Emergence of central mode in the paraelectric phase of ferroelectric perovskites

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THz-range dielectric spectroscopy and first-principle-based effective-Hamiltonian molecular dynamics simulations were employed to elucidate the dielectric response in the paraelectric phase of (Ba,Sr)TiO\textsubscript{3} solid solutions. Analysis of the resulting dielectric spectra suggests the existence of a crossover between two different regimes: a higher-temperature regime governed by the soft mode only versus a lower-temperature regime exhibiting a coupled soft mode/central mode dynamics. Interestingly, a single phenomenological coupling model can be used to adjust the THz dielectric response in the entire range of the paraelectric phase (i.e., even at high temperature). We conclude that the central peak is associated with thermally activated processes, and that it cannot be discerned anymore in the dielectric spectra when the rate of these thermally activated processes exceeds certain characteristic frequency of the system.

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It is well known that the static permittivity of ferroelectric materials is related to frequencies of all polar phonon modes through the Lyddane-Sachs-Teller formula \cite{1}. Near the phase transition, however, an additional low-frequency mode has to be often taken into account – the so-called central mode \cite{2,4,8,9}. A generic reason for this additional Debye-type excitation seems to be large-amplitude fluctuations between quasi-stable off-center ionic positions. Existence of such intrinsic central mode could be very clearly demonstrated, e.g., below the cubic-tetragonal phase transition $T_C$ of BaTiO\textsubscript{3} \cite{2}.

Similar central mode (CM) is also known to exist in the paraelectric phase. Phenomenological theories of the paraelectric CM have been developed by several authors \cite{2,6}. All these approaches lead to a coupled relaxator-oscillator dielectric response. However, an important question has been left open so far: whether the CM persists up to the highest temperatures, or rather it progressively disappears, or whether it disappears at some well-defined temperature $T_{CM}(>T_C)$.

Unfortunately, it is much more difficult to obtain a clear-cut experimental evidence for the dielectric CM in the cubic perovskite phase \cite{2,4,8,9}. The characteristic frequencies of the soft phonon-oscillator and CM in K\textsubscript{NbO}\textsubscript{3} and BaTiO\textsubscript{3} are so broad and close together that they can hardly be disentangled. The difficulty of the experimental analysis of the dielectric spectra of K\textsubscript{NbO}\textsubscript{3} and BaTiO\textsubscript{3} is caused, at least partly, by intrinsically large phonon damping factors, related to the fact that $T_C$ is quite high in these compounds (about 700 and 400 K, respectively). Therefore, it is of interest to study the CM also in the ferroelectric compounds in which the phase transition occurs at lower temperatures, which can be achieved for example by mixing BaTiO\textsubscript{3} and K\textsubscript{NbO}\textsubscript{3} with suitable incipient ferroelectrics, namely SrTiO\textsubscript{3} and KTaO\textsubscript{3}, respectively.

Here, we describe a combined experimental and theoretical study of the technologically-relevant mixed Ba\textsubscript{x}Sr\textsubscript{1-x}TiO\textsubscript{3} system (BST) aimed to establish the characteristic temperature trends in the model parameters of the relaxator-oscillator dielectric response in the polar perovskites. It turns out that this phenomenological theory allows to “easily” understand the existence of the temperature $T_{CM}$, at which the CM in the dielectric spectra is appearing or disappearing.

Basic dielectric properties of BST solid solutions and the concentration diagram of this system were thoroughly discussed, see e.g. Refs.\cite{10,11} and references therein. Experiments discussed below were carried out with a set of high-density BST ceramics with Ba:Sr ratio ranging from $x=0$ to $x=1$, prepared by methods described elsewhere (see Refs.\cite{12,13}). Low-frequency permittivity obtained from standard dielectric measurements (10 kHz) in the paraelectric phase was fitted to a Curie-Weiss law

$$\varepsilon(0)^{-1} = (T - T_0)/C .$$

As expected \cite{2,10}, Curie constants were of the order of $10^5 K$ for all concentrations, while the extrapolation temperature $T_0(x)$ turned out to be strongly dependent on the concentration (see the inset of Fig. 1a).

These findings may suggest that at a fixed temperature interval above the extrapolation temperature $T_0$, the static permittivity is roughly independent of $x$. However, this is not the case for the THz-range dielectric spectra of BST ceramics. In Fig. 1a, we compare dielectric loss spectra obtained similarly as in Refs.\cite{12,13} from simultaneous fits to time-domain THz transmission and far-IR reflectivity spectra. Although all these spectra are obtained at 100 K above the corresponding temperature $T_0$, we can see a clear crossover between two rather
distinct regimes: a broad-band regime for BaTiO$_3$-rich compounds, and a narrow-band regime for SrTiO$_3$-rich compounds. The narrow response band can be easily adjusted with a single damped harmonic oscillator (DHO) model, while the broad band suggests a more complex spectral shape, such as that of the coupled relaxator-oscillator model.

