Nanoscale properties of PbZrO₃ nanowires: phase competition for enhanced energy conversion and storage

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Abstract

Thin antiferroelectric PbZrO₃ nanowires simulated using a first-principles-based approach exhibit a strong competition between antiferroelectric and ferroelectric phases. The competition leads to a significant enhancement of energy-storing and converting properties, such as dielectric constant, recoverable energy, efficiency, and piezoelectric response. The temperature evolution of the spontaneous polarization and strain are favorable for the solid-state cooling applications.

Keywords: nanowires, ferroelectricity, antiferroelectricity, energy storage and conversion, computer simulations, PbZrO₃

1. Introduction

The ever increasing need for energy supply has propelled the quest for cleanly-generated and renewable energy. At present the electric energy demand is increasing twice as fast as overall energy use and expected to rise by more than two-thirds by 2035. For example, in 2012 42% of primary energy used was converted into electricity [1]. This in turn drives the demands for devices for efficient storing, absorbing, supplying, and converting electricity. These devices require high energy storage densities, high power density, high energy efficiency and conversion characteristics. The demand for the functional materials is even

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10 more urgent for miniaturized and integratable electronics and electrical systems.
11 Among bulk materials antiferroelectrics are receiving a lot of attention owing
12 to their potential for energy storage and conversion that stems from the large
13 saturation polarization, small remnant polarization, and excellent electrome-
14 chanical characteristics. For example, optimized $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.98}\text{Ti}_{0.02})\text{O}_3$
15 thick films can exhibit energy storage density of up to 60 J/cm^3 and nearly 40%
16 efficiency [2]. This is to be compared with a typical dielectric capacitor that
17 can only store up to 2 J/cm^3 of energy [3]. Another unique and technologically
18 desirable feature of antiferroelectrics is the large change in strain that accompa-
19 nies the antiferroelectric-to-ferroelectric phase transition induced by an electric
20 field. For example, in antiferroelectric bulk ceramics the difference in strain
21 between the antiferroelectric (AFE) and ferroelectric (FE) phases can reach up
22 to 0.4% making them excellent candidates for microactuators [4].
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25 While antiferroelectrics have emerged as strong competitors in the area of
26 materials for energy applications, their prospects for use as miniaturized devices
27 remain largely unknown. The majority of studies to date have focused on the
28 thin film geometry owing to the advances in the films' growth techniques [3, 4].
29 Antiferroelectric films have been reported to have an energy storage density
30 in the range of 7- 37 J/cm^3 [3] which is lower than the values found for the
31 bulk. Somewhat similar is the trend in the electromechanical response which
32 seems to become weaker in thin films. For instance, the strain in antiferro-
33 electric thin films can only reach up to 0.2% [5, 6]. Could this deterioration
34 of properties be caused by the tendency of the AFE thin films to develop FE
35 phases [7, 8, 9, 10, 11]? On the other hand, the properties of AFE nanos-
36 tructures beyond the planar geometry is even less investigated and understood
37 [12, 13, 14, 15, 16], which is especially true for AFE nanowires. Nanowires can be
38 synthesized using a variety of experimental techniques [12, 16, 17] and are partic-
39 ularly valuable as both interconnects and functional units in the fabrication of
40 electronic, optoelectronic, electrochemical, and electromechanical nanodevices
41 [18]. At the same time the prospects of AFE nanowires for energy related appli-
42 cations remain virtually unknown. Can antiferroelectric nanowires outperform
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their bulk counterparts for energy storing and converting properties or will the onset of ferroelectricity at the nanoscale indeed cause a deterioration in functionality? While a definite experimental answer is pending, the atomic-scale first-principles-based simulations can already provide some valuable guidelines.

