

(Ba,Sr)TiO₃ 拉伸应变薄膜的介电响应

于展波^{1,2}, 马兴越^{1,2}, 吴宗铄², 高志昊^{1,2}, 吴 迪^{1,2}, 杨玉荣^{1,2}

(1. 南京大学现代工程与应用科学学院, 材料科学与工程系, 南京 210093;

2. 南京大学, 固体微结构物理全国重点实验室, 南京 210093)

摘 要: 介电响应是铁电材料的重要物理性质之一, 然而, 铁电多畴结构的高频介电响应尚不明确。通过使用基于第一性原理的有效哈密顿量方法, 研究了(Ba_{0.8}Sr_{0.2})TiO₃ (BST_{0.8})薄膜在 1.55%面内拉伸应变下单畴结构和包含 180°和 90°畴壁的多畴结构的介电响应。动力学研究表明 180°和 90°畴壁都是稳定的, 并表现出类似的动力学自发振荡。单畴结构的介电响应谐振峰主要出现在太赫兹范围内, 改变外部电场的大小可以操纵 BST_{0.8} 中单畴结构介电响应的谐振峰频率。多畴结构的畴壁运动在低频的介电响应中占主导地位, 并且 180°和 90°畴壁都具有一个与畴壁谐振有关的低频模式。本工作对 BST_{0.8} 单畴和多畴介电响应的研究结果对微波介质陶瓷的应用有推动作用。

关键词: 多畴结构; 介电响应; 有效哈密顿量方法; 第一性原理

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1 Introduction

Ferroelectrics are characterized by switchable spontaneous polarization in an external electric field, which are key components in electronics, optics, sensors, and actuators^[1]. Ferroelectrics usually possess complex domain structures with domain walls (DWs) separating adjacent homogeneously polarized domains^[2]. The DWs have attracted much attention during the past two decades due to their properties and potential for device designing^[3-4]. The related issues include DW motion^[5], nonvolatile memory^[6], topological defects^[7], enhanced susceptibility^[8], enhanced quality factor^[9], low dielectric loss^[10], and others^[11-13].

(Ba_{0.8}Sr_{0.2})TiO₃ (BST_{0.8}) is a ferroelectric substance with multi-domain structures. Two typical multi-domain structures were found in previous work, *i.e.*, structures with 90° DWs and 180° DWs. The enhancement of dielectric response in 90° DW system is well

understood^[9], but the behavior of dielectric response in 180° DW system is still unclear. Clarifying how the 180° domain wall affects the dielectric response can thus enhance our comprehension of the effects in multi-domain systems. In this paper, the dielectric response of single domain in the lead-free BST_{0.8} solid solution was investigated by an effective Hamiltonian method. The multi-domain structures with 180° DWs and 90° DWs under tensile strains were simulated, and the dielectric response of multi-domain structures with 180° DWs and 90° DWs was analyzed. In addition, the multi-domain configurations and the dielectric response of multi-domain structures in equilibrated orthogonal phase of BST_{0.8} under different external conditions were also investigated based on the atomistic first-principle-based simulations.

2 Method

In this work, we performed molecular dynamics

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第一作者: 于展波(2000—), 男, 硕士研究生。

通信作者: 吴 迪(1974—), 男, 博士, 教授;

杨玉荣(1980—), 男, 博士, 教授。

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First author: YU Zhanbo (2000—), male, Master candidate.

E-mail: zhanboyu@smail.nju.edu.cn

Correspondent author: WU Di (1974—), male, Ph.D., Professor;

YANG Yurong (1980—), male, Ph.D., Professor.

E-mail: diwu@nju.edu.cn; yangyr@nju.edu.cn

using the ALFE-H code^[14], using the first-principles-based effective Hamiltonian^[15–16]:

$$E_{\text{tot}}(\{u_i\}, \{\eta_1\}, \{\eta_{\text{loc}}\}, \{\sigma_j\}, \eta_{\text{H}}) = E_{\text{ave}}(\{u_i\}, \{\eta_1\}, \eta_{\text{H}}) + E_{\text{loc}}(\{u_i\}, \{\eta_1\}, \{\eta_{\text{loc}}\}, \{\sigma_j\}) \quad (1)$$

where u_i is the local soft mode, $\eta_1, \dots, \eta_6$ are the homogeneous strain components with Voigt notation, $\{\sigma_j\}$ characterizes the atomic configuration, $\sigma_i = +1$ or -1 corresponds to the presence of a Ba or Sr atom, respectively. All the parameters of the effective Hamiltonian were given in a previous work^[16].

