**Terahertz field-induced ferroelectricity in quantum paraelectric SrTiO₃**

Xian Li¹, Tian Qiu², Jiahao Zhang², Edoardo Baldini³, Jian Lu¹*, Andrew M. Rappe³, Keith A. Nelson¹†

“Hidden phases” are metastable collective states of matter that are typically not accessible on equilibrium phase diagrams. These phases can host exotic properties in otherwise conventional materials and hence may enable novel functionality and applications, but their discovery and access are still in early stages. Using intense terahertz (THz) field excitation, we found that an ultrafast phase transition into a hidden ferroelectric phase can be dynamically induced in quantum paraelectric strontium titanate (SrTiO₃). The induced lowering in crystal symmetry yields substantial changes in the ferroelectric phase can be dynamically induced in quantum paraelectric SrTiO₃. Using intense terahertz (THz) light field to move the ions into their positions in the incipient crystalline phase. This case was forshadowed by molecular dynamics (MD) simulations of THz field–induced switching between different FE domain orientations, a closely related type of “collective coherent control” (12).

STO is a widely used dielectric material that has a cubic perovskite structure at room temperature. Many members of this crystal family (e.g., PbTiO₃) undergo first-order FE transitions into metastable collective states, or “hidden phases.” These phases are rarely accessible on equilibrium phase diagrams and may persist long after the external stimuli that induced them have ceased. Recent experiments (1–6) have illustrated some of the possibilities and expanded our understanding of nonequilibrium material properties and dynamics. In some cases, ultrafast resonant excitation of soft lattice vibrational modes (phonons) has played the key role in reaching hidden metallic and superconducting phases (1, 2). Here, we extend this capability in the discovery of a hidden ferroelectric (FE) phase in the paradigmatic material SrTiO₃ (STO). We accessed the hidden phase by selectively exciting the “soft” phonon mode that serves as a collective reaction coordinate along which ions move from their initial positions toward their positions in the new phase (Fig. 1). The resulting ultrafast control over ferroelectricity may find rich applications in memory devices (7), STO-based heterostructures (8), and high-TC superconductivity (9, 10). In other recent experiments (11), ionic displacements along soft-mode coordinates have been driven through nonlinear coupling between the soft modes and other phonon modes that were excited by long-wavelength infrared pulses. In the present case, we excite the soft mode directly, using a terahertz (THz) light field to move the ions into their positions in the incipient crystalline phase. This was foreshadowed by molecular dynamics (MD) simulations of THz field–induced switching between different FE domain orientations, a closely related type of “collective coherent control” (12).

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**Fig. 1. Hidden ferroelectric phase accessed through THz field excitation.** *(A)* Collective coherent control over material structure. A single-cycle THz-frequency electric field moves all the ions it encounters toward their positions in a new crystalline phase. In STO, the initial high-symmetry configuration around each Ti⁺⁺ ion has no dipole moment and the crystal is paraelectric. The incident field drives the “soft” lattice vibrational mode, moving the ions along the directions indicated into a lower-symmetry geometry with a dipole moment. Long-range ordering of dipole moments in the same direction yields a FE crystalline phase. *(B)* Experimental setup. THz field–induced lowering of the STO crystal symmetry is observed using 800-nm probe pulses that are partially depolarized (terahertz Kerr effect, or TKE) and which are partially converted to the second harmonic frequency (THz field–induced second harmonic, or TFISH). STO crystal cut is (100). The 800-nm probe pulses are polarized at 45° relative to the vertical THz polarization in the TKE experiments and 0° in the TFISH experiments, respectively. The reflected 400-nm signal is not polarization-resolved. DM, dichroic mirror; PMT, photomultiplier tube.
involves motions of the ions along the soft phonon coordinate illustrated in Fig. 1A. In contrast, upon reduction of the temperature to 105 K, STO undergoes an antiferrodistortive (AFD) structural phase transition into a second paraelectric phase of tetragonal symmetry \( (13, 14) \). Further cooling reveals mode softening (decrease in frequency \( \omega \)) in the usual Curie-Weiss form \( \omega \approx (T - T_c)^{1/2} \) with critical temperature \( T_c = 36 \) K \( (15) \), but at such a low temperature, the zero-point quantum uncertainties in ion positions prevent long-range FE ordering of their locations. Thus, STO is a textbook example of a so-called quantum paraelectric (QPE) phase \( (15) \), in which dipole correlation lengths do not extend beyond nanometer length scales \( (16) \). Recently, studies have shown that the QPE state in STO is a result of a more complex competition among three driving forces \( (17, 18) \): quantum fluctuations, AFD structural distortions (rotations of neighboring oxygen octahedra in opposite directions), and ferroelectric ordering. As a result, even subtle perturbations such as \( ^{18} \)O isotope substitution \( (19) \) are able to turn STO ferroelectric.

