

Spontaneous Polarization in One-Dimensional Pb(ZrTi)O₃ Nanowires

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Formation of spontaneous polarization in one-dimensional (1D) structures is a key phenomenon that reveals collective behaviors in systems of reduced dimensions, but has remained unsolved for decades. Here we report *ab initio* studies on finite-temperature structural properties of infinite-length nanowires of Pb(Zr_{0.5}Ti_{0.5})O₃ solid solution. Whereas existing studies have ruled out the possibility of phase transition in 1D chains, our atomistic simulations demonstrate a different conclusion, characterized by the occurrence of a ferroelectric polarization and critical behaviors of dielectric and piezoelectric responses. The difference is accounted for by the use of depolarizing effects associated with finite thickness of wires. Our results suggest no fundamental constraint that limits the use of ferroelectric nanowires and nanotubes arising from the absence of spontaneous ordering.

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Low-dimensional ferroelectrics (FE) are of considerable importance because of the demand in nonvolatile FE memory and device miniaturization [1–3], and because of their unusual properties that could be drastically different from bulks [4–9]. One-dimensional nanowire (1D NW) is an interesting system that bridges the 3D bulk ferroelectrics, for which no depolarizing fields exist along any dimension and possess at low temperature a ferroelectric ordering with formation of spontaneous polarization [10], and the 0D nanoparticles, for which depolarizing fields exist along all three possible dimensions and exhibit instead a peculiar ordering with formation of toroidal moment [9]. Experimentally, it has become possible to fabricate 1D ferroelectric nanowires and nanotubes out of different substances such as Pb(ZrTi)O₃, BaTiO₃, SrTiO₃, and SrBi₂Ta₂O₉ [11–14]. Theorywise, despite their obvious technological implication, the properties of these 1D systems—in particular, the structural, dielectric, and piezoelectric properties—remain unknown, which hampers the understanding of these novel forms of ferroelectrics.

Another key question of fundamental relevance is whether one-dimensional wires should exhibit any spontaneous ferroelectric ordering. The answer is not clear. On the one hand, it has been amply proved using a variety of statistical models that the 1D lattices with particle-particle interaction decaying as or faster than r^{-3} are impossible to have phase transformation at finite temperature [15–19], thereby imposing a fundamental constraint that limits the potential use of ferroelectric 1D nanowires and nanotubes. This conclusion has been widely accepted and formulated into a basic theory [20]. On the other hand, evidence of a *ferromagnetic* ordering was recently reported in a one-dimensional atomic chain on a metal supporting surface [21], questioning the applicability of the existing phase transition theory of 1D systems.

Here we investigate the fundamentals of phase transition in 1D FE system as well as study their dielectric and electromechanical properties, by means of two complementary techniques of (1) finite-temperature *ab initio*

simulations on 1D wires made of Pb(Zr_{0.5}Ti_{0.5})O₃ (PZT) solid solution and (2) analytical minimization of a free energy applicable for a general 1D FE system. We demonstrate that ferroelectric long-range ordering remarkably exists, at finite temperature and under zero external fields, in real 1D wires of diameter larger than 2 nm. The result is in difference from what has been known from the statistical models. Our results further show that the ordering in 1D infinite wires does not form any toroid moment and bears no similarity to the phase transition in 0D nanoparticles [9,22]. As another key outcome of our study, we determine the scaling law of the polarization in 1D systems.

Our simulations are based on a first-principle derived effective Hamiltonian [23,24], in which total energy E is a function of local modes \mathbf{u}_i , inhomogeneous strain \mathbf{v}_i , and alloy species σ_i at site i , as well as homogeneous strain η ,

$$E(\{\mathbf{u}_i\}, \{\mathbf{v}_i\}, \{\sigma_i\}, \{\eta\}) = E_{\text{VCA}}^{n\text{-dip}}(\{\mathbf{u}_i\}, \{\mathbf{v}_i\}, \{\eta\}) + E_{\text{VCA}}^{\text{dip}}(\{\mathbf{u}_i\}) + E_{\text{alloy}}(\{\mathbf{u}_i\}, \{\mathbf{v}_i\}, \{\sigma_i\}, \{\eta\}), \quad (1)$$

