






Theory of nonlinear terahertz susceptibility in ferroelectrics

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(Received 25 April 2024; revised 30 July 2024; accepted 5 August 2024; published 19 August 2024)

An analytical theory is developed for predicting the nonlinear susceptibility of ionic polarization to continuous electromagnetic waves in both bulk and strained thin film ferroelectrics. Using a perturbation method for solving the nonlinear equation of motion for ionic polarization within the framework of Landau-Ginzburg-Devonshire theory, the full second-order nonlinear susceptibility tensor is derived as a function of frequency, temperature, and strain. The theory predicts the coexistence of a significantly enhanced second-order dielectric susceptibility and a relatively low dielectric loss in BaTiO₃ films with a strain-stabilized monoclinic ferroelectric phase and in a strained SrTiO₃ film near its temperature-driven second-order ferroelectric-to-paraelectric phase transition. In this paper, we establish a theoretical framework for predicting and exploiting nonlinear interactions between terahertz waves and ferroelectric materials and, more generally, suggest exciting opportunities to strain-engineer nonlinear dynamical properties of ferroelectrics beyond the static and quasistatic limits.

DOI: [10.1103/PhysRevB.110.054311](https://doi.org/10.1103/PhysRevB.110.054311)

I. INTRODUCTION

Nonlinear susceptibility in the terahertz (THz) band (frequency: 0.1–10 THz) is critical to nonlinear THz wave interactions such as THz high-order harmonic generation [1–5], THz-field-induced second harmonic generation (SHG) [6–8], and THz field-induced Kerr effect [9]. These nonlinear processes underpin the development of a wide variety of THz applications ranging from nonlinear THz spectroscopy to high-power THz sources to THz imaging [10,11].

Ferroelectric materials, due to their noncentrosymmetric nature, permit even-order harmonic generation and have been widely used for nonlinear wave phenomena at optical frequencies ($\sim 10^{14}$ Hz). For example, LiNbO₃, a workhorse nonlinear optical material [12,13], is a uniaxial ferroelectric whose spontaneous polarization (denoted as \mathbf{P}^{ion} to indicate its origin in ionic displacements) aligns along the c axis of its hexagonal unit cell. More specifically, in displacive ferroelectric systems such as LiNbO₃, PbTiO₃, and BaTiO₃, \mathbf{P}^{ion} is caused by the condensation of a soft mode phonon below the Curie temperature and can be expressed as $\mathbf{P}^{\text{ion}} = Z_p^* \mathbf{Q}^p$, where Z_p^* and \mathbf{Q}^p are the Born effective charge density and the normal coordinates of the soft mode, respectively [14,15].

In the optical regime, frequency-dependent dynamic (linear or nonlinear) susceptibility of ferroelectric materials is primarily associated with the optical electric field-induced electronic polarization \mathbf{P}^e [16,17] (note that $\mathbf{P}^e = 0$ under zero electric field). In the THz and gigahertz (GHz) regimes, dynamic susceptibility of ferroelectrics contains contributions from both the \mathbf{P}^{ion} and \mathbf{P}^e because both types of polarizations

can promptly respond to the GHz-THz electric fields given their high resonant frequencies ($\sim 10^{12}$ Hz for \mathbf{P}^{ion} [18] and $\sim 10^{15}$ Hz for \mathbf{P}^e). However, the contribution of \mathbf{P}^{ion} to the dynamic susceptibility should be much more significant [19] because the linear dielectric susceptibility of \mathbf{P}^{ion} is much larger than the induced \mathbf{P}^e in the GHz-THz range and because the \mathbf{P}^{ion} can resonantly interact with the THz electric field.

Frequency-dependent nonlinear susceptibilities of \mathbf{P}^{ion} in bulk ferroelectric crystals have been analytically calculated by employing the perturbation method to solve the equation of motion for \mathbf{P}^{ion} within the framework of a Landau-Devonshire-type thermodynamic energy density function (a polynomial of \mathbf{P}^{ion}) [20–24]. However, the thermodynamic potential used in these works [20–24] does not incorporate the coupling between \mathbf{P}^{ion} and strain (i.e., the piezoelectric effect), which has recently been shown to have a significant influence on the resonant frequency of the \mathbf{P}^{ion} even in stress-free bulk ferroelectric materials [18,25]. Furthermore, these works [20–24] are largely focused on the mathematical derivation without extensively discussing the underlying physical picture, e.g., the relation between the nonlinear susceptibility and the landscape of the thermodynamic energy density.

In this paper, based on the equation of motion for \mathbf{P}^{ion} (specifically, the ionic polarization associated with the soft mode) and the Landau-Ginzburg-Devonshire (LGD) thermodynamical energy density function of \mathbf{P}^{ion} that incorporates the coupling between \mathbf{P}^{ion} and strain, we analytically derive the full nonlinear susceptibility tensor of \mathbf{P}^{ion} in monodomain ferroelectrics and incipient ferroelectrics as a function of frequency, temperature, and in the case of coherently strained thin films, the epitaxial strain.

While the theoretical framework presented in this paper is directly applicable to various types of THz nonlinear

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phenomena [e.g., third harmonic and sum frequency generation (SFG)/difference frequency generation (DFG)] in ferroelectrics, the examples are focused on THz SHG, where a nonlinear THz polarization \mathbf{P}^{ion} with an angular frequency 2ω is generated in the material by an incident THz field \mathbf{E} with an angular frequency ω . After calculating the THz second harmonic susceptibility in a few bulk ferroelectric single crystals, we predict a dramatically enhanced THz second harmonic susceptibility in monodomain BaTiO₃ films with a strain-stabilized monoclinic phase as well as near the temperature-driven ferroelectric-to-paraelectric phase transition in strained SrTiO₃ films. These findings indicate the potential application of using these strained ferroelectric films for source-current-free SHG at both the microwave and THz frequencies. The theory advances the physical understanding of the nonlinear interaction between THz waves and ferroelectrics. More broadly, in this paper, we suggest exciting opportunities for strain engineering of nonlinear dynamic properties in ferroelectrics beyond the static and quasistatic limits.

II. THEORY

The nonlinear THz susceptibilities refer to the third- and higher-rank χ tensors in the relation between the total ionic polarization \mathbf{P}^{ion} (hereafter \mathbf{P}) and the incident electric field \mathbf{E} . In ferroelectric materials that have a spontaneous polarization P_i^0 under zero electric field, the total polarization can be written as

$$P_i = P_i^0 + \Delta P_i = P_i^0 + \Delta P_i^{(1)} + \Delta P_i^{(2)} + \dots, \quad (1a)$$

$$\Delta P_i^{(1)}(\omega) = \kappa_0 \sum_j \chi_{ij}^{(1)}(\omega) E_j(\omega), \quad (1b)$$

$$\Delta P_i^{(2)}(\omega_n \pm \omega_m) = \kappa_0 \sum_{jk} \sum_{(mn)} \chi_{ijk}^{(2)}(\omega_n \pm \omega_m, \omega_n, \omega_m) \times E_j(\omega_n) E_k(\omega_m), \quad (1c)$$

where κ_0 is the vacuum permittivity, and E_i is the electric-field component of the incident THz wave. The subscripts $i, j, k = 1, 2, 3$ indicate crystal physics coordinates. Under the plane-wave assumption in the thin slab limit, i.e., the thickness of the ferroelectric is significantly smaller than THz wavelength $\lambda_c = \frac{2\pi}{k^{\text{Re}}}$ (k^{Re} is the real component of the complex wave number \mathbf{k} [25]), one has $E_i = E_i^0 \exp(-i\omega t)$. Equation (1c) follows the notation in Refs. [26,27] except that all \mathbf{P} 's hereafter referring to ionic polarization; ΔP_i in Eq. (1a) is the dynamic variation of the ionic polarization, which can be separated into a first-order polarization $\Delta P_i^{(1)}(\omega) = \Delta P_i^{(1),0} \exp(-i\omega t)$ that has the same angular frequency as the incident THz wave [Eq. (1b)] and second-order polarization $\Delta P_i^{(2)}(\omega_n \pm \omega_m) = \Delta P_i^{(2),0} \exp[-i(\omega_n \pm \omega_m)t]$ that can contain multiple frequency components [Eq. (1c)]. Here, i denotes the imaginary unit. Specifically, an incident THz wave containing waves of two angular frequencies ω_n and ω_m [the notation (mn) indicating that the $\omega_n \pm \omega_m$ is fixed, while ω_n and ω_m can individually vary] can generate two SHG polarization components $\Delta P_i^{(2)}(2\omega_n)$ and $\Delta P_i^{(2)}(2\omega_m)$,

a SFG component $\Delta P_i^{(2)}(\omega_n + \omega_m)$, a DFG component $\Delta P_i^{(2)}(\omega_n - \omega_m)$, and a dc polarization shift $\Delta P_i^{(2)}(0)$ induced by a static electric field rectified from complex electric fields $E_i(\omega) = E_i^0 \exp(-i\omega t)$ and its conjugate $E_i^*(\omega) = E_i(-\omega) = E_i^0 \exp(i\omega t)$.

Each second-order polarization component is associated with its own $\chi_{ijk}^{(2)}$ tensor, including $\chi_{ijk}^{(2)}(2\omega_n, \omega_n, \omega_n)$, $\chi_{ijk}^{(2)}(2\omega_m, \omega_m, \omega_m)$, $\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m)$, $\chi_{ijk}^{(2)}(\omega_n - \omega_m, \omega_n, -\omega_m)$, and $\chi_{ijk}^{(2)}(0, \omega_m, -\omega_m)$ and/or $\chi_{ijk}^{(2)}(0, \omega_n, -\omega_n)$. In this paper, the analytical formulae for all these $\chi_{ijk}^{(2)}$ tensors are derived. The examples focus on the THz SHG, where a monochromatic incident THz wave with an angular frequency ω , $\mathbf{E}(\omega)$, generates a second-order polarization $\Delta P_i^{(2)}(2\omega)$, i.e.,

$$\Delta P_i^{(2)}(2\omega) = \kappa_0 \sum_{jk} \chi_{ijk}^{(2)}(2\omega, \omega, \omega) E_j(\omega) E_k(\omega). \quad (2)$$

The analytical formulae for the frequency-dependent linear susceptibility $\chi_{ij}^{(1)}$ and second-order susceptibility $\chi_{ijk}^{(2)}$ can be obtained by finding the steady-state solution of the equation of motion for ΔP_i [25], which is analogous to the equation of motion for an anharmonic oscillator, given as

$$\begin{aligned} \mu \frac{\partial^2 \Delta P_i}{\partial t^2} + \gamma_{ij} \frac{\partial \Delta P_j}{\partial t} &= \Delta E_i^{\text{eff}} \\ &= E_i^{\text{Landau}} + E_i^{\text{Elast}} + E_i^{\text{d}} + E_i + E_i^{\text{rad}}, \end{aligned} \quad (3)$$

where the subscripts $i = 1, 2, 3$ of the polarization component indicate the Cartesian crystal physics coordinates of the paraelectric cubic phase within the framework of the LGD theory [28]. Here, $\mu = \frac{1}{\kappa_0 \omega_p^2}$ is the mass coefficient (polarization inertia) with an ionic plasma frequency $\omega_p = \sqrt{\frac{1}{\kappa_0 V_0} \sum_n \frac{q_n^2}{M_n}}$, where q_n and M_n are the charge and mass of the n th charged ion in a unit cell with a volume V_0 [29], and γ_{ij} is the phenomenological viscous damping coefficient that can be related to the crystal viscosity [30]; the temporal variation of the total effective electric field is $\Delta E_i^{\text{eff}} = E_i^{\text{eff}}(P_i) - E_i^{\text{eff}}(P_i^0)$. At the initial equilibrium state ($P_i = P_i^0$), one has $E_i^{\text{eff}}(P_i^0) = 0$, and thus, $\Delta E_i^{\text{eff}} = E_i^{\text{eff}}(P_i)$. Among the various (effective) electric fields contributing to the E_i^{eff} , $E_i^{\text{Landau}} = -\frac{\partial f^{\text{Landau}}}{\partial P_i}$ and $E_i^{\text{Elast}} = -\frac{\partial f^{\text{Elast}}}{\partial P_i}$ are nonlinear polynomials of P_i (f^{Landau} and f^{Elast} are the Landau and elastic energy densities, respectively) [25]. The derivation of Eq. (3) is provided in Appendix A.

Specific ferroelectric materials considered in this paper include (i) tetragonal perovskite ferroelectric single crystals BaTiO₃ and PbTiO₃, where the initial equilibrium polarization \mathbf{P}^0 aligns along the x axis in the lab coordinate system; (ii) trigonal ferroelectric single crystals LiTaO₃ and LiNbO₃, where the initial equilibrium polarization \mathbf{P}^0 also aligns along the x axis in the lab coordinate system; (iii) an anisotropically strained (001)_{pc} BaTiO₃ (pc: pseudocubic) thin film, which has a surface parallel to the (001) plane of its cubic paraelectric phase; and (iv) an biaxially strained (001)_{pc} SrTiO₃ film grown on an orthorhombic (o) DyScO₃ (110)_o substrate [31]. Normal incidence of a p -polarized THz wave is considered under the plane-wave assumption, where the THz electric

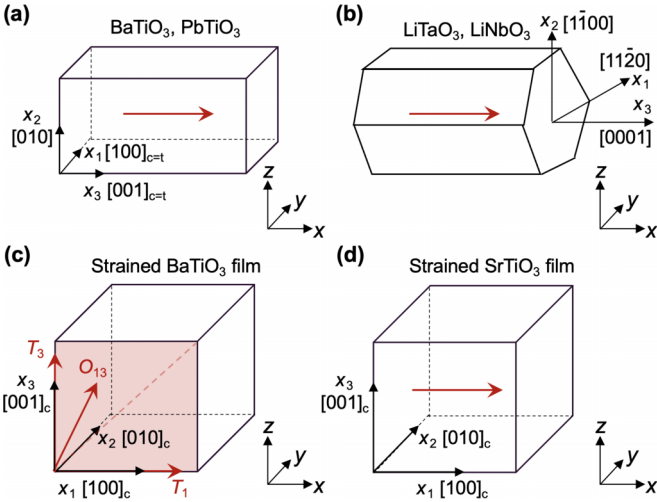


FIG. 1. Schematics of (a) the tetragonal unit cells of BaTiO₃ and PbTiO₃ and (b) the hexagonal unit cells of the LiTaO₃ and LiNbO₃. (c) and (d) Cubic representation of the pseudocubic (pc) unit cells of a (001)_{pc} strained BaTiO₃ film and a (001)_{pc} strained SrTiO₃ film. The red arrow indicates the direction of the spontaneous polarization. In (c) and (d), x_1 - x_2 - x_3 coordinates indicate the Cartesian axes of the cubic paraelectric unit cells of the BaTiO₃ and SrTiO₃, consistent with the notation P_i ($i = 1, 2, 3$) in the Landau-Ginzburg-Devonshire (LGD) thermodynamic energy density function. x - y - z coordinates indicate the lab coordinate system.

field inside the ferroelectric material, E_i in Eq. (3), only contains an x component in the lab coordinate system. The lab and the crystal physics coordinate systems in the above four cases are illustrated in Fig. 1. Expressions of f^{Landau} and f^{Elast} for BaTiO₃, PbTiO₃, SrTiO₃, LiTaO₃, and LiNbO₃ and the relevant material parameters are summarized in Appendix B.

Under the plane-wave assumption in the thin slab limit (i.e., the thickness of the ferroelectric slab is much smaller than the THz wavelength in the slab), the polarization-oscillation-induced radiation electric field can be calculated as $E_i^{\text{rad}} = (-\frac{d_0}{2\kappa_0 c} \frac{\partial P_x}{\partial t}, -\frac{d_0}{2\kappa_0 c} \frac{\partial P_y}{\partial t}, 0)$ for a single-domain ferroelectric [25], where d_0 is the thickness of the ferroelectric, and c is the speed of light in vacuum. For thick bulk crystals, E_i^{rad} has a complex analytical expression and varies spatially along the thickness direction, as derived in Ref. [25]. At the initial equilibrium state, both E_i and E_i^{rad} are zero. For a single-domain ferroelectric thin film with an infinitely large x - y plane and mobile screening charges (e.g., electrons, holes, and absorbed ions) at the top and bottom surfaces, the depolarization field at the initial equilibrium state is zero. Under the excitation by THz or higher-frequency electric fields, we assume that these charged species at the surfaces remain largely frozen. Consequently, the film is subjected to a dynamic depolarization field that is given by $\Delta E_i^{\text{d}} = (0, 0, -\frac{1}{\kappa_0 \kappa_b} \Delta P_z)$, where κ_b is the background dielectric constant accounting for the contribution from the electronic contribution [32,33]. Here, a typical value of $\kappa_b = 5$ [34] is used for all ferroelectric materials in the calculation. The lab coordinate system ($i = x, y, z$) is used in the above expressions for E_i , E_i^{rad} , and E_i^{d} .

The elastic energy $f^{\text{Elast}} = \frac{1}{2} c_{ijkl} (\epsilon_{kl} - \epsilon_{kl}^0) (\epsilon_{ij} - \epsilon_{ij}^0)$, where c_{ijkl} is the elastic stiffness tensor under constant electric field and temperature; the stress-free strain ϵ^0 is induced by the P_i through the electrostrictive effect. The solution of the total strain ϵ_{ij} at the initial equilibrium state depends on the mechanical boundary condition of the system. In the case of coherently strained BaTiO₃ and SrTiO₃ thin films, one has a mixed boundary condition [35] with $\epsilon_{11} = \epsilon_{11}^{\text{mis}}$, $\epsilon_{22} = \epsilon_{22}^{\text{mis}}$, $\epsilon_{12} = 0$, and $\sigma_{i3} = 0$ ($i = 1, 2, 3$) from which the expressions of the total strain ϵ_{i3} can be obtained. The mismatch strains $\epsilon_{11}^{\text{mis}}$ and $\epsilon_{22}^{\text{mis}}$ result from the lattice constant and/or thermal expansion coefficient mismatch between the epitaxial film and substrate. It is known that such mismatch strain can enable polymorphic ferroelectric phase transitions that are absent in the stress-free state or modulate the ferroelectric-to-paraelectric transition temperature in ferroelectric thin films [35,36] and that the static (i.e., driven by dc electric field) linear dielectric susceptibility $\chi_{ij}^{(1), \text{dc}} = \frac{\partial P_i}{\kappa_0 \partial E_j}$ can be significantly enhanced near such phase transitions [28,37].

