Dielectric response of BaZrO₃/BaTiO₃ superlattice

D. Wang^{*,‡} and Z. Jiang^{*,†}

^{*}*Electronic Materials Research Laboratory–Key Laboratory of the Ministry of Education
 Xi'an Jiaotong University, Xi'an 710049, P. R. China*

International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, P. R. China

[†]*Physics Department and Institute for Nanoscience and Engineering
 University of Arkansas, Fayetteville, Arkansas 72701, USA*

[‡]dawei.wang@mail.xjtu.edu.cn

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We use the first-principles-based molecular dynamic approach to simulate dipolar dynamics of BaZrO₃/BaTiO₃ superlattice, and obtain its dielectric response. The dielectric response is decomposed into its compositional, as well as the in-plane and out-of-plane parts, which are then discussed in the context of chemical ordering of Zr/Ti ions. We reveal that, while the in-plane dielectric response of BaZrO₃/BaTiO₃ superlattice also shows dispersion over probing frequency, it shall not be categorized as relaxor.

Keywords: Relaxor; molecular dynamics; dielectric response.

1. Introduction

Relaxor ferroelectrics possess unique static and dynamic properties, which make them excellent materials for practical applications. One important feature of relaxors, which gave birth to their name, is related to relaxational dipolar dynamics. The relaxation dynamics of canonical relaxors is intimately linked to their phonon dynamics as the relaxation is widely believed to be originated from the motion of polar nanoregions (PNRs), which appear upon cooling in nonpolar crystal at particular temperature due to local condensation of phonon optic soft (ferroelectric-type) mode.^{1–4} The relaxation spectrum is typically localized close to phonon frequencies at $T \gg T_m$, but broadens vastly upon cooling so that at $T < T_m$ the dynamics remain active at all frequencies available for measurements. The investigations of the spectrum have been implemented by means of dielectric spectroscopy at frequencies from $\nu \sim 5 \times 10^9$ down to $\sim 10^{-3}$ Hz.²

It is a common observation about relaxors that they are all disordered systems. For instance, in both Ba(Zr,Ti)O₃ (BZT) and Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN), it is the B-site atom that is random. In addition, in PMN, because Mg and Nb are heterovalent, it is generally recognized that random electric field is important for its relaxor properties. How important is the randomness for forming relaxors in typical perovskites? What happens if the atoms are in perfect order, are they still relaxors? Is the dispersion of T_m the key to define relaxor? Such important questions deserve careful consideration, but is challenging for experimental investigation. Therefore, in this case, theoretical studies or numerical simulations could avail to understand the strange dynamic behavior of relaxors.^{1–4} In

particular, a reliable and quantitative theoretical model on the atomistic level is desired.

Indeed, theoretical modeling from the microscopic perspective of relaxors have continuously progressed over previous years.^{5–13} However, while theoretical models for relaxors have existed for some time, realistic numerical simulations that connect with experiments are not as many as one may expect. In numerical simulations of relaxors, there are at least three challenges to tackle: (i) modeling the randomness in the structure and interaction of relaxor, which is evidenced in BZT by the connectivity of Ti ions and the inhomogeneous PNRs associated with Ti ions; (ii) as a consequence of the randomness, the “rugged free energy landscape”¹⁴ arises, which makes such systems’ evolution over temperature hard to grasp. For instance, most relaxors have no clear-cut phase transition, which is common in normal ferroelectrics; (iii) due to the special energy landscape, relaxors, similar to spin glasses, often have slow dynamics. In extreme cases, the relaxation process can extend over the order of days.^{15,16} In relaxors, the slow dynamics results in the complex low-frequency part in the dielectric responses. Different formulas, such as the Cole–Cole,¹⁷ Havriliak–Negami equations,¹⁸ and other models¹⁹ have been proposed to model the relaxation process, as polarization in such systems adopts complex dynamics due to various interactions.

