Terahertz field-induced ferroelectricity in quantum paraelectric SrTiO$_3$

Xian Li$^1$, Tian Qiu$^2$, Jiahao Zhang$^2$, Edoardo Baldini$^3$, Jian Lu$^1$, Andrew M. Rappe$^3$, Keith A. Nelson$^4$

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 electric field excitation, we found that an ultrafast phase transition into a hidden ferroelectric phase can be dynamically induced in quantum paraelectric strontium titanate (SrTiO$_3$). The induced lowering in crystal symmetry yields substantial changes in the ferroelectric phase transition. Our results demonstrate collective coherent control over material structures, in which a single-cycle field drives ions along the microscopic pathway leading directly to their locations in a new crystalline phase on an ultrafast time scale.

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$^{4+}$ 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 $\omega \propto (T - T_c)^{1/2}$ 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 overcame 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 (fig. S6) (14, 22).

![Fig. 2. STO symmetry breaking measured by optical second harmonic generation (TFISH).](image)

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.](image)

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.
direction break the symmetry, resulting in optical second harmonic signals that oscillate at twice the soft-mode frequency. There is also a non-oscillatory signal component due to THz-induced orientation of dipoles, whose decay becomes slower as $T$ is reduced because of the increasing dipolar correlation (23). In the QPE phase at $T < 36$ K, two features in the signals change substantially at high THz field amplitudes: (i) The nonoscillatory signal component grows in a highly nonlinear fashion as a function of the field strength, which indicates a pronounced growth with very different velocities in STO (21, 27), the strong THz absorption (28) that is coupled anharmonically to the soft mode. Similar nonlinear coupling has been observed in a highly nonlinear fashion with THz field strength amplitude. These features reveal additional atomic displacements that take place as the FE crystal structure is formed. At soft-mode amplitudes sufficient to reach the new phase, collective displacements of other phonon modes (coupled nonlinearly to the soft mode) are induced. The THz-induced ordered structure is noncentrosymmetric, so oscillations about this structure produce changes in the second harmonic signal level that oscillate at the phonon frequencies, not twice the frequencies. It is noteworthy that the three distinct low-frequency peaks in the TRISH response at high field strength are sharp as $T$ is reduced (fig. S9), as is known to occur for the soft modes in SrTiO$_3$ below its FE phase transition temperature (19). It is likely that we are observing these modes, with frequencies altered slightly as a result of the nonequilibrium transient crystal structure in which we are observing them, and that their sharp onset at high fields indicates their displacements associated with the FE crystal structure. We also observe a broad phonon feature at 1.3 THz whose frequency does not appear to change with temperature and whose signal strength does not increase as sharply as the lower-frequency peaks. We believe this behavior to be consistent with a Raman-active $A_{1g}$ mode (we retain the “$A_{1g}$” label even though the crystal symmetry has been changed; fig. SIB shows the AFD mode coordinate) (25) that is coupled anharmonically to the soft mode. Similar nonlinear coupling has been observed in a highly nonlinear fashion with THz field strength amplitude. These features whose strengths depend in a highly nonlinear fashion on the THz field strength, clearly similar to what we observed in TFIISH measurements. We conclude from all the experimental data and MD simulations for details of the mode assignments, whose calculated time-dependent response is 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, indicating 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 structure. Our results demonstrate collective coherent control of material structure that may be applicable to a wide range of classical and quantum phase transitions in which soft phonon modes play key roles in the collective structural transformations.

REFERENCES AND NOTES
ACKNOWLEDGMENTS

We thank T. Egami, A. Steinbacher, Y. Wang, and E. Demler for stimulating discussions. Funding: The work at MIT was supported in part by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, under award DE-SC0019126, and by Swiss National Science Foundation fellowship P2ELP2-172290 (E.B.). The work at Penn (T.Q., J.Z., and A.M.R.) was supported by the DOE, Office of Science, Office of Basic Energy Sciences, under grant DE-FG02-07ER46431. We acknowledge computational support from the NERSC of the DOE. Author contributions: K.A.N. conceived the project and the experiments together with X.L. and J.L.; the time-resolved THz setup was built by X.L., who performed the TFISH and TKE measurements and analyzed the data with support from E.B.; T.Q., J.Z., and A.M.R. provided MD calculations of the pump thresholds and mode displacements for the THz-driven ferroelectricity and the time- and mode-resolved responses; the manuscript was written by K.A.N., X.L., and E.B. with input from all authors. Competing interests: Authors declare no competing interests. Data and materials availability: All data are available in the manuscript or the supplementary materials.

SUPPLEMENTARY MATERIALS

science.sciencemag.org/content/364/6445/1079/suppl/DC1 Materials and Methods Supplementary Text Figs. S1 to S13 Table S1 References (30–47) 27 December 2018; accepted 20 May 2019 10.1126/science.aaw4913
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.

Science, this issue p. 1075, p. 1079