2. Computational Method

Recent developments in effective Hamiltonian models for (anti)ferroelectrics have made possible realistic simulations of a variety of nanoscale (anti)polar materials [19, 20, 21, 22, 23, 24]. We carried out such studies for PbZrO_3 antiferroelectric nanowires under an applied electric field and for a wide range of temperatures with the aims to address the aforementioned questions. Stress-free PbZrO_3 nanowires with lateral size, d , of 4.1 to 8.3 nm grown along the [001] pseudocubic direction are modeled by $N \times N \times 20$ supercells periodic along the nanowire axis. N varies from 8 to 20 unit cells. The energy of the supercell is given by the first-principles effective Hamiltonian for PbZrO_3 [24]. The degrees of freedom for the Hamiltonian include local modes, $\mathbf{u}_i$, that are proportional to the dipole moment in the unit cell, i , oxygen octahedron tilts about pseudocubic axes, ω_i , that describe oxygen octahedron rotation, and strain variables tensors (in Voigt notations), η_i , that are responsible for mechanical deformations of a unit cell. Note that the unit cell here refers to a five atom cell of cubic perovskite. The energy of the PbZrO_3 Hamiltonian includes dipole-dipole interactions in quasi-one-dimensional structures [23], short-range interactions, on-site self energies, elastic energy, coupling energy between the degrees of freedom and the interaction between the local modes and the electric field and is given in Ref.[24]. All the parameters of the effective Hamiltonian were computed from first-principles and are reported in Ref.[24]. The Hamiltonian correctly reproduces many of the electrical and thermodynamical properties of PbZrO_3 [24]. In particular, it accurately predicts the antiferroelectric phase transition and the dipole pattern associated with it, electric hysteresis loops, and the PbZrO_3 behavior under pressure.

To simulate different electrical boundary conditions we apply a homogeneous electric field that opposes the average depolarizing field in the nanostructure. The average depolarizing field in the supercell can be computed from the atomistic approach of Ref. 23 or from the continuum model approximation for the average depolarizing field [23]. Since for the nanostructure sizes considered in the present study both approaches give very similar results, we mostly use the continuum model approximation due to its computational efficiency. The amount of compensating charge is controlled by the percentage of the surface charge compensation, β . For example, $\beta = 92\%$ corresponds to the situation when the free carriers can compensate up to 92% of the surface charge due to the polarization. The parameter β can be related to the finite screening length of the electrodes, λ_{eff} , and the nanowire's lateral size, d , as follows $\beta = (1 + 2\frac{\lambda_{eff}}{d})^{-1}$. However, the surface charge compensation does not necessarily require electrodes. Examples include surface charge compensation due to molecular adsorbates, charge carriers, intrinsic surface states, oxygen or other ionic vacancies, and others [25, 26, 27, 28, 29]. In these cases the screening parameter could be related to the concentration of free carriers, n , as $\beta = \frac{qnd}{2P_{bulk}}$, where q is the free carrier charge and P_{bulk} is the spontaneous polarization in the bulk. A similar computational approach was previously used to model different electrical boundary conditions in ferroelectric nanostructures [22, 22, 21]. The energy given by the Hamiltonian is used in canonical Monte Carlo simulations. Typically 40,000 Monte Carlo sweeps are simulated in a single run. To obtain equilibrium phases all nanostructures were annealed from 1500 K down to 5 K using the simulated annealing technique.

3. Results and Discussion

We begin by considering the situation when the free charge could screen up to 92% of the polarization surface charge, which corresponds to a realistic case of partial surface charge compensation. Fig.1 shows the room temperature dependence of the polarization, P , on the electric field, E , for nanowires with different