All the calculations were performed in the *NPT* ensemble, employing an Evans-Hoover thermostat, with periodic boundary condition (PBC) along all three directions. To simulate the substrate, a uniform biaxial strain was fixed to the external strain $\eta_1 (\eta_{xx}) = \eta_2 (\eta_{yy}) = 1.55\%$, and $\eta_6 (\eta_{xy}) = 0$. The strain was chosen because 1) the 180° DWs and 90° DWs both coexisted stably, matching the experimental PFM observations^[9], 2) the dielectric responses of multi-domain with 90° DWs and 180° DWs showed a high similarity with strains from 1.45% to 1.85%, and 3) increasing strain to 1.55% reduces fluctuations significantly, ensuring a reliable extraction of intrinsic dielectric properties. The presence of the phase orthogonal in the BST_{0.8} phase diagram in a large temperature range (*i.e.*, 140 K) under this strain, which is beneficial for reducing the molecular dynamics (MD) simulations fluctuations.

To calculate the dielectric response, we extracted the trajectory of local mode u_i averaged over the supercell during MD simulations^[17]:

$$\varepsilon_{\alpha\beta}(\nu) = \frac{1}{\varepsilon_0 V k_B T} \left\{ \langle M_\alpha M_\beta \rangle - \langle M_\alpha \rangle \langle M_\beta \rangle + i2\pi\nu \int_0^\infty dt e^{i2\pi\nu t} \langle (M_\alpha(t=0) - \bar{M}_\alpha(t=0))(M_\beta(t) - \bar{M}_\beta(t)) \rangle \right\} \quad (2)$$

where M_α is the α Cartesian component of the total dipole moment, computed as $M_\alpha = \frac{Z^*}{N} \sum_i u_i$ (where Z^* is the Born effective charge of the local mode). $\langle \dots \rangle$ and bars both indicate the ensemble average.

In this work, the influence of different DW structures on the dielectric response was investigated. We obtained single domain structure and multi-domain structures with 180° DWs and 90° DWs based on the MD simulations, then the corresponding dielectric

response is computed. For the multi-domain structure, we began with a self-constructed initial multi-domain polarization configuration and performed 50 ps MD simulation under chosen strains for structural relaxation. In the initial configuration, the magnitude of non-zero component of soft mode u on each site was set to 0.1 Å, atomic occupations (alloying) were randomized, and unless otherwise specified, all other mode variables were set to zero. Subsequently, we examined the results of the structural relaxation *via* integrating experimental conditions and observed phenomena. Subsequent 8 ns additional simulations were performed to obtain autocorrelation function ($\langle M_\alpha M_\beta \rangle - \langle M_\alpha \rangle \langle M_\beta \rangle$ term in Eq. (2)) for any time t ranging from 0 to 1 ns by steps of 10 fs. The fast Fourier transformation (FFT) was performed to calculate the dielectric response according to Eq. (3). We used two uncoupled damped harmonic oscillators (DHOs) to fit the calculation data^[18]:

$$\varepsilon(\nu) = \frac{S_1}{\nu_1^2 - \nu^2 + i\nu\gamma_1} + \frac{S_2}{\nu_2^2 - \nu^2 + i\nu\gamma_2} \quad (3)$$

where ν_1, γ_1, S_1 (respectively, ν_2, γ_2, S_2) are the resonant frequency, damping constant, and oscillator strength of the first (respectively, second) oscillator.