where the first two terms describe the nondipolar and dipolar interaction between perovskite 5-atom cells in the virtual crystal approximation (VCA), and the third term includes the energy associated with species-dependent alloy interaction. Expressions for $E_{\text{VCA}}^{n\text{-dip}}$ and E_{alloy} as well as parameters for PZT were given in Ref. [25], and were recently used for studying PZT nanoparticles [9]. The effective-Hamiltonian approach has been proved to be very successful in predicting the unusual low-symmetry monoclinic phase of PZT [24,26] and the phase diagram of BaTiO₃ with the presence of quantum zero-point motion [27]. The Hamiltonian in Eq. (1) was initially proposed for 3D bulks [23] and applicable to systems possessing periodicity along all three dimensions (i.e., with no depolarizing fields). To include the depolarizing energy due to charges at the lateral surfaces of 1D systems, we formulate a dual-space approach by using periodic Green's function $\mathcal{G}(\mathbf{r}, \mathbf{r}')$, for which the dipole energy E^{dip} can be determined as [28]

$$E^{\text{dip}} = -\frac{1}{2\epsilon_\infty} \lim_{\mathbf{r} \rightarrow 0} \sum_{\alpha\beta, ij} \frac{\partial}{\partial r_\alpha} \frac{\partial}{\partial r_\beta} \times \mathcal{G}(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_i-\mathbf{r}_j} p_\alpha(\mathbf{r}_i) p_\beta(\mathbf{r}_j), \quad (2)$$

$$\mathcal{G}(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{R}_\parallel} \frac{1}{|\mathbf{r}-\mathbf{r}'+\mathbf{R}_\parallel|} = \frac{2}{h} \sum_{\mathbf{G}_\parallel} K_0(G_\parallel|\boldsymbol{\rho}-\boldsymbol{\rho}'|) e^{i\mathbf{G}_\parallel \cdot (\mathbf{z}-\mathbf{z}')} ,$$

where \mathbf{R}_\parallel (\mathbf{G}_\parallel) are the real (reciprocal) lattice vectors along the z -axis wire direction, and h is the periodicity along this direction. $p_\alpha(\mathbf{r}_i)$ is the α component of the dipole at site \mathbf{r}_i . ϵ_∞ is the dielectric constant, $\boldsymbol{\rho}$ the projection of \mathbf{r} on the (x, y) plane, and $K_0(x)$ is the 0th-order modified Bessel function of imaginary argument. Since the function $K_0(x)$ decays exponentially at large x , the summations in Eq. (2) thus converge rapidly over \mathbf{G}_\parallel .

We study PZT wires of infinite length, mimicked by means of periodicity along the longitudinal z axis but not along the lateral x and y axes. Wires are chosen to be of cylindrical shape with their x , y , and z axes along the pseudocubic [100], [010], and [001] directions of the perovskite structure, respectively. We have performed simulations for a variety of diameters d , varying from 3 to 40, while the z -axis periodic length h is chosen to be 14 (d and h are in units of bulk lattice constant $a = 4 \text{ \AA}$ unless specified otherwise). We consider disordered PZT where Zr and Ti are randomly distributed. Finite-temperature Monte Carlo simulations with statistical convergence are used to obtain local modes and dielectric and piezoelectric properties.

Local mode (that is directly proportional to electrical polarization) and homogeneous strain in a $d = 15$ NW are shown in Fig. 1 as a function of temperature. The perhaps most striking result is that the z component of the average soft mode, $\langle u_z \rangle$, sharply increases to nonvanishing values below a critical T_c temperature which is found to be 610 K for the studied wire, while the amplitudes of the other two components $\langle u_x \rangle$ and $\langle u_y \rangle$ remain null. This signals that the wire undergoes a phase transformation from a paraelectric cubic phase into a tetragonal structure. The corresponding homogeneous strain components, expressed in the Voigt notation and measured with respect to the LDA-calculated bulk cubic lattice constant, reveal that below the critical T_c temperature η_3 exhibits a steady increase, whereas the components η_1 and η_2 continue to decrease. As a result, the c/a ratio reaches a value of 1.020 at 10 K, which is remarkably close to 1.024 found for the PZT bulk [25], showing that the tetragonal strain does not deteriorate in this 6 nm wire.