For the lead-free relaxor BZT, new opportunities to study the relations between composition, local structure and properties appeared with the development of first-principles-based simulations.^{20,21} In this approach, the structure and composition sensitive interactions between atoms constituting the material are determined exactly based on quantum

mechanical calculations, and the macroscopic properties of particular materials can be calculated without involving adjustable parameters. In particular, the quantitative agreement between many simulated and experimentally measured macroscopic properties of ferroelectrics with perovskite structure has been achieved recently,^{22–26} which ensures that the local (experimentally unreachable) properties extracted from the model, would reliably reflect real behaviors. Interestingly, such an atomistic model has also led to the belief that disordered BZT is a soft pseudospin glass system,^{10,27} both of which resulting from quenched disorder and random interactions. This similarity is helpful in understanding BZT's relaxor properties since it partly explains why BZT shows many interesting and sometimes puzzling properties, such as the dielectric constant differs under the field-cooling and zero-field-cooling conditions. In addition, spin glass has achieved the critical position that connects many seemingly very different problems in different research areas, such as information theory, computational complexity, biology, and econophysics, etc.^{28–30} Therefore, detailed investigation on BZT will likely benefit other research areas.

As we can see, the aforementioned challenge (i) was solved with the construction of a first-principles-based effective Hamiltonian; the challenge (ii) in producing static properties was addressed using MC simulations.^{20,22,23} The last challenge, i.e., to accurately reproduce the low-frequency dielectric responses of BZT, is tackled recently in the investigation of disordered $\text{Ba}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$.^{24,31} Here, we continue this line of research, obtain the dielectric response of a perfectly ordered 1:1 $\text{BaZrO}_3/\text{BaTiO}_3$ and compare it to disordered $\text{Ba}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$. As we will show, such comparison deepens

our understanding about relaxor and emphasizes the importance of disorder in the making of true relaxors.

2. Dielectric Responses

In this study, we focus on the role of disorder on the formation of relaxors, and in this process show the precise meaning of relaxor. Our approach is to simulate a $\text{BaZrO}_3/\text{BaTiO}_3$ 1:1 superlattice, grown along the $[001]$ direction, where the chemical environment for each Ti ion is uniform.³² The setup of such BZT system and its static properties had been investigated in Ref. 32. After obtaining the dielectric response of ordered BZO/BTO superlattice, we will be able to understand how order/disorder of ions affect the formation of relaxors. Here, the effective Hamiltonian approach is used to model the $\text{BaZrO}_3/\text{BaTiO}_3$ 1:1 superlattice. Details and parameters of this effective Hamiltonian can be found in Ref. 21. With this effective Hamiltonian, we use MD simulations^{24,33–37} to simulate a chemically ordered $12 \times 12 \times 12$ supercell and compute its dielectric responses, where the techniques used are similar to that reported in Ref. 24. Between 15 and 1000 K, a series of dielectric responses of the ordered BZO/BTO system are obtained at different temperatures.

We first show the dielectric responses obtained at 900 K in Fig. 1. The top row shows ϵ_{zz} , the out-of-plane dielectric response, while the bottom row of Fig. 1 shows the dielectric response ϵ_{xx} , which is related to the in-plane (the x - y plane) dielectric response. To better understand the dielectric response, both of them are decomposed using the technique developed in Ref. 24. The dielectric response from all

Fig. 1. (Color online) The real (red curves) and imaginary (blue curves) part of the dielectric response obtained at 900 K. From all dipoles (a, d), dipoles associated with Ti ions (b, e), and dipoles associated with Zr ions (c, f). The top row is the dielectric response associated dipole oscillations in the z -direction, while the bottom row is with the dipole oscillation in the x - y plane.

Fig. 2. (Color online) The real (red curves) and imaginary (blue curves) parts of the dielectric response obtained at 100 K of the BaZrO₃/BaTiO₃ 1:1 superlattice. The top row is the dielectric response associated with dipole oscillations in the z -direction, while the bottom row is with the dipole oscillation in the x - y plane.

dipoles, and dipoles associated with Ti/Zr cells are shown in each column.

