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Finite-Temperature Properties of Ba(Zr, Ti)O₃ Relaxors from First Principles

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A first-principles-based technique is developed to investigate the properties of Ba(Zr, Ti)O₃ relaxor ferroelectrics as a function of temperature. The use of this scheme provides answers to important, unresolved and/or controversial questions such as the following. What do the different critical temperatures usually found in relaxors correspond to? Do polar nanoregions really exist in relaxors? If yes, do they only form inside chemically ordered regions? Is it necessary that antiferroelectricity develop in order for the relaxor behavior to occur? Are random fields and random strains really the mechanisms responsible for relaxor behavior? If not, what are these mechanisms? These ab initio based calculations also lead to deep microscopic insight into relaxors.

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Relaxor ferroelectrics are characterized by some striking anomalous properties (see, e.g., Refs. [1–21] and references therein). For instance, they adopt a peak in their ac dielectric response versus temperature function while they remain macroscopically paraelectric and cubic down to the lowest temperatures [1]. Furthermore, this dielectric response deviates from the “traditional” Curie-Weiss law [22] for temperatures lower than the so-called Burns temperature [2]. Other examples of anomalous properties include the plateau observed in their static dc dielectric response at low temperatures [23,24], and the unusual temperature behavior [16] of the Edwards-Anderson parameter [25]. Determining the origin of these intriguing effects has been a challenge to scientists since the discovery of ferroelectric relaxors.

The goal of this Letter is to report ab initio based calculations that not only reproduce all the aforementioned intriguing features but also offer deep microscopic insight into relaxors.

Practically, we decided to focus on a specific relaxor, namely disordered Ba(Zr₀.₅, Ti₀.₅)O₃ (BZT) solid solutions. (BZT is also fascinating because its parent compounds are rather different: BaZrO₃ is paraelectric while BaTiO₃ is a typical ferroelectric.) Here, we develop and use a first-principles-based effective Hamiltonian approach for which a detailed description is given in the supplemental material [26–39]. The total energy of this effective Hamiltonian is used in Monte Carlo (MC) simulations to compute finite-temperature properties of BZT alloys. We use 12 × 12 × 12 (8640 atoms) or 16 × 16 × 16 (20480 atoms) supercells in which the σᵢ variables are randomly placed and kept fixed during the MC simulations, in order to mimic disordered BZT solid solutions. These two supercells provide similar results, which attest to the convergency of the simulations. The temperature T is decreased in small steps from high temperature, and up to 10⁶ MC sweeps are used to get converged statistical properties.

Here, the uᵢ, local soft-mode vectors in each five-atom cell i (uᵢ is directly proportional to the local electric dipole moment centered in cell i) and the homogeneous strain tensor ηᵢ arising from the MC simulations indicate that Ba(Zr₀.₅, Ti₀.₅)O₃ bulk remains macroscopically cubic and nonpolar for any temperature down to the lowest one investigated here (which is 5 K), which is consistent with measurements [40]. We also computed the dielectric susceptibility, at different temperatures by progressively cooling down the system, from our MC simulations via two different approaches: (i) a “direct” method for which the resulting dielectric susceptibility is denoted as χₐₒ and is calculated as the change in polarization with respect to an applied electric field (with this field practically being oriented along the [111] pseudocubic direction and having a magnitude of 10⁷ V/m); and (ii) the “correlation-function” approaches of Refs. [41,42] for which the resulting dielectric susceptibility is referred to as χₐₒ and is provided by the fluctuation-dissipation theorem via χₐₒ = \( \frac{1}{4N} \sum_{\alpha,\beta} \left[ \left\langle u_\alpha u_\alpha \right\rangle - \left\langle u_\alpha \right\rangle \left\langle u_\beta \right\rangle \right] \), where \( \left\langle u_\alpha \right\rangle \) denotes the statistical average of the product between the α and β components of the supercell average of the local mode vectors, and where \( \left\langle u_\alpha \right\rangle \) (respectively, \( \left\langle u_\beta \right\rangle \)) is the statistical average of the α (respectively, β) component of the supercell average of the local mode vectors. N is the number of sites in the supercell while V is its volume. kₑ is Boltzmann’s constant, and εₒ is the permittivity of the vacuum. Strikingly, while previous work (see, e.g., Ref. [42]) found that these two different methods provide nearly identical dielectric susceptibilities in typical ferroelectrics, Fig. 1(a)
ac electric fields having frequencies ranging between freezing temperature ranging between 100 and 140 K has susceptibility arising from the fit of saturates to a plateau for lower temperature. Both the properties in disordered BaZrO3 centered on Ti and Zr ions. Consequently, the contribution of the static (dc) dielectric response while our simulated \( \chi_{\text{CF}} \) corresponds to observed low-frequency dielectric responses of BZT relaxors—which is reminiscent of the fact that the susceptibility given by the fluctuation-dissipation theorem is nearly the ac susceptibility in the Edwards-Anderson model of spin glasses [44].