Figure 2 describes the piezoelectric d_{33} coefficient and dielectric ϵ_{33} constant, obtained from the statistical average of the response correlation function [29], as a function of temperature for the $d = 15$ wire. Three most notable observations are the following: (1) Both d_{33} and ϵ_{33} responses show a sharp peak as temperature varies across T_c , which further confirms the existence of phase transformation consistent with the formation of spontaneous ferro-

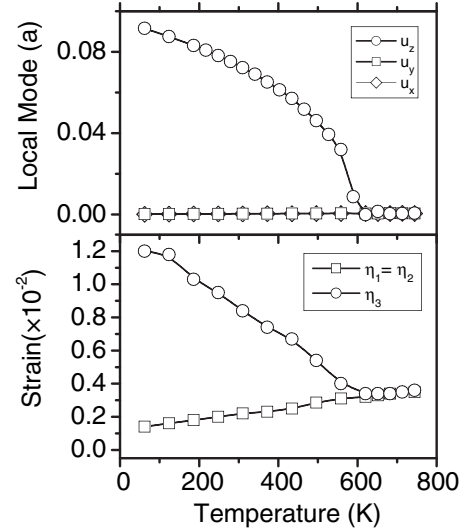


FIG. 1. Average local-mode displacements $\langle u_i \rangle$ (upper panel) and homogeneous strain η (lower panel) as a function of temperature in the $d = 15$ wire. $\langle u_i \rangle$ is in units of bulk lattice constant a . The temperature is rescaled so that the theoretical T_c of bulk PZT matches the experimental value of 640 K.

electric ordering. (2) Interestingly, the peak widths of d_{33} and ϵ_{33} curves are considerably *smaller* than those exhibited by bulk PZT, which is rather surprising when one recognizes the fact that thermal fluctuation is known to be strong in low-dimensional structures than in bulk [20]. (3) At room temperature, the d_{33} coefficient of the wire is predicted to be notably large at ~ 50 pC/N and, in fact, is comparable to the value in bulk PZT. Our calculations further reveal that the phase transition in 1D wires leads to an enormous ϵ_{33} peak value of $\sim 10\,000$ [Fig. 2(b)].

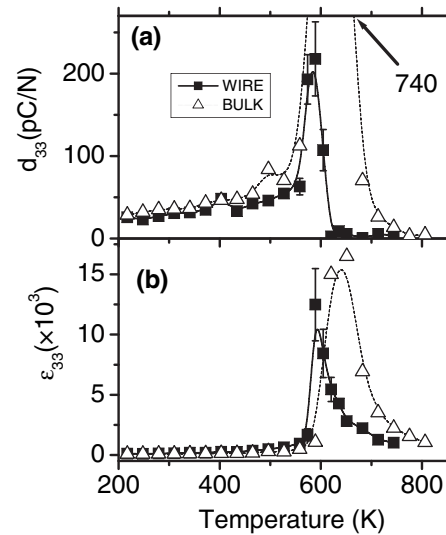


FIG. 2. (a) Piezoelectric d_{33} coefficient and (b) dielectric ϵ_{33} constant as a function of temperature for the $d = 15$ wire. The coefficients of bulk PZT, where the d_{33} peak reaches a value of 740 pC/N, is also shown for comparison.

