

Electronic Origin of Laser-Induced Ferroelectricity in SrTiO₃

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Supporting Information

ABSTRACT: Although ultrafast control of the nonthermally driven ferroelectric transition of paraelectric SrTiO₃ was achieved under laser excitation, the underlying mechanism and dynamics of the photoinduced phase transition remain ambiguous. Here, the determinant formation mechanism of ultrafast ferroelectricity in SrTiO₃ is traced by nonadiabatic dynamics simulations. That is, the selective excitation of multiple phonons, induced by photoexcited electrons through the strong correlation between electronic excitation and lattice distortion, results in the breaking of the crystal central symmetry and the onset of ferroelectricity. The accompanying population transition between $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals excites multiple phonon branches, including the two high-energy longitudinal optical modes, so as to drive the titanium ion away from the center of the oxygen octahedron and generate a metastable ferroelectric phase. Our findings reveal a cooperative electronic and ionic driving mechanism for the laser-induced ferroelectricity that provides new schemes for the optical control of ultrafast quantum states.



D ue to the fact that condensed matter can be nonthermally modulated by ultrafast laser pulses, photoinduced phase transitions have attracted much attention recently.¹⁻⁴ One of the major interests is the modulation of ferroelectricity by photoexcitation on the ultrafast time scale.⁵⁻²¹ Ferroelectricity, originating from a broken spatial inversion symmetry, is an important functionality of materials that have a spontaneous polarization, and the polarization direction is switchable by an external electric field. However, using ultrafast lasers to effectively modulate the ferroelectricity in materials remains a great challenge, and theoretical studies on ultrafast dynamics of ferroelectricity are scarce.

Strontium titanate $(SrTiO_3)$ is a prototypical incipient ferroelectric with a perovskite structure. The antiferrodistortive (AFD) phase transition occurs in bulk SrTiO₃ crystals at the temperature T = 105 K, which is associated with the soft phonon mode at the R point of the Brillouin zone boundary.^{22,23} This transition leads to extremely small lattice distortions, but is not accompanied by the discontinuity of the dielectric constant.²⁴ Further cooling shows that no ferroelectric phase transition occurs due to the suppression by quantum fluctuations.²⁵ However, weak modulations, such as external electric field, stress, strain, isotope substitution, or calcium doping, can lead to the ferroelectricity in SrTiO₃.²⁶⁻³¹ In addition, laser excitation has been proven to effectively induce a metastable ferroelectricity in SrTiO₃.^{5,32} Nova et al. applied femtosecond mid-infrared optical pulses to obtain a metastable polar state in SrTiO₃, where ionic displacements were driven through the nonlinear coupling between the ferroelectric soft mode and high-frequency phonons resonantly excited by ultrafast lasers.⁵ Li et al. used an intense terahertz light to directly drive the soft mode to obtain the "hidden"

ferroelectric phase, which was typically inaccessible in the equilibrium phase diagram. $^{\rm 32}$

Although experimental findings show obvious induced ferroelectricity in SrTiO₃ under laser excitations in the midinfrared frequency and THz regime, its microscopic formation mechanism (via pure ionic excitation or with the contribution of excited electrons) is presumptive and ambiguous. It is wellknown that SrTiO₃ is a centrosymmetric material with strong anharmonic lattice dynamics,^{33–35} caused by the competition between AFD and the ferroelectricity instability.^{36–38} Because of the complex electron–electron and electron–phonon interactions, understanding the driving force or microscopic mechanism of light-induced ferroelectric phase transitions is challenging.^{39–44} To this end, a quantitative analysis of the evolution of atomic and electronic dynamics based on firstprinciples time-dependent calculations is highly desirable.

