Relaxors exhibit unique dielectric response properties such as diffuse phase transitions and strong dispersion of the dielectric constant. The origin of these properties is still not fully understood. Here, we review our work on using first-principles-based methods to elucidate the connections between composition, local structure and dynamics in Pb-based relaxors.

Keywords: Relaxor; dielectric response; dynamics; relaxation time.

1. Introduction

Relaxor ferroelectrics have been used in a variety of applications, such as piezoelectrics, capacitors, and transducers. Relaxors exhibit broadened permittivity peaks with dispersion of the frequency-dependent dielectric constant. In particular, $T_{\epsilon,\text{max}}$, the temperature maximum of the $\epsilon(\omega)$, follows the Vogel–Fulcher relationship described by

$$\omega = \omega_0 e^{-U_0/k_B(T_{\epsilon,\text{max}}-T_f)},$$

where $\omega$ is a frequency of applied field, $\omega_0$ is an attempt frequency, $T_f$ is the freezing temperature at which the relaxation frequency vanishes, $k_B$ is the Boltzmann constant, and $U_0$ is the Vogel–Fulcher activation barrier.\(^1\) Following the work of Burns and Dacol,\(^2\) the unusual dielectric and structural properties of relaxors have been ascribed to the appearance of polar nanoregions (PNR) inside the nonpolar matrix at the Burns temperature $T_b$ above the Curie temperature $T_c$. For some years, the PNR were thought to be formed due to the presence of nanoscale compositional inhomogeneities. Such inhomogeneities would lead to strong random electric fields and a smearing out of the ferroelectric
phase transition.\textsuperscript{3,4} In this theory, the dipole moments of PNRs rotate slowly inside a nonpolar region and give rise to the dependence of the dielectric constant on frequency. However, reports of strong relaxor behavior in perovskites with long-range B-cation ordering (for which nanoscale compositional variation is therefore impossible) cast strong doubt on this model and suggest that a local-structure-based approach is more fruitful for understanding the relaxor behavior.\textsuperscript{5–7} In this paper, we review some of our earlier works\textsuperscript{8,9} and report our recent works on first-principles-based modeling of relaxors.

2. Methodology

The details of the first-principles density functional theory (DFT) calculations are given in Refs. 10–12. The molecular dynamics (MD) simulations for 0.75 Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–0.25 PbTiO\textsubscript{3} (0.75 PMN–0.25 PT) were performed with the bond valence (BV) model atomistic potential described in Ref. 13. The simulations were carried out in a 6 × 6 × 6 supercell and with a 1 fs timestep using the Nosé–Kleemann thermostat.

3. Results

In order to understand how compositional variations affect relaxor behavior, we first quantify the relative strength of dielectric dispersion in different materials by using $\Delta T_{\text{disp}}$, defined as

$$\Delta T_{\text{disp}} = T_{\text{c,max}}(10^2 \text{ Hz}) - T_{\text{c,max}}(10^6 \text{ Hz}),$$ \hspace{1cm} (2)

where $T_{\text{c,max}}(10^2 \text{ Hz})$ and $T_{\text{c,max}}(10^6 \text{ Hz})$ are the temperatures at which the dielectric constant is maximal for $\omega = 100 \text{ Hz}$ and $\omega = 1 \text{ MHz}$, respectively. The magnitude of $\Delta T_{\text{disp}}$ is directly related to $U_0$ in the Vogel–Fulcher formula and is equal to zero for normal ferroelectrics such as PT. Furthermore, in solid solutions of relaxor end-members and normal ferroelectrics such as (1 – $x$) Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} – $x$PbTiO\textsubscript{3} (PMN–PT) and (1 – $x$) Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} – $x$ Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3} (PMN–PSN), $\Delta T_{\text{disp}}$ exhibits a smooth monotonic trend from high values on the relaxor side of the phase diagram to zero on the ferroelectric side. This makes $\Delta T_{\text{disp}}$ suitable to serve as an order parameter for the compositional phase transitions between relaxor and ferroelectric phases. The characterization of relaxor behavior by a single parameter makes it possible to correlate composition and local structural properties with dielectric response. We examine the trends in $\Delta T_{\text{disp}}$ for the PMN–PT, PMN–PSN, (1 – $x$) Pb(Sc\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} – $x$PbTiO\textsubscript{3} (PSW–PT), (1 – $x$) Pb(Sc\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} – $x$PbZrO\textsubscript{3} (PSW–PZ), and (1 – $x$) Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} – $x$PbTiO\textsubscript{3} (PZN–PT) Pb-based perovskite solid solutions (Fig. 1(a)). A wide variety of $\Delta T_{\text{disp}}$ values is present, with some solutions (e.g., PMN–PT) exhibiting a sharp drop in $\Delta T_{\text{disp}}$ as the fraction of the ferroelectric end-member is increased, while for the others the decrease in $\Delta T_{\text{disp}}$ with increased ferroelectric fraction is quite gradual (e.g., PMN–PSN).