To analytically solve $\chi_{ijk}^{(2)}$, we first rewrite Eq. (3) into the following matrix form by expanding E_i^{Landau} and E_i^{Elast} in Taylor series and dropping the higher-order terms (see Appendix C):

$$\mu \frac{\partial^2 \Delta \mathbf{P}}{\partial t^2} + \boldsymbol{\gamma}^{\text{eff}} \frac{\partial \Delta \mathbf{P}}{\partial t} + \mathbf{K} \Delta \mathbf{P} + \mathbf{C} \Delta \mathbf{P}_{\text{II}} = \mathbf{E}, \quad (4)$$

where both the polarization change $\Delta \mathbf{P} = (\Delta P_1, \Delta P_2, \Delta P_3)^{\text{T}}$ and the incident THz electric field $\mathbf{E} = (E_1, E_2, E_3)^{\text{T}}$ are a 3×1 matrix; $\Delta \mathbf{P}_{\text{II}} = (\Delta P_1^2, \Delta P_2^2, \Delta P_3^2, 2\Delta P_1 \Delta P_2, 2\Delta P_1 \Delta P_3, 2\Delta P_2 \Delta P_3)^{\text{T}}$ is a 6×1 matrix; $\boldsymbol{\gamma}^{\text{eff}}$ is a 3×3 matrix which contains contributions from both the phenomenological intrinsic damping (related to crystal viscosity of the ferroelectric) and the radiation-induced damping [18,25]. For strained ferroelectric thin films in the thin slab limit, one has

$$\boldsymbol{\gamma}^{\text{eff}} \approx \begin{bmatrix} \gamma_{11} + \frac{1}{2} \frac{d_0}{\kappa_0 c} & 0 & 0 \\ 0 & \gamma_{22} + \frac{1}{2} \frac{d_0}{\kappa_0 c} & 0 \\ 0 & 0 & \gamma_{33} \end{bmatrix}, \quad (5)$$

where the off-diagonal components are assumed to be zero, and the intrinsic damping coefficients are assumed to be isotropic $\gamma_{11} = \gamma_{22} = \gamma_{33} = 2 \times 10^{-7} \Omega \text{ m}$ [25]. The additional term added to γ_{11} and γ_{22} describes the radiation-electric-field-induced damping [18], where the thickness of the ferroelectric film $d_0 = 10 \text{ nm}$ is small enough to ensure that the film is coherently strained by the substrate. For thick bulk crystals, the complex expression of the radiation electric field E_i^{rad} would result in a radiation-induced damping that varies along the thickness and does not have an explicit analytical expression [25]. For simplicity, we use the same $\boldsymbol{\gamma}^{\text{eff}}$ in the analytical calculation of both bulk and thin-film ferroelectrics in this paper. For the components of the 3×3 matrix \mathbf{K} , $K_{ij} = -A_{ij} - B_{ij}$ ($i, j = 1, 2, 3$). In the case of (001)_{pc} BaTiO₃ and SrTiO₃ thin films [Figs. 1(c) and 1(d)] under dynamic electric-field excitation ($\omega \neq 0$), we use $K_{33} = -A_{33} - B_{33} + \frac{1}{\kappa_0 \kappa_b}$, where the term $1/\kappa_0 \kappa_b$ results from the dynamic depolarization field $\Delta E_z^{\text{d}}(t) = -\Delta P_z(t)/\kappa_0 \kappa_b$ ($z \equiv 3$) in a thin film with infinitely large x - y plane (see

Appendix C). In the case of dc excitation ($\omega = 0$) and/or bulk ferroelectric crystals, the dynamic depolarization field does not need to be considered; thus, $K_{33} = -A_{33} - B_{33}$. For the components of the third-rank tensor \mathbf{C} , $C_{ijk} = -\frac{1}{2}A_{ijk} - \frac{1}{2}B_{ijk}$ ($i, j, k = 1, 2, 3$), where

$$A_{ij} = -\left. \frac{\partial^2 f^{\text{Landau}}}{\partial P_i \partial P_j} \right|_{\mathbf{P}=\mathbf{P}^0}, \quad A_{ijk} = -\left. \frac{\partial^3 f^{\text{Landau}}}{\partial P_i \partial P_j \partial P_k} \right|_{\mathbf{P}=\mathbf{P}^0}, \quad (6a)$$

$$B_{ij} = -\left. \frac{\partial^2 f^{\text{Elast}}}{\partial P_i \partial P_j} \right|_{\mathbf{P}=\mathbf{P}^0}, \quad B_{ijk} = -\left. \frac{\partial^3 f^{\text{Elast}}}{\partial P_i \partial P_j \partial P_k} \right|_{\mathbf{P}=\mathbf{P}^0}. \quad (6b)$$

Thus, K_{ij} and C_{ijk} represent, respectively, the local curvature of the total free energy density (a sum of the Landau and elastic energy density) at the initial equilibrium (spontaneous) polarization state \mathbf{P}^0 . Both the mismatch strain and the temperature can modulate the \mathbf{P}^0 , \mathbf{K} , and \mathbf{C} tensors.

We then employ the perturbation method, which has previously been used to derive the nonlinear susceptibility of electronic polarization at optical frequencies [26], to analytically solve Eq. (3) for both the linear and nonlinear susceptibility (see Appendix C). The linear susceptibility $\chi_{ij}^{(1)}(\omega)$ is given as

$$\chi_{ij}^{(1)}(\omega) = \frac{1}{\kappa_0} \left[\begin{array}{ccc} D_{11}(\omega) & K_{12} & K_{13} \\ K_{21} & D_{22}(\omega) & K_{23} \\ K_{31} & K_{32} & D_{33}(\omega) \end{array} \right]^{-1}, \quad (7)$$

$i, j = 1, 2, 3,$

In Eq. (7), the diagonal components $D_{ii}(\omega) = \mu(\omega_i^2 - \omega^2) - \mathbf{i}\gamma_{ii}^{\text{eff}}\omega$, where the resonant frequency of polarization oscillation $\omega_i = \sqrt{K_{ii}/\mu}$ [25]. Under the application of a static (dc) electric field ($\omega = 0$), one has $\chi_{ij}^{(1),\text{dc}} = 1/\kappa_0 K_{ij}$ ($i, j = 1, 2, 3$).

The THz SHG susceptibility $\chi_{ijk}^{(2)}(2\omega, \omega, \omega)$ is given by

$$\chi_{ijk}^{(2)}(2\omega, \omega, \omega) = -\kappa_0^2 \sum_{\alpha, \beta, \gamma=1,2,3} C_{\alpha\beta\gamma} \chi_{i\alpha}^{(1)}(2\omega) \chi_{\beta j}^{(1)}(\omega) \chi_{\gamma k}^{(1)}(\omega), \quad (8)$$

$i, j, k = 1, 2, 3.$

Equation (8) indicates that $\chi_{ijk}^{(2)}$ can be expressed as a function of linear susceptibilities $\chi_{ij}^{(1)}$, which is consistent with the theory by Garret [38] and Mayer and Keilmann [39]. A notable finding of our theory is that the coefficient $C_{\alpha\beta\gamma}$, which was referred to as the generalized Miller's coefficient [39] and typically fitted to experimental measurement [11, 39], is now specifically connected to the third-order derivatives of the LGD energy density with respect to the equilibrium polarization \mathbf{P}^0 . For SHG, the tensor $d_{ijk} = \frac{1}{2}\chi_{ijk}^{(2)}$ is also used. In this paper, we use $\chi_{ijk}^{(2)}$ to show its relation with $\chi_{ij}^{(1)}$, as in Eq. (8).

To demonstrate the validity of Eq. (8), two tests are performed (see details in Appendix D). First, the expression of $\chi_{ijk}^{(2),\text{dc}}$ directly from thermodynamic analysis is the same as the expression obtained by letting $\omega = 0$ in Eq. (8). As an example, in the case of a tetragonal BaTiO₃ bulk crystal, we first calculate the static $\chi_{333}^{(2),\text{dc}}$ based on Eq. (8), which describes the generation of static nonlinear polarization ΔP_3 by a static electric field E_3 [$\equiv E_x$ in the lab coordinate system, see Fig. 1(a)]. The calculate value [$\chi_{333}^{(2),\text{dc}} = -1.573 \times$

10^{-6} m/V] agrees well with the value of -1.576×10^{-6} m/V extracted by fitting a static $P_3 - E_3$ curve obtained from thermodynamic analysis. Second, the numbers of nonzero and independent elements in the third-rank tensor $\chi_{ijk}^{(2),\text{dc}}$ for stress-free BaTiO₃ crystals of cubic, tetragonal, orthorhombic, or rhombohedral phase are consistent with those of the second-order susceptibility tensor of the electronic polarization (optical SHG) under the same crystal symmetry [26].

III. RESULTS AND DISCUSSION

We first calculate the frequency-dependent nonlinear susceptibility at room temperature (25 °C) in the bulk tetragonal BaTiO₃ and PbTiO₃ as well as the trigonal LiNbO₃ and LiTaO₃ single crystals. As shown in Figs. 1(a) and 1(b), the initial equilibrium polarization \mathbf{P}^0 aligns along the polar axis of BaTiO₃, PbTiO₃, LiNbO₃, and LiTaO₃ in the crystal physics coordinates, which is the x axis in the lab coordinate system. When the incident THz wave is polarized only along x in the lab coordinate system ($E_x \equiv E_3$), one has

$$\Delta P_3^{(2)}(2\omega) = \kappa_0 \chi_{333}^{(2)} E_3(\omega)^2. \quad (9)$$

Since the amplitude of the incident THz electric field inside the material has a time-dependence $E_3(\omega) = E_3^0 \exp(-\mathbf{i}\omega t)$, the amplitude and the phase of the second-order nonlinear polarization $\Delta P_3^{(2)}(2\omega) = \Delta P_3^{(2),0} \exp\{\mathbf{i}[-2\omega t + \varphi^{(2)}]\}$ are related to the modulus $|\chi_{333}^{(2)}|$ and the argument θ of $\chi_{333}^{(2)}$, respectively, i.e.,

$$\Delta P_3^{(2),0} = \frac{\kappa_0}{2} |\chi_{333}^{(2)}| E_3^0{}^2, \quad \varphi^{(2)} = \theta. \quad (10)$$

Figure 2(a) shows the frequency-dependent $|\chi_{333}^{(2)}|$ for the four ferroelectric materials. Notably, in the case of LiTaO₃, by tuning the Landau parameters provided in Ref. [40], good agreement with the experimental measurement [39] is achieved both in the nonlinear susceptibility modulus $|\chi_{333}^{(2)}|$ and the resonant frequencies. Based on Eq. (8), one has

$$\chi_{333}^{(2)} = -\kappa_0^2 C_{333} \chi_{33}^{(1)}(2\omega) \chi_{33}^{(1)}(\omega)^2. \quad (11)$$

Equation (11) also suggests the existence of two peaks for $|\chi_{333}^{(2)}|$ at $\omega = \omega_3, \omega_3/2$, where $\chi_{33}^{(1)}(\omega)$ and $\chi_{33}^{(1)}(2\omega)$ reach their maximum, respectively, as shown in Fig. 2(a). By comparison, $\chi_{33}^{(1)}(\omega)$ resonates only at ω_3 , as shown in Fig. 2(b). The $|\chi_{333}^{(2)}|$ at $\omega_3/2$ is at about the same order of magnitude with its value at ω_3 . Furthermore, the dielectric loss of the ferroelectric [41], which is represented by the imaginary part of the linear susceptibility $\chi_{33}^{(1),\text{Im}}$, is three orders of magnitude smaller at $\omega_3/2$ [see bottom panel of Fig. 2(b)]. Therefore, for potential applications of THz SHG, it is an attractive option to set the frequency of the incident THz wave at the half-resonance frequency of the ionic polarization in ferroelectrics.

By letting $\omega = 0$ in Eq. (11), one has $\chi_{333}^{(2),\text{dc}} = -\kappa_0^2 C_{333} \chi_{33}^{(1),\text{dc}^3}$. Therefore, materials with large dc dielectric susceptibility $\chi_{33}^{(1),\text{dc}}$ also tend to have large $\chi_{333}^{(2),\text{dc}}$. From Fig. 2(a), it is evident that the tetragonal BaTiO₃ has a substantially larger $\chi_{333}^{(2),\text{dc}}$ and larger peak values of $|\chi_{333}^{(2)}|$ than

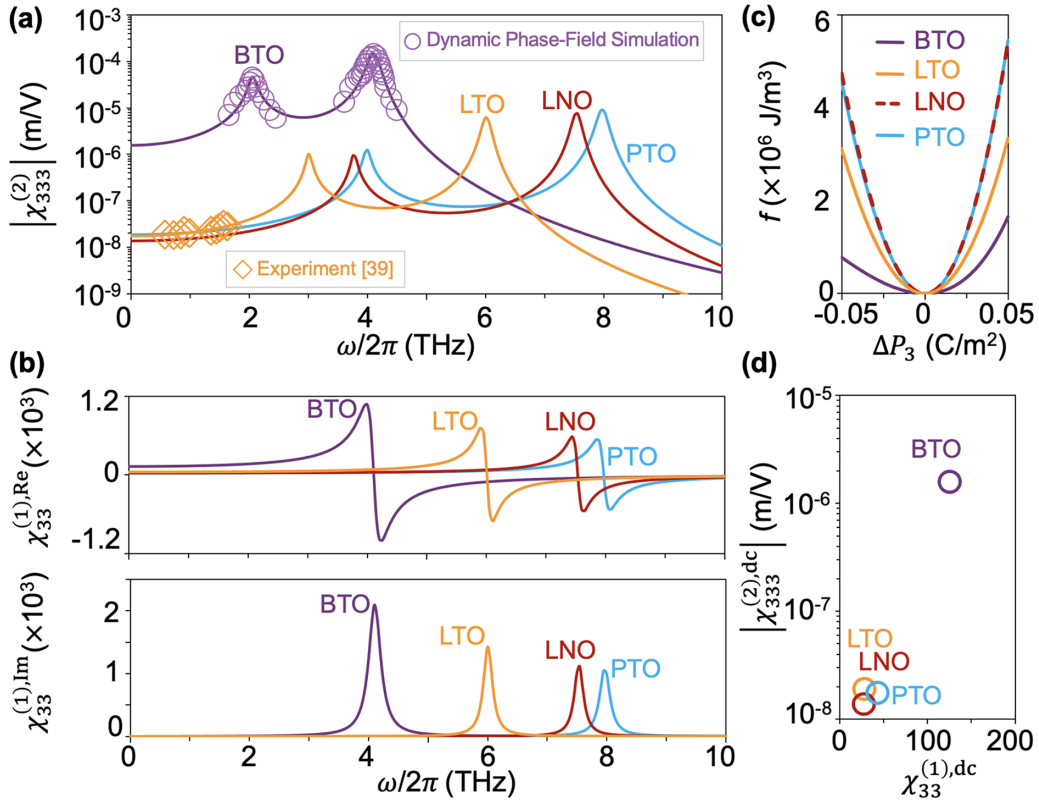


FIG. 2. Frequency-dependent (a) modulus of the nonlinear susceptibility $|\chi_{333}^{(2)}|$ and (b) real and imaginary components of the linear susceptibility $\chi_{33}^{(1)}$ in tetragonal BaTiO₃ (BTO) and PbTiO₃ (PTO) as well as the trigonal LiTaO₃ (LTO) and LiNbO₃ (LNO) bulk ferroelectric crystals. (c) Free energy density f as a function of $\Delta P_3 = P_3 - P_3^0$ in these four materials. (d) dc linear susceptibility $\chi_{33}^{(1),\text{dc}}$ and the magnitude of the dc second-order nonlinear susceptibility $|\chi_{333}^{(2),\text{dc}}|$ of these four materials. The temperature is 298 K, which is below the Curie temperature of the four ferroelectric materials studied herein.

the other three ferroelectric materials. As shown in Fig. 2(c), the local curvature of the energy landscape near P_3^0 is the smallest in the tetragonal BaTiO₃. As a result, the tetragonal BaTiO₃ has the largest $\chi_{33}^{(1),\text{dc}}$ and hence $|\chi_{333}^{(2),\text{dc}}|$ among the four materials, as shown in Fig. 2(d). Furthermore, the analytically calculated $|\chi_{333}^{(2)}|$ of the tetragonal BaTiO₃ agrees well with the values extracted independently from dynamical phase-field simulations (see Appendix E), demonstrating that the analytical model is valid.

We now calculate $\chi_{111}^{(2)}$ in an anisotropically strained (001)_{pc} BaTiO₃ film at room temperature (25 °C). Here, $\chi_{111}^{(2)}$ is associated with the generation of second-order nonlinear polarization ΔP_1 by a dynamic electric field $E_1 \equiv E_x$ in the lab coordinate system, see Fig. 1(c). The BaTiO₃ film is subjected to a fixed mismatch strain $\varepsilon_{22}^{\text{mis}} = -1\%$, yet the strain $\varepsilon_{11}^{\text{mis}}$ can vary. This strain condition is considered for three reasons. First, varying $\varepsilon_{11}^{\text{mis}}$ from 2 to -1% leads to a transition from an in-plane tetragonal T_1 phase with $(P_1^0 \neq 0, 0, 0)$ to an out-of-plane orthorhombic O_{13} phase with $(P_1^0 \neq 0, 0, P_3^0 \neq 0)$, followed by a transition to an out-of-plane tetragonal T_3 phase with $(0, 0, P_3^0 \neq 0)$, as shown in Fig. 3(a). We can therefore study how these two typical polymorphic ferroelectric phase transitions influence $\chi_{111}^{(2)}$. Second, the zero P_2^0 component in such an anisotropically strained film allows for excluding the contribution of $\chi_{2i}^{(1)}$ ($i = 1, 2, 3$) to $\chi_{111}^{(2)}$ [see Eq. (7)], thereby simplifying the analysis. Third, the three

strain-stabilized polar phases (T_1 , O_{13} , and T_3) have all been experimentally observed in BaTiO₃, where the O_{13} phase is also defined as a monoclinic M_C phase if $|P_3^0| > |P_1^0|$ [42,43].

