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# First-principles study for surface tension and depolarizing effect on ferroelectric properties of BaTiO<sub>3</sub> nanowires

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**Abstract:** The spontaneous polarization in ferroelectric (FE) nanowires (NWs) can be considerably enhanced due to the nanosize confinement by the first-principles calculations. The spontaneous polarization in a fully-relaxed  $BaTiO_3$  NW with 2.0 nm in diameter is 1.18 times higher than that of bulk counterpart. The ferroelectric properties of the wire are found to generally depend on its dimensions through effects of the surface tension and near-surface depolarizing effect. The surface tension seems to be crucial for the giant enhancement of spontaneous polarization.

Key words: ferroelectric nanowires; surface stress; depolarization; first-principles

## **1** Introduction

Low-dimensional ferroelectrics (FEs) have attracted intense attention due to their potential applications in leading toward miniaturized devices for nanoscaled actuators, nanoscaled sensors, nonlinear optics, and especially non-volatile ferroelectric random access memories with large storage density [1-3]. Much experimental effort has been made recently in preparing understanding FE nanorings[4], and nanowires (NWs)[5-7], and nanoparticles[8-9]. Theoretically, NAUMOV and FU[10-12] have used a first-principlesderived effective-Hamiltonian approach to investigate the ferroelectricity in zero-dimensional (0D) BaTiO<sub>3</sub> nanodots, Pb(Zr, Ti)O<sub>3</sub> nanodisks, nanorods and one-dimensional (1D) NWs, and revealed the vortex structure dipoles in nanodots, nanodisks, and nanorods.

It is well known that the ferroelectricity is generally caused by atomic off-center displacements which result from a delicate balance between long-range (LR) Coulomb interaction and short-range (SR) covalent interaction[13]. In 1D FE nanostructures, the LR interaction is truncated due to the lack of periodicity and the SR one is significantly modified near the surface boundary. Thus, both interactions and the corresponding balance are changed with regard to the bulk. Therefore, the depolarizing effect would come into being because of the lack of periodicity and the modified surface boundary, which causes the spontaneous polarization decreasing [2, 12]. On the other hand, the surface compressive stress caused by the surface restructuring of 1D nanostructures produces an effective tension in the length direction[14], which leads to a large off-center displacements. Importantly, the large off-center displacements would arise the spontaneous polarization. NAUMOV and FU[10] reported theoretically the scaling law of the spontaneous polarization in Pb(Zr, Ti)O<sub>3</sub> NWs based on the depolarizing effect. However, there have not been any theoretical and experimental studies of spontaneous polarization simultaneously involved in both the depolarizing effect and surface stress in 1D FE NWs.

In this work, the first-principles calculations were carried out to pursue the spontaneous polarization in the fully-relaxed 1D BaTiO<sub>3</sub> FE NWs, taking the near-surface depolarizing effect associated with finite thickness of wires in the radial direction and the large surface tension induced by the 1D confinement into account.

### 2 Model and calculating method

The BaTiO<sub>3</sub> NWs are extended to infinity along the longitudinal z axis through the periodic repetition of

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supercell. 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. The schematic illustrations of NWs are shown in Fig.1. The polarity axis lies along the NWs length. The vacuum space with about 8 nm in thickness surrounds the nanowires, which ensures that the NWs in neighboring supercells do not interact with each other and cause the surface-induced atomic relaxation and the cell-shape changes. Thus, these treatments would affect both the local modes and the local inhomogeneous strains. We perform the simulations for a variety of diameters d, varying from 1.4 to 4.2 nm, while the z-axis periodical length h is chosen to be the bulk lattice constant. Other internal parameters used here are those of bulk BaTiO<sub>3</sub>. First-principles density functional theory (DFT) with local density approximation is performed using the Vienna *ab initio* simulation package (VASP), within the projector augmented wave (PAW) pseudo potential method[15]. These calculations are performed with a  $1 \times 1 \times 5$  Monkhorst-Pack k-point mesh centered at  $\Gamma$  and a 460 eV plane-wave cutoff, both of which result in good convergence of the computed ground-state properties. The forces on the atoms are calculated using the Hellmann-Feynman theorem[15], which is used to perform a conjugate gradient relaxation, and shown to be feasible in our previous reports[16-18]. Structural optimizations are continued until the forces on the atoms converge to less than 1 meV/Å. Moreover, the electronic polarization P via  $P = Z_{eff}^* \cdot U_{eff}$  of the BaTiO<sub>3</sub> NWs is performed by the Berry phase method[19], where  $Z_{eff}^*$ is the Born effective charge of the local mode; and  $U_{\rm eff}$  is the local model of the cell to describe the ferroelectric instability. The method is considered to be a good description for the electronic polarization of an insulating groundstate system[17]. It is noted that, in order to keep to be insulating and close to circular, the configurations of the nanowires are stoichiometric with the BaO and TiO<sub>2</sub> surface-terminations at the same time. It is not the only BaO- or TiO<sub>2</sub>-surface-terminations. Of course, the whole structure would be kept symmetrical corresponding to the central z axis. In our simulated structures, the BaTiO<sub>3</sub> nanowires are insulating with stoichiometric configuration. As shown in Fig.2, we plot the orbital-resolved densities of states (DOSs) of BaTiO<sub>3</sub> nanowires(NWs) with diameter d=2.0 nm. There is a



**Fig.1** Schematic illustrations of 1D BaTiO<sub>3</sub> NWs viewed from [100] (a) and [001] (b) directions, and internal ferroelectric perovskite structure (c)



**Fig.2** Orbital-resolved densities of states (DOSs) of  $BaTiO_3$  nanowires(NWs) with diameter d=2.0 nm(Fermi energy is set to zero)

band-gap about 1.7 eV between the O 2p and Ti 3d states. It is shown that the simulated wires are insulators.