In this work, we apply real-time time-dependent density functional theory (rt-TDDFT) for first-principles simulations of ultrafast dynamics in photoexcited $SrTiO_3$, to reveal the electronic origin of laser-induced ferroelectricity. We find that the paraelectric-to-ferroelectric transition in $SrTiO_3$ originates from the spatial inversion symmetry breaking induced by photoexcited electrons through the strong correlation between electronic excitation and lattice distortion. The femtosecond laser pulse drastically changes the charge density between the

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Figure 1. (a) Lattice structure of cubic SrTiO₃ in a unit cell. (b) Potential energy surfaces of SrTiO₃. Here we vary the lattice length of SrTiO₃ along the [001] direction. The distortion ratio Δ (%) is defined as $\Delta = \frac{c-c_0}{c_0} \times 100$, where c_0 is the optimized lattice parameter and *c* is the lattice length along the [001] direction under deformation. The total energy of optimized cubic SrTiO₃ structure is set to zero, where the Ti ion is located in the center of the oxygen octahedron.



Figure 2. (a) Time evolution of the laser field waveform (upper panel) and the $SrTiO_3$ lattice parameters (lower panel). The applied Gaussianshaped electric field is polarized along the [001] direction of bulk $SrTiO_3$ with a peak intensity of 0.077 V/Å and a photon energy of 1.55 eV. The laser field reaches the maximum intensity at 16 fs with a fwhm of 10 fs. (b) Time evolution of the polarization formation in $SrTiO_3$. (c) Snapshots of the atomic structure of $SrTiO_3$ and the charge density difference of the (010) plane across the Ti ion upon photoexcitation at t = 0, 20, 40, 120, and 200 fs, respectively. The charge density range is from -0.001 to +0.001 e/bohr³.

top O and Ti ions along the laser polarization direction, which induces a transient uniaxial tensile deformation. The electron– phonon interactions lead to the selective excitation of multiple phonon branches, especially the two high-energy longitudinal optical (LO) modes, which drives the Ti ions away from the center of the oxygen octahedron and into new positions favoring the ferroelectric phase on an ultrafast time scale. Meanwhile, we also find that in the early excitation stage the charge carrier excitation on Ti ions is dominated by the $3d_{z^2}$ orbital, while in the ferroelectric phase the charge transfer is mainly coupled to the $3d_{x^2-y^2}$ orbital, both of which are accompanied by a gradual accumulation of charge population on the $3d_{xz}$ and $3d_{yz}$ orbitals, indicating the occurrence of interorbital mixing. This mechanism, namely, cooperative interplay between directly irradiated electrons and induced phonon excitation, is rather different from the assumption of nonlinear couplings between phonon coordinates and the crystal stress.⁵ Such nonthermal controlling of ferroelectricity by ultrafast laser excitation of materials opens a wide range of potential applications, such as optical switches and memory devices, where optical responses can be efficiently modulated by ultrafast laser pulses.

The optimized structure of cubic $SrTiO_3$ is shown in Figure 1a with a calculated lattice parameter of 3.876 Å, in good

agreement with the experimental value of 3.905 Å.⁴⁵ Due to the centrosymmetric structure, the cubic phase of SrTiO₃ has no ferroelectricity. Then we first apply stretching forces along the [001] direction of SrTiO₃, and the calculated energy surfaces indicate that the uniaxial tensile distortion accounts for the paraelectric-to-ferroelectric phase transition of SrTiO₃, as shown in Figure 1b. We define the distortion ratio (%) of lattice length as $\Delta = \frac{c - c_0}{c_0} \times 100$, where c_0 is the optimized lattice parameter of cubic $SrTiO_3$ and c is the lattice length under deformation along the [001] direction. In Figure 1b, we show that the potential energy surface along the [001] direction changes from a single well to a double well as the tensile distortion is applied. In addition, the depth of the double well increases with the rise of the distortion ratio (Δ). The potential barrier (depth) of double well is 20 meV when Δ = 5%, and it increases to 79 meV when Δ = 10%. The applied tensile distortion drives Ti ions away from the center of the oxygen octahedron, breaking the centrosymmetry of SrTiO₃. Such symmetry breaking generates a nonzero electric dipole moment in SrTiO₃. When the lattice is stretched by 10%, the position of the Ti ions deviates from the center of the oxygen octahedron by 0.23 Å along the [001] direction, resulting in a ferroelectric polarization of 0.234 C/m^2 . In contrast, lattice compression along the [001] direction of SrTiO₃, corresponding to a negative Δ , fails to form the double well potential energy surface and the transit polar state.