It is also important to recall that, while \( \chi_{\text{CF}} \) possesses a peak at \( T_f \), our MC simulations indicate that Ba(Zr_{0.5}Ti_{0.5})O_3 bulk remains macroscopically cubic and nonpolar for any temperature—which is consistent with what is expected for relaxors [1]. Moreover, the temperature behaviors of \( \chi_{\text{CF}} \) and \( \chi_{\text{direct}} \) allow the introduction of four different regions: namely, (1) Region I that concerns temperatures, \( T \), above \( T_b \approx 450 \) K and for which \( \chi_{\text{CF}} \) and \( \chi_{\text{direct}} \) can be nicely fitted by the Curie-Weiss formula [22]; i.e., they are both directly proportional to \( 1/[T - T_0] \) (where \( T_0 \) is practically found here to be very close to \( -120 \) K); (2) Region II that extends between \( T^* \approx 240 \) K and \( T_b \) for which \( \chi_{\text{CF}} \) increases as the temperature decreases but no longer follows the Curie-Weiss law, unlike \( \chi_{\text{direct}} \); (3) Region III that is located in between \( T_f \) and \( T^* \) for which neither \( \chi_{\text{CF}} \) nor \( \chi_{\text{direct}} \) obey the Curie-Weiss law; and (4) Region IV that occurs for temperatures lower than \( T_f \), and for which \( \chi_{\text{CF}} \) decreases as \( T \) is reduced while \( \chi_{\text{direct}} \) is nearly constant there. \( T_b \) can be assigned to be the Burns temperature [2] while \( T^* \) can be thought of as being the novel critical temperature recently found in relaxors [11,12]. The facts that \( \chi_{\text{CF}} \) follows the Curie-Weiss law only for temperatures above the Burns temperature and that this Burns temperature is of the order of 450 K have both been observed in Ba(Zr_{0.5}Ti_{0.5})O_3 [40]. Similarly, a negative \( T_0 \) Curie temperature has also been experimentally extracted in BZT samples [40].

Figure 1(b) reports the temperature evolution of the so-called Edwards-Anderson parameter [25], \( q_{\text{EA}} \), that is calculated as \( q_{\text{EA}} = \langle \mathbf{u}_i \mathbf{u}_j \rangle / j \), where the inner averaging is made over the \( t \) Monte Carlo sweeps while the outer averaging is made over the \( i \) lattice sites. The behavior of the simulated \( q_{\text{EA}} \) of BZT bulk versus temperature bears some striking resemblance with those predicted by the spherical random bond–random field model and measured from nuclear magnetic resonance for the PbMg_{1/3}Nb_{2/3}O_3 relaxor [16]. For instance, (1) it is small and increases nearly linearly with decreasing temperature at high temperatures (in Region I); (2) it is large and also increases linearly with decreasing temperature at low temperatures (in Region IV); and (3) the \( q_{\text{EA}} \)-versus-\( T \) function is curved upward in between (in Regions II and III). Figure 1(b) also reveals that the temperature behavior and values of the overall Edward-Anderson parameter (for any temperature) almost entirely originate from the electric dipoles centered on Ti ions. Consequently, the contribution of the dipoles belonging to BaZrO3 unit cells to the total reveals that it is not the case for disordered BZT: \( \chi_{\text{CF}} \) exhibits a peak around \( T_f \approx 130 \) K, while \( \chi_{\text{direct}} \) increases when decreasing the temperature down to \( T_f \) and then saturates to a plateau for lower temperature. Both the temperature behavior of \( \chi_{\text{CF}} \) and the temperature at which \( \chi_{\text{CF}} \) is maximum are fully consistent with the dielectric experiments of Ref. [40] in Ba(Zr_{0.5}Ti_{0.5})O_3 relaxors under ac electric fields having frequencies ranging between 100 Hz and 100 kHz. Moreover, the depicted behavior of \( \chi_{\text{direct}} \) is exactly the one expected for the perfectly static dielectric response of relaxors [23,24], which allows us to identify \( T_f \) as the so-called freezing temperature [7–10] (a freezing temperature ranging between 100 and 140 K has been reported for BZT systems [43], in good agreement with our value of \( \approx 130 \) K). Our \( \chi_{\text{direct}} \) thus provides the static (dc) dielectric response while our simulated \( \chi_{\text{CF}} \)
Edwards-Anderson parameter nearly vanishes. Other dramatic differences between local properties associated with Zr versus Ti atoms are revealed in Fig. 1(c), which shows that not only is the average magnitude of the local dipoles centered on Zr ions much smaller than those centered on Ti ions, but its temperature behavior is also strikingly different: the dipoles belonging to BaZrO$_3$ unit cells continuously shrink on average as the temperature is reduced, while the dipoles located inside BaTiO$_3$ cells suddenly become enlarged with decreasing temperature below $T_f$. Electric diffraction measurements [39] and a model emphasizing the importance of the BaTiO$_3$ soft mode on the relaxor behavior of BZT [45] are also consistent with our prediction that the Ti sites carry much larger dipoles than the Zr sites. Moreover, the results from Fig. 1(c) imply that, at the lowest temperatures, the Ti atoms displace on average about 0.16 Å, while the Zr atoms move by 0.03 Å from their cubic, equilibrium positions. Such numbers are in remarkable agreement with the values of 0.17 and 0.03 Å, respectively, obtained by the first-principles calculations of Ref. [46] for a BZT supercell containing 135 atoms [47].