In order to prove the intrinsic origin of this spectral broadening phenomenon, we have also calculated dielectric spectra of disordered BST solutions by conducting molecular dynamics (MD) simulations using the effective Hamiltonians of Ref. 11 – as previously reported in Refs. 7, 9. Chemical disorder in the Ba and Sr ion sublattice has been included directly by specifying randomly chosen Ba and Sr ion positions within a simulation supercell representing a 12x12x12 perovskite formula units of BST, assuming periodic boundary conditions. To verify that the results are independent of the particular configuration, simulations were also carried out for several different configurations.

The resulting spectra (see Fig.1b) are quite monotonously varying with the average Ba concentration in the simulated supercell, even though the Ba ion distribution is obviously different for each concentration. This also confirms that the observed trends are driven by the overall concentration, rather than by the degree of the occupational disorder. As consistent with the experiments, the predicted static dielectric permittivity above $T_C$ obeyed the Curie-Weiss law (Eq. 1). Moreover, simulated loss spectra for temperatures about 100 K above $T_0$ indeed confirmed a similar broadening for BaTiO$_3$-rich compounds as in the measurements (see Fig.1b).

Despite of this considerable broadening, spectra of Fig.1 do not show a very clear 2-maximum dielectric loss response, such as the one observed in the A$_1$ spectra of the tetragonal phase of BaTiO$_3$ single crystal [7]. We expect that CM and soft mode (SM) components are much better separated in the spectra within the first few tens of K above $T_C$. However, in this temperature range the THz measurements were not feasible even with very thin ceramic samples because they become too opaque for THz radiation.

Motivated by this difficulty, we have calculated dielectric spectra of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST50) in a broad range of frequencies and temperatures down to the vicinity of the ferroelectric phase transition using the effective-Hamiltonian approach of Ref. 11. In order to obtain well-behaved smooth dielectric spectra especially closer to $T_0$ in the low THz regime, MD time-step was chosen to be 0.5fs and the simulations were conducted for a length of 13.2 ns in order to obtain 10000 samples for averaging the autocorrelation functions [8]. Figure 2 displays the frequency dependence of the imaginary part of dielectric permittivity derived from MD simulations at 270 K ($C = 0.6 \times 10^5$ K and $T_0 = 245$ K for simulated BST50). The presence of a lower frequency Deyeb-like CM in addition to the higher frequency SM is clearly seen there.

To account for the simultaneously appearing SM and CM, we have used the coupled oscillator-relaxator model
The quantities $\Omega_D$, $\omega_D$, $\Gamma_D$ related to the CM have analogous meaning as $\Omega_S$, $\omega_S$, $\Gamma_S$. The coupling term $\Delta$ can be chosen positive. Indeed, in the Debye-relaxator limit ($\omega \ll \Gamma_D$ and $\omega \ll \omega_D$) the $\omega^2$ term can be neglected against $\omega_D^2 - i\omega\Gamma_D$ and the above matrix reduces to that of the coupled relaxator-oscillator model [2]. In this case, four parameters $\Omega_D$, $\omega_D$, $\Gamma_D$ and $\Delta$ can be replaced by only three parameters: the relaxation frequency $\gamma_D$, the coupling frequency $\delta$, and an auxiliary frequency $\rho$

$$\gamma_D = \omega_D^2/\Gamma_D, \quad \delta = \Delta/\omega_D, \quad \rho = \omega_D\Omega_S/\Omega_D. \quad (5)$$

With these substitutions (Eq. 5) and for $\omega \ll \Gamma_D$, $\omega \ll \omega_D$, and $\Omega_S \gg \Omega_D$ or $\rho \gg \delta$, the expression of Eq. 3 reduces to the formula of Eq. 2.

Previously, several authors [2, 4, 6] treated the problem of paraelectric CM in perovskites and derived a frequency dependence of the dielectric permittivity in the form equivalent to eqs. 2 or 3. Common assumption in all these approaches [2, 4, 6] is that the Curie-Weiss behavior of the static permittivity results from the Cochran-like temperature dependence of the SM frequency $\omega_S^2 = A/(T - T_0)$ with a "Cochran" temperature $T_0 < T < T_C$. This is indeed well obeyed here (with $A = 50 \text{cm}^{-2}\text{K}^{-1}$ and $T_C = 165 \text{K}$ for BST50, see Fig. 3). However, the implications for the temperature dependence of $\delta$ and $\gamma_D$ are quite different among these models. In the spirit of Ref. 2 one could assume that $\delta$ and $\gamma_D$ either do not change with temperature since the bare D-mode is not contributing to the ordering mechanism, or perhaps, that (model A)

$$\delta^2 = \text{const}. \quad (6)$$

and

$$\gamma_D \sim 1/T, \quad (7)$$

when assuming in Eq. 5 that the D-mode damping increases with the temperature like $\Gamma_D \sim T$. Bare pseudospins in the model of Ref. 2 are considered as freely fluctuating bistable dipoles forming an ideal paraelectric gas with Arrhenius relaxation law, which leads to (model B)

