

Fano resonance in lead-free relaxor Ba(Zr,Ti)O₃

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In many different physical systems, the interference of a discrete state with a continuum of states results in a Fano resonance. Here, we use an *ab-initio* molecular dynamic scheme to reveal such resonance between the bare optical phonon mode of the Zr sublattice (the discrete state) and the bare optical phonon mode of the Ti sublattice (the continuum of states) in disordered lead-free Ba(Zr,Ti)O₃ relaxor [1]. In addition, a terahertz relaxation mode reflecting reorientations of Ti dipoles and showing an Arrhenius-like behavior is predicted, in agreement with experiments.

Canonical relaxor ferroelectrics are a special class of material that have broad dielectric response over a large temperature range, which are also strongly frequency dependent. Because of their large dielectric permittivity, property measurements in their GHz–THz range are challenging and, as a result, very few data are currently available for this frequency range [2–6]. Here, we investigate, analyze and compare with experiments the complex dielectric response of disordered lead-free Ba(Zr,Ti)O₃ (BZT) relaxor numerically obtained in the terahertz regime, via a combination of a first-principles-based effective Hamiltonian [7–9] and a molecular dynamics (MD) technique [10, 11]. One particular feature of BZT is that it is also experimentally known [6] to demonstrate a separate relaxation mechanism at the frequencies that are in the order of a few cm⁻¹, which are accessible by the present simulations. BZT has also been selected here because recent simulations [7–9] did reveal the importance of polar nanoregion (PNRs, inside which Ti dipoles are parallel to each other) and the existence of all three known characteristic temperatures of relaxors (i.e., the Burns temperature $T_B \simeq 450$ K, $T^* \simeq 240$ K, and the freezing temperature $T_f \simeq 130$ K).

The studied material is made of 50% of Zr and Ti ions that are randomly distributed inside a 12×12×12 supercell (8,640 atoms). The latter is periodic along the *x*-, *y*- and *z*-axes, which lie along the pseudocubic [100], [010] and [001] directions, respectively. We perform effective-Hamiltonian-based MD simulations [10, 11] to obtain complex dielectric responses of the disordered BZT for temperatures between 10 K to 1000 K. The complex electric susceptibility $\chi_{\alpha\beta}(\nu)$, can be obtained using the following equation:

$$\chi_{\alpha\beta}(\nu) = \frac{1}{\varepsilon_0 V k_B T} \left[\langle d_\alpha(t) d_\beta(t) \rangle + i 2\pi\nu \int_0^\infty dt e^{i2\pi\nu t} \langle d_\alpha(t) d_\beta(0) \rangle \right] \quad (1)$$

where ν is the frequency while α and β define Cartesian components, V is the volume of the chosen supercell and ε_0 is the vacuum permittivity. $\mathbf{d}(t)$ is the electric dipole moment of the system at time t , and $\langle \dots \rangle$ represents thermal averages. Due to the complexity of the system, the total dielectric response of BZT is rather challenging to fit. To solve this problem, we use the fact that the total electric dipole moment, \mathbf{d} , of the system in Eq. (1) consists of two parts $\mathbf{d} = \mathbf{d}^{\text{Zr}} + \mathbf{d}^{\text{Ti}}$, where \mathbf{d}^{Zr} (respectively, \mathbf{d}^{Ti}) is the dipole moment originating from the electric dipoles centered on Zr (respectively, Ti) sites, to obtain and fit the constitutional dielectric responses, $\chi_{\alpha\beta}^{\text{Zr,Zr}}$, $\chi_{\alpha\beta}^{\text{Ti,Ti}}$, which represent the “sole” contributions of the Zr-centered and Ti-centered sites, respectively, and $\chi_{\alpha\beta}^{\text{Ti,Zr}}$ that quantifies the role of the correlations between the Zr and Ti-centered sites in that total response.