3 Results and discussion

3.1 Single domain simulations

We first characterize the phase transition of bulk and epitaxially strained BST_{0.8} system ($\eta = 1.55\%$) at finite temperatures, as shown in Figs. 1(a) and 1(b), respectively. The MD simulations are performed for $12 \times 12 \times 12$ supercell (corresponding to 8640 atoms). For a bulk system, static properties are simulated by the annealing method with a temperature step of 10 K. For each temperature step, we use 10000 Hybrid Monte Carlo (HMC) steps. As the temperature decreases from 500 K to 10 K, the paraelectric cubic phase (C) subsequently transforms into ferroelectric tetragonal (T), orthogonal (O), rhombohedral (R) at T_{C1} of (515 ± 5) K, T_{C2} of (335 ± 5) K and T_{C3} of (205 ± 5) K, respectively, which is consistent with the previous results^[16]. For strained system, we average several randomly distributed Sr and Ba configurations to obtain the converged results *via* running annealing simulations with 20000 HMC steps at each temperature. It is the phase C at a high temperature

of larger than 400 K. C-O and O-M_B transitions are observed at T_{C1} of (355 ± 5) K and T_{C2} of (215 ± 5) K, respectively, as the temperature decreases. M_B is a monoclinic phase with polarization $P_x \approx P_y > P_z$ introduced by Vanderbilt and Cohen^[19].

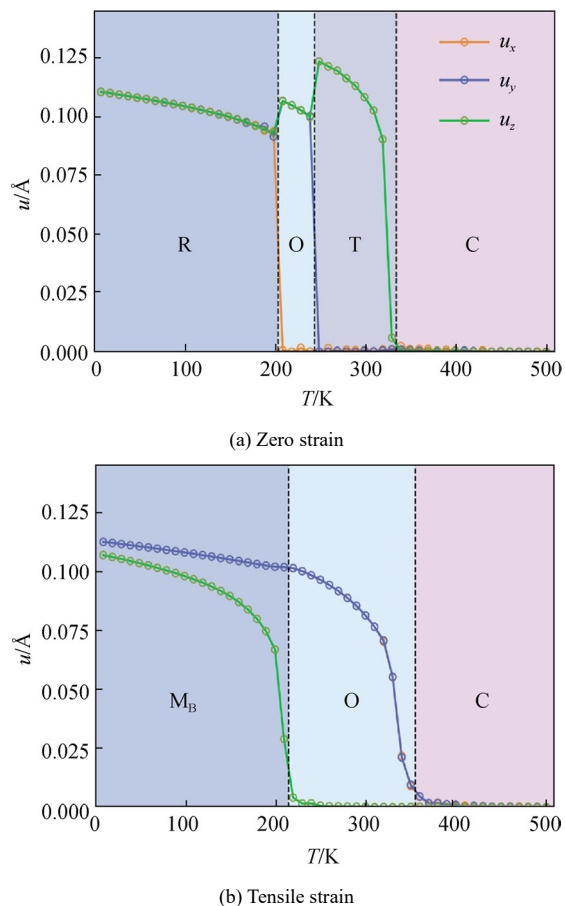


Fig. 1 Phase diagram of BST_{0.8} under zero strain and tensile strain ($\eta=1.55\%$), u_x , u_y and u_z are the components of local mode u along x , y , and z directions, respectively. (C, T, O, R and M_B represent cubic, tetragonal, orthorhombic, rhombohedral and monoclinic phases, respectively)

To clarify the dynamic properties of the strained system, we compute the dielectric response at 300 K with the electric fields along $[110]$ from 0 to 2 MV/cm. We first slowly cool down the system from 700 K to 300 K with obtain the equilibrated structure, and then 50 ps MD simulations are performed with the corresponding electric field, which is sufficiently enough to equilibrate the system. Fig. 2 shows the real and imaginary parts of the response as a function of frequency in different external electric fields at 300 K.

The computational results can be well fitted with the

model of two uncoupled DHOs. For $E=0$ MV/cm, the results exhibit two peaks at 300 GHz and 3 THz. One peak at 300 GHz gradually disappears as the electric field increases to 1.0 MV/cm. Another peak at 3 THz for E of 0 MV/cm continuously shifts to 7 THz in the electric field of 3 MV/cm. A high frequency peak appears at 8 THz as the electric field reaches 1 MV/cm, and then shifts to 9 THz slowly as the electric field increases to 3 MV/cm.