Let us now focus on Fig. 2, which displays dipolar snapshots within a given $(y, z)$ plane at different temperatures, in order to gain a microscopic understanding of relaxors. Figure 2(a) reveals that Region I consists of randomly oriented dipoles that are centered on Ti ions and that are surrounded by much smaller dipoles located inside BaZrO$_3$ cells. As indicated in Fig. 2(b), some of these Ti sites act as nuclei to the formation of small clusters inside which the dipoles begin to be parallel to each other in Region II. We numerically found that the polarization of these small clusters in Region II does not automatically lie along a $(111)$ direction. For instance, the average direction of the local modes inside the bottom cluster of Fig. 2(b) is different: the dipoles belonging to Ti and Zr ions, respectively.

[Figure 2: Snapshots of the dipolar configurations in a given $(y, z)$ plane for different temperatures. Panels (a), (b), (c), (d), (e), and (f) correspond to temperatures of 550 K (Region I), 250 K (Region II), 150 K (Region III), 100 K (Region IV), 50 K (Region IV) and 10 K (Region IV), respectively. Blue colors and red colors indicate that the corresponding local modes are centered on Ti and Zr ions, respectively.]
supercell, \( \mathbf{k}_{\text{max}} = \frac{2\pi}{a_{\text{lat}}} (-y + z) \), where \( a_{\text{lat}} \) is the lattice constant of the five-atom primitive cell and where \( y \) and \( z \) are unit vectors along the \( y \)- and \( z \)-axes, respectively. Figure 1(d) shows the temperature evolution of the square of the Fourier transform of the local dipoles configuration at \( \mathbf{k}_{\text{max}} \). One can clearly see that, in Regions I and II, this quantity is nearly zero. On the other hand, it increases when the temperature decreases below \( T^* \) while still remaining fairly small (around 1.5% of the total spectra gathering the Fourier transforms at all possible \( k \)-points, at 5 K). We interpret such latter results as indicative that the different nanopolar regions slightly interact in Regions III and IV in an antiferroelectriclike (or incommensurate [50] or dipolar-wave-like) fashion. Interestingly, antiferroelectricity has been previously reported in some relaxor systems [14,15].