We next investigate how the critical T_c temperature associated with the *longitudinal* z -axis FE ordering may be tuned by varying the *lateral* diameter of wires. Our results, depicted in Fig. 3(a), reveal two regimes for which the T_c behaves very differently. For wires of large diameter, T_c is nearly size independent and shows only a marginal decrease with respect to bulk PZT. However, as d is shrunk below the length of 11 bulk cells, T_c decreases dramatically in a completely different fashion, with the slope $\partial T_c / \partial d$ determined to be $15.5 \text{ K}/\text{\AA}$. As a result, the critical temperature in PZT wires is predicted to be widely tunable by as much as 300 K, which is important since it allows one to obtain very high dielectric and/or electromechanical performances by controllably shifting T_c to the room temperature at which devices normally operate.

The sudden and drastic decrease of T_c in Fig. 3(a) can be attributed to the possible existence of a threshold length for the dipole-dipole correlation. One key difference between FE wire and bulk is the dipoles at the wire surface. However, effects of these surface dipoles are screened by other dipoles within the correlation length. When the wire diameter is smaller than the correlation length, the surface dipoles cannot be fully screened and start to dominate in affecting the ferroelectric properties, causing a sharp change in T_c . Our calculations reveal this correlation length to be around 44 \AA . The existence of the dipole-dipole correlation length also explains a similar plunge of the transition temperature observed in PbTiO_3 ultrathin films [7] as well as the T_c behavior of the toroidal-moment A phase reported in *zero-dimensional* nanodisks [9]. By

revisiting the study of Ref. [9], the correlation length in toroidal phase is found to be 52 \AA , which agrees reasonably well with the value in this study as one bears in mind that the correlation depends on the dimensionality of the system.

Let us now turn attention to the determination of the scaling law for the polarization in 1D wires, by examining the z -axis polarization in different wires at a fixed and low temperature of 64 K [Fig. 3(b)]. Two most important conclusions are evident. First, our simulations show that the lateral size can be used to impose a significant control over the magnitude of polarization. Second, the polarization in 1D wires follows an interesting scaling law of $P = P_{\text{bulk}} - A/d$, where A is predicted to be $5.592 \times 10^{-10} \text{ C/m}$. We further find that our realistic $T_c \sim P$ relation cannot be simply described by the empirical formula of $T_c = \text{const} \times P^\alpha$ with $\alpha = 2$. Instead, T_c is proportional to P as d is larger than 11, but behaves like $P^{2.44}$ for the thinner NWs (i.e., α is size dependent).

We have performed other simulations using different periodic length h up to 200 bulk cells, which is the limit of our computing power. We find that the above results virtually do not change. Our results thus differ from the statistical models that predict no phase transition in 1D wires [16–19]. We now show, by examining the free energy and taking into account the entropy and depolarizing-field effects as well as the parameters of real materials, that the system length for disorder to appear in 1D wires is on the order of millimeter, and the spontaneous ordering of local dipoles that occurs in our simulations is thus a macroscopic and real effect.

First, it is important to realize that the polarization perpendicular to the NWs is suppressed by the depolarizing fields under the open-circuits boundary condition, and local dipoles in NWs are thus allowed to be parallel or antiparallel to the z -axis direction, which is further confirmed by examining the dipole pattern of our simulation results. In other words, the disorder that may potentially destroy the single-domain FE ordering is mainly due to the 180° domains, formed thermodynamically as well as with the domain wall perpendicular to the z axis. Assume that all domains have the same average length l , and let n be the number of domains that exist within the wire length L . Using the weak solution theory of Landau [20], the free energy for 1D wires with the presence of domains can be written as $\Phi = \Phi_0 + nk_B T \ln(na/L) + n\psi + U$, where Φ_0 is the thermodynamic potential, without allowance for the existence of domains. The second term describes the entropy contribution due to the appearance of domains, while the third term is the domain-wall energy caused mainly by the strain on the domain boundary. Surface charges on 180° domain walls will also lead to a long-range depolarizing field \mathbf{E} , though it averages to zero over the entire wire length. The energy U associated with this depolarizing field is $U = -n\Omega \mathbf{P} \cdot \mathbf{E}/2$, where $\Omega = \pi d^2 l/4$ is the volume of each domain and \mathbf{P} the volume