### **3** Results and discussion

Fig.3 shows the longitudinal *z*-axis FE spontaneous polarization as a function of the varying diameter of free-standing NWs under the open-boundary condition. In order to display the different ferroelectric order of the BaTiO<sub>3</sub> NWs, the ratio of  $P_{\text{nanowires}}/P_{\text{bulk}}$  is also presented. The spontaneous polarization is different along the radial direction, and thus the calculated spontaneous polarization is an average value. Remarkably, we can see the giant enhancement of spontaneous polarization in the BaTiO<sub>3</sub> NWs with 2.0 nm in diameter compared with that of the bulk counterpart. In detail, there is a critical size of about 1.4 nm in the spontaneous polarization of



**Fig.3** Longitudinal *z*-axis spontaneous polarization as function of NWs diameter under open-boundary condition (Dot line: value of bulk polarization of  $BaTiO_3$ )

BaTiO<sub>3</sub> NWs, which further confirms the existence of the FE phase transition in 1D NWs when their diameter is less than a definite size[10]. Interestingly, a maximal value of spontaneous polarization that is about 1.18 times higher than that of bulk can be obtained for the BaTiO<sub>3</sub> NWs with 2.0 nm in diameter. Then, the spontaneous polarization gradually decreases with increasing the diameter of BaTiO<sub>3</sub> NWs and trends to the bulk value. However, the spontaneous polarization drops quickly when the diameter of NWs is less than 2.0 nm. It has been recognized that, in general, the near-surface depolarizing effects associated with finite thickness of wires are known to be strong in low-dimensional structures to cause the considerably smaller spontaneous polarization than that of bulk[2, 10, 12], which implies that FE nanostructures are not expected to be promising in the applications of nanodevices. Then, our studies show that the strong enhancement of spontaneous polarization can be achieved in 1D FE NWs, which actually opens a door toward the application of FE nanostructures.

At the atomistic scale, the spontaneous polarization is mainly caused by the displacement of Ti atoms deviating from the centre positions (the paraelectric phase) in the displacive FE BaTiO<sub>3</sub>[13]. Fig.4(a) shows the average displacement of Ti  $\langle u_{Ti} \rangle$  atoms along the *x*, y, and z directions of the  $BaTiO_3$  NWs. Surprisingly, there are the same trends of  $\langle u_{Ti} \rangle$  as the spontaneous polarization along its length axis with varying the NWs diameter. However, the average displacement of  $\langle u_{Ti} \rangle$  is zero in the x and y directions. Thus, the results are responsible for the zero spontaneous polarization in the perpendicular direction of the BaTiO<sub>3</sub> NWs, which is similar to the previous studies[10, 12]. Fig.4(b) shows the schematic illustration of the displacements of the symmetric four Ti atoms along the x and y directions for the 2.6 nm BaTiO<sub>3</sub> NWs. Although there are considerable displacements for every Ti atom in the x and y directions, the whole displacement vector is zero in the parallel-to-surface direction to cause the zero polarization. Thus, our calculations indicate that the FE ordering in 1D infinite BaTiO<sub>3</sub> NWs does not form any toroid moments, which is different from the phase transition of 0D nanoparticles[10-12].

NAUMOV and FU[10] reported the spontaneous polarization of the infinite length Pb(Zr,Ti)O<sub>3</sub> NWs and the scaling law of the spontaneous polarization in the (001) direction ( $P=P_{bulk}-A/d$ ) based on the depolarizing effects, in which the spontaneous polarization in NWs is less than that of bulk and decreases with reducing NWs diameter. To understand the difference between our results and NAUMOV's studies, and the origin of the



**Fig.4** Average displacement of Ti atoms along *x*, *y*, and *z* directions of BaTiO<sub>3</sub> NWs (a) and schematic illustration (b) of displacements of symmetric four Ti atoms along *x* and *y* directions for 2.6 nm BaTiO<sub>3</sub> NWs ( $|u_{1x}| = |u_{2x}| = |u_{2x}| = |u_{4x}|$ ,  $|u_{1y}| = |u_{2y}| = |u_{3y}| = |u_{4y}|$ )

enhancement of the polarization along z, we plot the in-plane lattice constant of the nanowires as a function of NW diameter in Fig.5, where the  $d_1$  represents the unoptimized NW diameter, and  $d_2$  represents the optimized NW diameter. Evidently, the surface compressive stress is pointed to be at the origin of the enhancement of the polarization along z. The surface stress of NWs can greatly enhance the spontaneous polarization by counteracting the depolarizing effects. It is noted that there is very large surface stress below the critical size. Because of the large depolarized effects corresponding to the surface-stress effects, the polarization of the NWs is zero under the critical sizes. In fact, the enhanced polarization by the stress has been confirmed in the FE superlattices[20].



**Fig.5**  $(d_2-d_1)/d_1$  function of BaTiO<sub>3</sub> NW diameter

#### **4** Conclusions

1) Taking the near-surface depolarizing effect and the surface tension induced by 1D confinement into account, there is the giant enhancement of spontaneous polarization in the fully-relaxed 1D BaTiO<sub>3</sub> NWs using first-principles calculation.

2) The calculated results show the spontaneous polarization in the BaTiO<sub>3</sub> NWs with 2.0 nm in diameter is 1.18 times higher than that of the bulk counterpart.

3) The physical mechanisms of the unusual spontaneous polarization in 1D FE NWs are suggested to be the competition between near-surface depolarizing effect and the surface tension on the basis of *ab initio* calculations.

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