lateral sizes. The $P(E)$ loops were obtained by applying the electric field perpendicular to the nanowire axis ([100] pseudocubic direction in our case), which models the experimental setups for measuring electric and piezoelectric response in nanowires [16, 30]. The most striking feature is the transition from the AFE to a FE behavior below the critical thickness of 7.4 nm. Such a transition is similar to the one found in PbZrO_3 ultrathin films [7, 8, 9, 10, 11, 31] and could be explained by the recently proposed surface effect [31]. The surface eliminates energetically costly short range interactions between the neighboring dipoles in the PbZrO_3 thus stabilizing the FE phase. It is well known that the equilibrium phases in polar nanostructures are extremely sensitive to the surface charge compensation [28, 32, 22, 30, 33]. Yet the exact amount of the compensating charge remains impossible to measure or control experimentally. In fact, often times it is the nature of the nanostructure's equilibrium phase that suggests whether the surface charge compensation is efficient. In particular, polar phases with polarization perpendicular to the nanostructure surface are usually associated with good surface charge compensation [30, 32, 28], while patterns with no net polarization are typically attributed to poor surface charge compensation [22, 33]. On the other hand, the surface charge compensation due to extrinsic free carriers or molecular adsorbates is likely to vary from nanowire to nanowire or even within the same nanowire. To accommodate for both the uncertainty and variation in the amount of compensating charge we carry out simulations for the range of β from 80 to 95% that is associated with relatively good surface charge compensation. Then the data are averaged over the entire range of β . Such an approach models closely real experiments where the compensating charge is only known at a qualitative level.

Fig.2(a) shows the room temperature $P(E)$ loops for nanowires with d of 5.0 and 8.3 nm. Note that for the remainder of the paper we report data averaged over the entire range of β . We notice that the thinner nanowire exhibits a FE behavior while the thicker nanowire responds to the electric field similar to a lossy dielectric. Interestingly, our computational data for the thicker nanowire resemble closely the loops obtained for 22-100 nm thick PbZrO_3 films

[9, 8, 7] which suggests that our model of variable surface charge compensation captures well the polarization charge screening in nanoscale antiferroelectrics. One remarkable feature of the $P(E)$ loops is the relatively large dP/dE slope as compared to a typical dielectric. The reason behind such a large response is the mixed AFE-FE character of the room temperature phase. Both FE and AFE phases share large saturation polarization, however, the AFE phase leads to a reduced value of remnant polarization. We computed the dielectric response of different nanowires using the zero-field dP/dE slopes. Because our computational method underestimates the dielectric susceptibility, χ , of bulk PbZrO_3 , the values for the nanowires are reported in Fig.2(b) relative to the computational susceptibility of bulk PbZrO_3 . Our computations predict a dramatic (up to eight times) increase of χ in nanowires as compared to the bulk. The improvement in the dielectric response is attributed to the contribution from the FE phase.

The combination of large polarization with slim hysteresis loops is favorable for the energy storage. To estimate the performance of PbZrO_3 nanowires in energy storage applications we calculated the recoverable energy density, W_r , and efficiency, η_{eff} , using the approach of Ref.[34]. The data computed for the maximum electric field of 4.0 MV/cm are given in Fig.2(c) and (d). The straight horizontal lines give the value for bulk PbZrO_3 . We first note that the bulk value of 53 J/cm² compares well with the experimental values of 37-53 J/cm² obtained for optimized $(\text{Pb}_{0.2}\text{La}_{0.02})(\text{Zr}_{0.95}\text{La}_{0.05})\text{O}_3$ thick films under comparable electric fields [35]. Secondly, our model predicts that PbZrO_3 nanowires could significantly outperform their bulk counterparts in terms of the recoverable energy density. Indeed W_r for thicker nanowires is about 50% larger than the bulk value. The enhancement in W_r is attributed to smaller electric hysteresis in the thicker nanowires [see Fig.2(a)]. Thinner nanowires develop a FE phase which increases the electric hysteresis leading to a reduction in W_r , while the efficiency is comparable to bulk. Based on our numerical data we conclude that PbZrO_3 nanowires are promising candidates for energy storage applications in miniaturized devices.