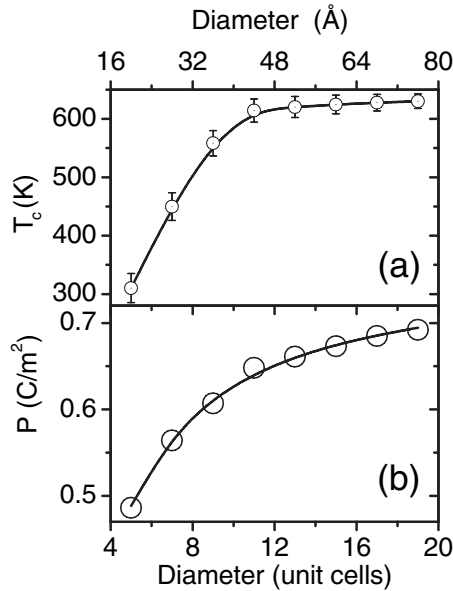


FIG. 3. (a) Critical T_c temperature, and (b) magnitude of polarization at 64 K , as a function of wire diameter. The diameter is in units of \AA (bulk lattice constant) for the upper (lower) horizontal axis. The fitted result using the $1/d$ scaling law is shown as a solid line in (b).

polarization. For domains with length $l \gg d$, the depolarizing field can easily be obtained from a uniformly polarized ellipsoid [30] with semiaxis s_1 and radius s_2 in the limit $s_1/s_2 \rightarrow \infty$, yielding $\mathbf{E} = -4\pi(l/d)^{-2} \ln(2l/d)\mathbf{P}$. The free energy is thus

$$\Phi = \Phi_0 + nk_B T \ln\left(\frac{na}{L}\right) + n\psi - \frac{n\pi^2 d^4 P^2}{2l} \ln\left(\frac{nd}{2L}\right). \quad (3)$$

Minimizing the free energy with respect to n , along with the fact that (1) $\ln(nd/2L)$ is on the same order as $\ln(na/L)$ and (2) domain-wall energy $\psi > 0$, results in the average length l_{ave} of domain as

$$l_{\text{ave}} = \pi^2 d^4 P^2 / k_B T. \quad (4)$$

Adopting realistic parameters of $d \sim 3$ nm, $P \sim 0.6$ C/m², and $T \sim 300$ K, we obtain $l_{\text{ave}} \sim 10^6$ nm (this value will further increase as $T \rightarrow 0$). This shows that the ferroelectric ordering can exist over a macroscopic length scale of 10^6 nm in 1D ferroelectric NWs, similar to the smectic phase observed in liquid crystals [31]. The critical temperature as predicted in our *ab initio* simulations thus describes a transition from a paraelectric into a ferroelectric phase within one domain.

Our studies provide new insights of phase transitions in 1D systems. First, our results demonstrate that phase transitions in 1D wires occur on a remarkable macroscopic length scale, but not necessarily on an infinite length scale as assumed in the general theories of 1D phase transition. In reality, phase transitions in bulk FEs also occur on a finite length scale. Our theories further yield quantitatively that a large spontaneous polarization of the bulk magnitude exists in 1D wires, showing that there are no fundamental constraints on the technological use of novel ferroelectric wires. Moreover, the large d_{33} , χ_{33} responses and the large c/a strain as predicted in the present study are all previously unknown and difficult to obtain from the general theories. The physical reason why thermal fluctuation in FE NWs is less disruptive than previously thought is rather simple. Results of the studies using spin-lattice models [18,19] do not apply here because of the existence of (strong) depolarizing fields arising from the truncation of lateral dimension. In contrast, the depolarizing effects in FE wires force the collective polarization to prefer along the longitudinal direction, and the ordered phase is an energy minimum stabilized by large surrounding energy barriers.

We believe that our results will stimulate further work on ferroelectric nanowires as well as the interest of utilizing the polarization formed in these novel structures for technological purposes. The existence of ferroelectric phase transitions with formation of spontaneous polarization also points to the possible need of reformulating the phase transition theory in one-dimensional systems.

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