The out-of-plane dielectric response (top row of Fig. 1) clearly shows two peaks at 152 and 345 cm⁻¹. Interestingly, phonon calculation of the BZO/BTO superlattice indeed confirms that two resonances with dipoles along z exist at ~ 135 and ~ 376 cm⁻¹,³⁸ consistent with the MD calculation here. Figure 1(c) shows the main resonance of Zr is at 152 cm⁻¹, while Ti has two peaks of similar magnitude. A close examination of the total response [Fig. 1(a)] indicates that the two peaks from Ti are redistributed in the total response, resulting in the larger lower-in-frequency peak.

The in-plane dielectric response (bottom row of Fig. 1) indicates a broad Ti peak [Fig. 1(e)] and a sharp Zr peak [Fig. 1(f)], resulting in a Fano resonance in the total dielectric response. The broad peak is likely because the weak correlation between the in-plane dipoles (Ti ions).³² Furthermore, both the total and Ti dielectric response [Figs. 1(d) and 1(e)] show signatures of a low-frequency ($\lesssim 100$ cm⁻¹) relaxation. In the next section, we will perform further investigation to understand if such relaxation make the BZO/BTO superlattice a true relaxor.

Comparison of the in-plane and out-of-plane dielectric response also reveals that they have a common peak at ~ 152 cm⁻¹, which indicates that, at this frequency, the out-of-plane and in-plane dipole dynamics are coupled. Such coupling may explain the large absorption of ϵ_{zz} at ~ 152 cm⁻¹ relative to that at ~ 376 cm⁻¹ [Fig. 1(a)] since the oscillation of dipoles along z can be damped by the in-plane dynamics.

Similarly, in Fig. 2 we show the dielectric response of the BZO/BTO superlattice at 100 K. Comparing to 900 K, the dielectric response obtained at 100 K has much smaller noise. The out-of-plane dielectric response still has two resonances, but with their peak frequencies shifted to ~ 124 and ~ 309 cm⁻¹. The in-plane dielectric responses are even more interesting, showing a few irregular resonances close to ~ 300 cm⁻¹. As previous studies have shown, the BZO/BTO superlattice has a phase transition at $T_C \simeq 220$ K. Below T_C , dipoles in the x - y planes become partially correlated and the dipole configuration partially antiferroelectric.³² The resonances in Figs. 2(d) and 2(e) are characteristics of such an antiferroelectric phase. Another difference between Figs. 1 and 2 is that, at 100 K, the in-plane dielectric response from Ti has a resonance at around ~ 300 cm⁻¹, close to the higher-in-frequency resonance, rather than the first peak that happens at 900 K.

3. Relaxor or Not?

Having shown the dielectric response above and below the phase transition of the BZO/BTO superlattice, we now focus on the low-frequency part (< 100 cm⁻¹), investigate the relaxation signature seen in Fig. 1, and compare ordered and disordered systems. As we can see from Figs. 1(d)–1(f), dipoles associated with Ti ions dominate the low-frequency dielectric response as it exhibits relaxation signatures. Therefore, we will also examine the in-plane dielectric response associated with Ti ions, in addition to the in-plane total response, where relaxation signature is strong.

Fig. 3. (Color online) The real part of the in-plane susceptibility $[(\chi_{xx} + \chi_{yy})/2]$ from Ti versus temperature calculated at different frequencies (a)–(c). Since the susceptibility at $\nu = 0 \text{ cm}^{-1}$ is quite large (its peak value is larger than 4000), we have removed the $\nu = 0 \text{ cm}^{-1}$ curve in Panel (a). The T_m variation with respect to frequency is shown in Panel (b), where the solid blue dots are the positions of maximum susceptibility obtained from curves in Panel (a) and the red curve is the best fit line. Panel (c) shows that the resonance frequency (solid blue dots) of the DHO mode as a function of temperature. To compare to disordered BZT, the counterparts of Panels (a)–(c) are shown as Panels (d)–(f)^{24,31} (see text).