Here, we show that intense coherent THz excitation of the FE soft modes in STO can lead to highly nonlinear phonon responses that overcome the quantum fluctuations and yield clear signatures of an ultrafast QPE-to-FE phase transition. The observed signals reveal a substantial rise in ferroelectric ordering and restructuring of phonon spectra beyond a threshold THz field strength, indicating the emergence of the collective FE phase.

We carried out two complementary experiments with single-cycle THz pump pulses and time-delayed optical probe pulses (Fig. 1B). THz field–induced second harmonic (TFISH) generation spectroscopy \( (20) \) was conducted to observe signals that arise from inversion-symmetry breaking due to coherent soft-mode lattice vibrational motion away from the initially centrosymmetric structure of the QPE phase. THz field–induced optical birefringence (THz Kerr effect, or TKE) spectroscopy \( (21) \) was performed to characterize Raman-active phonon responses that were driven nonlinearly by the THz-initiated soft-mode lattice vibrations. Figure 2 shows TFISH measurement results from STO and their Fourier transforms at several temperatures and THz field amplitudes. At temperatures above 30 K, a single mode that softens with decreasing temperature, consistent with the FE soft mode, is observed \( (14, 22) \).

**Fig. 2.** STO symmetry breaking measured by optical second harmonic generation (TFISH). (A and B) Temperature-dependent TFISH signals recorded at 550 kV/cm field amplitude from STO (A) and their Fourier transforms (B). The FE soft mode is observed above 30 K, and new phonon peaks as well as nonoscillatory signals appear at lower temperatures. (C and D) THz field strength–dependent TFISH signals measured at 5 K (C) and their Fourier transforms (D). Signals at low field strengths are magnified by the amounts indicated in (D) for better visibility. Pronounced changes in the nonoscillatory signal components and the phonon spectra occur when the THz field level is increased above 340 kV/cm. The numerical first derivatives of the time-domain signals were calculated before Fourier transformation to reduce the relative amplitude of the nonoscillatory components.