$$\delta^2 = \alpha_0/T \quad (8)$$

and

$$\gamma_D = \gamma_\infty \exp \left[-U/kT\right], \quad (9)$$

where $U$ is a potential barrier and $\gamma_\infty$ is an attempt frequency. In a similar model applied to BaTiO$_3$ in Ref. 5 one assumes that bare pseudospin subsystem would order at a finite temperature $T_L < T_C$, with $T_L \approx T_C$ and the resulting formulas for $\delta$ and $\gamma_D$ read (model C)

$$\delta^2 = \alpha_0/(T - T_L) \quad (10)$$

where $T$ is a potential barrier and $\gamma_\infty$ is an attempt frequency. In a similar model applied to BaTiO$_3$ in Ref. 5 one assumes that bare pseudospin subsystem would order at a finite temperature $T_L < T_C$, with $T_L \approx T_C$ and the resulting formulas for $\delta$ and $\gamma_D$ read (model C)
and

\[ \gamma_D = \gamma_\infty \exp \left( \frac{U}{kT} \right) \frac{T - T_1}{T} \].

(11)

Comparison of the anticipated temperature trends with the outcome of our MD simulations shown in Fig. 3 indicates that none of the above three models is fully satisfactory. As a matter of fact, the MD results suggest that the coupling term \( \delta \) is constant (or it perhaps slightly increases with the increasing temperature), which is compatible with the model A only, while the increasing \( \gamma_D \) rather supports the thermally activated flipping, assumed in models B or C. Tentatively, we have fitted the temperature dependence of \( \gamma_D \) to the Arrhenius law of Eq. 9 in the 260-400K temperature range. It gives reasonable values of \( U = 84 \text{ meV} \) and \( \gamma_\infty = 1160 \text{ cm}^{-1} \).

In fact, it turns out that the BST50 dielectric spectra can be well fitted at all temperatures (i.e., even above \( T_{\text{CM}} \)) when keeping \( \delta = 57 \text{ cm}^{-1} \) and \( \gamma_D \) described by the aforementioned Arrhenius law (fitted parameters are shown by open symbols in Fig. 3). In other words, the coupled relaxor-oscillator model (Eq. 2) can be used in the whole temperature range above \( T_C \), without any particular discontinuity in the temperature course of the model parameters near the temperature \( T_{\text{CM}} \).

So why does the CM seem to "disappear" from the BST50 spectrum at \( T_{\text{CM}} \)? In order to understand this behavior, it is convenient to consider the formula of Eq. 2 as the response of a DHO with a frequency-dependent self-energy term

\[ \hat{\Pi}(\omega) = -\frac{\delta^2 \gamma_D^2}{\gamma_D^2 + \omega^2} - i \omega \left( \Gamma_S + \frac{\delta^2 \gamma_D}{\gamma_D^2 + \omega^2} \right) \].

(12)

From this expression, it is obvious that the simple DHO formula is recovered when \( \gamma_D \gg \delta^2 / \Gamma_S \), since in this case the imaginary part of the self-energy becomes simply \( \text{Im}[\Pi] = -\omega \Gamma_S \). Therefore, it is reasonable to define the temperature \( T_{\text{CM}} \) as the temperature at which \( \delta^2 \approx \gamma_D \Gamma_S \). Since the temperature dependence of \( \gamma_D \) is steep, the temperature-driven crossover between \( \gamma_D \ll \delta^2 / \Gamma_S \) and \( \gamma_D \gg \delta^2 / \Gamma_S \) is quite sharp. With the data of Fig. 3, this crossover temperature is about \( T_{\text{CM}} \approx 360 - 370 \text{ K} \). Moreover, in case of Arrhenius law for \( \gamma_D \), one obtains

\[ T_{\text{CM}} \approx \frac{U}{k \ln(\gamma_\infty \Gamma_S / \delta^2)} \],

(13)

showing that \( T_{\text{CM}} \) scales with the activation energy \( U \).

This kind of crossover temperature \( T_{\text{CM}} \) likely bears some resemblance with the so-called Burns temperature and \( T^* \) temperature, that have been observed in some complex perovskite materials [18–20], since they all may be associated with change of dynamics.

In summary, we provide interpretation of experiments and MD simulations suggesting that permittivity of BST system in the paraelectric phase shows a crossover between a high-temperature spectrum with a simple SM and a lower-temperature spectrum with a more complex shape involving an additional CM that is coupled to the SM. Analysis of MD simulations allowed us to select convenient formula for the temperature evolution of the model parameters, leading to a deviation with respect to previous theoretical predictions when CM and SM are coupled. As a matter of fact, these MD results indicate a thermally activated dynamics in a postulated pseudospin subsystem and their almost temperature-independent pseudospin-phonon coupling coefficient. Furthermore and interestingly, the dielectric spectra of BST50 from MD simulations could also be analyzed using this original coupled CM-SM model at \( T > T_C \), in the high-temperature regime. As a result, the appearance of the CM in the dielectric spectra is understood as a crossover between fast and slow pseudospin dynamics. Arrhenius-type temperature dependence of bare pseudospin dynamics allows to understand the abrupt change of the spectrum at this crossover, which thus appears almost as a phase transition.

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