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Ultrafast light-induced symmetry changes in single $BaTiO_3$ nanowires

Electronic Supplementary Information

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Modeling Second Harmonic from a Single Nanowire

In this section we discuss how the second harmonic intensity depends on the polarization of incident light for a nanowire with arbitrary crystallographic orientation as shown in the Figure S1.

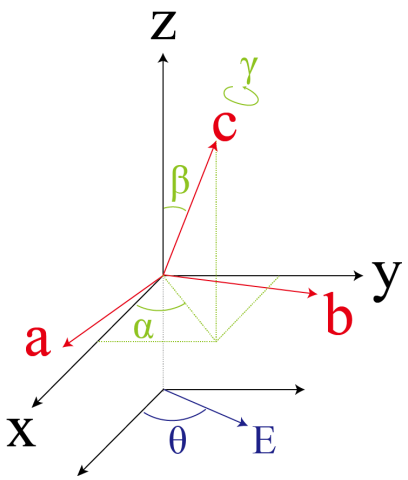

Figure S1. Schematic diagram showing the coordinates system of lab frame (described by x, y, z), and crystal axes (a, b, c) with Euler's angles α, β, γ, and the polarization $\vec{E}$ of the incident light.

The second harmonic generation (SHG) from a nonlinear material with tetragonal symmetry, such as $BaTiO_3$ (BTO), is described by

$$\begin{bmatrix} P_a(2\omega) \\ P_b(2\omega) \\ P_c(2\omega) \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_a^2(\omega) \\ E_b^2(\omega) \\ E_c^2(\omega) \\ 2E_b(\omega)E_c(\omega) \\ 2E_a(\omega)E_c(\omega) \\ 2E_a(\omega)E_b(\omega) \end{bmatrix},$$

where $E_i(\omega)$ and $P_i(2\omega)$ are components of the electric field and the induced second harmonic polarization along the i'th axis, respectively, and the d_{ij}'s are the components of the second harmonic tensor. Due to the symmetry of the material, the Euler angle γ has no role in determining the second harmonic and is set to 0. Since the tensor equation for SHG is written in the crystal frame, to calculate SHG, one needs to transform the electric field from the lab frame into the crystal coordinate through

$$E_a = \vec{E} \cdot \hat{a},$$

$$E_b = \vec{E} \cdot \hat{b},$$

$$E_c = \vec{E} \cdot \hat{c},$$

By applying the SHG equation, one can then obtain the induced nonlinear polarization in the crystal frame. This is then transformed back into the lab frame by

$$\vec{P}(2\omega) = P_a(2\omega)\hat{a} + P_b(2\omega)\hat{b} + P_c(2\omega)\hat{c}\ .$$

The SHG can be treated as electric dipole radiation driven by the nonlinear polarization $\vec{P}(2\omega)V$, where V is the excited volume of the material.[1] The detected SHG intensity will depend on the details of the setup of the collection optics. We make an approximation that only the emitted second harmonic light propagating along the +z direction is collected. Under the experimental settings, the measured second harmonic intensity is described by

$$I(2\omega) = A\left[\left|\vec{P}(2\omega)\cdot\hat{y}\right|^2 + \left|\vec{P}(2\omega)\cdot\hat{x}\right|^2\right],$$

where A is an overall proportional factor that depends on factors such as the excited volume and the efficiency of the collection and detection system.

The electric field distribution inside a nanowire is different from that of the incident field in both magnitude and direction. To simplify the model, one can assume that the nanowire is infinitely long. Under such approximation, the electric field inside the nanowire will be

$$\vec{E}_{nanowire} = \vec{E}_{axial} + t_1 \vec{E}_{transverse},$$

where $\vec{E}_{axial}$ and $\vec{E}_{transverse}$ are the components of incident field parallel and perpendicular to the long axis of the nanowire (see **Figure S2**), and t_1 is a coupling coefficient, which depends on the shape and dielectric constant.

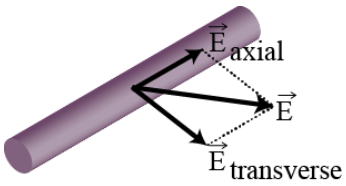

Figure S2. Schematic diagram showing input field $\vec{E}$ decomposed into axial component $\vec{E}_{axial}$ and transverse component $\vec{E}_{transverse}$.

It can be shown that there is a similar reduction effect for the induced SHG polarization due to the induced charge screening and depolarization field. The effective nonlinear polarization is

$$\vec{P}(2\omega) = \vec{P}_{axial}(2\omega) + \mathrm{t}_2 \vec{P}_{transverse}(2\omega) .$$

where $\vec{P}_{axial}$ and $\vec{P}_{transverse}$ are axial and transverse components of the induced nonlinear polarization inside the nanowire, and t_2 is a coupling coefficient. Therefore, the second harmonic intensity is a function of the Euler angles, α and β, and the coupling coefficients, t_1 and t_2.