The variation of $\chi_{111}^{(2),\text{dc}}$ with $\varepsilon_{11}^{\text{mis}}$, as shown in Fig. 3(b), can be understood by analyzing the strain modulation of the local curvature and asymmetry of the energy landscape. For the tetragonal T_1 and T_3 phases, one can analogously derive that $\chi_{111}^{(2),\text{dc}} = -\kappa_0^2 C_{111} \chi_{11}^{(1),\text{dc}^3}$. In the T_3 phase, $C_{111} = 0$ since the local energy landscape is symmetric with respect to ΔP_1 ; thus, $\chi_{111}^{(2),\text{dc}} = 0$. In the T_1 phase, $\chi_{111}^{(2),\text{dc}}$ decreases as $\varepsilon_{11}^{\text{mis}}$ increases, which is attributed to the decreasing $\chi_{11}^{(1),\text{dc}}$, as shown in Fig. 3(c). For the O_{13} phase:

$$\chi_{111}^{(2),\text{dc}} = -\kappa_0^2 [C_{111} \chi_{11}^{(1),\text{dc}^3} + 3C_{113} \chi_{11}^{(1),\text{dc}^2} \chi_{13}^{(1),\text{dc}} + 3C_{133} \chi_{11}^{(1),\text{dc}} \chi_{13}^{(1),\text{dc}^2} + C_{333} \chi_{13}^{(1),\text{dc}^3}]. \quad (12)$$

As shown in Fig. 3(c), the diagonal component $\chi_{11}^{(1),\text{dc}}$ is much larger than $\chi_{13}^{(1),\text{dc}}$ in the M_C phase, especially near the O_{13}/T_3 phase boundary. Thus, the significant increase in $\chi_{111}^{(2),\text{dc}}$ of the M_C phase is mainly caused by the associated increase in $\chi_{11}^{(1),\text{dc}}$.

Let us now discuss the frequency dependence of $|\chi_{111}^{(2)}|$ for the O_{13} and T_1 phases under different strain $\varepsilon_{xx}^{\text{mis}}$, noting that $|\chi_{111}^{(2)}| = 0$ in the T_1 phase. The $\chi_{111}^{(2)}$ of the tetragonal T_1 phase

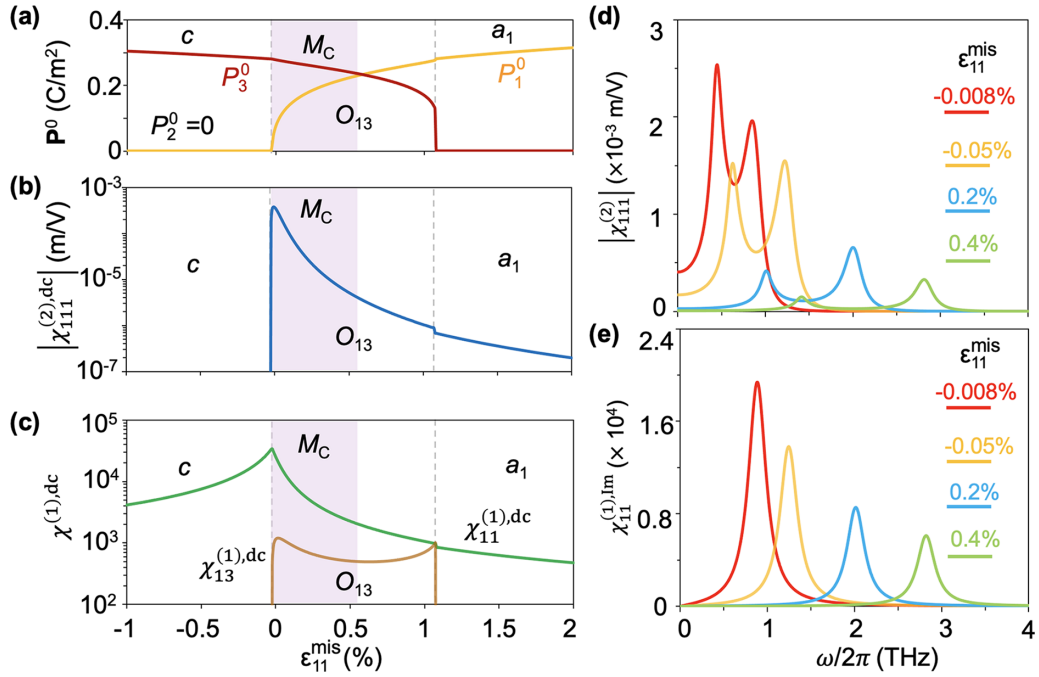


FIG. 3. Strain-dependent (a) equilibrium polarization state \mathbf{P}^0 , (b) dc nonlinear susceptibility absolute value $|\chi_{111}^{(2),dc}|$, and (c) dc nonlinear susceptibility $\chi_{11}^{(1),dc}$ and $\chi_{13}^{(1),dc}$ in a coherently strained (001)_{pc} BaTiO₃ film. $\varepsilon_{22}^{\text{mis}}$ is fixed at 1%. The shade indicates the monoclinic M_C phase, which belongs to the O_{13} phase but with $|P_3^0| > |P_1^0|$. Frequency-dependent (d) $|\chi_{111}^{(2)}|$ and (e) $\chi_{11}^{(1),lm}$ under different mismatch strains $\varepsilon_{11}^{\text{mis}}$. The temperature is 298 K.

is given by

$$\chi_{111}^{(2)} = -\kappa_0^2 C_{111} \chi_{11}^{(1)} (2\omega) \chi_{11}^{(1)} (\omega)^2. \quad (13)$$

Notably, Eq. (13) above is also approximately applicable to the O_{13} phase since it is reasonable to consider $\chi_{i3}^{(1)} = \chi_{3i}^{(1)} \approx 0$ because the large dynamical depolarization field tends to suppress the magnitude of the out-of-plane polarization variation [i.e., $|\Delta P_3(t)|$ is much smaller than $|\Delta P_1(t)|$]. Based on Eq. (13), there should be two peaks at ω_1 , $\omega_1/2$, in the frequency spectrum of $|\chi_{xxx}^{(2)}|$, consistent with the results in Fig. 3(d). The locations of ω_1 can be seen more clearly at the peaks in the frequency spectrum of $\chi_{11}^{(1),lm}$, as shown in Fig. 3(e).

As the strain $\varepsilon_{11}^{\text{mis}}$ becomes less compressive (e.g., from -0.05 to -0.008%) in the O_{13} phase, K_{11} decreases [see Fig. 3(c)], leading to a smaller $\omega_1 = \sqrt{K_{11}/\mu}$. As a result, the discrepancy between ω_1 and $\omega_1/2$ also decreases. Since the peaks of ω_1 , $\omega_1/2$ both have a finite linewidth due to the nonzero damping, these two peaks can partially overlap when they are close. This explains why $|\chi_{111}^{(2)}|$ at $\omega_1/2$ is larger than its value at $\omega_1/2$ at $\varepsilon_{11}^{\text{mis}} = -0.008\%$. Together, Figs. 3(d) and 3(e) demonstrate the effectiveness of using strain to enhance $|\chi_{111}^{(2)}|$ yet keeping $\chi_{11}^{(1),lm}$ (dielectric loss) at a relatively low value. Specifically, at $\varepsilon_{11}^{\text{mis}} = -0.008\%$, $|\chi_{111}^{(2)}|$ reaches a value of $\sim 2.54 \times 10^{-3}$ m/V at 0.45 THz, yet $\chi_{xx}^{(1),lm}$ is ~ 636.5 (one order of magnitude smaller than its peak value). This value of $|\chi_{111}^{(2)}|$ is one order of magnitude larger than $|\chi_{\text{eff}}^{(2)}|$ ($\sim 10^{-4}$ m/V) reported in the superconducting NbN thin film [44].

The above analyses indicate that a significant enhancement in $\chi_{111}^{(2)}$ simultaneously requires a vanishing curvature

(in other words, a large dielectric susceptibility) and a non-vanishing asymmetry ($C_{111} \neq 0$) of the energy landscape, which can be achieved in BaTiO₃ with a monoclinic M_C phase, occurring near the strain-driven second-order $O_{13} - T_3$ ferroelectric phase transition in coherently strained BaTiO₃ film. With this understanding, we further evaluate $\chi_{111}^{(2)}$ near the second-order ferroelectric-to-paraelectric transition in an equiaxially strained (001)_{pc} SrTiO₃ film with $\varepsilon_{11}^{\text{mis}} = \varepsilon_{22}^{\text{mis}} = 1\%$. As shown in Fig. 4(a), the calculated equilibrium polarization \mathbf{P}^0 is $(P_1^0, 0, 0)$, which is consistent with the recent experimental observation in a coherently SrTiO₃ film grown on (110)_o DyScO₃ substrate with a largely single polarization domain after in-plane electric poling [31]. As the temperature T approaches the Curie point T_c , P_1^0 gradually decreases to zero [Fig. 4(a)]; $\chi_{111}^{(2),dc} = -\kappa_0^2 C_{111} \chi_{11}^{(1),dc^3}$ increases dramatically and then drops to zero in the paraelectric phase, as shown in Fig. 4(b). Likewise, this is mainly because $\chi_{11}^{(1),dc}$ is enhanced significantly at near T_c [see Fig. 4(c)] and because C_{111} is zero in the cubic paraelectric phase.

The frequency spectrum of $|\chi_{111}^{(2)}|$ of the in-plane tetragonal SrTiO₃ film should likewise only display two peaks at $\omega_1/2$ and ω_1 , which are tens of GHz due to the reduced soft mode frequency near T_c [45]. Furthermore, at close to T_c , the two peaks of the $|\chi_{xxx}^{(2)}|$ spectrum at $\omega_1/2$ and ω_1 can merge into one; see, for example, the cases of 243.7 and 243.5 K in Fig. 4(d). Importantly, these features allow for identifying the frequency of the incident THz/GHz wave for obtaining significantly enhanced $|\chi_{111}^{(2)}|$ together with a relatively low $\chi_{11}^{(1),lm}$. For example, at $T = 242$ K, $|\chi_{111}^{(2)}|$ has a value of 0.466 m/V, yet $\chi_{11}^{(1),lm}$ is ~ 56.46 at 1 GHz; at $T = 242$ K, $|\chi_{111}^{(2)}|$ has a value of 0.611 m/V at 16 GHz, yet $\chi_{11}^{(1),lm}$ is

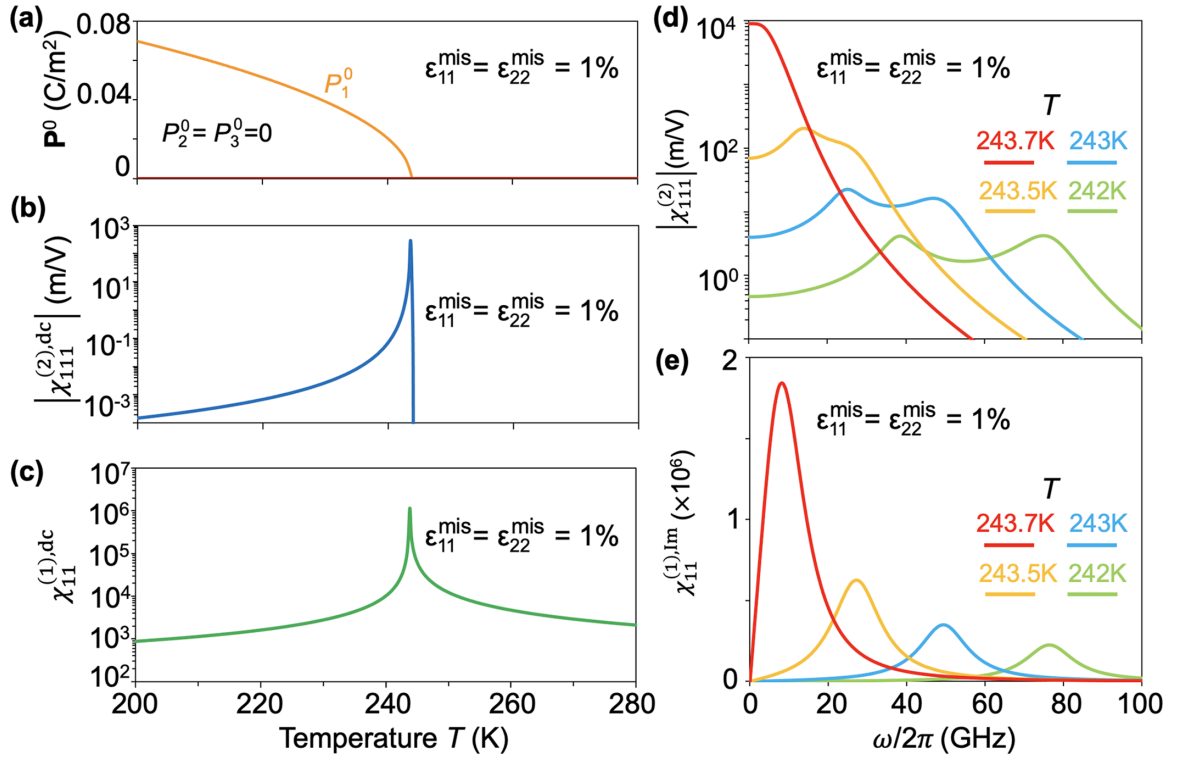


FIG. 4. Temperature-dependent (a) equilibrium polarization state \mathbf{P}^0 , (b) dc nonlinear susceptibility absolute value $|\chi_{111}^{(2),dc}|$, and (c) dc linear susceptibility $\chi_{111}^{(1),dc}$ in a coherently strained (001)_{pc} SrTiO₃ film at $\epsilon_{11}^{\text{mis}} = \epsilon_{22}^{\text{mis}} = 1\%$. Frequency-dependent (d) $|\chi_{111}^{(2)}|$ and (e) $\chi_{111}^{(1),lm}$ under different temperature at $\epsilon_{11}^{\text{mis}} = \epsilon_{22}^{\text{mis}} = 1\%$. The structural order parameter $q_1 = q_2 = q_3 = 0$ under these strain and temperature conditions.

~ 985 . These values of $|\chi_{111}^{(2)}|$ are three orders of magnitude larger than $|\chi_{\text{eff}}^{(2)}|$ ($\sim 10^{-4}$ m/V) reported in the superconducting NbN thin film [44]. Such a high $|\chi^{(2)}|$, along with manageable dielectric loss, suggests an exciting prospect of using coherently strained SrTiO₃ film as a structurally simple, source-current-free (and hence ultralow power dissipation) frequency doubler operating in the GHz/millimeter-wave band for high-data-rate wireless communication.

IV. CONCLUSIONS

We have developed an analytical theory for predicting the dynamic nonlinear dielectric susceptibility of monodomain ferroelectric crystals as a function of frequency, temperature, and in the case of strained thin films, the epitaxial strain. Our theory reveals the important role of the strain-polarization coupling in ferroelectrics, which has been ignored in existing theoretical works [20–24], in determining the nonlinear dielectric susceptibility through the modulation of the curvature and asymmetry of the local energy landscape.

Based on the well-established LGD thermodynamic energy density function and the kinetic parameters of different ferroelectric materials, the theory predicts a route to enhancing the modulus of the second-harmonic susceptibility $\chi_{111}^{(2)}$ and simultaneously maintaining the dielectric loss at a low level in a (001)_{pc} BaTiO₃ film with strain-stabilized monoclinic M_C phase and a strained (001)_{pc} SrTiO₃ film near its temperature-driven second-order ferroelectric-to-paraelectric phase transition. These results reveal the critical importance

of stabilizing the M_C phase in enhancing $\chi_{111}^{(2)}$ of BaTiO₃ and similar ferroelectric systems, which is analogous to the critical role of the M_C phase in enhancing the nonlinear optical and piezoelectric property coefficients of BaTiO₃ [42,43]. In addition to $\chi_{111}^{(2)}$ which is relevant to the THz SHG, the analytical formulae of other second-order $\chi_{ijk}^{(2)}$'s, including THz SFG/DFG and THz wave rectification (dc shift), are also derived (see Appendix C). By comparing the predicted $\chi_{ijk}^{(2)}$ to experimental measurements (e.g., THz SHG), one can refine the LGD coefficients [e.g., here, we refine the coefficients of LiTaO₃, as shown in Fig. 1(a)] and the kinetic parameters such as the mass and damping coefficients of a wide range of ferroelectric materials. The procedures of derivations can be readily extended to calculate the higher-order susceptibilities [e.g., $\chi_{ijkl}^{(3)}$] as well.

Overall, in this paper, we provide a theoretical basis for studying the nonlinear interaction between a THz (typical frequency range: 0.1–10 THz) or lower-frequency electromagnetic (EM) wave and a ferroelectric material. The analytically calculated nonlinear susceptibility of the ferroelectric polarization \mathbf{P}^{ion} (soft mode) is obtained by finding the *steady-state* solution to the equation of motion for \mathbf{P}^{ion} , thus only applicable to continuous THz wave or multicycle narrowband THz pulse. However, the theoretical framework can be readily generalized to calculate the nonlinear susceptibility of ferroelectric polarization to single-cycle broadband THz pulse, as used in many experiments [46–50], by finding the *transient-state* solution to the equation of motion for \mathbf{P}^{ion} .

Moreover, by (i) extending the LGD potential (a polynomial of \mathbf{P}^{ion}) to incorporate the coupling between \mathbf{P}^{ion} and the ionic polarization associated with the higher-frequency infrared (IR) active phonons (denoted as $\mathbf{P}^{\text{ion,IR}}$), and (ii) solving the coupled equations of motion for both \mathbf{P}^{ion} and $\mathbf{P}^{\text{ion,IR}}$, it is possible to analytically calculate the nonlinear susceptibility of \mathbf{P}^{ion} to a mid-IR (frequency: ~ 20 THz) pulse, as has been studied in many computational [51–53] and experimental [14,54–56] studies (a.k.a. the nonlinear phononics approach). Furthermore, by introducing a nonlinear coupling between \mathbf{P}^{ion} and the electric field of a near-IR pulse (frequency: tens of THz) in the framework of impulsive stimulated Raman scattering (ISRS) into the equation of motion for \mathbf{P}^{ion} (like Refs. [57–60]), it is possible to analytically calculate the nonlinear susceptibility of \mathbf{P}^{ion} to a near-IR pulse via the ISRS.