We first concentrate on the MD data for the imaginary part of these different dielectric responses at $T = 900$ K. Figure 1 shows that the imaginary part of $\chi^{\text{Zr,Zr}}$ consists of a single narrow peak centered around 155 cm⁻¹, while $\text{Im}(\chi^{\text{Ti,Ti}})$ appears to have two (rather than one) significant broad peaks centered around 130 cm⁻¹ and 250 cm⁻¹, respectively. However, it is known that there is no PNR at 900 K [7], which implies that the anisotropy of PNRs can *not* be the cause of the two peaks seen in $\text{Im}(\chi^{\text{Ti,Ti}})$. To search for the mechanism that is responsible for the occurrence of these two peaks, we consider two linearly *coupled* damped harmonic oscillators (DHO) – one of them (with bare frequency $\nu_{\text{Ti},0}$, bare damping constant $\Gamma_{\text{Ti},0}$, and bare plasma frequency $\Omega_{\text{Ti},0}$) representing the intrinsic, bare dynamical response of the Ti sublattice, the other (with $\nu_{\text{Zr},0}$, $\Gamma_{\text{Zr},0}$, and $\Omega_{\text{Zr},0}$) representing the intrinsic, bare dynamical response of the Zr sublattice. Application of this coupled model to the simulated dielectric response at 900 K is shown in Fig. 1. We find that: (i) the bare Zr oscillator is described by $\Omega_{\text{Zr},0} = 450$ cm, $\nu_{\text{Zr},0} = 170$ cm⁻¹, and $\Gamma_{\text{Zr},0} = 19$ cm⁻¹; (ii) the bare Ti oscillator is described by $\Omega_{\text{Ti},0} = 1250$ cm⁻¹, $\nu_{\text{Ti},0} = 193$ cm⁻¹, and $\Gamma_{\text{Ti},0} = 205$ cm⁻¹; and (iii) the coupling constants are $\Delta_{\text{Ti,Zr}} = -8435$ cm⁻¹ and $\Gamma_{\text{Ti,Zr}} = -41$ cm⁻¹. The resulting

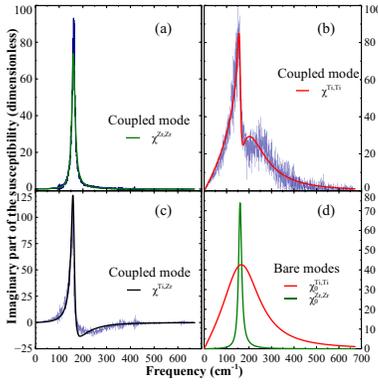


FIG. 1. Imaginary part of different dielectric responses of BZT is shown as a function of frequency at $T = 900$ K.

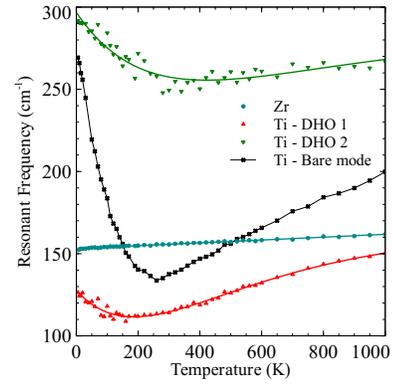


FIG. 2. Resonant frequencies of the DHO modes associated with the Zr and of Ti sublattices, as a function of temperature.

bare dielectric response, $\chi_0^{\text{Zr,Zr}}$ and $\chi_0^{\text{Ti,Ti}}$, associated with these parameters, are shown in Fig. 1(d). It is important to realize that the bare Ti oscillator is clearly much more damped than the Zr one and that these two oscillators overlap in frequency. As a result, it is clear that the mechanism we are looking for is the so-called Fano resonance, for which the broad bare Ti response provides the background component while the sharp bare Zr response provides the discrete state (that are the two ingredients for the Fano resonance). To further demonstrate that the proposed Fano resonance exists in BZT relaxors, we performed additional MD simulations in which the resonance of $\chi^{\text{Zr,Zr}}$ is artificially tuned to 450 cm^{-1} , that is far away from the (bare) resonance of $\chi_0^{\text{Ti,Ti}}$. In such a case, we numerically found that, e.g., $\chi^{\text{Ti,Ti}}$, has now only *one* (broad) peak rather than two, which confirms the adequacy of the Fano interference in our investigated system. Moreover, Figure 2 reports the temperature evolution of the resonant frequencies of all the DHO modes associated with the Zr and Ti dielectric responses, as well as the bare resonant frequency $\nu_{\text{Ti},0}$ associated with $\chi_0^{\text{Ti,Ti}}$ (note that the bare resonant frequency $\nu_{\text{Zr},0}$ associated with $\chi_0^{\text{Zr,Zr}}$ is very similar to $\nu_{\text{Zr-Zr}}$, and not shown for clarity). Interestingly, the characteristic temperatures of BZT, T_f , T_B and T^* , reveal themselves in Fig. 2, either as the crossing of bare frequencies or the temperature at which $\nu_{\text{Ti},0}$ hits its minimum. However, whether this is a coincidence for BZT or a general feature of relaxors needs further investigation.

In addition to the Fano resonance, our simulations also predict a thermally activated THz relaxation mode, in agreement with experiment [6], which follows an Arrhenius law above the freezing temperature. Finally, if time allows, we will show that our computations can naturally reproduce and explain at a microscopic level the frequency dependence of the peak in the dielectric response of BZT, which is often taken as the defining property of a relaxor.

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