a**, Schematic of strain
 571 gradient induced flexoelectric polarization under illumination. **b-d** Phase-field simulation on
 572 domain structures of highly-strained BFO. **(b)** The simulated domain structure before light
 573 illumination, where the green arrow indicates the net in-plane polarization. **(c)** Simulated
 574 equilibrium domain structure under dome-like strain/stress distribution in the illuminated area. **(d)**
 575 Simulated equilibrium domain structure when the induced flexoelectric field effectively points
 576 along $[110]_{pc} / [\bar{1}\bar{1}0]_{pc}$. The red and blue arrows in **(c)** and **(d)** indicate the net in-plane polarization
 577 of the switched T-BFO. **e**, Topography and **f**, corresponding surface potential image take at the same
 578 illuminated region. **g**, Schematic illustration of light-induced domain formation driven by the
 579 combination of laser heating and flexoelectric effect. In **(g)**, the bold arrows in black and red colors
 580 present the net in-plane polarizations of non-illuminated and illuminated area, respectively. The
 581 short colored arrows in the extended sketches show the possible in-plane polarization variants of
 582 M_C and M_A BFO phases. The radiative orange arrows represent the effective flexoelectric field,
 583 which drift the hot carriers from the photo-excited region to the illumination boundaries.

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588 **Fig. 5 Optical control of room-temperature multiferroicity in BFO and creating designer**589 **domain architectures via laser-spot motion. a,** IP PFM and XLD/XMCD-PEEM images taken at

590 the same illuminated region. Strong black and white contrast in the XLD-PEEM image indicates the

591 strong dichroism resulting from antiferromagnetic order of BFO; while the red/blue contrast in

592 XMCD-PEEM image show the existence of ferromagnetic moments lying parallel/antiparallel to

593 k -vector of the incident X-ray, respectively. **b,** Schematics of the optical driven domain

594 transformation and domain percolation with continually moving light spot towards right hand side.

595 The yellow and brown arrows indicate the net in-plane polarization in the center of illumination

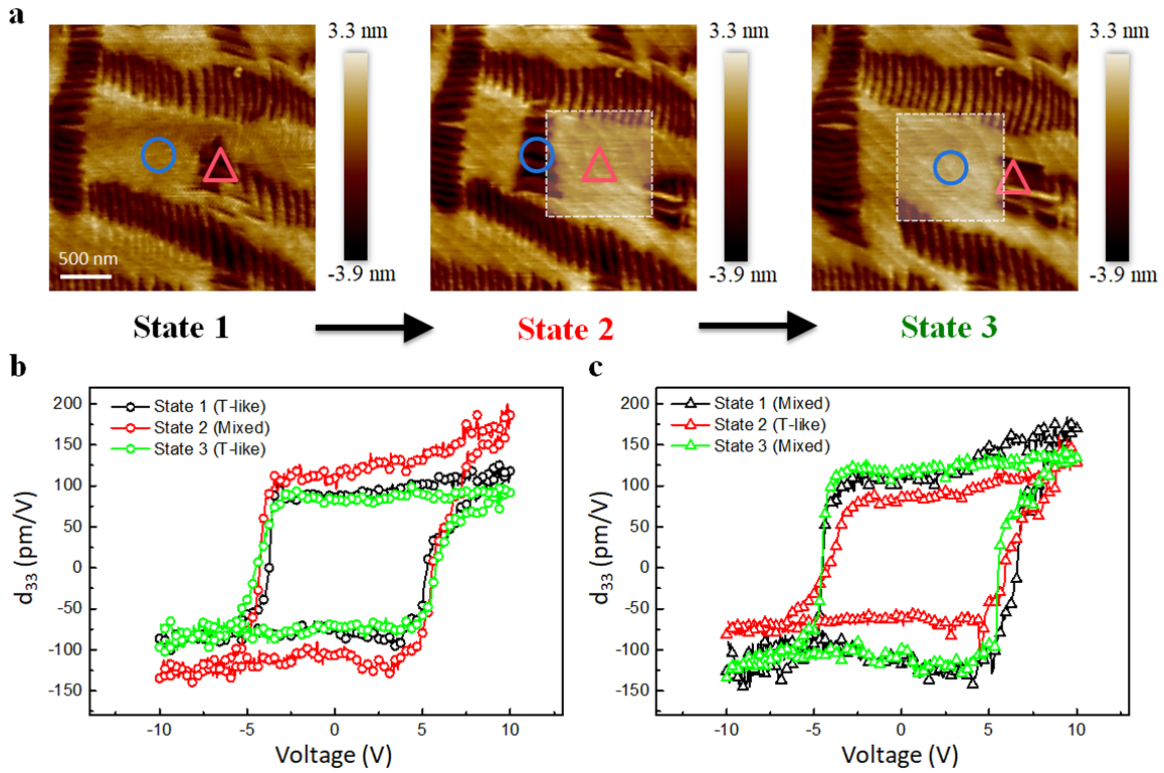
596 spot, while green arrow indicates the moving direction of the laser spot. The in-plane electric fields

597 of domains at rear parts of the illumination trajectory determine the polarization preference of

598 resultant domains. **c,** Experimental demonstration of optical controlled designer domain599 architectures by moving the light spot along $\langle 100 \rangle_{pc}$ directions.

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Fig. 6 Deterministic optical control of piezoelectric property in mixed-phase BFO. a, Topography images of mixed-phase BFO after repeatedly illumination taken in the same area. The d_{33} loop measured b, at blue circle and c, at red triangle with respect to state 1, 2 and 3. An enhanced d_{33} value can be observed with the formation of mixed-phase state, while a lower d_{33} value is obtained at the location of T-BFO.