To explore the electronic evolution and ionic dynamics of laser-induced paraelectric-to-ferroelectric phase transition in SrTiO₃, we now apply a Gaussian-shaped laser pulse with a wavelength of 800 nm and field polarization lying along the [001] direction of SrTiO₃. A maximum intensity of 0.077 V/Å and a full width at half-maximum (fwhm) of 10 fs are chosen for the applied laser field, as shown in the upper panel of Figure 2a. The photoinduced structural change and associated phase transition are well captured in our rt-TDDFT molecular dynamic (MD) simulations. In the lower panel of Figure 2a, we present the variation of the lattice vectors of SrTiO₃ as a function of time upon photoexcitation. It shows that after the first 100 fs of the short period oscillation, the lattice parameter c along the [001] direction is stretched to ~4.2 Å, while the changes in lattice parameters a and b remain oscillating around the initial values. Moreover, the polarization in the [001] direction rises to ~ 0.57 C/m² after 100 fs, as reported in Figure 2b, contrary to the slight thermal fluctuations in other axial directions. Upon the transition from the paraelectric to ferroelectric state, the volume change of the SrTiO₃ unit cell in our simulation is about 1%. The lattice stretching along c direction obtained here is overestimated to some extent compared to the strain ratios achieved in experiments with longer-wavelength laser.⁵ This is related to limitations of the model system we used, which include two main aspects: the lack of boundary constrains in the constant-pressure-energy (NPE) ensemble (see Figure S1) and the direct action of the laser pulse on the interior of the lattice, resulting in a high sensitivity of the lattice response. We emphasize that the nonequilibrium phenomena probed by our simulation show the laser-induced transient strain effects, which may correlate with the steady-state phenomena. In contrast, the strain measured in the experiment is a macroscopic observation at near equilibrium.

Our simulations indicate that the ultrafast laser pulse induces a spatial inversion symmetry breaking in $SrTiO_3$, forming the electric dipole moment along the light polarization direction. The system transforms into a metastable ferroelectric state after 150 fs, with a maximum polarization value of ~ 0.57 C/m^2 along the [001] direction, which has the same order of magnitude as the spontaneous polarization of typical ferroelectric materials, such as BaTiO₃, PbTiO₃, and KNbO₃.⁴⁶

Since the calculated direct band gap obtained with LDA is 2.01 eV, as shown in Figure S2, which is underestimated with respect to the experimental value,⁴⁷ we further clarify the quantitative effect of the calculated band gap value. We raise the energy level of the conduction band to achieve an experimental value of 3.75 eV for the direct band gap of SrTiO₃ crystal by a scissor correction, and repeat the nonadiabatic quantum simulations of the photoexcitation by applying the same laser pulse. We find that although the overall excitation amount becomes smaller (about one-third of that obtained with LDA gap), the ultrafast laser-induced polarization is still formed in SrTiO₃ along the [001] direction albeit with a reduced amplitude, as shown in Figure S3.

We further analyze the motion of atoms in SrTiO₃ to reveal the key factors affecting the formation of ferroelectricity. As displayed in the upper panel of Figure 2c, the Ti ion, at the center of the oxygen octahedron in the ground state (0 fs), deviates from the center under the action of the laser field (20-200 fs), leading to the anisotropic lattice distortion and thus the formation of electric dipole moments in the [001] direction. In the lower panel of Figure 2c, we present the distribution of charge density difference between timedependent Kohn-Sham orbitals and the corresponding ground-state orbitals during the process of ferroelectric phase transition. It clearly shows that due to the choice of [001] laser field polarization, the charge density distribution along the top O¹ and Ti ion is drastically modulated, while the variation between the lateral O^2/O^3 and Ti ions is very small. The charge density along the O¹ and Ti direction shows an increase in the presence of light, indicating an enhanced interatomic force on ions in the light polarization direction. We present in Figure S4 the variation of the interatomic forces on the Ti and O¹ ions with time during the early stages of light irradiation. It shows that at the end of the direct action of light, Ti is subjected to a force along the z-axis, while O^1 is subjected to a force in the opposite direction, leading to an enhanced interaction between O¹ and Ti, thus a compression of the lattice. This fact explains the instantaneous *c*-axis compression before the formation of polarization.