To extract relaxation properties, we fit the dielectric response using the Cole–Cole equation¹⁷ plus a damped harmonic oscillator (DHO)^a

$$\chi(\nu) = \frac{\Delta\chi_1}{1 + (i\nu\tau)^{1-\alpha}} + \frac{\Delta\chi_2}{\nu_0^2 - \nu^2 + i\nu\gamma}, \quad (1)$$

where $\Delta\chi_1$, α , τ , $\Delta\chi_2$, ν_0 , and γ are fitting parameters. Here $\Delta\chi_1$ ($\Delta\chi_2$) is the spectra weight of the Cole–Cole (DHO) mode, τ is the relaxation time of the Cole–Cole mode and α ($0 < \alpha < 1$) characterize how far the relaxation mode is different from the Debye relaxation, and finally ν_0 and γ are the resonance frequency and damping constant, respectively. For accuracy, we confine the frequency range of fitting to be between 0 and 40 cm^{-1} . We note the DHO function only provides a background for the dielectric response, which is not our main concern here.

Several variations of the above fitting scheme have been tested. For instance, we have tried (i) a modified version of Eq. (1), using a piecewise function (i.e., the Cole–Cole function for temperatures with strong relaxation signatures, but polynomials for others), and (ii) an over damped DHO for the relaxation part [i.e., replacing the Cole–Cole function in Eq. (1) with the DHO]. We have verified that different fitting schemes, if performed carefully (e.g., by visually inspecting the curves to make sure the fittings are satisfactory), will lead to the same conclusion.

In Fig. 3, we show the in-plane susceptibility averaged over the x - and y -directions [i.e., we plot the susceptibility $\chi = (\epsilon_{xx} + \epsilon_{yy})/2$] associated with dipoles on Ti sites. The reason of choosing the susceptibility from Ti is to avoid the sharp peak from Zr in the total dielectric response, while dealing with the relaxation-like peak. Figure 3(a) shows the

^aIn this work, we have obtained the real and imaginary part of the dielectric response, χ' and χ'' . Together they form the dielectric permittivity as $\epsilon(\omega) = 1 + \chi'(\omega) - i\chi''(\omega)$ from the electromagnetic field point of view. Therefore, when we fit the dielectric permittivity using Debye or Cole–Cole equations, it is necessary to use $-\chi''(\omega)$ as the imaginary part. Sometimes, the different choices are referred to as engineering and physics conventions. This subtle point needs to be noted as both the real and imaginary parts of the susceptibility need to be fitted.

real part of $\chi(\nu)$, where ν is the probing frequency, ranging between 0.5 and 30 cm⁻¹. As we can see, each curve at a given frequency peaks at a temperature (T_m) between 200 and 500 K, and T_m shifts toward higher temperature as the frequency increases. In addition, $\chi(\nu)$ has a large dispersion over temperature between 200 and 600 K. Furthermore, the sudden change in susceptibility at ~ 200 K also indicates a phase transition, consistent with the partially antiferroelectric phase we have seen in previous work.³² The flat susceptibility below ~ 200 K in Fig. 3(a) is likely a feature of antiferroelectric phase.

The strong dispersion and shift of T_m shown in Fig. 3(a) raises an interesting question, that is whether the BZO/BTO superlattice can be categorized as true relaxor. To answer this question, we need the quantitative relation between T_m and ν , which is shown in Fig. 3(b). Since a reliable fitting of susceptibility versus temperature is unknown yet, we simply choose the position of maximum susceptibility as T_m , therefore causing some rough edges in Fig. 3(b). However, we verified that T_m versus ν can be fitted well with the relation $T_m = T_0 + a\sqrt{\nu}$, where a is a fitting parameter. This result clearly distinguishes BZO/BTO superlattice from disordered BZT, where the T_m versus ν follows the Vogel–Fulcher law,³¹ and shows that BZO/BTO superlattice cannot be categorized as relaxor. As a matter of fact, a generally accepted definition of relaxor is hard to find.³⁹ Bokov and Ye provided an empirical definition of relaxors, specifying that the Vogel–Fulcher law shall be followed for ferroelectrics to be taken as relaxors.² While it may not be the ultimate answer about what relaxor is, this definition does exclude BZO/BTO superlattice from being classified as relaxor, although its susceptibility shows a strong dispersion.