More broadly, the theory in this paper can also be extended to calculate susceptibilities of the ferroelectric polarization under the excitation of a circularly polarized THz wave which can enable emergent phenomena from the dynamic multiferroicity [15,61,62], to ferroelectrics under mechanical boundary conditions such as an uniaxially stretched ferroelectric membrane [63], and to other polar materials that have a spontaneous ionic polarization such as wurtzite III-nitride semiconductors [64].

ACKNOWLEDGMENTS

This paper is primarily supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award No. DE-SC0020145 as part of the Computational Materials Sciences Program (V.G., L.-Q.C., and J.-M.H.). J.-M.H. also acknowledges the partial support from the National Science Foundation (NSF) under Grant No. DMR-2237884 on the dynamical phase-field simulations in this paper. The dynamical phase-field simulations were performed using Bridges at the Pittsburgh Supercomputing Center through Allocation No. TG-DMR180076 from the Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) program, which is supported by National Science Foundation Grants No. 2138259, No. 2138286, No. 2138307, No. 2137603, and No. 2138296. Part of this work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. DE-AC52-07NA27344 (B.W.). A.R. acknowledges the support of the National Science Foundation Graduate Research Fellowship Program under Grant No. DGE1255832.

APPENDIX A: DERIVATION OF THE EQUATION OF MOTION FOR THE IONIC POLARIZATION (SOFT MODE) IN FERROELECTRICS

We begin by writing the equation of motion for the soft mode, which has a coordinate \mathbf{Q}^p (Q_i^p , $i = 1, 2, 3$, with units of m) based on the Newton's second law, i.e.,

$$\mathbf{F}^{\text{ext}} + \mathbf{F}^{\text{restoring}} + \mathbf{F}^{\text{f}} = \rho^* \frac{d^2 \mathbf{Q}^p}{dt^2}, \quad (\text{A1})$$

where ρ^* is the effective mass density of the soft mode (unit: kg/m^3). Here, \mathbf{F}^{ext} is the volumetric coulombic force (unit:

N/m^3), given by

$$\mathbf{F}_i^{\text{ext}} = Z_p^* (E_i + E_i^{\text{d}} + E_i^{\text{rad}}), \quad (\text{A2})$$

where E_i , E_i^{d} , and E_i^{rad} are the electric field of the incident THz EM wave, the depolarization electric field, and the radiation electric field inside the ferroelectric, respectively, as mentioned in the main text. The subscript $i = x, y, z$ indicates that these electric fields are typically defined in the lab coordinate system, with $x \equiv 1$, $y \equiv 2$, and $z \equiv 3$ for the case of the (001)_{pc} strained BaTiO₃ film and the (001)_{pc} strained SrTiO₃ film [see Figs. 1(c) and 1(d)]. The Born effective charge Z_p^* describes the charge density associated with the soft mode. It has units of C/m^3 and relates \mathbf{Q}^p and ferroelectric polarization \mathbf{P}^{ion} (or simply \mathbf{P} hereafter) via $Q_i^p = P_i/Z_p^*$, as mentioned in the introduction.

The volumetric restoring force $F_i^{\text{restoring}}$, which is analogous to the restoring force that drives the electron back to its equilibrium position in nonlinear optical phenomena [26], is related to the local slope of the potential energy density landscape of the soft mode with contribution from both the Landau free energy density and elastic energy density. When P is spatially uniform and oscillates in-phase in the ferroelectric (as is the case in the thin slab limit), $F_i^{\text{restoring}}$ is expressed as

$$\begin{aligned} F_i^{\text{restoring}} &= -\frac{\partial(f^{\text{Landau}} + f^{\text{Elast}})}{\partial Q_i^p} = -Z_p^* \frac{\partial(f^{\text{Landau}} + f^{\text{Elast}})}{\partial P_i} \\ &= Z_p^* (E_i^{\text{Landau}} + E_i^{\text{Elast}}), \end{aligned} \quad (\text{A3})$$

where the expressions of f^{Landau} and f^{Elast} are provided in Appendix B. Furthermore, the volumetric frictional force is assumed to be linearly proportional to the velocity of the soft mode, given by

$$F_i^{\text{f}} = -\gamma_{ij}^* \frac{dQ_j^p}{dt} = -\frac{\gamma_{ij}^*}{Z_p^*} \frac{dP_j}{dt}. \quad (\text{A4})$$

Substituting Eqs. (A2)–(A4) into Eq. (A1) and using P_i as the variable, one has, after some rearrangement,

$$\frac{\rho^*}{Z_p^{*2}} \frac{d^2 P_i}{dt^2} + \frac{\gamma_{ij}^*}{Z_p^{*2}} \frac{dP_j}{dt} = E_i + E_i^{\text{d}} + E_i^{\text{rad}} + E_i^{\text{Landau}} + E_i^{\text{Elast}}. \quad (\text{A5})$$

By letting $\mu = \frac{\rho^*}{Z_p^{*2}}$, $\gamma_{ij} = \frac{\gamma_{ij}^*}{Z_p^{*2}}$, and using a total effective electric field E_i^{eff} to represent the summation of all the fields on the right-hand side of Eq. (A5), the latter can be rewritten into a concise form, i.e.,

$$\mu \frac{d^2 P_i}{dt^2} + \gamma_{ij} \frac{dP_j}{dt} = E_i^{\text{eff}}, \quad (\text{A6})$$

which is equivalent to Eq. (3) because $P_i = P_i^0 + \Delta P_i$ and $E_i^{\text{eff}} = \Delta E_i^{\text{eff}}$, as discussed in the main text. Equation (3) can alternatively be derived based on an Euler-Lagrange approach by generalizing the procedures in Ref. [65] to consider the complete set of driving forces mentioned above.

APPENDIX B: DETAILED EXPRESSIONS OF f^{Landau} AND f^{Elast} FOR BaTiO₃, PbTiO₃, SrTiO₃, LiTaO₃, AND LiNbO₃ AND THE ASSOCIATED MATERIALS PARAMETERS

Eighth-, sixth-, and fourth-order f^{Landau} 's are used for BaTiO₃, PbTiO₃, and SrTiO₃, respectively, given as [66]

$$\begin{aligned} f^{\text{Landau}} = & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2P_2^2 + P_2^2P_3^2 + P_1^2P_3^2) + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) \\ & + \alpha_{112}[P_1^2(P_2^4 + P_3^4) + P_2^2(P_1^4 + P_3^4) + P_3^2(P_1^4 + P_2^4)] + \alpha_{123}P_1^2P_2^2P_3^2 + \alpha_{1111}(P_1^8 + P_2^8 + P_3^8) \\ & + \alpha_{1112}[P_1^6(P_2^2 + P_3^2) + P_2^6(P_1^2 + P_3^2) + P_3^6(P_1^2 + P_2^2)] + \alpha_{1122}(P_1^4P_2^4 + P_2^4P_3^4 + P_1^4P_3^4) \\ & + \alpha_{1123}(P_1^4P_2^2P_3^2 + P_2^4P_1^2P_3^2 + P_3^4P_2^2P_1^2), \end{aligned} \quad (\text{B1})$$

$$\begin{aligned} f^{\text{Landau}} = & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2P_2^2 + P_2^2P_3^2 + P_1^2P_3^2) + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) \\ & + \alpha_{112}[P_1^2(P_2^4 + P_3^4) + P_2^2(P_1^4 + P_3^4) + P_3^2(P_1^4 + P_2^4)] + \alpha_{123}P_1^2P_2^2P_3^2, \end{aligned} \quad (\text{B2})$$

$$\begin{aligned} f^{\text{Landau}} = & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2P_2^2 + P_2^2P_3^2 + P_1^2P_3^2) + \beta_1(q_1^2 + q_2^2 + q_3^2) + \beta_{11}(q_1^4 + q_2^4 + q_3^4) \\ & + \beta_{12}(q_1^2q_2^2 + q_2^2q_3^2 + q_1^2q_3^2) - t_{11}(P_1^2q_1^2 + P_2^2q_2^2 + P_3^2q_3^2) - t_{12}(P_1^2(q_2^2 + q_3^2) + P_2^2(q_1^2 + q_3^2) + P_3^2(q_1^2 + q_2^2)) \\ & - t_{44}(P_1P_2q_1q_2 + P_2P_3q_2q_3 + P_1P_3q_1q_3). \end{aligned} \quad (\text{B3})$$

Note that f^{Landau} of SrTiO₃ also includes the terms that describe the coupling between the polarization P_i and the structural order parameter q_i ($i = 1, 2, 3$), which represents the linear oxygen displacement associated with oxygen octahedra rotation [67].

The elastic free energy density is given as $f^{\text{Elast}} = \frac{1}{2}c_{ijkl}e_{kl}e_{ij}$, where e_{ij} and e_{kl} are the elastic strains, and c_{ijkl} is the elastic stiffness tensor at constant electric field E and temperature T and can be related to the density of the electrical Helmholtz free energy f (see its definition in Appendix D) via the relation $c_{ijkl} = (\frac{\partial^2 \sigma_{ij}}{\partial e_{kl}})_{T,E} = (\frac{\partial^2 f}{\partial e_{kl} \partial e_{ij}})_{T,E}$. For the pseudocubic BaTiO₃, PbTiO₃, and SrTiO₃ films, f^{Elast} is expanded as

$$f^{\text{Elast}} = \frac{1}{2}c_{11}(e_{11}^2 + e_{22}^2 + e_{33}^2) + c_{12}(e_{11}e_{22} + e_{11}e_{33} + e_{22}e_{33}) + 2c_{44}(e_{12}^2 + e_{13}^2 + e_{23}^2), \quad (\text{B4})$$

where c_{11} , c_{12} , and c_{44} are the independent components of the 6×6 elastic stiffness matrix c_{mn} ($m, n = 1, 2, \dots, 6$), which represents the elastic stiffness tensor c_{ijkl} following the convention described in Ref. [68]. The $e_{ij} = \varepsilon_{ij} - \varepsilon_{ij}^0$ ($i, j = 1, 2$) is the elastic strain, where ε_{ij} is the total strain, and ε_{ij}^0 is the stress-free (eigen)strain. For BaTiO₃ and PbTiO₃, one has

$$\varepsilon_{11}^0 = Q_{11}P_1^2 + Q_{12}(P_2^2 + P_3^2), \quad \varepsilon_{22}^0 = Q_{11}P_2^2 + Q_{12}(P_1^2 + P_3^2), \quad \varepsilon_{33}^0 = Q_{11}P_3^2 + Q_{12}(P_1^2 + P_2^2); \quad (\text{B5a})$$

$$\varepsilon_{23}^0 = Q_{44}P_2P_3, \quad \varepsilon_{13}^0 = Q_{44}P_1P_3, \quad \varepsilon_{12}^0 = Q_{44}P_1P_2, \quad (\text{B5b})$$

where Q_{11} , Q_{12} , and Q_{44} are the electrostrictive coefficients. For SrTiO₃, one has

$$\varepsilon_{11}^0 = Q_{11}P_1^2 + Q_{12}(P_2^2 + P_3^2) + \Lambda_{11}q_1^2 + \Lambda_{12}(q_2^2 + q_3^2), \quad (\text{B6a})$$

$$\varepsilon_{22}^0 = Q_{11}P_2^2 + Q_{12}(P_1^2 + P_3^2) + \Lambda_{11}q_2^2 + \Lambda_{12}(q_1^2 + q_3^2), \quad (\text{B6b})$$

$$\varepsilon_{33}^0 = Q_{11}P_3^2 + Q_{12}(P_1^2 + P_2^2) + \Lambda_{11}q_3^2 + \Lambda_{12}(q_1^2 + q_2^2), \quad (\text{B6c})$$

$$\varepsilon_{23}^0 = Q_{44}P_2P_3 + \Lambda_{44}q_2q_3, \quad \varepsilon_{13}^0 = Q_{44}P_1P_3 + \Lambda_{44}q_1q_3, \quad \varepsilon_{12}^0 = Q_{44}P_1P_2 + \Lambda_{44}q_1q_2, \quad (\text{B6d})$$

where Λ_{11} , Λ_{12} , and Λ_{44} are the linear quadratic coupling coefficient between the strain and structural order parameter. At the initial equilibrium state, the total strain ε_{ij} is determined based on the mechanical boundary condition. In monodomain (P_i and q_i are spatially homogeneous), stress-free bulk crystals, $\varepsilon_{ij} = \varepsilon_{ij}^0$. In biaxially strained films, as indicated in Sec. II, $\varepsilon_{11} = \varepsilon_{11}^{\text{mis}}$, $\varepsilon_{22} = \varepsilon_{22}^{\text{mis}}$, $\varepsilon_{33} = -\frac{c_{12}}{c_{11}}(\varepsilon_{11}^{\text{mis}} + \varepsilon_{22}^{\text{mis}} - \varepsilon_{11}^0 - \varepsilon_{22}^0) + \varepsilon_{33}^0$, and $\varepsilon_{23} = \varepsilon_{23}^0$, $\varepsilon_{13} = \varepsilon_{13}^0$, $\varepsilon_{12} = 0$.

For trigonal crystals LiTaO₃ and LiNbO₃ that are uniaxial ferroelectrics, the Landau free energy density is written as [40]

$$f^{\text{Landau}} = -\frac{\alpha_1}{2}P_3^2 + \frac{\alpha_2}{4}P_3^4 + \frac{\alpha_3}{2}(P_1^2 + P_2^2). \quad (\text{B7})$$

Following Ref. [40], the elastic energy density f^{Elas} of LiTaO₃ and LiNbO₃ is written, in contrast with Eqs. (B4)–(B6), using Voigt notation, i.e.,

$$\begin{aligned} f^{\text{Elas}} = & \beta_1\varepsilon_3^2 + \beta_2(\varepsilon_1 + \varepsilon_2)^2 + \beta_3[(\varepsilon_1 - \varepsilon_2)^2 + \varepsilon_6^2] + \beta_4\varepsilon_3(\varepsilon_1 + \varepsilon_2) + \beta_5(\varepsilon_4^2 + \varepsilon_5^2) + \beta_6[(\varepsilon_1 - \varepsilon_2)\varepsilon_4 + \varepsilon_5\varepsilon_6] \\ & + \gamma_1(\varepsilon_1 + \varepsilon_2)P_3^2 + \gamma_2\varepsilon_3P_3^2 + \gamma_3[(\varepsilon_1 - \varepsilon_2)P_2P_3 + \varepsilon_6P_1P_3] + \gamma_4(\varepsilon_5P_1P_3 + \varepsilon_4P_2P_3) + \gamma_5(\varepsilon_1 + \varepsilon_2)(P_1^2 + P_2^2) \\ & + \gamma_6\varepsilon_3(P_1^2 + P_2^2) + \gamma_7[(\varepsilon_1 - \varepsilon_2)(P_1^2 - P_2^2) + 2\varepsilon_6P_1P_2] + \gamma_8[\varepsilon_4(P_1^2 - P_2^2) + 2\varepsilon_5P_1P_2], \end{aligned} \quad (\text{B8})$$

TABLE I. List of the coefficients in the Landau and elastic free energy densities of BaTiO₃, PbTiO₃, and SrTiO₃. The temperature is in units of °C for BaTiO₃ and PbTiO₃ and K for SrTiO₃.