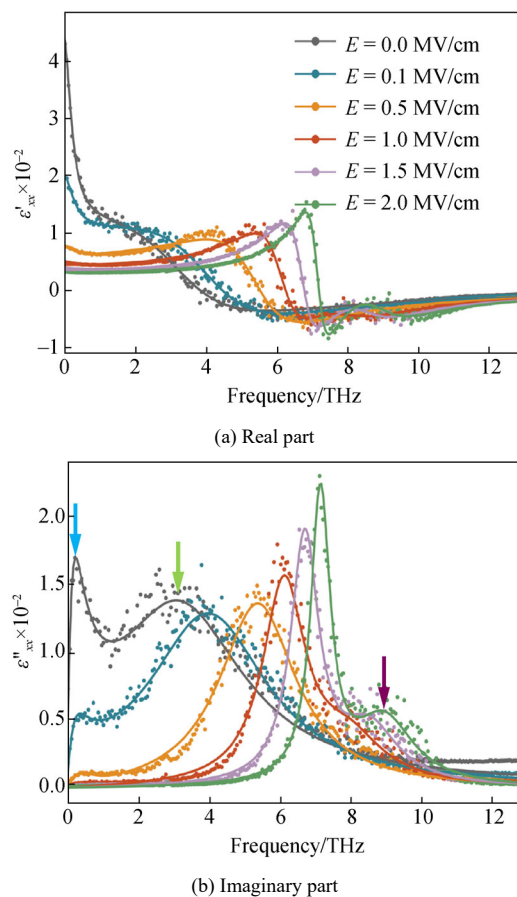


Fig. 2 Real (a) and imaginary (b) parts of dielectric response for BST_{0.8} in different external electric fields ($E_x=E_y=E$) at 300 K. (Symbols represent computational data, while solid lines provide the fitting results from damped harmonic oscillators. The arrows in the inset of panel (b) indicate the corresponding peaks. The blue arrow indicates that the peak disappears in a higher electric field, the green peak shifts to a higher frequency in a higher electric field, and the purple arrow indicates a new peak in a high electric field)

Clearly, the real and imaginary parts of the predicted dielectric response at each chosen electric field both exhibit two peaks. A low-frequency mode with 300 GHz at zero field in the system gradually disappears as the

electric field increases, and a high-frequency mode larger than 8 THz appears when electric field is larger than 1 MV/cm. The high frequencies modes of 3 THz at zero field and 8 THz under 1 MV/cm shift towards higher frequencies as the electric field increases. The simulations reveal that it is possible to manipulate the frequency of peaks in dielectric response *via* changing the magnitude of the external electric field.

3.2 Multi-domain simulations

According to some previous experiments^[13, 20], there are three types of multi-domain structures in BST_{0.8}, with the DWs aligning in (110), (010) and (100) planes in films, respectively. According to the *xy*-plane symmetry in phase O with the uniform biaxial strains, multi-domains with DWs aligning in (010) or (100) are equivalent to each other. Here, we perform MD simulations to further analyze the multi-domain structures with DWs aligning in (110) and (100) with η of 1.55% at 300 K. The simulations are performed with the size of $120 \times 120 \times 5$ supercell (corresponding to 360 000 atoms) for the multi-domain with 180° DWs aligning in direction (110) in supercell and $48 \times 48 \times 5$ supercell (corresponding to 57 600 atoms) for the multi-domain with 90° DWs aligning in direction (100) in supercell.

Fig. 3(a) shows the *xy*-plane dipolar configuration of multi-domain structure with 180° DWs in the bottom layer of the considered supercell, which is obtained *via* averaging configurations over the last 10 ps MD^[21] configuration at 300 K. Red regions and blue regions exhibit antiparallel in-plane polarizations (see white arrows in Fig. 3(a)). Fig. 3(b) shows the layer-resolved $\bar{u}$ averaged perpendicular to the green line and indexed along the green line in Fig. 3(a). $\bar{u}_\alpha$ represents the average dipole moment of the bottom layer in supercell, which is calculated by

$$\bar{u}_\alpha = \frac{1}{N_t} \sum_t \left(\frac{1}{N} \sum_i Z^* u_{\alpha,i,t} \right) \quad (4)$$

where N_t and N are the time range^[22] and number of supercells used for averaging, respectively. α denotes the cartesian components. The width of 180° DWs is approximately 10 unit cells. Within DWs, the local mode u changes from one domain continuously towards another domain, which is similar to that in a previous research^[23]. Fig. 3(c) shows the spontaneous oscillations of 180° DWs in the absence of external electric fields. The proportion of the width of single domains with $+u_x$ and $-u_x$ is approximately 1:1 over the simulations. These results indicate that the multi-domains with 180° DW aligning in (110) are stable.