To rationalize these trends, we focus on two local structure criteria that have been experimentally shown to influence relaxor dispersion. First, in a classic 1980 paper, Setter and Cross\textsuperscript{15} have shown that PbSc\textsubscript{1/2}Ta\textsubscript{1/2}O\textsubscript{3} (PST) shows a large dispersion...
(\(\Delta T_{\text{disp}}\)) when the Sc and Ta B-cations are disordered on the B-site by rapid quenching. This is in contrast to the slowly annealed PST which exhibits a rock-salt B-cation arrangement and a standard ferroelectric behavior. A disordered B-cation arrangement produces overbonded and underbonded oxygen atoms\(^1\) and strong variations in the local potential energy surface. The results of Setter and Cross, as well as the more recent work of Juhás \etal\(^7\) on the effects of B-cation disorder in PSW–PT solid solutions, imply that the presence of overbonded and underbonded oxygen atoms is related to relaxor dispersion. We therefore choose the second moment of the B-cation valence of an oxygen atom (\(\langle V^2 \rangle \)) as a local structural parameter to characterize the magnitude of variation in the local structure. This is defined as

\[
\langle V^2 \rangle = \frac{1}{N_O} \sum_i (V_{i,1}^B + V_{i,2}^B - 2\overline{V^B})^2,
\]

where \(V_{i,1}^B\) and \(V_{i,2}^B\) are the valences of the two nearest B-cation neighbors of an O atom. The third term, \(\overline{V^B}\), is charge on B-cations in the chemical formula of perovskite solid solutions; the value is equal to four for all of the perovskites in this paper.

The second key local parameter is the average off-center displacement (\(D_{\text{avg}}^B\)) of the B-cations in the material. The importance of \(D_{\text{avg}}^B\) can be deduced from the comparison of the PZN and PMN materials. As shown in Fig. 1(a), the dispersion of PZN is much weaker with \(\Delta T_{\text{disp}}\) of only 8 K, as opposed to \(\Delta T_{\text{disp}} = 24\) K for PMN. Both PZN and PMN exhibit a random-site ordered B-cation arrangement in which the B-cations assume a rock-salt arrangement with one site fully occupied by the Nb\(^{5+}\) ion and the other one occupied by a random mixture of 2/3 Mg\(^{2+}\) or Zn\(^{2+}\) ions and 1/3 Nb\(^{5+}\) ions. The ionic sizes of Mg and Zn are essentially identical, so the difference in \(\Delta T_{\text{disp}}\) can be ascribed to neither the ionic size nor to the ionic valence effects. Comparison of the local B-cation off-center displacements obtained by DFT calculations shows a clear difference between PZN and PMN. The average displacement magnitude of Zn ions in PZN is 0.14 Å, comparable to the average displacement magnitude for the ferroelectrically active Nb ions and significantly larger than the 0.05 Å average displacement magnitude obtained for Mg ions in PMN.\(^1\) This suggests that the higher average B-cation displacement is correlated with lower \(\Delta T_{\text{disp}}\). Further support for the importance of \(D_{\text{avg}}^B\) can be seen in Samara’s\(^1\) experimental study of the effect of pressure on the dielectric properties of La-doped Pb(Zr,Ti)O\(_3\) (PLZT). As shown in Fig. 1(b), \(\Delta T_{\text{disp}}\) decreases with increasing pressure and decreasing volume, moving from the PZN-like value of 6 K at ambient pressure to the PMN-like value of 18 K at a pressure of 20 kbar. DFT calculations have shown that a decrease in perovskite volume leads to a strong decrease in the magnitude of off-center displacements.\(^7\) Therefore, the enhancement of \(\Delta T_{\text{disp}}\) observed by Samara is fully consistent with the correlation between lower \(D_{\text{avg}}^B\) and higher \(\Delta T_{\text{disp}}\).

The dependence of \(\Delta T_{\text{disp}}\) on \(\langle V^2 \rangle\) for the PMN–PSN solid solution (for which \(D_{\text{avg}}^B\) is constant) is similar to the dependence of the order parameter on temperature in standard Landau theory of a second-order phase transition (Fig. 2(a)).

![Graph](image-url)

Fig. 2. (a) The dependence of dispersion measure \(\Delta T_{\text{disp}}\) on \(\langle V^2 \rangle\) for the PMN–PSN solid solution, showing a strong resemblance to the behavior of the order parameter in a second-order phase transition. (b) Comparisons of the \(\Delta T_{\text{disp}}\) results of the Landau theory fit with experimental \(\Delta T_{\text{disp}}\) values. All of the data points fall close to the \(y = x\) line, indicating that the fit quantitatively captures the trends in the experimental \(\Delta T_{\text{disp}}\) data.
We therefore combine the two local criteria in a Landau theory equation for the compositional ferroelectric to relaxor phase transition with $\Delta T_{\text{disp}}$ as the order parameter:

$$ G = G_0 - \frac{1}{2} A \langle V^2 \rangle, D_{\text{avg}}^B $$

$$ \times \Delta T_{\text{disp}}^2 + \frac{1}{4} \Delta T_{\text{disp}}^4, \quad (4) $$