Coefficients	BaTiO ₃	PbTiO ₃	SrTiO ₃
α_1 (N m ² C ⁻²)	$4.124 \times 10^5 (T-115)$ [69]	$3.8 \times 10^5 (T-479)$ [70]	$4.05 \times 10^7 [\coth(\frac{54}{T}) - \coth(\frac{54}{30})]$ [71]
α_{11} (N m ⁶ C ⁻⁴)	-2.097×10^8 [69]	-0.73×10^8 [70]	2.899×10^9 [31]
α_{12} (N m ⁶ C ⁻⁴)	7.974×10^8 [69]	7.5×10^8 [70]	7.766×10^9 [67]
α_{111} (N m ¹⁰ C ⁻⁶)	1.294×10^9 [69]	2.6×10^9 [70]	0
α_{112} (N m ¹⁰ C ⁻⁶)	-1.950×10^9 [69]	6.1×10^8 [70]	0
α_{123} (N m ¹⁰ C ⁻⁶)	-2.500×10^9 [69]	-37×10^8 [70]	0
α_{1111} (N m ¹⁴ C ⁻⁸)	3.863×10^{10} [69]	0	0
α_{1112} (N m ¹⁴ C ⁻⁸)	2.529×10^{10} [69]	0	0
α_{1122} (N m ¹⁴ C ⁻⁸)	1.637×10^{10} [69]	0	0
α_{1123} (N m ¹⁴ C ⁻⁸)	1.367×10^{10} [69]	0	0
β_1 (N m ⁻⁶)	0	0	$1.32 \times 10^{29} [\coth(\frac{145}{T}) - \coth(\frac{145}{105})]$ [71]
β_{11} (N m ⁻⁶)	0	0	1.688×10^{50} [71]
β_{12} (N m ⁻⁶)	0	0	3.879×10^{50} [71]
t_{11} (N m ² C ⁻²)	0	0	-1.902×10^{29} [31]
t_{12} (N m ² C ⁻²)	0	0	-1.014×10^{29} [71]
t_{44} (N m ² C ⁻²)	0	0	5.865×10^{29} [71]
c_{11} (GPa)	178 [69]	174.6 [70]	336 [71]
c_{12} (GPa)	96.4 [69]	79.37 [70]	107 [71]
c_{44} (GPa)	122 [69]	111 [70]	127 [71]
Q_{11} (m ⁴ C ⁻²)	0.1 [69]	0.089 [70]	0.0536 [71]
Q_{12} (m ⁴ C ⁻²)	-0.034 [69]	-0.026 [70]	-0.0154 [71]
Q_{44} (m ⁴ C ⁻²)	0.029 [69]	0.03375 [70]	0.00472 [71]
Λ_{11} (N C ⁻²)	0	0	8.820×10^{18} [71]
Λ_{12} (N C ⁻²)	0	0	-7.774×10^{18} [71]
Λ_{44} (N C ⁻²)	0	0	-4.528×10^{18} [71]

where the ε_i 's here are the total strain. For monodomain, stress-free bulk crystals, ε_i can be obtained by solving the mechanical boundary condition $\sigma_j = \partial f^{\text{Elast}} / \partial \varepsilon_j = 0$, $j = 1, 2, 3, 4, 5, 6$, given by

$$\varepsilon_1 = \Gamma_1 P_1^2 + \Gamma_2 P_2^2 + \Gamma_3 P_3^2 + \Gamma_4 P_2 P_3, \quad \varepsilon_2 = \Gamma_2 P_1^2 + \Gamma_1 P_2^2 + \Gamma_3 P_3^2 - \Gamma_4 P_2 P_3, \quad (\text{B9a})$$

$$\varepsilon_3 = \Gamma_5 P_1^2 + \Gamma_5 P_2^2 + \Gamma_6 P_3^2, \quad \varepsilon_4 = \Gamma_7 P_1^2 - \Gamma_7 P_2^2 + \Gamma_8 P_2 P_3, \quad (\text{B9b})$$

$$\varepsilon_5 = \Gamma_8 P_1 P_3 + 2\Gamma_7 P_1 P_2, \quad \varepsilon_6 = 2\Gamma_4 P_1 P_3 + \Gamma_9 P_1 P_2, \quad (\text{B9c})$$

Here, the coefficients Γ_i are $\Gamma_1 = \frac{\beta_1(-8\beta_3\beta_5\gamma_5+2\beta_6^2\gamma_5-8\beta_2\beta_5\gamma_7+4\beta_2\beta_6\gamma_8)+\beta_4(4\beta_3\beta_5\gamma_6-\beta_6^2\gamma_6-2\beta_4\beta_5\gamma_7+\beta_4\beta_6\gamma_8)}{2(4\beta_1\beta_2-\beta_4^2)(4\beta_3\beta_5-\beta_6^2)}$, $\Gamma_2 = \frac{\beta_1(-8\beta_3\beta_5\gamma_5+2\beta_6^2\gamma_5+8\beta_2\beta_5\gamma_7-4\beta_2\beta_6\gamma_8)+\beta_4(4\beta_3\beta_5\gamma_6-\beta_6^2\gamma_6-2\beta_4\beta_5\gamma_7+\beta_4\beta_6\gamma_8)}{2(4\beta_1\beta_2-\beta_4^2)(4\beta_3\beta_5-\beta_6^2)}$, $\Gamma_3 = \frac{-2\beta_1\gamma_1+\beta_4\gamma_2}{2(4\beta_1\beta_2-\beta_4^2)}$, $\Gamma_4 = \frac{-2\beta_5\gamma_3+\beta_6\gamma_4}{2(4\beta_3\beta_5-\beta_6^2)}$, $\Gamma_5 = \frac{\beta_4\gamma_5-2\beta_2\gamma_6}{4\beta_1\beta_2-\beta_4^2}$, $\Gamma_6 = \frac{\beta_4\gamma_1-2\beta_2\gamma_2}{4\beta_1\beta_2-\beta_4^2}$, $\Gamma_7 = \frac{\beta_6\gamma_7-2\beta_3\gamma_8}{4\beta_3\beta_5-\beta_6^2}$, $\Gamma_8 = \frac{\beta_6\gamma_3-2\beta_3\gamma_4}{4\beta_3\beta_5-\beta_6^2}$, and $\Gamma_9 = \frac{2\beta_6\gamma_8-4\beta_5\gamma_7}{4\beta_3\beta_5-\beta_6^2}$.

Tables I and II list the coefficients in the Landau and elastic free energy densities of the four ferroelectric materials. The mass coefficient $\mu = 1.35 \times 10^{-18}$ J m s² C⁻² for BaTiO₃ [29], $\mu = 1.59 \times 10^{-18}$ J m s² C⁻² for PbTiO₃ [29], $\mu = 22 \times 10^{-18}$ J m s² C⁻² for SrTiO₃ [72], and $\mu = 1.81 \times 10^{-18}$ J m s² C⁻² for LiNbO₃ [29]. The μ value of LiTaO₃, which is not yet available in literature to our knowledge, is set to be the same as LiNbO₃.

APPENDIX C: LINEAR AND NONLINEAR SUSCEPTIBILITY DERIVATION BY PERTURBATION METHOD

Given that $E_i^{\text{Landau}}(t) = E_i^{\text{Landau}}(P_i^0) + \Delta E_i^{\text{Landau}}(t)$, $E_i^{\text{Elast}}(t) = E_i^{\text{Elast}}(P_i^0) + \Delta E_i^{\text{Elast}}(t)$, $E_i^{\text{d}} = E_i^{\text{d}}(P_i^0) + \Delta E_i^{\text{d}}(t)$, and that $E_i^{\text{Landau}}(P_i^0) + E_i^{\text{Elast}}(P_i^0) + E_i^{\text{d}}(P_i^0) = 0$ in the initial equilibrium state ($P_i = P_i^0$), the equation of motion for polarization [Eq. (3)] can be rewritten as

$$\mu \frac{\partial^2 \Delta P_i}{\partial t^2} + \gamma_{ij} \frac{\partial \Delta P_j}{\partial t} = \Delta E_i^{\text{Landau}} + \Delta E_i^{\text{Elast}} + \Delta E_i^{\text{d}} + E_i + E_i^{\text{rad}}, \quad (\text{C1})$$

where $\Delta E_i^{\text{Landau}}$ and $\Delta E_i^{\text{Elast}}$ can be expanded through Taylor series expansion, i.e., $\Delta E_i^{\text{Landau}} = A_{ij} \Delta P_j + \frac{1}{2} A_{ijk} \Delta P_j \Delta P_k + \dots$, $\Delta E_i^{\text{Elast}} = B_{ij} \Delta P_j + \frac{1}{2} B_{ijk} \Delta P_j \Delta P_k + \dots$, where the expressions of A_{ij} , A_{ijk} , B_{ij} , and B_{ijk} are provided in Sec. II, with $i, j = 1, 2, 3$; $\Delta E_i^{\text{d}} = (0, 0, -\frac{1}{\kappa_0 \kappa_b} \Delta P_z)$ and $E_i^{\text{rad}} = (-\frac{d_0}{2\kappa_0 c} \frac{\partial P_x}{\partial t}, -\frac{d_0}{2\kappa_0 c} \frac{\partial P_y}{\partial t}, 0)$ are often expressed in the x - y - z lab coordinate system, with $x \equiv 1$, $y \equiv 2$, and $z \equiv 3$. Moreover, we assume that only the diagonal components of the 3×3 matrix γ_{ij} are nonzero. This assumption is also adopted in the derivation of the nonlinear susceptibility of electronic polarization to optical light waves

TABLE II. List of the coefficients in the Landau and elastic free energy densities of LiTaO₃ and LiNbO₃ at room temperature (298 K).

Coefficients	LiTaO ₃	LiNbO ₃
α_1 (N m ² C ⁻²)	1.25×10^9 (fitted from [39])	2.012×10^9 [40]
α_2 (N m ² C ⁻²)	6×10^8 (fitted from [39])	3.608×10^9 [40]
α_3 (N m ² C ⁻²)	1.3×10^9 (fitted from [39])	1.345×10^9 [40]
β_1 (N m ⁻²)	13.55×10^{10} [40]	12.25×10^{10} [40]
β_2 (N m ⁻²)	6.475×10^{10} [40]	6.4×10^{10} [40]
β_3 (N m ⁻²)	4.925×10^{10} [40]	3.75×10^{10} [40]
β_4 (N m ⁻²)	7.4×10^{10} [40]	7.5×10^{10} [40]
β_5 (N m ⁻²)	4.8×10^{10} [40]	3×10^{10} [40]
β_6 (N m ⁻²)	-1.2×10^{10} [40]	0.9×10^{10} [40]
γ_1 (N m ² C ⁻²)	-0.202×10^9 [40]	0.216×10^9 [40]
γ_2 (N m ² C ⁻²)	1.317×10^9 [40]	1.848×10^9 [40]
γ_3 (N m ² C ⁻²)	-2.824×10^9 [40]	-0.33×10^9 [40]
γ_4 (N m ² C ⁻²)	4.992×10^9 [40]	3.9×10^9 [40]

[26]. The values of γ_{11} , γ_{22} , and γ_{33} determine the linewidth of a peak in the frequency spectra of both the linear and nonlinear susceptibilities and therefore can be calibrated by comparing the theoretically predicted and experimentally measured linewidth. If only keeping the first two terms in the expanded expressions of $\Delta E_i^{\text{Landau}}$ and $\Delta E_i^{\text{Elast}}$, Eq. (C1) can be expanded into the following equations:

$$\begin{aligned} \mu \frac{\partial^2 \Delta P_1}{\partial t^2} + \left(\gamma_{11} + \frac{d_0}{2\kappa_0 c} \right) \frac{\partial \Delta P_1}{\partial t} - (A_{11} + B_{11}) \Delta P_1 - (A_{12} + B_{12}) \Delta P_2 - (A_{13} + B_{13}) \Delta P_3 - \frac{1}{2} (A_{111} + B_{111}) \Delta P_1^2 \\ - \frac{1}{2} (A_{122} + B_{122}) \Delta P_1^2 - \frac{1}{2} (A_{133} + B_{133}) \Delta P_1^2 - (A_{123} + B_{123}) \Delta P_2 \Delta P_3 - (A_{113} + B_{113}) \Delta P_1 \Delta P_3 - (A_{112} + B_{112}) \Delta P_1 \Delta P_2 = E_1, \end{aligned} \quad (\text{C2a})$$

$$\begin{aligned} \mu \frac{\partial^2 \Delta P_2}{\partial t^2} + \left(\gamma_{22} + \frac{d_0}{2\kappa_0 c} \right) \frac{\partial \Delta P_2}{\partial t} - (A_{21} + B_{21}) \Delta P_1 - (A_{22} + B_{22}) \Delta P_2 - (A_{23} + B_{23}) \Delta P_3 - \frac{1}{2} (A_{211} + B_{211}) \Delta P_1^2 \\ - \frac{1}{2} (A_{222} + B_{222}) \Delta P_1^2 - \frac{1}{2} (A_{233} + B_{133}) \Delta P_1^2 - (A_{223} + B_{223}) \Delta P_2 \Delta P_3 - (A_{213} + B_{213}) \Delta P_1 \Delta P_3 - (A_{212} + B_{212}) \Delta P_1 \Delta P_2 = E_2, \end{aligned} \quad (\text{C2b})$$

$$\begin{aligned} \mu \frac{\partial^2 \Delta P_3}{\partial t^2} + \gamma_{33} \frac{\partial \Delta P_3}{\partial t} - (A_{31} + B_{31}) \Delta P_1 - (A_{32} + B_{32}) \Delta P_2 - \left(A_{33} + B_{33} - \frac{1}{\kappa_0 \kappa_b} \right) \Delta P_3 - \frac{1}{2} (A_{311} + B_{311}) \Delta P_1^2 \\ - \frac{1}{2} (A_{322} + B_{322}) \Delta P_1^2 - \frac{1}{2} (A_{333} + B_{333}) \Delta P_1^2 - (A_{323} + B_{323}) \Delta P_2 \Delta P_3 - (A_{313} + B_{313}) \Delta P_1 \Delta P_3 - (A_{312} + B_{312}) \Delta P_1 \Delta P_2 = E_3. \end{aligned} \quad (\text{C2c})$$

Equations (C2a)–(C2c) can be written into a matrix form as shown by Eq. (4), reproduced below:

$$\mu \frac{\partial^2 \Delta \mathbf{P}}{\partial t^2} + \boldsymbol{\gamma}^{\text{eff}} \frac{\partial \Delta \mathbf{P}}{\partial t} + \mathbf{K} \Delta \mathbf{P} + \mathbf{C} \Delta \mathbf{P}_{\text{II}} = \mathbf{E}, \quad (\text{C3})$$

where the expanded expressions of the matrices $\Delta \mathbf{P}$, \mathbf{E} , $\Delta \mathbf{P}_{\text{II}}$, and $\boldsymbol{\gamma}^{\text{eff}}$ as well as the tensors \mathbf{K} and \mathbf{C} are provided in the main paper, as shown by Eqs. (4), 6(a), 6(b), and the related text. To solve Eq. (C3) by the perturbation method, we begin by replacing \mathbf{E} with $\lambda \mathbf{E}$, where λ is a parameter that characterizes the strength of the perturbation and ranges continuously between 0 and 1 and will be set equal to 1 at the end of calculation. In the framework of the perturbation method, the solution of Eq. (C3) can be written as $\Delta \mathbf{P} = \lambda \Delta \mathbf{P}^{(1)} + \lambda^2 \Delta \mathbf{P}^{(2)} + \lambda^3 \Delta \mathbf{P}^{(3)} + \dots$, where $\Delta \mathbf{P}^{(1)}$ is the lowest-order (linear) contribution to $\Delta \mathbf{P}$, calculated as $\Delta \mathbf{P}^{(1)} = \Delta P_i^{\text{Linear}} = \kappa_0 \chi_{ij}^{(1)} E_j$; $\Delta \mathbf{P}^{(2)}$ is the second-order nonlinear term of nonlinear polarization oscillation, calculated as $\Delta \mathbf{P}^{(2)} = \kappa_0 \chi_{ijk}^{(2)} E_j E_k$; and so forth.

It is worth emphasizing that the premise of the perturbation theory in the present application is that the center of polarization oscillation is always at $P_i = P_i^0$, which is only valid when the amplitude of E_i^{inc} is not too large. Under strong excitation, the dc polarization shift $\Delta P_i^{(2)}(0)$, as discussed in the text after Eqs. (6a) and (6b), would be large and therefore shifts the center of polarization oscillation from P_i^0 to $P_i^0 + \Delta P_i^{(2)}(0)$. Alternatively, the polarization dynamics under strong excitation can

be obtained by numerical solutions from a dynamical phase-field model with coupled strain-polarization-EM wave dynamics [18,25]. With this in mind, we proceed by writing the term $\Delta\mathbf{P}_{\text{II}}$ as

$$\begin{aligned}\Delta\mathbf{P}_{\text{II}} &= \left\{ \left[\sum_{i=1}^2 \lambda^i \Delta P_1^{(i)} \right], \left[\sum_{i=1}^2 \lambda^i \Delta P_2^{(i)} \right]^2, \left[\sum_{i=1}^2 \lambda^i \Delta P_3^{(i)} \right]^2, \right. \\ &\quad \left. 2 \left[\sum_{i=1}^2 \lambda^i \Delta P_2^{(i)} \right] \left[\sum_{i=1}^2 \lambda^i \Delta P_3^{(i)} \right], 2 \left[\sum_{i=1}^2 \lambda^i \Delta P_1^{(i)} \right] \left[\sum_{i=1}^2 \lambda^i \Delta P_3^{(i)} \right], 2 \left[\sum_{i=1}^2 \lambda^i \Delta P_1^{(i)} \right] \left[\sum_{i=1}^2 \lambda^i \Delta P_2^{(i)} \right] \right\}^T \\ &= \lambda^2 [\Delta P_1^{(1)2}, \Delta P_2^{(1)2}, \Delta P_3^{(1)2}, 2\Delta P_2^{(1)} \Delta P_3^{(1)}, 2\Delta P_1^{(1)} \Delta P_3^{(1)}, 2\Delta P_1^{(1)} \Delta P_2^{(1)}]^T \\ &\quad + \lambda^3 [2\Delta P_1^{(1)} \Delta P_1^{(2)}, 2\Delta P_2^{(1)} \Delta P_2^{(2)}, 2\Delta P_3^{(1)} \Delta P_3^{(2)}, \\ &\quad 2\Delta P_2^{(1)} \Delta P_3^{(2)} + 2\Delta P_3^{(1)} \Delta P_2^{(2)}, 2\Delta P_1^{(1)} \Delta P_3^{(2)} + 2\Delta P_3^{(1)} \Delta P_1^{(2)}, 2\Delta P_1^{(1)} \Delta P_2^{(2)} + 2\Delta P_2^{(1)} \Delta P_1^{(2)}]^T + \dots \\ &= \lambda^2 \Delta\mathbf{P}_{\text{II}}^{(1)} + \lambda^3 \Delta\mathbf{P}_{\text{II}}^{(1,2)} + \dots\end{aligned}\quad (\text{C4})$$

Plugging in the expression $\Delta\mathbf{P} = \lambda\Delta\mathbf{P}^{(1)} + \lambda^2\Delta\mathbf{P}^{(2)} + \lambda^3\Delta\mathbf{P}^{(3)} + \dots$ and Eq. (C4) into Eq. (C3), Eq. (C3) can be rewritten into a form given by $\lambda(\text{Eq.}u_1) + \lambda^2(\text{Eq.}u_2) + \lambda^3(\text{Eq.}u_3) + \dots = \lambda\mathbf{E}^{\text{inc}}$. The solution to this equation requires that $\text{Eq.}u_1 = \mathbf{E}^{\text{inc}}$ and that $\text{Eq.}u_n = 0$ ($n = 2,3,4, \dots$), which can be expanded into a series of linear equations as follows:

$$\mu \frac{\partial^2 \Delta\mathbf{P}^{(1)}}{\partial t^2} + \boldsymbol{\gamma}^{\text{eff}} \frac{\partial \Delta\mathbf{P}^{(1)}}{\partial t} + \mathbf{K}\Delta\mathbf{P}^{(1)} = \mathbf{E}^{\text{inc}}, \quad (\text{C5a})$$

$$\mu \frac{\partial^2 \Delta\mathbf{P}^{(2)}}{\partial t^2} + \boldsymbol{\gamma}^{\text{eff}} \frac{\partial \Delta\mathbf{P}^{(2)}}{\partial t} + \mathbf{K}\Delta\mathbf{P}^{(2)} + \mathbf{C}\Delta\mathbf{P}_{\text{II}}^{(1)} = 0, \quad (\text{C5b})$$

$$\mu \frac{\partial^2 \Delta\mathbf{P}^{(3)}}{\partial t^2} + \boldsymbol{\gamma}^{\text{eff}} \frac{\partial \Delta\mathbf{P}^{(3)}}{\partial t} + \mathbf{K}\Delta\mathbf{P}^{(3)} + \mathbf{C}\Delta\mathbf{P}_{\text{II}}^{(1,2)} = 0. \quad (\text{C5c})$$

Under a single-frequency continuous incident THz wave in the thin slab limit $E_i^{\text{inc}}(t) = E_i^{\text{inc},0} \exp(-i\omega t)$, one can write $\Delta\mathbf{P}^{(1)} = \Delta\mathbf{P}^0 \exp[i(-\omega t + \varphi)]$ as a steady-state solution, where φ is the phase difference between the incident THz wave and the excited polarization wave. Accordingly, Eq. (C5a) can be rewritten as

$$-\mu\omega^2 \Delta\mathbf{P}^{(1)} - i\boldsymbol{\gamma}^{\text{eff}} \omega \Delta\mathbf{P}^{(1)} + \mathbf{K}\Delta\mathbf{P}^{(1)} = \mathbf{E}^{\text{inc}}. \quad (\text{C6})$$

Rearranging Eq. (C6), one has $\Delta\mathbf{P}^{(1)} = (\mathbf{K} - \mu\omega^2 - i\boldsymbol{\gamma}^{\text{eff}} \omega)^{-1} \mathbf{E}^{\text{inc}} = \kappa_0 \chi_{ij}^{(1)} E_j^{\text{inc}}$, from which the expression of $\chi_{ij}^{(1)}$ can be derived, as shown by Eq. (4) in Sec. II.