To understand the dispersion of T_m and why T_m versus ν follows the square root law, we further investigate the in-plane relaxation-like peak in the dielectric responses associated with Ti ions [e.g., Fig. 1(e)]. It is found that, for all temperatures above 200 K, this resonance can be well fitted with a DHO function [i.e., the second term of Eq. (1)]. Therefore, we extract the resonance frequency ν_0 and plot ν_0 versus temperature in Fig. 3(c). Below 450 K and close to the transition temperature (~ 200 K), it can be easily verified that $\nu_0 = \nu_t \sqrt{T - T_0}$ ($T_0 \simeq 200$ K), where ν_t is a fitting parameter [see the red curve in Fig. 3(c)]. This interesting feature is a phenomenon of ferroelectrics, such as Pb(Zr,Ti)O₃,³⁴ known as the softening of the soft mode, but differs significantly from the relation between the characteristic frequency of a relaxation mode and temperature in a true relaxor.^{24,31} Here the change of ν_0 is associated with the global phase transition, and is the major cause of the dispersion of the susceptibility over frequency as shown in Fig. 3(a). Finally, the deviation of ν_0 for $T > 450$ K is likely due to the influence of Zr ions, which have a strong resonance between 100 and 200 cm⁻¹ [see Fig. 1(f)].

As a comparison, Fig. 3 also includes results obtained from disordered Ba(Zr_{0.5}Ti_{0.5})O₃. Figure 3(d) is from Ref. 31 and shows the real part of the susceptibility and its

dependence on the probing frequency. In contrast to Fig. 3(a), the disordered BZT still has large susceptibility even below 200 K. Figure 3(e) is from Ref. 31 and shows that T_m versus ν can only be fitted by the Vogel–Fulcher law, i.e., $\nu = \nu_a \exp[-U/(T_m - T_{VF})]$ (ν_a and T_{VF} are constants), unlike Fig. 3(b), where a square-root law is used (i.e., $T_m = T_0 + a\sqrt{\nu}$). Finally, the resonance frequency and relaxation frequency also obey very different laws as Figs. 3(c) and 3(f) (from Ref. 24) show that the disordered system follows the Arrhenius law ($\nu = \nu_a \exp(-E_a/k_B T)$), while the superlattice follows the square-root law. All the difference shown in Fig. 3 highlights the unique properties belong to relaxors. With results from both ordered and disordered BZT systems, we may conclude that quenched disorder is a necessary condition in making a true relaxor. Without such an element: (i) there will be no susceptibility dispersion below a critical temperature (compare Fig. 3(a) to Fig. 2(a)), and (ii) the relation of T_m versus ν will not follow the Vogel–Fulcher law. Judging from these two facts, the BZO/BTO superlattice cannot be categorized as a relaxor.

4. Summary

In summary, molecular dynamics simulations are performed to obtain the complex dielectric responses of BaZrO₃/BaTiO₃ superlattice. We further analyzed the relaxation-like part of the dielectric response and find the shift of T_m versus ν of this system, however, does not follow the usual Vogel–Fulcher law that are usually obeyed by relaxors. Such results indicate that the BaZrO₃/BaTiO₃ superlattice is not relaxor. The comparison to disordered Ba(Zr_{0.5}Ti_{0.5})O₃ emphasize the importance of disorder in forming relaxors. Furthermore, given that BaTiO₃ layers in BaZrO₃/BaTiO₃ are rather independent from each other,³² it is likely that period modulation in BaZrO₃/BaTiO₃ superlattice will not strongly influence the dielectric response shown here, and neither can such system be categorized as true relaxors.

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