Let us now compute the correlation between Ti dipoles (we decided to focus on Ti-Ti dipolar correlations because Fig. 2 revealed that the polar clusters only contain Ti sites and because Fig. 1(b) shows that the overall Edwards-Anderson parameter mainly only originates from Ti dipoles). This correlation is practically defined by \( \theta \left( \mathbf{r} \right) = \frac{1}{N_T \sum_{i \in \text{NTi}} \mathbf{u}_i \cdot \mathbf{u}_{i+r} \quad \text{where the index} \ i \ \text{runs over all the} \ N_T \ \text{Ti sites of the system and where} \ \mathbf{u}_i \ \text{and} \ \mathbf{u}_{i+r} \ \text{are the local modes in cell} \ i \ \text{and in the cell centered on the Ti atom (if any) distant from} \ \mathbf{r} \ \text{from the cell} \ i, \ \text{respectively} \ [51]. \) A value of 1 (respectively, \( -1 \)) for \( \theta \left( \mathbf{r} \right) \) for a given \( \mathbf{r} \) would indicate that Ti dipoles and their neighboring Ti dipoles distant from \( \mathbf{r} \) are aligned along the same (respectively, opposite) direction. Figure 1(c) shows the value of \( \theta \left( \mathbf{r} \right) \) for various representative \( \mathbf{r} \) vectors, as a function of temperature. One can see that, in Region I and on average, the Ti dipoles are only (and slightly) correlated with the Ti dipoles centered at their first nearest neighbor cells. Such a correlation further increases in strength when the polar nanoclusters form and become greater in size and in polarization, as the temperature is reduced in Regions II, III, and IV. Second- and third-nearest neighbors also begin to be more correlated on average as the temperature decreases in Regions III and IV. Interestingly, a significant anticorrelation (see the negative sign of the correlation) between Ti dipoles that are distant by three lattice constants along the \( z \)- (or \( x \)- or \( y \)-) axis also strongly develops in Regions III and IV, which reinforces the previous finding that antiferroelectriclike interactions exist within the BZT relaxor system. Note that the supplemental material [26] also provides and discusses the \( \theta \left( \mathbf{r} \right) \) function for all the \( \mathbf{r} \)-vectors lying in the \( (y, z) \) plane at 10 K.

A particularly important feature of our scheme is that we can switch on and off some interactions in order to determine their effect on physical properties. We numerically found that turning off random fields and random strains does not significantly affect the results shown in Fig. 1 and 2, which contrasts with a common belief on the microscopic origins of relaxors [4,16,17] while being more consistent with models proposed for the homovalent (K, Li)TaO\(_3\) relaxor [52,53]. On the other hand, our computations reveal that it is the difference in ferroelectric strength between Ti and Zr ions that leads to the relaxor behavior in BZT. As a matter of fact, annihilating such differences in the simulations leads to (1) \( \chi \) direct and \( \chi \) CF being equal to each other and continuously decreasing as the temperature decreases down to 0 K (with the system remaining cubic and nonpolar), (2) the Edwards-Anderson parameter being around 10 times smaller than the one depicted in Fig. 1(b) at low temperature, and (3) the polar nanoclusters disappearing. It should also be emphasized that our simulation results depicted in Figs. 1 and 2 imply that relaxor behavior can occur in BZT even if no large chemically ordered region exists in that system (since our computations were performed on disordered solid solutions). Such a finding seems to contrast with models recently proposed to explain the relaxor behavior of heterovalent Pb(Sc, Nb)\(_3\)O\(_3\) and Pb(Mg, Nb)\(_3\)O\(_3\) alloys [13], while agreeing with a study [39] downplaying the role of chemical short-range ordering on the formation of polar nanoregions in BZT. In fact, our simulations indicate that the relaxor behavior already occurs in disordered BZT solid solutions because some regions of space can be more Ti rich than others because of the random process of assigning sites in a disordered solid solution. Such a feature bears resemblance to the Anderson localization phenomenon for which electronic wave functions become localized in a region of space [of an overall disordered \( (A', A'') \) solid solution] that is much richer in \( A' \) than in \( A'' \) [54]. Finally, we also increased the antiferroelectriclike interactions (by playing with the so-called \( j_5 \) short-range coefficient [27]). We found that such an increase leads to a shift towards higher temperatures of the peak of \( \chi \) CF, in addition to enhancing at low temperatures (i) the Edwards-Anderson parameter, (ii) the average magnitude of the local modes centered on Ti ions, (iii) the square of the Fourier transform of the local dipoles configuration at \( \mathbf{k}_{\text{max}} \), and (iv) the strength of the anticorrelation between Ti dipoles that are distant by three lattice constants along the \( z \)- (or \( x \)- or \( y \)-) axis. Such findings emphasize the importance of the antiferroelectriclike interactions between Ti-rich nanopolar clusters for the relaxor behavior.

We therefore hope that our study helps in achieving a better understanding of the fascinating relaxor ferroelectrics. In order to further enhance such understanding, future studies could examine the influence of static and dynamic (GHz–THz) electric fields [20,21] on the behaviors of BZT materials, and determine if the results found here also hold for heterovalent relaxors [such as Pb(Sc, Nb)O\(_3\) and Pb(Mg, Nb)O\(_3\)].

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