Substituting the steady-state solution of $\Delta\mathbf{P}^{(1)}$ into Eq. (C5b) allows for deriving the steady-state solution of $\Delta\mathbf{P}^{(2)}$ and therefore $\chi_{ijk}^{(2)}$. To do this, we first expand the terms that are contained in the expression $\Delta\mathbf{P}_{\text{II}}^{(1)}$ as follows:

$$\begin{aligned}\Delta P_j^{(1)}(\omega) \Delta P_k^{(1)}(\omega) &= \kappa_0^2 |\chi_{jm}| E_m^{\text{inc},0} \cos(\omega t + \varphi^{jm}) |\chi_{kn}| E_n^{\text{inc},0} \cos(\omega t + \varphi^{kn}) \\ &= \kappa_0^2 (|\chi_{jm}| E_m^{\text{inc},0}) (|\chi_{kn}| E_n^{\text{inc},0}) \left[\frac{1}{2} \cos(\varphi^{jm} - \varphi^{kn}) + \frac{1}{2} \cos(2\omega t + \varphi^{jm} + \varphi^{kn}) \right] \\ &\equiv \frac{\kappa_0^2}{2} \chi_{jm}^{(1)} \chi_{kn}^{(1)*} E_m^{\text{inc},0} E_n^{\text{inc},0} + \frac{\kappa_0^2}{2} \chi_{jm}^{(1)} \chi_{kn}^{(1)} E_m^{\text{inc},0} E_n^{\text{inc},0} \exp(-i2\omega t) = \Delta\mathbf{P}^{(2)}(0) + \Delta\mathbf{P}^{(2)}(2\omega),\end{aligned}\quad (\text{C7})$$

which therefore contains both a dc shift $\Delta\mathbf{P}^{(2)}(0)$ and a second-order harmonic component $\Delta\mathbf{P}^{(2)}(2\omega)$. Here, φ^{jm} refers to the phase difference between the oscillatory polarization component $\Delta P_j^{(1)}(t)$ and the excitation electric field component E_m^{inc} , and so forth, for φ^{kn} . Also, $\chi_{kn}^{(1)*} = \chi_{kn}^{(1),\text{Re}} - i\chi_{kn}^{(1),\text{Im}}$ is the conjugation of the complex susceptibility of $\chi_{kn}^{(1)} = \chi_{kn}^{(1),\text{Re}} + i\chi_{kn}^{(1),\text{Im}}$. Plugging both the steady-state solution of $\Delta\mathbf{P}^{(1)}$ and Eq. (C7) into Eq. (C5b), and if only considering $\Delta\mathbf{P}^{(2)}(2\omega)$, Eq. (C5b) can be rewritten as

$$-\mu 4\omega^2 \Delta\mathbf{P}^{(2)} - i\boldsymbol{\gamma}_{ii}^{\text{eff}} 2\omega \Delta\mathbf{P}^{(2)} + \mathbf{K}\Delta\mathbf{P}^{(2)} = -\frac{\kappa_0^2}{2} \sum_{j,k=1,2,3} C_{ijk} \left[\sum_{j,m=1,2,3} \chi_{jm}^{(1)} E_m^{\text{inc},0} \right] \left[\sum_{k,n=1,2,3} \chi_{kn}^{(1)} E_n^{\text{inc},0} \right]. \quad (\text{C8})$$

Thus, the SHG susceptibility $\chi_{ijk}^{(2)}(2\omega)$ can be expanded as

$$\begin{aligned}
\chi_{ijk}^{(2)}(2\omega, \omega, \omega) &= -\kappa_0^2 \sum_{\alpha, \beta, \gamma=1,2,3} C_{\alpha\beta\gamma} \chi_{i\alpha}^{(1)}(2\omega) \chi_{\beta j}^{(1)}(\omega) \chi_{\gamma k}^{(1)}(\omega) \\
&= \begin{bmatrix} \chi_{111}^{(2)} & \chi_{122}^{(2)} & \chi_{133}^{(2)} & \chi_{123}^{(2)} & \chi_{113}^{(2)} & \chi_{112}^{(2)} \\ \chi_{211}^{(2)} & \chi_{222}^{(2)} & \chi_{233}^{(2)} & \chi_{223}^{(2)} & \chi_{213}^{(2)} & \chi_{212}^{(2)} \\ \chi_{311}^{(2)} & \chi_{322}^{(2)} & \chi_{333}^{(2)} & \chi_{323}^{(2)} & \chi_{313}^{(2)} & \chi_{312}^{(2)} \end{bmatrix} \\
&= -\kappa_0^2 \begin{bmatrix} \chi_{11}^{(1)}(2\omega) & \chi_{12}^{(1)}(2\omega) & \chi_{13}^{(1)}(2\omega) \\ \chi_{21}^{(1)}(2\omega) & \chi_{22}^{(1)}(2\omega) & \chi_{23}^{(1)}(2\omega) \\ \chi_{31}^{(1)}(2\omega) & \chi_{32}^{(1)}(2\omega) & \chi_{33}^{(1)}(2\omega) \end{bmatrix} \cdot \begin{bmatrix} C_{111} & C_{122} & C_{133} & C_{123} & C_{113} & C_{112} \\ C_{211} & C_{222} & C_{233} & C_{223} & C_{213} & C_{212} \\ C_{311} & C_{322} & C_{333} & C_{323} & C_{313} & C_{312} \end{bmatrix} \\
&\quad \cdot \begin{bmatrix} \chi_{11}^{(1)2}(\omega) & \chi_{12}^{(1)2}(\omega) & \chi_{13}^{(1)2}(\omega) & 2\chi_{12}^{(1)}(\omega)\chi_{13}^{(1)}(\omega) \\ \chi_{21}^{(1)2}(\omega) & \chi_{22}^{(1)2}(\omega) & \chi_{23}^{(1)2}(\omega) & 2\chi_{22}^{(1)}(\omega)\chi_{23}^{(1)}(\omega) \\ \chi_{31}^{(1)2}(\omega) & \chi_{32}^{(1)2}(\omega) & \chi_{33}^{(1)2}(\omega) & 2\chi_{32}^{(1)}(\omega)\chi_{33}^{(1)}(\omega) \\ 2\chi_{21}^{(1)}(\omega)\chi_{31}^{(1)}(\omega) & 2\chi_{22}^{(1)}(\omega)\chi_{32}^{(1)}(\omega) & 2\chi_{23}^{(1)}(\omega)\chi_{33}^{(1)}(\omega) & 2\chi_{22}^{(1)}(\omega)\chi_{33}^{(1)}(\omega) + 2\chi_{23}^{(1)}(\omega)\chi_{32}^{(1)}(\omega) \\ 2\chi_{11}^{(1)}(\omega)\chi_{31}^{(1)}(\omega) & 2\chi_{12}^{(1)}(\omega)\chi_{32}^{(1)}(\omega) & 2\chi_{13}^{(1)}(\omega)\chi_{33}^{(1)}(\omega) & 2\chi_{12}^{(1)}(\omega)\chi_{33}^{(1)}(\omega) + 2\chi_{13}^{(1)}(\omega)\chi_{32}^{(1)}(\omega) \\ 2\chi_{11}^{(1)}(\omega)\chi_{21}^{(1)}(\omega) & 2\chi_{12}^{(1)}(\omega)\chi_{22}^{(1)}(\omega) & 2\chi_{13}^{(1)}(\omega)\chi_{23}^{(1)}(\omega) & 2\chi_{12}^{(1)}(\omega)\chi_{23}^{(1)}(\omega) + 2\chi_{13}^{(1)}(\omega)\chi_{22}^{(1)}(\omega) \\ 2\chi_{11}^{(1)}(\omega)\chi_{13}^{(1)}(\omega) & 2\chi_{11}^{(1)}(\omega)\chi_{12}^{(1)}(\omega) \\ 2\chi_{21}^{(1)}(\omega)\chi_{23}^{(1)}(\omega) & 2\chi_{21}^{(1)}(\omega)\chi_{22}^{(1)}(\omega) \\ 2\chi_{31}^{(1)}(\omega)\chi_{33}^{(1)}(\omega) & 2\chi_{31}^{(1)}(\omega)\chi_{32}^{(1)}(\omega) \\ 2\chi_{21}^{(1)}(\omega)\chi_{33}^{(1)}(\omega) + 2\chi_{23}^{(1)}(\omega)\chi_{31}^{(1)}(\omega) & 2\chi_{21}^{(1)}(\omega)\chi_{32}^{(1)}(\omega) + 2\chi_{22}^{(1)}(\omega)\chi_{31}^{(1)}(\omega) \\ 2\chi_{11}^{(1)}(\omega)\chi_{33}^{(1)}(\omega) + 2\chi_{13}^{(1)}(\omega)\chi_{31}^{(1)}(\omega) & 2\chi_{11}^{(1)}(\omega)\chi_{32}^{(1)}(\omega) + 2\chi_{12}^{(1)}(\omega)\chi_{31}^{(1)}(\omega) \\ 2\chi_{11}^{(1)}(\omega)\chi_{23}^{(1)}(\omega) + 2\chi_{13}^{(1)}(\omega)\chi_{21}^{(1)}(\omega) & 2\chi_{11}^{(1)}(\omega)\chi_{22}^{(1)}(\omega) + 2\chi_{12}^{(1)}(\omega)\chi_{21}^{(1)}(\omega) \end{bmatrix}, \quad i, j, k = 1, 2, 3 \quad (\text{C9})
\end{aligned}$$

The dc shift component $\Delta \mathbf{P}^{(2)}(0)$ can be derived from the following equation:

$$\mathbf{K} \Delta \mathbf{P}^{(2)}(0) = -\frac{\kappa_0^2}{2} \sum_{j,k=1,2,3} C_{ijk} \left[\sum_{j,m=1,2,3} \chi_{jm}^{(1)} E_m^{\text{inc},0} \right] \left[\sum_{k,n=1,2,3} \chi_{kn}^{(1)*} E_n^{\text{inc},0} \right]. \quad (\text{C10})$$

Accordingly, the nonlinear electric susceptibility $\chi_{ijk}^{(2)}(0)$ can be derived as

$$\begin{aligned}
\chi_{ijk}^{(2)}(0, \omega, -\omega) &= -\kappa_0^2 \sum_{\alpha, \beta, \gamma=1,2,3} C_{\alpha\beta\gamma} \chi_{i\alpha}^{(1)}(0) \chi_{\beta j}^{(1)}(\omega) \chi_{\gamma k}^{(1)*}(\omega) \\
&= \begin{bmatrix} \chi_{111}^{(2)} & \chi_{122}^{(2)} & \chi_{133}^{(2)} & \chi_{123}^{(2)} & \chi_{113}^{(2)} & \chi_{112}^{(2)} \\ \chi_{211}^{(2)} & \chi_{222}^{(2)} & \chi_{233}^{(2)} & \chi_{223}^{(2)} & \chi_{213}^{(2)} & \chi_{212}^{(2)} \\ \chi_{311}^{(2)} & \chi_{322}^{(2)} & \chi_{333}^{(2)} & \chi_{323}^{(2)} & \chi_{313}^{(2)} & \chi_{312}^{(2)} \end{bmatrix} \\
&= -\kappa_0^2 \begin{bmatrix} \chi_{11}^{(1)}(0) & \chi_{12}^{(1)}(0) & \chi_{13}^{(1)}(0) \\ \chi_{21}^{(1)}(0) & \chi_{22}^{(1)}(0) & \chi_{23}^{(1)}(0) \\ \chi_{31}^{(1)}(0) & \chi_{32}^{(1)}(0) & \chi_{33}^{(1)}(0) \end{bmatrix} \begin{bmatrix} C_{111} & C_{122} & C_{133} & C_{123} & C_{113} & C_{112} \\ C_{211} & C_{222} & C_{233} & C_{223} & C_{213} & C_{212} \\ C_{311} & C_{322} & C_{333} & C_{323} & C_{313} & C_{312} \end{bmatrix}
\end{aligned}$$

$$\begin{aligned}
& \left[\begin{array}{cccc}
|\chi_{11}^{(1)}(\omega)|^2 & |\chi_{12}^{(1)}(\omega)|^2 & |\chi_{13}^{(1)}(\omega)|^2 & 2\chi_{12}^{(1)}(\omega)\chi_{13}^{(1),*}(\omega) \\
|\chi_{21}^{(1)}(\omega)|^2 & |\chi_{22}^{(1)}(\omega)|^2 & |\chi_{23}^{(1)}(\omega)|^2 & 2\chi_{22}^{(1)}(\omega)\chi_{23}^{(1),*}(\omega) \\
|\chi_{31}^{(1)}(\omega)|^2 & |\chi_{32}^{(1)}(\omega)|^2 & |\chi_{33}^{(1)}(\omega)|^2 & 2\chi_{32}^{(1)}(\omega)\chi_{33}^{(1),*}(\omega) \\
2\chi_{21}^{(1)}(\omega)\chi_{31}^{(1),*}(\omega) & 2\chi_{22}^{(1)}(\omega)\chi_{32}^{(1),*}(\omega) & 2\chi_{23}^{(1)}(\omega)\chi_{33}^{(1),*}(\omega) & 2\chi_{22}^{(1)}(\omega)\chi_{33}^{(1),*}(\omega) + 2\chi_{23}^{(1)}(\omega)\chi_{32}^{(1),*}(\omega) \\
2\chi_{11}^{(1)}(\omega)\chi_{31}^{(1),*}(\omega) & 2\chi_{12}^{(1)}(\omega)\chi_{32}^{(1),*}(\omega) & 2\chi_{13}^{(1)}(\omega)\chi_{33}^{(1),*}(\omega) & 2\chi_{12}^{(1)}(\omega)\chi_{33}^{(1),*}(\omega) + 2\chi_{13}^{(1)}(\omega)\chi_{32}^{(1),*}(\omega) \\
2\chi_{11}^{(1)}(\omega)\chi_{21}^{(1),*}(\omega) & 2\chi_{12}^{(1)}(\omega)\chi_{22}^{(1),*}(\omega) & 2\chi_{13}^{(1)}(\omega)\chi_{23}^{(1),*}(\omega) & 2\chi_{12}^{(1)}(\omega)\chi_{23}^{(1),*}(\omega) + 2\chi_{13}^{(1)}(\omega)\chi_{22}^{(1),*}(\omega) \\
2\chi_{11}^{(1)}(\omega)\chi_{13}^{(1),*}(\omega) & & 2\chi_{11}^{(1)}(\omega)\chi_{12}^{(1),*}(\omega) & \\
2\chi_{21}^{(1)}(\omega)\chi_{23}^{(1),*}(\omega) & & 2\chi_{21}^{(1)}(\omega)\chi_{22}^{(1),*}(\omega) & \\
2\chi_{31}^{(1)}(\omega)\chi_{33}^{(1),*}(\omega) & & 2\chi_{31}^{(1)}(\omega)\chi_{32}^{(1),*}(\omega) & \\
2\chi_{21}^{(1)}(\omega)\chi_{33}^{(1),*}(\omega) + 2\chi_{23}^{(1)}(\omega)\chi_{31}^{(1),*}(\omega) & 2\chi_{21}^{(1)}(\omega)\chi_{32}^{(1),*}(\omega) + 2\chi_{22}^{(1)}(\omega)\chi_{31}^{(1),*}(\omega) & & \\
2\chi_{11}^{(1)}(\omega)\chi_{33}^{(1),*}(\omega) + 2\chi_{13}^{(1)}(\omega)\chi_{31}^{(1),*}(\omega) & 2\chi_{11}^{(1)}(\omega)\chi_{32}^{(1),*}(\omega) + 2\chi_{12}^{(1)}(\omega)\chi_{31}^{(1),*}(\omega) & & \\
2\chi_{11}^{(1)}(\omega)\chi_{23}^{(1),*}(\omega) + 2\chi_{13}^{(1)}(\omega)\chi_{21}^{(1),*}(\omega) & 2\chi_{11}^{(1)}(\omega)\chi_{22}^{(1),*}(\omega) + 2\chi_{12}^{(1)}(\omega)\chi_{21}^{(1),*}(\omega) & &
\end{array} \right], \quad i, j, k = 1, 2, 3.
\end{aligned} \tag{C11}$$

It is noteworthy that $\chi_{ijk}^{(2)}(0, \omega, -\omega)$ in Eq. (C11), which describes the rectification of two THz waves with the frequencies ω and $-\omega$, is conceptually different from the second-order dc nonlinear susceptibility $\chi_{ijk}^{(2),dc}$. The latter can be obtained by letting $\omega = 0$ in Eq. (C9). Like the expression of $\chi_{ijk}^{(2)}(2\omega, \omega, \omega)$ in Eq. (C9), the expression of $\chi_{ijk}^{(2)}(0, \omega, -\omega)$ is only valid when the amplitude of E_i^{inc} is not too large. On one hand, the derivation of $\chi_{ijk}^{(2)}(0, \omega, -\omega)$ assumes that the center of polarization oscillation is always at $P_i = P_i^0$ as the premise of the perturbation theory. On the other hand, the resulting dc shift component $\Delta\mathbf{P}^{(2)}(0, \omega, -\omega)$ describes a shift of the oscillation center away from P_i^0 , which would cause sizable change in the coefficient matrices \mathbf{K} and \mathbf{C} if the magnitude of $\Delta\mathbf{P}^{(2)}(0, \omega, -\omega)$ is sufficiently large.