After the duration of the laser pulse (40 fs), the interatomic force between the O^1 and Ti ions falls and the distance between the top O^1 and Ti begins to grow. Since 120 fs, the stretched lattice vector *c* and electric polarization have been formed and retained in the remaining simulation time. The photoinduced charge density variation promotes the symmetry breaking of SrTiO₃ lattice structure along the *c*-axis. In the whole process of ferroelectric phase transition in SrTiO₃, the position of the Ti ion with respect to the center of the oxygen octahedron is the key structural order parameter to produce the polarization and ferroelectricity of the photoexcited material.

The tensile distortion induced by laser excitation is a nonthermal process and the ultrafast laser directly excites the electronic subsystem rather than the ionic subsystem in $SrTiO_3$. For $SrTiO_3$ in the ground state, the electronic states in the energy range from -5 to 0 eV are dominated by the O_{2p} orbitals, and the unoccupied electronic states in the energy



Figure 3. (a) Distribution of excited electrons and holes (gray region) in $SrTiO_3$ and the partial density of states of O_{2p} and Ti_{3d} orbitals. The electrons are mainly excited from the O_{2p} (red lines) to Ti_{3d} (blue lines) orbitals. Fermi energy E_F is set to zero, which is the highest occupied state at the edge of the valence band. Black arrows indicate a multiphoton process. (b) Time evolution of the effective charge for all atoms in $SrTiO_3$ and the charge population on the Ti_{3d} orbitals.

range from 0 to 5 eV are mainly the Ti_{3d} states.⁴⁷⁻⁴⁹ Upon laser illumination, electrons are transferred to the conduction bands, and holes are generated in the valence bands simultaneously. We calculate the distribution of excited electrons and holes in SrTiO₃, compared with the partial density of states of O_{2p} and Ti_{3d} orbitals in Figure 3a. Since the calculated band gap of 2.01 eV is larger than the incident photon energy (hv = 1.55 eV), the excitation process is mainly a multiphoton process, as illustrated in Figure 3a. We vary the electric field strength of the laser pulses and show the corresponding distribution of excited carriers in Figure S5. We note that the electron excitation processes are dominated by two-photon absorption and the number of excited electrons is quartic as a function of electric field. Subsequently, the excitation energy is rapidly transferred to the lattice degrees of freedom through electron-phonon couplings, leading to further ion displacements. Hot electrons and holes enter the relaxation stage by carrier-carrier and carrier-phonon scatterings. After the direct action of the laser pulse (40 fs), the number of excited electrons maintains at about 0.005 electrons per unit cell, but the system continues to evolve, forming the nonthermal ferroelectricity in SrTiO₃. Cohen has demonstrated that the hybridization between the 3d states of Ti and the 2p states of O is essential for the ferroelectricity in perovskite oxides.⁵⁰ The variation of partial density of states for $O_{2\mathfrak{p}}$ and Ti_{3d} with time indicates the development of orbital hybridization in SrTiO₃, which is essential to weaken the shortrange repulsions and to promote the ferroelectric distortions.

The stretching of lattice is closely related to the change of atomic effective charges. Mulliken charge analysis is used to characterize the charge distributions on each atom and typical orbitals. We present the variation in the effective charge of all