**Fig. 3.** Strongly nonlinear phonon responses appear in the low-symmetry STO phase. (A and B) Temperature dependence of THz-induced optical depolarization (TKE) signals recorded with 630 kV/cm THz pump field amplitude (A) and their Fourier transforms (B). The numerical first derivatives of the time-domain signals were calculated before Fourier transformation to reduce the relative amplitude of the nonoscillatory components. At temperatures of 60 K and above \( (22) \), no oscillatory signal is observed after THz excitation. The 1.3-THz peak and additional low-frequency modes appear at low temperatures. (C) THz field strength dependence of the TKE spectra at 10 K. New peaks grow in sharply as the THz field level is increased from 470 to 630 kV/cm. Inset: Quadratic fit to the 1.3-THz \( A_{1g} \) mode. The 0.8-THz mode shows faster than quadratic scaling in the THz field strength.
are observing these modes, with frequencies a ss h a r l y as h o w e r - f r e q u e n c y p e a k s. W e b e -
ture and whose signal strength does not increase
with the FE crystal structure. We also observe a
fields indicates their displacements associated
serving them, and that their sharp onset at high
altered slightly as a result of the nonequilibrium
transition temperature (T).
in the extent of steady-state (nonoscillatory) di-
stantially at high THz field amplitudes: (i) The
nonoscillatory signal component grows in a
nonoscillatory signal due to THz-induced
fig. S1B shows the AFD mode coordinate (25) that
is coupled anharmonically to the soft mode. Similar nonlinear coupling has been observed in
room-temperature STO using femtosecond x-ray
diffraction (26).
Figure 3 shows TKE data recorded at several
sample temperatures and THz field strengths. Although the optical and THz pulses propagate
with very different velocities in STO (21, 27), the
strong THz absorption (28) ensures that this does
not affect the time-dependent signals. At high
temperatures (Fig. 3A), only nonoscillatory signals are observed. Unlike such signals in the TFISH
data, these signals show only weakly T-dependent
decay kinetics and they do not increase substan-
tially as functions of either temperature or THz
field amplitude (figs. S7 and S8). They are asso-
ciated with dipole alignment rather than FE
orientation or polarity (22). We also observe the
A mode at 1.3 THz, which increases quadra-
tically with THz field strength, indicating ordi-
nary anharmonic coupling to the FE soft mode as
suggested above. By far most striking is the
emergence of several low-frequency phonon fea-
tures whose strengths depend in a highly non-
linear fashion on the THz field strength, clearly
similar to what we observed in TFISH measure-
ments. We conclude from all the experimental
evidence that at sufficiently large soft-mode
amplitudes, an ultrafast FE phase transition is
triggered. The strong nonlinear TFISH sig-
nals reveal the associated increase in FE order-
ing. The modes that grow in sharply as the THz
field amplitude is increased reveal collective dis-
placements of ions along multiple vibrational
modes that are coupled nonlinearly to the soft
mode and also reveal the change in lattice sym-
metry. It has been suggested that excitation of
the Raman modes may provide constructive
feedback to the FE soft mode that drives them by
disrupting the balance between AFD and FE
structural distortions (17, 18, 29), thereby
dynamically destabilizing the paraelectric ground
state on a multidimensional energy landscape.
To reach a clearer understanding of THz-
induced effects, we conducted classical MD simu-
lations for a supercell of 20 × 20 × 20 unit cells
in an isothermal-isobaric ensemble, with the inter-
atomic interaction described by the bond valence
model and with external pressure applied (22).
For each MD simulation, the system was first
relaxed for 100 ps to reach equilibrium at 5 K,
and then a Gaussian-profile electric field pulse
duration 0.66 ps, full width at half maximum)
was applied in either the z or x crystallographic
direction. Trajectories of the system were col-
lected for 50 ps, with the electric field reaching
its maximum at 11.5 ps. To evaluate whether the
electric field could induce ferroelectricity in STO,
we performed simulations with different field
amplitudes, and in each case we calculated the
global polarization of the system from the col-
lected trajectories. As shown in Fig. 4A, the in-
duced polarization rises sharply over a narrow
range of applied field amplitudes, saturating at
around 300 kV/cm along both the x and z direc-
tions. The important result of the simul-
ations is the confirmation that a single-cycle THz
field can induce a substantial global FE polari-
zation when the field is above a threshold level
on the order of 200 kV/cm. By calculating the
projections of the MD simulation trajectory along
different lattice vibrational mode coordinates, we
also confirmed that the key displacements occur
along the FE soft mode and the coupled AFD
mode coordinates (see (22) for details of the mode
assignments), whose calculated time-dependent
responses are shown in Fig. 4B. The soft-mode
response is driven directly by the THz field and
reaches its peak at the same time as the peak
field. The AFD modes are driven indirectly
through their anharmonic coupling to the FE
soft mode, and their peak displacements are
delayed as a result. The soft mode and the AFD
modes show steady-state displacements that
persist well after the THz field is gone, indi-
cating relaxation of the coupled system into the
FE structure.
The experimental data and MD simulations
together demonstrate a THz-induced ultrafast
QPE-to-FE phase transition in STO. The THz field
drives the soft mode, and additional coupled-
mode displacements occur to reach the FE struc-
ture. Our results demonstrate collective coherent
control of material structure that may be applica-
table to a wide range of classical and quantum
phase transitions in which soft phonon modes play
critical roles in the collective structural transfor-
mations.

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Fig. 4. MD simulation of response to STO THz excitation. (A) The peak global polarization
induced by excitation with a THz field along different crystallographic axes. A threshold electric field
amplitude of about 300 kV/cm is needed in order to fully polarize the crystal. (B) MD simulation
trajectory projection onto different vibrational mode coordinates. The soft-mode response is
driven directly and peaks at the same time as the z-polarized THz field (dashed vertical line).
The antiferrodistortive (AFD) modes are driven through coupling to the FE soft mode and reach their
maximum displacements after a delay. A steady-state AFD mode displacement (dashed green line
shows time-averaged value) as well as FE soft-mode displacement remain well after the THz driving
field has ceased.
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SUPPLEMENTARY MATERIALS
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Materials and Methods
Supplementary Text
Figs. S1 to S13
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**Driving strontium titanate ferroelectric**

Hidden phases are metastable collective states of matter that are typically not accessible on equilibrium phase diagrams. Nova *et al.* used infrared pulses to excite higher-frequency lattice modes that drive the crystal into a metastable ferroelectric phase, a phase that can persist for many hours. X. Li *et al.* used terahertz fields to drive the soft mode that moves the ions in the crystal into the positions they occupy in the new phase. The ferroelectric phase in this case was transient, lasting on the order of 10 picoseconds. Because these hidden phases can host exotic properties in otherwise conventional materials, the accessibility to and control of such hidden phases may broaden potential functionality and applications.

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