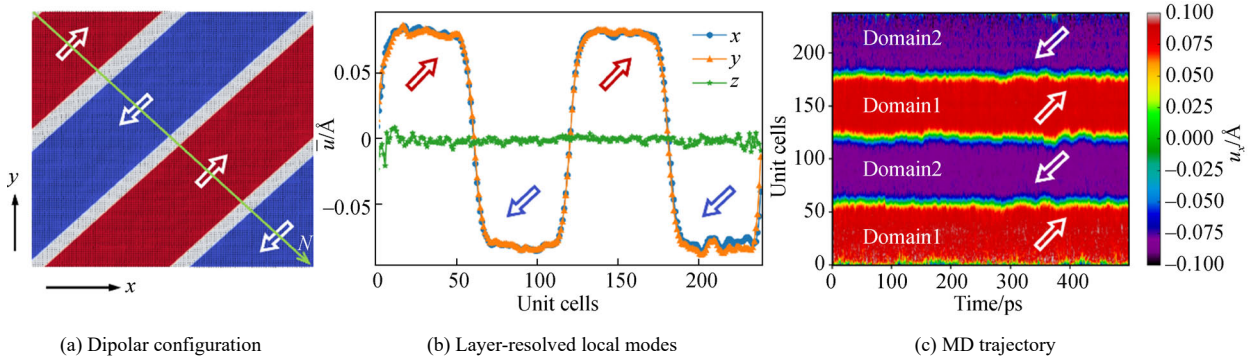


Fig. 3 Illustration of the molecular dynamic simulations of multi-domains with 180° DWs. (Panel (a) shows the local mode (polarization) configuration in the bottom layer (*x*-*y* plane) in the supercell. The 180° DWs (white regions) separating P along $[110]$ domains (red color) and P along $[\bar{1}\bar{1}0]$ (blue color) domains. Panel (b) displays the layer-resolved local modes u_x , u_y and u_z , which are the averaged local modes perpendicular to the green line in panel (a). Panel (c) displays the trajectory layer-resolved u_x of molecular dynamics during 500 ps simulations at 300 K for multi-domains with 180° DWs shown in panel (a). The fluctuations of domain edges indicate the oscillations of 180° DWs. The arrows are schematics of the polarizations in the corresponding domains)

Fig. 4(a) shows the *xy*-plane dipolar configuration of multi-domain structure with 90° DWs obtained *via* averaging configurations over the last 10 ps MD trajectory at 300 K. Blue and red regions exhibit local

moment u along $[\bar{1}\bar{1}0]$ and $[1\bar{1}0]$, respectively. Fig. 4(b) shows the layer-resolved $\bar{u}$ averaged perpendicular to the green line and indexed along the green line in Fig. 4(a). The width of 90° DWs is 3–4 unit cells. Fig. 4(c)

shows the spontaneous oscillations of 90° DWs in the absence of external electric fields. The oscillations of 90° DWs show the similar features with 180° DWs. The proportion of each domain is approximately 1:1 (see Fig. 4(c)), which is similar to the oscillations of 180° DWs (see Fig. 3(c)).

The influence of 90° DWs on the quality factor Q was investigated in a previous work^[9]. However, there are still two aspects that need to be further considered. First, the dielectric response of multi-domain with 90°

DWs in $\text{BST}_{0.8}$ is still unknown. Second, the difference between the dielectric responses of single domain structures and multi-domain structures with 180° DWs and 90° DWs is ambiguous. Previous work attributed the unique behavior of quality factor Q (calculated from dielectric response) to the stochastic oscillations of 90° DWs in an external electric field ($E_x=0.6$ MV/cm). Note that 180° DWs and 90° DWs exhibit slight oscillations that do not change the proportion of single domains width in the absence of external electric field.