atoms in SrTiO₃ and the 3d orbitals of Ti over time in Figure 3b. As shown in the upper panel of Figure 3b, laser irradiation has the most significant effect on the effective charge of the Ti and O^1 ions along the *c* axis. The effective charge of the Ti ion increases by about 0.1 e and that of the O¹ ion decreases by about 0.13 e in the period right after laser action (blue span in Figure 3b). Such a major charge transfer between the Ti and O¹ ions leads to a strong ion-ion interaction, accounting for the *c*-axis transient compression right after photoexcitation. On the other hand, the effective charge variation of the O^2 and O^3 ions is relatively small, thus with no obvious change in the lattice vectors a and b in the early excitation stage (<80 fs). After about 40 fs electron-hole relaxation process (orange span in Figure 3b), more holes are located on O^2 and O^3 , resulting in the lattice subsequent compressing along a and bdirections and stretching along the c axis (gray span in Figure 3b). Attributed to the charge-transfer-assisted breaking of spatial inversion symmetry, photoinduced ferroelectric polarization is formed after ~120 fs. Meanwhile, we also find that charge carrier excitation on the Ti ion in the early stage is dominated by the $3d_{z^2}$ orbital, while in the ferroelectric phase, the carrier motion is mainly coupled with the $3d_{x^2-y^2}$ orbital of titanium. The different behaviors involving $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals are a clear indication of the breaking of crystal centrosymmetry, which eventually leads to the emergence of uniaxial lattice stretching along the laser polarization direction. We also note that there is a gradual accumulation of electrons in the t_{2g} orbital of Ti ions (more specifically, the $3d_{xz}$ and $3d_{yz}$ orbitals) during the both stages, which is responsible for the occurrence of metastable tensile distortion of photoexcited SrTiO₃. The force analysis of the Sr ion indicates that the effective charge change of the Sr ion has little effect on

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Figure 4. (a) Phonon dispersion spectrum and time evolution of all 15 Gamma-point projected phonon branches in $SrTiO_3$. Five excited phonons are three LO branches (LO-1 at 4.82 THz, LO-2 at 13.44 THz, LO-3 at 23.75 THz) and a degenerated T_{2u} mode (6.63 THz). (b) Vibrational modes of five excited phonons. (c) Schematic diagram of photoinduced ferroelectric phase transition process in $SrTiO_3$.

breaking the central symmetry of the crystal, although the charge fluctuations of Sr during the process is similar to those of Ti.

In order to identify the phonons established during the ferroelectric phase transition of SrTiO₃ by vibrational excitation, we calculate the phonon dispersion spectrum and all 15 eigenvectors of phonons at the Gamma point, as shown in Figure 4a and Figure S6. The time evolution of each phonon branch is explored by projecting the displacement of ions in the trajectory onto the 15 phonon eigenvectors calculated from the equilibrium ground state. The projection intensity is defined as $\sum_{i} e_{i} \cdot u_{i}$, where u_{i} is the displacement vector of atom j from its original position at t = 0 and e_i is the *i*th phonon eigenvector at the Gamma point. As shown in Figure 4a, three LO phonons and a degenerate (T_{2u}) phonon are mainly excited by laser, labeled as LO-1, LO-2, LO-3, and T_{2u} modes, with the corresponding frequencies located at 4.82 THz, 13.44 THz, 23.75 THz, and 6.63 THz, respectively. The vibrational modes of five excited phonons are shown in Figure 4b. Since the polarization direction of the ultrafast laser is along the [001] direction, the excited phonons are mainly LO phonons rather than transverse optical (TO) phonons or acoustic phonons. The ultrafast laser field exerts directly on the electronic subsystem instead of the SrTiO₃ lattice, yielding the electronic excitation of the system. Through the electronphonon coupling, the lattice begins to undergo a vibrational excitation after 20 fs. The excited vibrational phonon modes, especially LO-2 and LO-3, collectively control the structural deformation, driving the ferroelectric phase transition of SrTiO₃. Recently, Zhou et al. also demonstrated that LO-2 and LO-3 phonons exhibit the strongest coupling with electrons.³⁹ Therefore, such paraelectric-to-ferroelectric structure transition in SrTiO₃ is a nonthermal process, driven by the strong couplings between specific phonon modes and electronic states excited by the ultrafast laser.

Clearly, ultrafast lasers open an effective channel to change the potential energy surface in a nonthermal way, allowing the system to reach a metastable ferroelectric phase. As illustrated in Figure 4c, femtosecond laser induces anisotropic lattice distortion and breaks the inversion symmetry of $SrTiO_3$ by directly changing the charge distribution between the O and Ti ions. Electron-phonon interactions drive the Ti ions away from the center of the oxygen octahedron to a metastable position with the minimum local energy, so as to form a ferroelectric state along the polarization direction of light. Therefore, $SrTiO_3$ is excited from the low-energy ground state to the metastable high-energy double-well state, transforming into a ferroelectric phase. The fundamental strategy for the photoinduced ferroelectricity under ultrafast intense laser excitation is the strong correlation between electronic excitation and lattice distortion, which is different from the resonant excitation under longer wavelength pulses, e.g., 15- μ m lasers.⁵ Therefore, it can be used to dynamically control complex functions in ferroic materials, such as ultrafast switching and polarization reversion. Moreover, changing the potential energy surface by ultrafast laser excitation and triggering a new metastable nonequilibrium state is a feasible approach with a variety of potential applications.^{51–53}