Next we turn to the temperature evolution of the remnant polarization, P_r , in the nanowires. The data were obtained by heating the poled nanowires from 5 to 1200 K. Fig.3(a) gives a representative dependence $P_r(T)$ for the $d=5$ nm nanowire. We notice the gradual onset of remnant polarization which originates from the coexistence of the FE and AFE phases that compete with each other. The AFE phase is favored at higher temperatures, while the FE phase is preferred at lower temperatures. This is in agreement with the experimental findings for ultra thin PbZrO_3 films [36]. Such broad $P(T)$ dependence is highly desirable for cooling applications that utilize the electrocaloric effect. Fig.3(b) shows the dependence of the temperature associated with the onset of polarization, T_P , on the nanowires' lateral size. T_P increases with the decrease in d consistent with the stabilizing role of the surface in the formation of the FE phase in PbZrO_3 nanostructures.

Next we discuss the electromechanical properties of PbZrO_3 nanowires. Fig.4(a) and (b) shows the dependence of the η_1 and η_3 components of the strain tensor on the electric field for one representative nanowire ($d=8.3$ nm). The $\eta_1(E)$ loop for the nanowire is in excellent qualitative agreement with the standard ferroelectric amplitude curve for NaNbO_3 nanowires [16]. One interesting feature of the $\eta(E)$ loops is the diffused character of the field induced AFE-FE phase transition. Similar features were previously reported for AFE PLZST films [4]. In both cases the effect originates from the modified competition between the AFE and FE phases. In films the perturbation was attributed to the thermal mismatch between the film and substrate, while in nanowires considered here the perturbation is due to the surface charge compensation. Such diffused character of the AFE-FE phase transition is very attractive for analog actuation applications that require a faster response and more precise micropositioning [4]. We have used the $\eta_1(E)$ and $\eta_3(E)$ dependencies to compute the piezoelectric coefficients d_{11} and d_{13} , respectively. The computational data are given in Fig.4(c). The coefficients are in the range of 20 to 30 pC/N which is comparable to the coefficients in PZT away from the morphotropic phase boundary. Both coefficients are more than an order of magnitude larger

than the coefficients of 1.1 pC/N computed for bulk PbZrO_3 . The enhancement of the piezoelectric coefficients is a consequence of the diffused character of the field induced AFE-FE phase transition in the nanowires. We also computed the temperature evolution of the spontaneous strain in the nanowires. A representative data for $d = 5.0$ nm nanowire are given in Fig.4(d). The data predict a large variation of spontaneous strain in a wide temperature range which is very desirable for piezocaloric applications. In such applications the temperature is controlled by the application of external stress [37]. Our computational data suggest that PbZrO_3 nanowires have promising electromechanical properties.

4. Conclusions

In summary, our simulations predict that PbZrO_3 nanowires with imperfect surface charge compensation exhibit a strong competition between AFE and FE phases that is strongly influenced by the surface effects. This competition leads to the onset of ferroelectricity in ultra thin nanowires, and strong enhancement of both dielectric susceptibility and energy storage characteristics. The electric-field-induced phase transition acquires a diffused character leading to the enhancement of the piezoelectric constants in comparison with bulk. In fact, the piezoelectric coefficients in PbZrO_3 nanowires are predicted to exceed the ones for a typical piezoelectric material, ZnO. Furthermore, the temperature dependencies of the spontaneous polarization and strain in PbZrO_3 nanowires have a rather monotonic character which is attractive for potential applications in solid-state coolers.

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Figure 1: Dependence of the polarization on the electric field in nanowires of different lateral sizes (a)-(c) for $\beta = 92\%$ and bulk (d).

Figure 2: Dependence of the polarization on the electric field for nanowires of different lateral sizes (a); the electric susceptibility reported relative to bulk as a function of d (b); recoverable energy density (c) and efficiency (d) as a function of nanowire lateral size.

Figure 3: Temperature dependence of the remnant polarization (a). Dependence of the temperature associated with the onset of spontaneous polarization on the nanowire size.

Figure 4: Dependence of the different components of the strain tensor on the electric field in 8.3 nm nanowire (a) and (b); Dependence of the piezoelectric coefficients on the nanowire size (c); Temperature evolution of spontaneous strain in 5 nm nanowire (d).