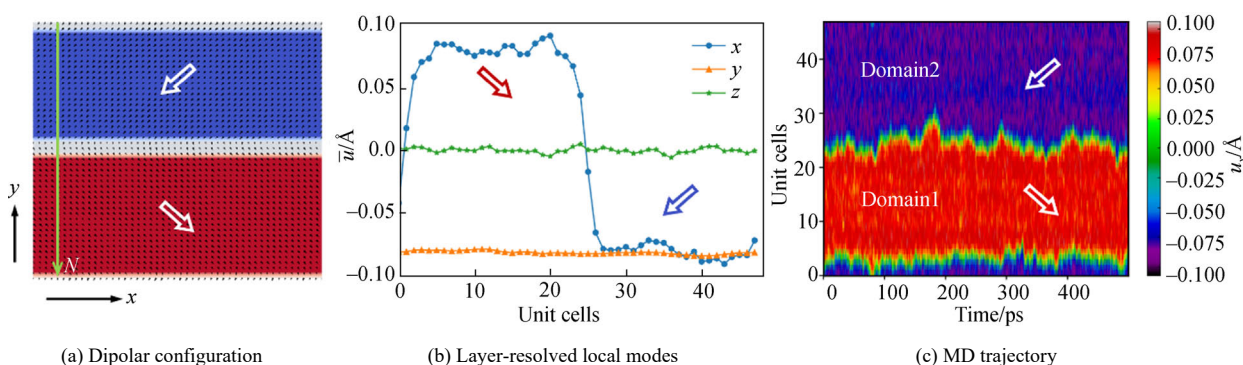


Fig. 4 Illustration of the molecular dynamic simulations of multi-domains with 90° DWs. (Panel (a) shows the local mode (polarization) configuration in the bottom layer (x - y plane) in the supercell. The 90° DWs (white regions) separating P along $[1\bar{1}0]$ domains (red color) and P along $[1\bar{1}0]$ (blue color) domains. Panel (b) displays the layer-resolved local modes u_x , u_y and u_z , which are the averaged local modes perpendicular to the green line in panel (a). Panel (c) displays the trajectory layer-resolved u_x of molecular dynamics during 500 ps simulations at 300K for multi-domains with 90° DWs shown in panel (a). The fluctuations of domain edges indicate the oscillations of 90° DWs. The arrows are schematic of the polarizations in the corresponding domains)

According to a previous study^[24], we extend the MD simulation time to 16 ns for multi-domain with 180° DW and 8 ns for multi-domain with 90° DW to accurately mimic the low-frequency part of the dielectric response (ϵ_{xx}). We firstly perform a uniform filter method from SciPy^[25] package to smooth the raw computational data, and then use DHOs to fit smoothed data. Fig. 5 shows the dielectric responses for single domain and multi-domains with 180° DWs and 90° DWs at 300 K. For the response of multi-domain structure with 180° DWs, two peaks located at 8 GHz and 120 GHz appear, respectively, and no peaks occur at > 200 GHz (see the orange line in Fig. 5(b)). The multi-domain structure with 90° DWs only exhibits one peak at 10 GHz in dielectric response (see Fig. 5(c)), which is at the similar frequency position with the peak at 8 GHz in 180° DWs system.

The analysis of the dielectric response of single domain structure and multi-domain structures shows that

the single domain structure exhibits high-frequency peaks at > 300 GHz, whereas the multi-domain structure has low-frequency peaks at 8 GHz and 120 GHz for 180° DWs system and at 10 GHz for 90° DWs system, revealing that there exists a low-frequency mode related to collective oscillation of DWs in multi-domain structures. In addition, the frequencies of peaks in multi-domain with DWs are in a gigahertz range, whereas the single domain structure has peaks in a terahertz range, which is similar to the different $Q(f)$ behaviors of domain-wall layers and bulk-like layers^[9]. The contribution of DWs to the dielectric response primarily arises from the timescale of DWs motion, such as sliding or breathing, which differs from the high-frequency vibrations of optical phonon modes. Specifically, the vibrational frequency of DWs is much lower, with relaxation times in the order of nanoseconds, resulting in a response frequency in GHz range, which is

far below the terahertz range of optical phonon modes. Therefore, DWs oscillations dominate the dielectric response at a low frequency. Moreover, multi-domain structure with 180° DWs has a unique low frequency mode at 120 GHz, which is significantly different from

single domain and 90° DWs system. In other words, multi-domain structures with 180° DWs and 90° DWs exhibit different dielectric responses. There exists a common low-frequency mode related to the oscillations of DWs in BST_{0.8}.