Because only noncentrosymmetric structures can produce second harmonic signals, the second harmonic generation (SHG) can be used to detect the polarization intensity of ferroelectric materials.^{5,32} Considering that the SHG intensity is approximately proportional to the square of the polarization intensity ($I_{\rm SHG} \propto P^2$), we repeat the ab initio rt-TDDFT dynamics simulations of SrTiO₃ using 800 nm and 2 μ m pulses with different fluences. Based on the calculated photoinduced polarizations, we report second harmonic signals as a function of fluence for the 800 nm and 2 μ m pumps in Figure 5a,b,



Figure 5. Fluence dependence of the second harmonic generation (SHG) intensity at a laser wavelength of (a) 800 nm and (b) 2 μ m, respectively. Blue dashed lines represent the fitting curves using the function $f(F) = \alpha(1 - e^{-\gamma(F-\beta)})$, where *F* is the fluence, and α , β , and γ are the saturation value, threshold fluence, and photosusceptibility, respectively. The saturation value α is 0.93 at 800 nm and 0.89 at 2 μ m.

respectively. The nonlinear pump fluence-dependent behavior of the SHG intensity can be described by a scaled exponential growth function $f(F) = \alpha(1 - e^{-\gamma(F-\beta)})$, where *F* is the fluence, and α , β , and γ are the saturation value, fluence threshold, and photosusceptibility, respectively. The photosusceptibility γ measures the efficiency of the laser field to produce the polarization. The calculated value obtained from data fitting is $\gamma_{800 \text{ nm}} = 0.74$ and $\gamma_{2 \ \mu\text{m}} = 15.31$, suggesting a higher efficiency for long-wavelength lasers. The fluence dependence also indicates a minimum fluence threshold for generating the SHG signal, 0.321 mJ/cm² for the 800 nm laser and 0.074 mJ/cm² for the 2 μ m laser.

At a longer wavelength of 10 μ m, a laser with a fluence of 0.009 mJ/cm^2 produces a uniaxial tensile deformation along the [001] direction, resulting in a polarization of 0.6 C/m², shown in Figure S7a. In comparison, to achieve the same polarization intensity, 2 μ m and 800 nm wavelength requires a laser fluence of 0.15 mJ/cm² and 1.8 mJ/cm², respectively, as shown in Figure S8. It clearly suggests stronger laser irradiation at shorter wavelength results in the same polarization intensity in SrTiO₃ as weaker laser irradiation at longer wavelength. In addition, the Mulliken charge analysis reveals quite similar charge transfer mechanisms resulting from 800 nm and 10 $\mu \rm m$ pulses (Figure S7b,c), which further suggests that our proposed mechanism for ultrafast laser-induced ferroelectric phase transition of SrTiO₃ is generally applicable. What we focus on here is the transient polarization with large fluctuations occurring in a short time (hundred femtoseconds), and moreover, nonlinear absorption is essential for the excitation of short-wavelength lasers. The macroscopic polarization might attenuate with electronic relaxation, and deexcitation occurs over a long time.