If the incident electrical field contains two frequencies ω_n and ω_m ($\omega_n > \omega_m$), the linear polarization oscillation $\Delta\mathbf{P}^{(1)} = \Delta\mathbf{P}^{(1)}(\omega_n) + \Delta\mathbf{P}^{(1)}(\omega_m)$. Substituting the steady-state different-frequencies solutions $\Delta\mathbf{P}^{(1)}(\omega_n)$ and $\Delta\mathbf{P}^{(1)}(\omega_m)$ into Eq. (C5b) allows for deriving the steady-state solution of $\Delta\mathbf{P}^{(2)}(\omega_n \pm \omega_m)$ and therefore $\chi_{ijk}^{(2)}(\omega_n \pm \omega_m, \omega_n, \omega_m)$. To do this, we likewise expand the terms that are contained in the expression $\Delta\mathbf{P}_{\text{II}}^{(1)}$ into the following expression:

$$\begin{aligned}
\Delta\mathbf{P}_j^{(1)}(\omega_n)\Delta\mathbf{P}_k^{(1)}(\omega_m) &= \kappa_0^2 |\chi_{jm}| E_m^{\text{inc},0} \cos(\omega_n t + \varphi^{jm}) |\chi_{kn}| E_n^{\text{inc},0} \cos(\omega_m t + \varphi^{kn}) \\
&= \kappa_0^2 (|\chi_{jm}| E_m^{\text{inc},0}) (|\chi_{kn}| E_n^{\text{inc},0}) \left\{ \frac{1}{2} \cos[(\omega_n - \omega_m)t + \varphi^{jm} - \varphi^{kn}] + \frac{1}{2} \cos[(\omega_n + \omega_m)t + \varphi^{jm} + \varphi^{kn}] \right\} \\
&\equiv \frac{\kappa_0^2}{2} \chi_{jm}^{(1)} \chi_{kn}^{(1),*} E_m^{\text{inc},0} E_n^{\text{inc},0} \exp[-\mathbf{i}(\omega_n - \omega_m)t] + \frac{\kappa_0^2}{2} \chi_{jm}^{(1)} \chi_{kn}^{(1)} E_m^{\text{inc},0} E_n^{\text{inc},0} \exp[-\mathbf{i}(\omega_n + \omega_m)t] \\
&= \Delta\mathbf{P}^{(2)}(\omega_n - \omega_m) + \Delta\mathbf{P}^{(2)}(\omega_n + \omega_m),
\end{aligned} \tag{C12}$$

Following similar procedures as the derivation of $\chi_{ijk}^{(2)}(2\omega)$ and $\chi_{ijk}^{(2)}(0)$, we can derive that

$$\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) = -\kappa_0^2 \sum_{\alpha, \beta, \gamma=1,2,3} C_{\alpha\beta\gamma} \chi_{i\alpha}^{(1)}(\omega_n + \omega_m) [\chi_{\beta j}^{(1)}(\omega_n) \chi_{\gamma k}^{(1)}(\omega_m) + \chi_{\beta j}^{(1)}(\omega_m) \chi_{\gamma k}^{(1)}(\omega_n)], \tag{C13}$$

$$\chi_{ijk}^{(2)}(\omega_n - \omega_m, \omega_n, \omega_m) = -\kappa_0^2 \sum_{\alpha, \beta, \gamma=1,2,3} C_{\alpha\beta\gamma} \chi_{i\alpha}^{(1)}(\omega_n - \omega_m) [\chi_{\beta j}^{(1)}(\omega_n) \chi_{\gamma k}^{(1),*}(\omega_m) + \chi_{\beta j}^{(1),*}(\omega_m) \chi_{\gamma k}^{(1)}(\omega_n)]. \tag{C14}$$

APPENDIX D: THERMODYNAMIC VALIDATION AND SYMMETRY VALIDATION

1. Thermodynamic validation

Let us first show that the dc nonlinear susceptibility $\chi_{ijk}^{(2),dc}$, which can be obtained by letting $\omega = 0$ in Eq. (C9), can equivalently be obtained from thermodynamic analyses. To this end, we consider a monodomain ferroelectric material, which has an electric Helmholtz free energy density given as

$$f(T, P_i, E_i, \varepsilon_{ij}) = g_0(T) + f^{\text{Landau}}(T, P_i) - \frac{1}{2} \kappa_0 \kappa_b E_i E_j - E_i P_i + f^{\text{Elast}}(\varepsilon_{ij}, P_i), \tag{D1}$$

where $g_0(T)$ is the Gibbs free energy density of the initial nonequilibrium state with zero spontaneous polarization; the Landau free energy density $f^{\text{Landau}}(T, P_i)$ is a function of temperature and ionic polarization; and the elastic energy density $f^{\text{Elast}}(\varepsilon_{ij}, P_i)$ is a function of the total strain ε_{ij} and ionic polarization, where the total strain ε_{ij} depends on the mechanical boundary condition

of the system. If omitting the depolarization field, the total electric field E_i (E_j) in Eq. (D1) is the same as the applied electric field. Minimizing $f(T, P_i, E_i, \varepsilon_{ij})$ with respect to P_i under a constant electric field E_j yields a relationship between P_i and E_i , that is,

$$E_i = \left[\frac{\partial(f^{\text{Landau}} + f^{\text{Elast}})}{\partial P_i} \right]_{T, E_i, \varepsilon_{ij}}. \quad (\text{D2})$$

Performing Taylor expansion for Eq. (D2), one has

$$E_i = \sum_{j=1,2,3} \left(\frac{\partial^2 f^{\text{Landau}}}{\partial P_i \partial P_j} + \frac{\partial^2 f^{\text{Elast}}}{\partial P_i \partial P_j} \right) \Delta P_j + \frac{1}{2} \sum_{j,k=1,2,3} \left(\frac{\partial^3 f^{\text{Landau}}}{\partial P_i \partial P_j \partial P_k} + \frac{\partial^3 f^{\text{Elast}}}{\partial P_i \partial P_j \partial P_k} \right) \Delta P_j \Delta P_k + \dots \quad (\text{D3})$$

Equation (D3) can be rewritten in the matrix form, i.e., $\mathbf{E} = \mathbf{K}\Delta\mathbf{P} + \mathbf{C}\Delta\mathbf{P}\Delta\mathbf{P}$ (see Sec. II for the definitions of the coefficient matrices \mathbf{K} and \mathbf{C}), or in its expanded form:

$$\begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} = \begin{bmatrix} K_{11} & K_{12} & K_{13} \\ K_{21} & K_{22} & K_{23} \\ K_{31} & K_{32} & K_{33} \end{bmatrix} \begin{bmatrix} \Delta P_1 \\ \Delta P_2 \\ \Delta P_3 \end{bmatrix} + \begin{bmatrix} C_{111} & C_{122} & C_{133} & C_{123} & C_{113} & C_{112} \\ C_{211} & C_{222} & C_{233} & C_{223} & C_{213} & C_{212} \\ C_{311} & C_{322} & C_{333} & C_{323} & C_{313} & C_{312} \end{bmatrix} \begin{bmatrix} \Delta P_1^2 \\ \Delta P_2^2 \\ \Delta P_3^2 \\ 2\Delta P_2 \Delta P_3 \\ 2\Delta P_1 \Delta P_3 \\ 2\Delta P_1 \Delta P_2 \end{bmatrix}, \quad (\text{D4})$$

Since Eqs. (D2)–(D4) are derived for the thermodynamic equilibrium state of polarization under an applied dc electric field, the polarization does not change with time. Therefore, the time derivatives of the polarization are zero, i.e., $\partial^n \Delta\mathbf{P} / \partial t^n = 0$, $n = 1, 2$. Under this condition, Eq. (D4) is equivalent to Eq. (3). Accordingly, $\chi_{ij}^{(1), \text{dc}}$ derived from Eq. (D4), with $\chi^{(1), \text{dc}} = \mathbf{K}^{-1}$ is equivalent to the solution shown in Eq. (4) under $\omega = 0$. Likewise, the solution of $\chi_{ijk}^{(2), \text{dc}}$ derived from Eq. (D4) via the perturbation method is equivalent to the solution shown in Eq. (C9) under $\omega = 0$, as listed below (where the superscript dc is omitted for brevity):

$$\begin{aligned} & \begin{bmatrix} \chi_{111}^{(2)} & \chi_{122}^{(2)} & \chi_{133}^{(2)} & \chi_{123}^{(2)} & \chi_{113}^{(2)} & \chi_{112}^{(2)} \\ \chi_{211}^{(2)} & \chi_{222}^{(2)} & \chi_{233}^{(2)} & \chi_{223}^{(2)} & \chi_{213}^{(2)} & \chi_{212}^{(2)} \\ \chi_{311}^{(2)} & \chi_{322}^{(2)} & \chi_{333}^{(2)} & \chi_{323}^{(2)} & \chi_{313}^{(2)} & \chi_{312}^{(2)} \end{bmatrix} \\ &= -\kappa_0^2 \begin{bmatrix} \chi_{11}^{(1)} & \chi_{12}^{(1)} & \chi_{13}^{(1)} \\ \chi_{21}^{(1)} & \chi_{22}^{(1)} & \chi_{23}^{(1)} \\ \chi_{31}^{(1)} & \chi_{32}^{(1)} & \chi_{33}^{(1)} \end{bmatrix} \begin{bmatrix} C_{111} & C_{122} & C_{133} & C_{123} & C_{113} & C_{112} \\ C_{211} & C_{222} & C_{233} & C_{223} & C_{213} & C_{212} \\ C_{311} & C_{322} & C_{333} & C_{323} & C_{313} & C_{312} \end{bmatrix} \\ & \begin{bmatrix} \chi_{11}^{(1)2} & \chi_{12}^{(1)2} & \chi_{13}^{(1)2} & 2\chi_{12}^{(1)}\chi_{13}^{(1)} & 2\chi_{11}^{(1)}\chi_{13}^{(1)} & 2\chi_{11}^{(1)}\chi_{12}^{(1)} \\ \chi_{21}^{(1)2} & \chi_{22}^{(1)2} & \chi_{23}^{(1)2} & 2\chi_{22}^{(1)}\chi_{23}^{(1)} & 2\chi_{21}^{(1)}\chi_{23}^{(1)} & 2\chi_{21}^{(1)}\chi_{22}^{(1)} \\ \chi_{31}^{(1)2} & \chi_{32}^{(1)2} & \chi_{33}^{(1)2} & 2\chi_{32}^{(1)}\chi_{33}^{(1)} & 2\chi_{31}^{(1)}\chi_{33}^{(1)} & 2\chi_{31}^{(1)}\chi_{32}^{(1)} \\ 2\chi_{21}^{(1)}\chi_{31}^{(1)} & 2\chi_{22}^{(1)}\chi_{32}^{(1)} & 2\chi_{23}^{(1)}\chi_{33}^{(1)} & 2\chi_{22}^{(1)}\chi_{33}^{(1)} + 2\chi_{23}^{(1)}\chi_{32}^{(1)} & 2\chi_{21}^{(1)}\chi_{33}^{(1)} + 2\chi_{23}^{(1)}\chi_{31}^{(1)} & 2\chi_{21}^{(1)}\chi_{32}^{(1)} + 2\chi_{22}^{(1)}\chi_{31}^{(1)} \\ 2\chi_{11}^{(1)}\chi_{31}^{(1)} & 2\chi_{12}^{(1)}\chi_{32}^{(1)} & 2\chi_{13}^{(1)}\chi_{33}^{(1)} & 2\chi_{12}^{(1)}\chi_{33}^{(1)} + 2\chi_{13}^{(1)}\chi_{32}^{(1)} & 2\chi_{11}^{(1)}\chi_{33}^{(1)} + 2\chi_{13}^{(1)}\chi_{31}^{(1)} & 2\chi_{11}^{(1)}\chi_{32}^{(1)} + 2\chi_{12}^{(1)}\chi_{31}^{(1)} \\ 2\chi_{11}^{(1)}\chi_{21}^{(1)} & 2\chi_{12}^{(1)}\chi_{22}^{(1)} & 2\chi_{13}^{(1)}\chi_{23}^{(1)} & 2\chi_{12}^{(1)}\chi_{23}^{(1)} + 2\chi_{13}^{(1)}\chi_{22}^{(1)} & 2\chi_{11}^{(1)}\chi_{23}^{(1)} + 2\chi_{13}^{(1)}\chi_{21}^{(1)} & 2\chi_{11}^{(1)}\chi_{22}^{(1)} + 2\chi_{12}^{(1)}\chi_{21}^{(1)} \end{bmatrix}. \end{aligned} \quad (\text{D5})$$

To demonstrate Eq. (D5) is valid, we consider a tetragonal BaTiO₃ single crystal with a spontaneous polarization $\mathbf{P}^0 = (0, 0, P_3^0)$ under zero electric field ($E_3^{\text{dc}} = 0$), as shown in Fig. 1(a). The $\chi_{333}^{(2), \text{dc}}$ calculated via Eq. (D5) is -1.573×10^{-6} m/V, while $\chi_{33}^{(1), \text{dc}}$ calculated by setting $\omega = 0$ in Eq. (7) is 125.55. In parallel, we evaluate the value of P_3 under different bias electric fields E_3^{dc} at thermodynamic equilibrium by numerically minimizing (via the random search method) the corresponding electric Helmholtz free energy density $f(T, P_i, E_i, \varepsilon_{ij})$ in the Mathematica software and obtain a static $P_3 - E_3^{\text{dc}}$ curve, as shown in Fig. 5. Next, we fit this static curve using the equation $P_3 = P_3^0 + \kappa_0[\chi_{33}^{(1), \text{dc}} E_3^{\text{dc}} + \chi_{333}^{(2), \text{dc}} E_3^{\text{dc}2}]$, through which we determine that $\chi_{33}^{(1), \text{dc}} = 125.2$ and $\chi_{333}^{(2), \text{dc}} = -1.576 \times 10^{-6}$ m/V, which agree well with the analytically calculated values.

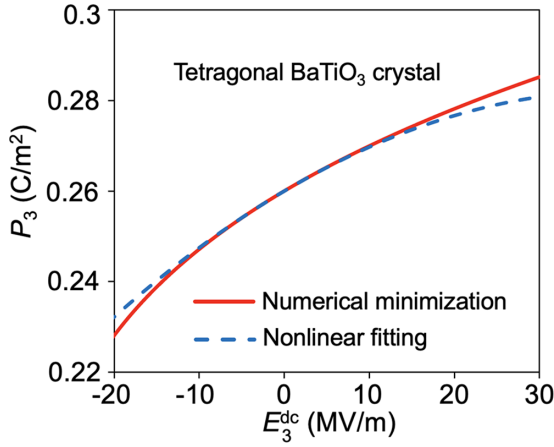


FIG. 5. P_3 as a function of an applied dc electric field E_3^{dc} obtained by thermodynamic analysis in a bulk tetragonal BaTiO_3 single crystal [shown in Fig. 1(a)] at 25°C, and its nonlinear fitting as explained in Appendix C.

2. Symmetry validation

The numbers of nonzero and independent elements of both $\chi_{ij}^{(1),\text{dc}}$ and $\chi_{ijk}^{(2),\text{dc}}$ can be mathematically evaluated based on Eq. (D5), which depends on the coefficient tensors \mathbf{C} and \mathbf{K} (in other words, the symmetry of f^{Landau} and f^{Elast} with respect to the equilibrium polarization state and the mechanical boundary condition of the system). As an example, considering a stress-free boundary condition, the numbers of nonzero (independent) elements of $\chi_{ij}^{(1),\text{dc}}$ for cubic, $P4mm$, $Amm2$, and $R3m$ BaTiO_3 bulk crystals are determined to be 3(1), 3(2), 5(3), and 9(2), respectively, in the cubic coordinate system. The numbers of nonzero (independent) elements of $\chi_{ijk}^{(2),\text{dc}}$ for cubic, $P4mm$, $Amm2$, and $R3m$ BaTiO_3 bulk crystals are 0(0), 5(2), 10(3), and 18(3), respectively, in the cubic coordinate system. By transforming $\chi_{ij}^{(1),\text{dc}}$ and $\chi_{ijk}^{(2),\text{dc}}$ tensors from the cubic to principal coordinate system (PCS), one can diagonalize the $\chi_{ij}^{(1),\text{dc}}$ tensor and simplify the matrix for the $\chi_{ijk}^{(2),\text{dc}}$ tensor. We perform this transformation by first transforming the polarization P_j in the Landau free energy from the cubic coordinate system (indicated as the x_1 - x_2 - x_3 coordinates in Table III) to P'_i in the PCS (indicated as the x'_1 - x'_2 - x'_3 coordinates in Table III) via $P'_i = T_{ij}P_j$, and then calculating the $\chi_{ij}^{(1),\text{dc}}$ and $\chi_{ijk}^{(2),\text{dc}}$ tensors in the PCS based on Eqs. (D4) and (D5). The transformation matrix T_{ij} is calculated as

$$\mathbf{T} = \begin{bmatrix} \cos \varphi_1 & -\sin \varphi_1 & 0 \\ \sin \varphi_1 & \cos \varphi_1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \Phi & -\sin \Phi \\ 0 & \sin \Phi & \cos \Phi \end{bmatrix} \\ \times \begin{bmatrix} \cos \varphi_2 & -\sin \varphi_2 & 0 \\ \sin \varphi_2 & \cos \varphi_2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (\text{D6})$$

where the Euler angles φ_1 , Φ , and φ_2 (also illustrated in Table III) describe the sequence of rotating x_1 - x_2 - x_3 (cubic) to x'_1 - x'_2 - x'_3 (PCS). Specifically, the rotation starts with an initial rotation φ_1 about the x_3 axis, followed by a rotation Φ about the x_1 axis, and then a final rotation φ_2 about the x_3 axis again.