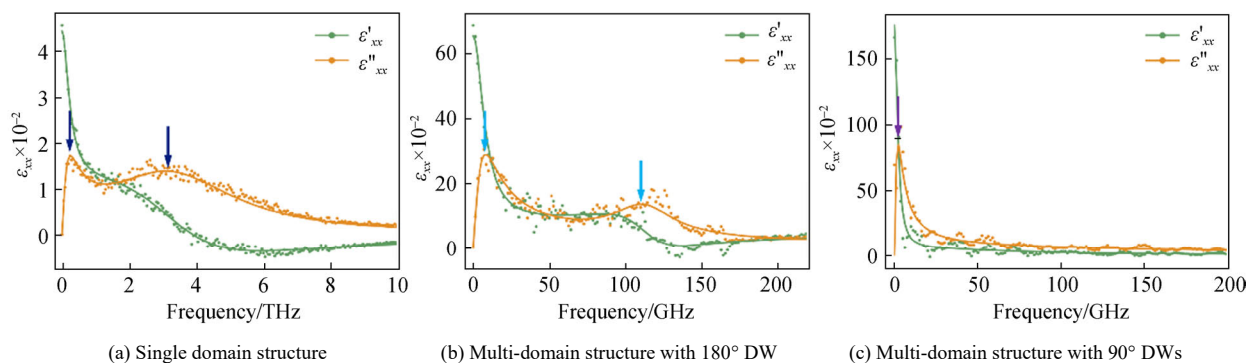


Fig. 5 Real and imaginary parts of dielectric response of single domain structure and multidomain structures with 180° DWs and 90° DWs. (Symbols represent computational data, while solid lines provide the fitting results from damped harmonic oscillators. The arrows with different colors are the frequencies of the peaks of ϵ'' associated with Eq. 1 in different domain structures)

4 Conclusions

The multi-domain structures and dielectric response of single domain structure and multi-domain structures with 180° DWs and 90° DWs in BST_{0.8} under tensile strains were investigated via first-principles-based effective Hamiltonian (ALFE-H code). The simulations showed that changing the magnitude of the external electric field could manipulate the frequency of peaks in dielectric response of single domain. Domain walls oscillations could dominate the dielectric response in a low frequency GHz range, whereas the single domain structures had peaks in a terahertz range. Moreover, multi-domain structures with different domain walls in BST_{0.8} exhibited different dielectric responses, and both multi-domain structures had a same low-frequency mode at 10 GHz related to the domain walls oscillations. The results of this study demonstrate the dielectric response behaviors of ferroelectrics induced by an external electric field and internal multidomain configurations and provided the potential mechanisms and guidance for optimizing the application performance.

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Dielectric Response of $(\text{Ba}, \text{Sr})\text{TiO}_3$ Thin Films under Tensile Strain

YU Zhanbo^{1,2}, MA Xingyue^{1,2}, WU Zongshuo², GAO Zhihao^{1,2}, WU Di^{1,2}, YANG Yurong^{1,2}

(1. College of Engineering and Applied Sciences, Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, China; 2. National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China)

Extended Abstract

Introduction Frequency-dependent dielectric response is one of the important properties of ferroelectrics, reflecting the polarization response to high-frequency electric fields. Polarizations are closely related to ferroelectric domain structures, such as single domain, which represents the region with homogeneous polarizations direction. Ferroelectrics usually possess complex domain structures with domain walls (DWs) separating adjacent homogeneously polarized domains. DWs have attracted much attention during the past two decades due to their properties and potential for device designing. The related issues include DW motion, nonvolatile memory, topological defects, enhanced susceptibility, enhanced quality factor, low dielectric loss, and others. $(\text{Ba}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ ($\text{BST}_{0.8}$) is a ferroelectric usually with multi-domain structures. Previous work identified two typical types of domain walls (DWs), *i.e.*, 90° DWs and 180° DWs. The enhancement of dielectric response in systems with 90° DWs is now well understood, and the behavior of dielectric response in multi-domain systems with 180° DWs remains unclear. Therefore, gaining insights into how 180° DWs affect the dielectric response can clarify the effects in multidomain systems.