We report nonadiabatic quantum dynamics simulations of the laser-induced ferroelectric phase transition process in SrTiO₃, where quantum motions of charge carriers and time evolution of excited states are captured within the rt-TDDFT framework. Under laser irradiation, the electronic subsystem of SrTiO₃ is directly excited, which in turn triggers selective excitation of multiple phonon branches through electronphonon couplings. Photoinduced uniaxial tensile distortion is formed along the laser polarization direction, breaking the spatial centrosymmetry of the SrTiO₃ lattice. The optically stretched SrTiO₃ shows a polar order associated with the photoinduced metastable ferroelectric phase. We identify that the driving force of ferroelectric phase transition is the strong couplings between photoexcited electronic states and induced phonon deformation. Upon photoexcitation, electron transfer from the O_{2p} orbital to Ti t_{2g} is observed, accompanied by a population transition between the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. Multiple phonon branches, including LO-2 and LO-3 modes, are subsequently excited, breaking the centrosymmetry of the crystal and leading to the uniaxial tensile distortion. Upon the femtosecond laser excitation, the electrons and the lattice are driven far from equilibrium and hidden states of materials can be reached, which is inaccessible under equilibrium conditions. Our study significantly advances the understanding on how photoexcited charge transfer exerts forces on the motion of ions through the interaction of electron-phonon couplings, to achieve the hidden metastable ferroelectric states that cannot be obtained by equilibrium thermal means. We expect this study may inspire new applications in ultrafast optical switching and optical data storage materials by optically inducing nonthermal phase transitions.

COMPUTATIONAL METHODS

The crystal SrTiO₃ structural optimization and static total energy calculations are performed with the SIESTA software.⁵⁴ According to ref 5, the mid-IR-induced second harmonic signal remains detectable up to room temperature and appears to be

unaffected by the cubic-to-tetragonal structural transition in $SrTiO_3$ at 105 K; therefore, we choose to simulate the cubic phase of $SrTiO_3$ consisting of 5 atoms with periodic boundary conditions. We use the local-density approximation (LDA) to describe the exchange and correlation energy.⁵⁵ Norm-conserving pseudopotentials and the numerical atomic orbital basis set with an energy cutoff of 400 Ry are adopted. The Brillouin zone of cubic unit cell is sampled by a $6 \times 6 \times 6$ Monkhorst–Pack k-point mesh. The lattice parameters are allowed to relax until all components of forces are smaller than 0.01 eV/Å. Phonon calculations are performed within the framework of density functional perturbation theory (DFPT) using Quantum Espresso.⁵⁶

The rt-TDDFT molecular dynamic (MD) simulations are performed using the time-dependent ab initio package (TDAP).^{57,58} The calculation of atomic forces is based on Ehrenfest dynamics, which has a similar formulation to the Hellmann–Feynman theorem, but is not related to the latter. To investigate the photoinduced ferroelectric phase in SrTiO₃, an external 800 nm laser field with a Gaussian envelope

$$E(t) = E_0 \cos(\omega t) \exp[-(t - t_0)^2 / 2\sigma^2]$$

is exerted, where the maximum field intensity E_0 is 0.077 V/Å and the time to the peak t_0 is 16 fs. A fwhm of 10 fs is chosen for the applied field. The time-dependent Kohn-Sham wave functions of the system evolve in a constant-pressure-energy (NPE) ensemble with a time step of 40 attoseconds, and the pressure is controlled by the Parrinello-Rahman method.59 The generalized mass of the Parrinello-Rahman variable is 100 Ry·fs². The variable determines the time scale of the Parrinello-Rahman variable dynamics and its coupling to the physical system. Partial phonon-phonon interactions such as optical phonon-phonon interactions are included, but some dissipation channels such as acoustic phonon-phonon interactions are not considered due to the limitation of cell size. We believe that the ultrafast dynamics discussed here (<1 ps) will not be greatly affected by considering more dissipation channels of phonon-phonon interactions that typically occur on a relatively slow time scale (>1 ps).

ASSOCIATED CONTENT

Supporting Information

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Additional method details of constant-pressure-energy (NPE) simulations, band structure of cubic SrTiO₃, effects of the calculated band gap, interatomic forces on ions, multiphoton excitation process, phonon dispersion spectrum of SrTiO₃, response of laser-induced ferroelectricity in SrTiO₃ at longer wavelengths, and the comparison of effectiveness of lasers with different wavelengths (PDF)

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Author Contributions

[#]C.S. and Q.Y. contributed equally. C.Z. and S.M. conceptualized the work. The ab initio simulations were performed by C.S. and Q.Y. The paper was written by C.S., Q.Y., C.Z., and S.M. All authors contributed to the discussions and analyses of the data, and approved the final version.

Notes

The authors declare no competing financial interest.

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