As shown in Table III, the numbers of nonzero (independent) elements of $\chi_{ijk}^{(2),\text{dc}}$ for cubic, $P4mm$, $Amm2$, and $R3m$ BaTiO_3 bulk crystals are 0(0), 5(2), 5(3), and 8(3), respectively, in the PCS. The obtained number of independent and nonzero elements for $\chi_{ijk}^{(2),\text{dc}}$ are consistent with Ref. [26].

APPENDIX E: EVALUATING $|\chi_{333}^{(2)}(2\omega)$ AND $\chi_{333}^{(1),\text{Im}}(\omega)$ FROM DYNAMICAL PHASE-FIELD SIMULATIONS

A dynamical phase-field model with coupled dynamics of strain, polarization, and EM waves [18,25] was used to simulate the excitation of polarization oscillation in a freestanding tetragonal BaTiO_3 slab by a monochromatic continuous THz wave with an angular frequency ω . The BaTiO_3 slab has an initial equilibrium polarization $(P_1^0, P_2^0, P_3^0) = (0, 0, 0.26 \text{ C/m}^2)$ at 298 K. The slab thickness is set to be 10 nm (which is far smaller than the THz wavelength) to ensure that the excited polarization is spatially uniform along the thickness direction and in-phase. A sinusoidal source current $J_x = J_x^0 \sin(\omega t)$ was injected to generate a continuous incident THz wave with an electric field component that is spatially uniform in the thin BaTiO_3 slab, i.e., $E_x(t) = E_x^0 \exp(-i\omega t)$, with $x \equiv 3$ [see Fig. 1(a)]. We consider 36 different ω 's in total near the two peaks of the analytically calculated $|\chi_{333}^{(2)}(2\omega)$, shown in Fig. 2(a), and performed 36 groups of simulations to extract $|\chi_{333}^{(2)}(2\omega)$ at each ω . In all simulations, we set $J_x^0 = 2 \times 10^{12} \text{ A/m}^2$, leading to $E_x^{\text{inc},0}$ of 376 730 V/m. Under this electric field, the BaTiO_3 slab will be driven into the anharmonic regime, but the magnitude of the dc polarization shift $\Delta P_3^{(2)}(0)$ arising from $\chi_{333}^{(2)}(0, \omega, -\omega)$, see Eq. (C11), remains relatively small. For such a weakly nonlinear oscillation, one can expect that the numerical simulation results would agree

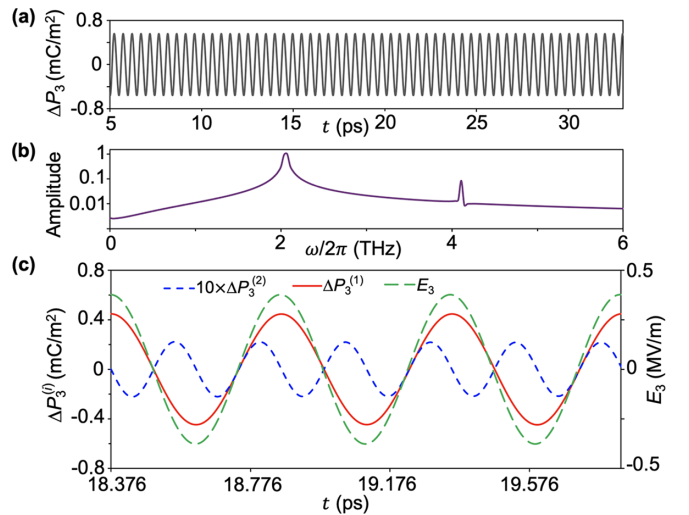
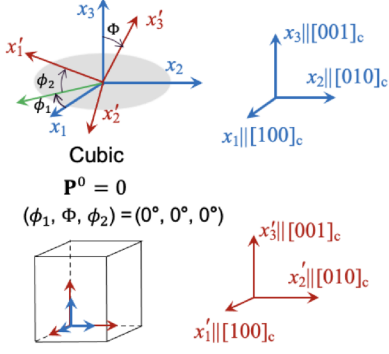
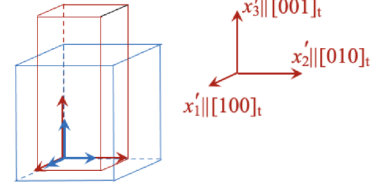
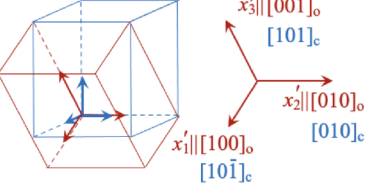
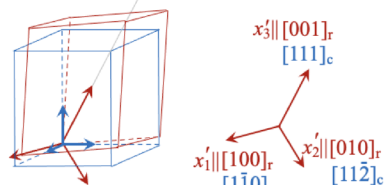


FIG. 6. (a) Steady-state evolution of the dynamically excited polarization $\Delta P_3(t) = P_3(t) - P_3^0$ in a thin freestanding (100) BaTiO_3 slab under a continuous terahertz (THz) wave with $\omega = 2\pi \times 2.0542 \text{ THz}$ at 298 K. (b) Frequency spectrum of $\Delta P_3(t)$ for the duration of $t = 5 - 33 \text{ ps}$. (c) Reconstructed temporal profiles of $\Delta P_3^{(1)}$ and $\Delta P_3^{(2)}$ as well as the profile of the incident THz electric field $E_3(t)$ obtained from a reference simulation without the (100) BaTiO_3 slab. $t = 0 \text{ ps}$ is the moment the source current is injected.

TABLE III. List of elements in $\chi_{ij}^{(1),dc}$ and $\chi_{ijk}^{(2),dc}$ of a stress-free BaTiO₃ bulk crystal.

 <p>Cubic $\mathbf{P}^0 = 0$ $(\phi_1, \Phi, \phi_2) = (0^\circ, 0^\circ, 0^\circ)$</p> <p>T=200 °C $\mathbf{P}^0 = 0$</p>	<p>$\chi_{ij}^{(1)}$ in the cubic and the principal coordinate systems</p> $\begin{pmatrix} \chi_{11}^{(1)} & 0 & 0 \\ 0 & \chi_{11}^{(1)} & 0 \\ 0 & 0 & \chi_{11}^{(1)} \end{pmatrix}$ $\begin{pmatrix} \chi'_{11}^{(1)} & 0 & 0 \\ 0 & \chi'_{11}^{(1)} & 0 \\ 0 & 0 & \chi'_{11}^{(1)} \end{pmatrix}$ <p>$\chi_{11}^{(1)} = \chi'_{11}^{(1)} = 1610.96$</p>	<p>$\chi_{ijk}^{(2)}$ in the cubic and the principal coordinate systems</p> $\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$ $\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$
<p>Tetragonal P4mm $\mathbf{P}^0 = (0, 0, P_3^0)$ $(\phi_1, \Phi, \phi_2) = (0^\circ, 0^\circ, 0^\circ)$</p>  <p>T=25 °C $\mathbf{P}^0 = (0, 0, 0.26) \text{ C/m}^3$</p>	<p>$\chi_{ij}^{(1)}$ in the tetragonal and the principal coordinate systems</p> $\begin{pmatrix} \chi_{11}^{(1)} & 0 & 0 \\ 0 & \chi_{11}^{(1)} & 0 \\ 0 & 0 & \chi_{33}^{(1)} \end{pmatrix}$ $\begin{pmatrix} \chi'_{11}^{(1)} & 0 & 0 \\ 0 & \chi'_{11}^{(1)} & 0 \\ 0 & 0 & \chi'_{33}^{(1)} \end{pmatrix}$ <p>$\chi_{11}^{(1)} = \chi'_{11}^{(1)} = 3599.76$ $\chi_{33}^{(1)} = \chi'_{33}^{(1)} = 187.85$</p>	<p>$\chi_{ijk}^{(2)}$ in the tetragonal and the principal coordinate systems</p> $\begin{pmatrix} 0 & 0 & 0 & 0 & 2\chi_{311}^{(2)} & 0 \\ 0 & 0 & 0 & 2\chi_{311}^{(2)} & 0 & 0 \\ \chi_{311}^{(2)} & \chi_{311}^{(2)} & \chi_{333}^{(2)} & 0 & 0 & 0 \end{pmatrix}$ $\begin{pmatrix} 0 & 0 & 0 & 0 & 2\chi'_{311}^{(2)} & 0 \\ 0 & 0 & 0 & 2\chi'_{311}^{(2)} & 0 & 0 \\ \chi'_{311}^{(2)} & \chi'_{311}^{(2)} & \chi'_{333}^{(2)} & 0 & 0 & 0 \end{pmatrix}$ <p>$\chi_{311}^{(2)} = \chi'_{311}^{(2)} = 8.74 \times 10^{-5} \text{ m/V}$ $\chi_{333}^{(2)} = \chi'_{333}^{(2)} = 4.37 \times 10^{-6} \text{ m/V}$</p>
<p>Orthorhombic Amm2 $\mathbf{P}^0 = (P_1^0, 0, P_3^0)$ $P_1^0 = P_3^0$ $(\phi_1, \Phi, \phi_2) = (90^\circ, 45^\circ, -90^\circ)$</p>  <p>T=-10 °C $\mathbf{P}^0 = (0.225, 0, 0.225) \text{ C/m}^3$</p>	<p>$\chi_{ij}^{(1)}$ in the orthorhombic and the principal coordinate systems</p> $\begin{pmatrix} \chi_{11}^{(1)} & 0 & \chi_{13}^{(1)} \\ 0 & \chi_{22}^{(1)} & 0 \\ \chi_{13}^{(1)} & 0 & \chi_{11}^{(1)} \end{pmatrix}$ $\begin{pmatrix} \chi'_{11}^{(1)} & 0 & 0 \\ 0 & \chi'_{22}^{(1)} & 0 \\ 0 & 0 & \chi'_{33}^{(1)} \end{pmatrix}$ <p>$\chi_{22}^{(1)} = \chi'_{22}^{(1)} = 2464.09$ $\chi_{11}^{(1)} = 698.7$ $\chi_{13}^{(1)} = -466.1$ $\chi'_{11}^{(1)} = 1164.8$ $\chi'_{33}^{(1)} = 232.6$</p>	<p>$\chi_{ijk}^{(2)}$ in the orthorhombic and the principal coordinate systems</p> $\begin{pmatrix} \chi_{111}^{(2)} & \chi_{122}^{(2)} & \chi_{133}^{(2)} & 0 & 2\chi_{133}^{(2)} & 0 \\ 0 & 0 & 0 & 2\chi_{133}^{(2)} & 0 & 2\chi_{122}^{(2)} \\ \chi_{122}^{(2)} & \chi_{111}^{(2)} & \chi_{133}^{(2)} & 0 & 2\chi_{122}^{(2)} & 0 \end{pmatrix}$ $\begin{pmatrix} 0 & 0 & 0 & 0 & 2\chi'_{311}^{(2)} & 0 \\ 0 & 0 & 0 & 2\chi'_{322}^{(2)} & 0 & 0 \\ \chi'_{311}^{(2)} & \chi'_{322}^{(2)} & \chi'_{333}^{(2)} & 0 & 0 & 0 \end{pmatrix}$ <p>$\chi_{111}^{(2)} = 7.65 \times 10^{-5} \text{ m/V}$ $\chi_{122}^{(2)} = 3.85 \times 10^{-5} \text{ m/V}$ $\chi_{133}^{(2)} = -2.32 \times 10^{-5} \text{ m/V}$ $\chi'_{311}^{(2)} = 7.05 \times 10^{-5} \text{ m/V}$ $\chi'_{322}^{(2)} = 5.45 \times 10^{-5} \text{ m/V}$ $\chi'_{333}^{(2)} = 4.92 \times 10^{-6} \text{ m/V}$</p>
<p>Rhombohedral R3m $\mathbf{P}^0 = (P_1^0, P_2^0, P_3^0)$ $P_1^0 = P_2^0 = P_3^0$ $(\phi_1, \Phi, \phi_2) = (0^\circ, 54.736^\circ, 45^\circ)$</p>  <p>T=-100 °C $\mathbf{P}^0 = (0.221, 0.221, 0.221) \text{ C/m}^3$</p>	<p>$\chi_{ij}^{(1)}$ in the rhombohedral and the principal coordinate systems</p> $\begin{pmatrix} \chi_{11}^{(1)} & \chi_{12}^{(1)} & \chi_{12}^{(1)} \\ \chi_{12}^{(1)} & \chi_{11}^{(1)} & \chi_{12}^{(1)} \\ \chi_{12}^{(1)} & \chi_{12}^{(1)} & \chi_{11}^{(1)} \end{pmatrix}$ $\begin{pmatrix} \chi'_{11}^{(1)} & 0 & 0 \\ 0 & \chi'_{11}^{(1)} & 0 \\ 0 & 0 & \chi'_{33}^{(1)} \end{pmatrix}$ <p>$\chi_{11}^{(1)} = 636.58$ $\chi_{12}^{(1)} = -237.93$ $\chi'_{11}^{(1)} = 874.51$ $\chi'_{33}^{(1)} = 160.72$</p>	<p>$\chi_{ijk}^{(2)}$ in the rhombohedral and the principal coordinate systems</p> $\begin{pmatrix} \chi_{111}^{(2)} & \chi_{122}^{(2)} & \chi_{122}^{(2)} & \chi_{123}^{(2)} & 2\chi_{122}^{(2)} & 2\chi_{122}^{(2)} \\ \chi_{122}^{(2)} & \chi_{111}^{(2)} & \chi_{122}^{(2)} & 2\chi_{122}^{(2)} & \chi_{123}^{(2)} & 2\chi_{122}^{(2)} \\ \chi_{122}^{(2)} & \chi_{122}^{(2)} & \chi_{111}^{(2)} & 2\chi_{122}^{(2)} & 2\chi_{122}^{(2)} & \chi_{123}^{(2)} \end{pmatrix}$ $\begin{pmatrix} 0 & 0 & 0 & 0 & 2\chi'_{311}^{(2)} & -2\chi'_{222}^{(2)} \\ -\chi'_{222}^{(2)} & \chi'_{222}^{(2)} & 0 & 2\chi'_{311}^{(2)} & 0 & 0 \\ \chi'_{311}^{(2)} & \chi'_{311}^{(2)} & \chi'_{333}^{(2)} & 0 & 0 & 0 \end{pmatrix}$ <p>$\chi_{111}^{(2)} = 6.66 \times 10^{-5} \text{ m/V}$ $\chi_{122}^{(2)} = -1.65 \times 10^{-5} \text{ m/V}$ $\chi_{123}^{(2)} = 3.58 \times 10^{-5} \text{ m/V}$ $\chi'_{222}^{(2)} = -6.21 \times 10^{-5} \text{ m/V}$ $\chi'_{311}^{(2)} = 2.81 \times 10^{-5} \text{ m/V}$ $\chi'_{333}^{(2)} = 1.87 \times 10^{-6} \text{ m/V}$</p>

well with the results calculated analytically based on the perturbation theory because a negligibly small $\Delta P_i^{(2)}(0)$ is the premise of the present analytical model, as discussed in Appendix C [see the paragraph before Eq. (C4)]. Details of the dynamical phase-field model and the setup of the numerical simulations are provided in Ref. [25].

As an example, Fig. 6(a) shows the steady-state evolution of $\Delta P_3(t)$ in the middle layer of the BaTiO₃ slab (note that ΔP_3 is spatially uniform in the slab) under a continuous THz wave excitation with $\omega = 0.5\omega_3 = 2\pi \times 2.0542$ THz, corresponding to the first peak of $|\chi_{333}^{(2)}(2\omega)$ in Fig. 1(a). Figure 6(b) shows the frequency spectrum of $\Delta P_3(t)$, which display two prominent peaks. The first peak at $\omega/2\pi = 2.0542$ THz is related to the linear polarization oscillation $\Delta P_3^{(1)}(t) = \Delta P_3^{(1),0} \exp\{i[-\omega t + \varphi^{(1)}]\}$ that has the same frequency as the incident THz wave. The second peak at $\omega/2\pi = 4.1084$ THz corresponds to the second-harmonic component of the polarization

oscillation, given by $\Delta P_3^{(2)}(t) = \Delta P_3^{(2),0} \exp\{i[-2\omega t + \varphi^{(2)}]\}$. Performing the inverse Fourier transform for the second peak allows for reconstructing the temporal profile of $\Delta P_3^{(2)}(t)$, as shown in Fig. 6(c), from which both the amplitude $\Delta P_3^{(2),0}$ ($=0.027762$ mC/m²) and phase $\varphi^{(2)}$ ($=1.48140$ rad) (84.878°) can be extracted. Thus, $|\chi_{333}^{(2)}(2\omega)| = 2\Delta P_3^{(2),0}/\kappa_0(E_3^{\text{inc},0})^2$ is calculated to be 4.454×10^{-5} m/V, which agrees well with the analytically calculated value of 4.67×10^{-5} m/V. Likewise, performing the inverse Fourier transform for the first peak enables the reconstruction of $\Delta P_3^{(1)}(t)$, from which we obtain $\Delta P_3^{(1),0} = 0.569$ mC/m² and $\varphi^{(1)} = 0.0515$ rad (2.951°). Therefore, $|\chi_{33}^{(1)}(\omega)| = \Delta P_3^{(1),0}/\kappa_0 E_3^{\text{inc},0} = 170.5995$. Given that $\chi_{33}^{(1)} = |\chi_{33}^{(1)}| \exp[i\varphi^{(1)}] = \chi_{33}^{(1),\text{Re}} + i\chi_{33}^{(1),\text{Im}}$, one has $\chi_{33}^{(1),\text{Im}} = |\chi_{33}^{(1)}| \sin\varphi^{(1)} = 8.651$, which agrees well with the analytically calculated $\chi_{33}^{(1),\text{Im}}$ of 7.259 at $\omega = 2\pi \times 2.0542$ THz.

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