$$ \Delta T_{\text{disp, equil}}^2 = A \langle V^2 \rangle, D_{\text{avg}}^B, \quad (5) $$

$$ A \langle V^2 \rangle, D_{\text{avg}}^B = a_0 + a_i \langle V^2 \rangle + a_d e^{-kD_{\text{avg}}^B}, \quad (6) $$

where $G$ is the free energy of the relaxor phase, $G_0$ is the energy of the parent ferroelectric phase and the Landau coefficient $A$ is a function of $\langle V^2 \rangle$ and $D_{\text{avg}}^B$ ($a_0$, $a_i$, $a_d$, and $k$ are constants). The $b$ coefficient is set to unity for simplicity.

We choose the exponential form for the dependence of $A \langle V^2 \rangle, D_{\text{avg}}^B$ on $D_{\text{avg}}^B$, as it was found to better fit the experimental $\Delta T_{\text{disp}}$ results. To obtain the coefficients in Eq. (4) we use the $\Delta T_{\text{disp}}$ for the 22 different types of $B$-cation ordering allows us to precisely evaluate $\langle V^2 \rangle$. The results of the fit are compared with the experimental $\Delta T_{\text{disp}}$ values in Fig. 2(b).

The agreement between the fit and the experimental values is quite good, indicating that local, Angstrom-scale structure does in fact control the dielectric dispersion in Pb-based relaxor ferroelectrics. The finding that local effects govern the magnitude of dispersion in relaxors motivated our molecular dynamics study of dielectric response in the 0.75 PMN–0.25 PT material using small $6 \times 6 \times 6$ supercells. We ran the simulations for $1.5$ ns in order to be able to study the dielectric response in GHz frequencies. We used a random-site ordering of $B$-cations in which all Ti and Mg atoms have only Nb nearest-neighbors. Each Nb atom has a random mixture of Mg and Ti nearest neighbor ions.

The dielectric loss obtained from the analysis of MD trajectories shows a shift to lower frequency below the Burns temperature $T_b = 550$ K, with three clear peaks apparent at 400 K (Fig. 3(a)). The higher frequency peak, soft mode (SM), is slightly shifted from the dielectric loss peak for $T > T_b$. The two lower-frequency peaks show a dramatic redshift, moving into the GHz range. The finding of two additional dielectric loss peaks, central modes (CM), for $T < T_b$ is in agreement with the experimental dielectric spectroscopy results of Bovtun et al. for PMN. To analyze the local characteristics of the dielectric response, we examine the relaxation lifetimes of the autcorrelation functions for the dipole moments of the individual $B$-cation sites. Here, we split the $B$-cations into six groups, based on the variation in their local $B$-cation arrangement along a Cartesian direction. In our supercell, all Mg atoms and all the Ti atoms have two Nb neighbors along a Cartesian direction. However, for Nb atoms four different possible arrangements along a Cartesian direction are possible. Some Nb atoms have two Mg neighbors, some have two Ti neighbors, some have Mg to the left and Ti to the right, and some have a Ti neighbor to the left and Nb neighbor to the right. We label these as Nb$^{MM}$, Nb$^{TT}$, Nb$^{MT}$, and Nb$^{TM}$, respectively.

Comparison of the relaxation lifetimes (Fig. 3(b)) shows that at $T > T_b$ (600 K), the dynamics are fast for all atoms, although Nb$^{TT}$ exhibit slightly higher lifetimes. Just below $T_b$, at 500 K the lifetimes jump up for some Ti sites and increases for the Nb$^{TT}$ sites.
Finally, close to the freezing temperature at 400 K, most of the sites exhibit large relaxation lifetimes, with the notable exception of Nb$_{MM}$ for which $\tau_i$ are only slightly increased from their paraelectric phase values. This dispersion in the values of the dipole relaxation timescales is consistent with relaxor behavior and explains the presence of both the high and the low frequency peaks in the dielectric loss spectrum. The sites with small $\tau_i$ even for $T < T_b$ are responsible for the high-frequency peak while the sites with large $\tau_i$ values are responsible for the lower frequency peaks that are redshifted as the temperature is lowered.

To characterize the temperature dependence of the relaxation lifetimes, we plot the lifetime distribution at different temperatures (Fig. 4(a)). A splitting off of the higher $\tau$ peaks starts at $T_b$, resulting in a broad $\tau$ distribution at 400 K (Fig. 4(b)). This is in agreement with the analysis of the experimental dielectric spectroscopy data performed by Kamba et al.,$^{19}$ who showed that the shortest lifetimes always follow Arrhenius kinetics, while the longest and median lifetimes follow Vogel–Fulcher kinetics.

In summary, first principles DFT studies and MD simulations of the dielectric response in relaxors show that the interactions that give rise to the fascinating relaxor behavior are of a short-range type and are controlled by the variations in the local chemical bonding in perovskites.

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