Methods We performed molecular dynamics simulations using the ALFE-H code with the first-principles-based effective Hamiltonian method to study the $\text{BST}_{0.8}$ system. All the calculations were performed in the NPT ensemble using the Evans-Hoover thermostat, and periodic boundary condition (PBC) along all three directions. To simulate the substrate, a uniform biaxial strain was fixed to the 1.55% in-plane strain. To analyze the multi-domain with different DWs, the simulations started with a self-constructed initial multi-domain polarization configuration. Subsequent 50 ps MD simulation was performed under chosen strains for structural relaxation. In the initial configuration, the magnitude of non-zero components of soft mode on each site was set to 0.1 Å, atomic occupations (alloying) were randomized, and unless otherwise specified, all other mode variables were set to zero. The trajectory of local mode averaged over the supercell during MD simulations was extracted to calculate the dielectric response. The 8 ns MD simulations were performed to obtain an autocorrelation function for any time t ranging from 0 to 1 ns by one step of 10 fs. The fast Fourier transformation (FFT) was performed to calculate the dielectric response. Then two uncoupled damped harmonic oscillators (DHOs) were used to fit the data of dielectric response.

Results and discussion The dielectric response of single domain at 300 K with the different electric fields along [110] from 0 to 2 MV/cm was computed. The computational results can be well fitted with the model of two uncoupled DHOs. The real and imaginary parts of the predicted dielectric response at each chosen electric field both exhibit two peaks. As the electric field increases, the low-frequency mode with 300 GHz at zero field in the system gradually disappears, and a high-frequency mode of larger than 8 THz appears when electric field is larger than 1 MV/cm. The high frequencies modes of 3 THz at zero field and 8 THz under 1 MV/cm

shift towards higher frequencies as the electric field increases. In other words, the present simulations reveal that it is possible to manipulate the frequency of peaks in dielectric response *via* changing the magnitude of the external electric field.

The dielectric responses of multi-domain with 90° DWs and 180° DWs are further analyzed. According to the experimental PFM results, the multi-domain structures are simulated and the dielectric response through MD simulations is calculated. The analysis of the dielectric response of single domain structure and multi-domain structures shows that the single domain structures exhibit high-frequency peaks at > 300 GHz, whereas the multi-domain structures exhibit low-frequency peaks at 8 GHz and 120 GHz for 180° DWs system and at 10 GHz for 90° DWs system, revealing that there exists a low-frequency mode related to collective oscillation of DWs in multi-domain structures. In addition, the frequencies of peaks in multi-domain with DWs are in a gigahertz range, whereas the single domain structure exhibits peaks in a terahertz range. The contribution of DWs to the dielectric response primarily arises from the timescale of DWs motion, such as sliding or breathing, which differs significantly from the high-frequency vibrations of optical phonon modes. The vibrational frequency of DWs is much lower, with relaxation times in the order of nanoseconds, resulting in a response frequency in GHz range, which is far below the terahertz range of optical phonon modes. Therefore, DWs oscillations dominate the dielectric response at a low frequency. Moreover, multi-domain structure with 180° DWs exhibits a unique low frequency mode at 120 GHz, which is significantly different from single domain and 90° DWs system. In other words, multi-domain structures with 180° DWs and 90° DWs exhibit different dielectric responses. There exists a common low-frequency mode related to the oscillations of DWs in BST_{0.8}.

Conclusions It was possible to manipulate the frequency of peaks in dielectric response of single domain through changing the magnitude of the external electric field. Domain walls oscillations dominated the dielectric response in a low frequency gigahertz range, whereas the single domain structures exhibited resonant peaks in a terahertz range. Moreover, multi-domain structures with different domain walls in BST_{0.8} had different dielectric responses, but the both have a same low-frequency mode at 10 GHz related to the domain walls oscillations. The results of this study indicated the dielectric response behaviors of ferroelectrics induced in an external electric field and internal multi-domain configurations and provided the potential mechanisms and guidance for optimizing application performance.

Keywords multi-domain; dielectric response; effective Hamiltonian method; first-principles