Fitting of Second Harmonic Intensity

The second harmonic intensity is a function of orientation, coupling coefficients, and input polarization.

$$\mathrm{I}^{2\omega}(\theta;\alpha,\beta,t_1,t_2)$$

By fitting the measured second harmonic intensity at different input polarization θ, we are able to extract those parameters by minimizing the square error:

$$\sum_{\theta}[\mathrm{I}^{2\omega}_{measured}(\theta)-\mathrm{I}^{2\omega}(\theta;\alpha,\beta,t_1,t_2)]^2,$$

Notice that there are intrinsic symmetries of $\mathrm{I}^{2\omega}(\theta;\alpha,\beta,t_1,t_2)$ associated with the crystal symmetry. To show this, let $\alpha=0$ without loss of generality. The coupling coefficients are also set to one because they will not change the symmetry properties. The induced second harmonic nonlinear polarization in the lab frame is

$$P_x=\{(2d_{15}+d_{31}-d_{33})\cos^2\beta\cos^2\theta+d_{31}\sin^2\theta+d_{33}\cos^2\theta\}\sin\beta$$

$$P_y=d_{15}[\sin\theta\cos\theta]\sin\beta$$

Therefore, for tetragonal crystal, $\mathrm{I}^{2\omega}\propto P_x^2+P_y^2$ is invariant under a $\beta\rightarrow-\beta$ transformation.[2] $\mathrm{I}^{2\omega}$ is also invariant under $\theta\rightarrow-\theta$ transformation, and therefore $\mathrm{I}^{2\omega}$ shows two mirror planes with respect to the direction parallel and perpendicular to the spontaneous polarization.

Finite Difference Time Domain Simulations

We performed 3D finite difference time domain (FDTD) using CST-Microwave Studio to study the pump energy deposition. We simulated the case that a nanowire with dimension $100\ nm$ by $100\ nm$ by $2\ \mu m$ with square cross section and input optical constants taken from bulk values, lying on a glass substrate. The nanowire is excited by a 266 nm plane wave and

the absorption power density is recorded. **Figure S3** shows the absorption power density at 2 difference cross sections, with pump beam propagated from top to bottom. Taking into account the pulse duration of the laser, the energy absorption per pulse is about 4 pJ, corresponding to a temperature jump of 80K averaged over the whole nanowire and carrier density of $3\times10^{20}\ cm^{-3}$.

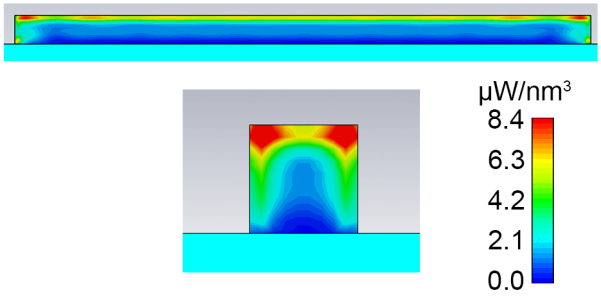

Figure S3. Power absorption density simulated by finite difference time domain calculations.

XRD and SEM Patterns from Synthesized BTO nanowires

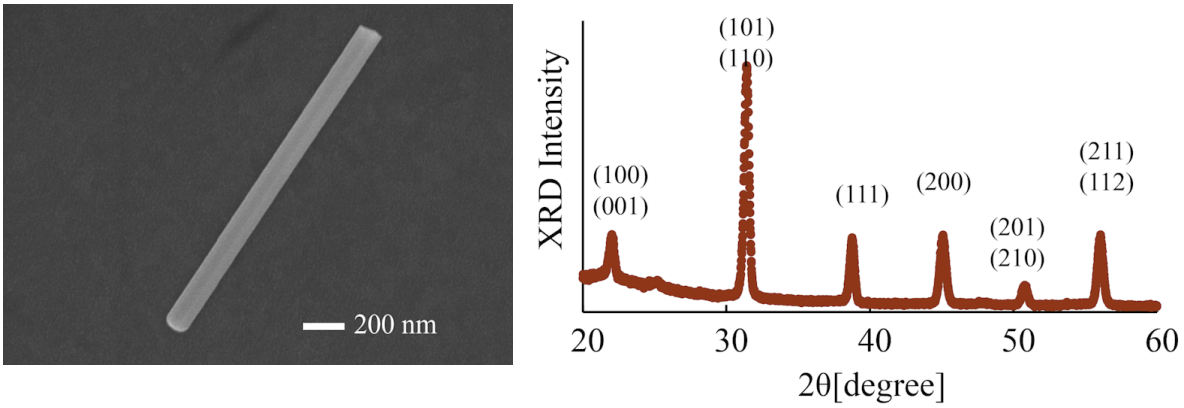

Figure S4. (left) SEM from a single nanowire and (right) XRD pattern from powder sample, showing identified peaks within tetragonal phase.

References

(1) Long, J. P.; Simpkins, B. S.; Rowenhorst, D. J.; Pehrsson, P. E. *Nano Lett*. **2007**, *7* (3), 831–836.

(2) Hsieh, C.-L.; Pu, Y.; Grange, R.; Psaltis, D. *Opt. Express* **2010**, *18* (11), 11917.