



Ab initio modeling of wall structure and shape in perovskite-based nanotubes



Andrei V. Bandura*, Dmitry D. Kuruch, Robert A. Evarestov

Department of Quantum Chemistry, St. Petersburg State University, Universitetsky Prospekt 26, Petergof, St. Petersburg 198504, Russia

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ABSTRACT

A large-scale first-principles simulation of the structure and stability of SrZrO₃ and BaZrO₃ single- and double-wall nanotubes with different chiralities and diameters was performed using the periodic PBE0 method and the basis set of localized Gaussian-type atomic orbitals. The initial structures of nanotubes were obtained by the rolling up of slabs cut from perovskite bulk phases and consisting of two or four alternating (001) ZrO₂, SrO or BaO layers. Significant structural reconstruction was found in 4-layer single-walled and in double-walled nanotubes. If the distance between the single-wall components of double-walled nanotubes is less than approximately 5.0 Å, they inclined to merge to stable polyhedron-shaped tubular objects consisting of blocks with distorted cubic perovskite structure. A comparison of the data obtained with the results of our previous works shows that the stability of perovskite nanotubes with merged walls increases in the following sequence of the parent phases: SrZrO₃ < BaZrO₃ ≈ SrTiO₃ < BaTiO₃. Calculated stability correlates with a ratio R_{II}/R_{IV} of ionic radii of group II and IV metals.
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1. Introduction

Presently, ABO₃ type perovskites are widely studied objects that demonstrate unique electronic, magnetic and optical properties. Due to their high chemical and mechanical stability and high proton conductivity at elevated temperatures they exhibit great promise as solid fuel cells and hydrogen sensors [1]. Nanoscale systems based on SrTiO₃ and BaTiO₃ (hereinafter STO and BTO), as well as on SrZrO₃ and BaZrO₃ (hereinafter SZO and BZO) are observed in a wide variety of realizations such as nanotubes [2–7], nanorods [8–10], and nanocrystals [8,11,12]. These nanomaterials can significantly improve the performance of a variety of electronic, electro-optical, electrochemical, and electromechanical devices and systems [13].

Though a relatively large number of experimental data were obtained [2–7] for synthesized perovskite NTs, these data were difficult to analyze due to lack of models accurately describing the chemical structure and morphology of the perovskite-based NTs. Most of the modern theoretical models [14] of the rolled-up NTs are created through folding of layers cut from bulk crystals. However this procedure usually provides NTs with thin (monolayer) walls only. As a result, most of the theoretical calculations are performed for the inorganic NTs with the wall thickness of about 2 Å.

Nevertheless, the minimum wall thickness of synthesized STO and BTO NTs was found to be about several tens of Angstroms [2,5–7].

In recently published works [15–18] we studied the structural and electronic properties of perovskite-based nanotubes. Thus, a large-scale first-principles simulations of the structure and stability of STO single-walled (SW) and double-walled (DW) nanotubes (NTs) with different chiralities were performed [15,16]. In the majority of the cases considered [15,16], the inner or outer TiO₂ shells of 4-layer NTs underwent a notable reconstruction through the shrinkage or stretching of interatomic distances during the structure optimization. Double-wall NTs constructed from two 2-layer SWNTs with the intertube distance of less than 4.5–5.0 Å merged to stable polyhedron-shaped tubular objects consisting of blocks which have a distorted cubic perovskite structure. It was shown [17] that SWNTs folded from layers of BTO phases (cubic, tetragonal, or orthorhombic) were more stable than STO-based NTs. We also found [17] that BTO-based NTs scarcely exhibit ferroelectric properties unlike BTO nanolayers, nanorods and nanocrystals. Spontaneous splitting of SrO-terminated 4-layer SWNTs folded from the SZO cubic phase into two separated NTs was found in our last work [18] of this series. It was proved that NTs folded from the orthorhombic SZO phase preserved the atomic distortions inherent to the bulk orthorhombic phase.

The review [14] of published papers on theoretical modeling of inorganic NTs shows that perovskite NTs were studied only in a few works. Thus, Piskunov and Spohr [19] demonstrated that the

* Corresponding author. Tel.: +7 812 3482119; fax: +7 812 4286939.
E-mail address: andrei@ab1955.spb.edu (A.V. Bandura).

density functional theory (DFT) predicted negative strain energies for some NTs folded from thin 2D SrTiO₃ nanosheets. The authors pointed out that “negative strain energy minimizes the NT formation energy with respect to the SrTiO₃ bulk”. Hence, one of the possible reasons for negative calculated strain energies is the large positive (relative to the bulk crystal) formation energy of the nanolayer (slab) used for NT folding. As a rule, this is due to the presence of dangling bonds on the slab surface. The arrangement of the dangling bonds on the bended surface may be more favorable than on the flat slab surface.

In this work we extend our previous studies and perform first-principles computations of the single- and double-walled SZO and BZO NTs, emphasizing the structure of NT walls produced by the relaxation or reconstruction of the initial rolled-up configuration. To the best of our knowledge such a study is so far absent. However, this is important due to the fact that the experimental data cannot provide a detailed description of the atomic-level morphology of perovskite NTs. Another goal of this work is to compare the properties of the NTs folded from layers of different perovskites Me^{II}Me^{IV}O₃ (Me^{II} = Sr, Ba; Me^{IV} = Ti, Zr) for clearing up which of them are the most suitable for NT folding.

The outline of the article is as follows. In Section 2, we describe the symmetry of the SW and DW nanotubes considered. The computational details of this study are given in Section 3. In Section 4, the calculation results are presented and discussed for SZO and BZO nanolayers and nanotubes. At the end of this section we briefly compare the stability of nanotubes folded from layers of SZO, BZO, STO and BTO perovskites. Finally, our conclusions are given.

2. Symmetry of single- and double-walled nanotubes

The folding procedure is applied to the (001) slabs cut from SZO and BZO cubic bulk crystals with space group 221 ($Pm\bar{3}m$) and from the orthorhombic SZO phase with space group 62 ($Pbnm$). The slab translational symmetry corresponds to square or rectangular plane lattices for cubic or orthorhombic space groups, respectively. The layer symmetry group of the slab depends on the bulk phase symmetry and the number of atomic layers included in the folding procedure. The perovskite (001) slabs consist of Me^{II}O and Me^{IV}O₂ alternating layers. For even number of layers all the slabs are stoichiometric. The thinnest stoichiometric slab includes one Me^{II}O and one Me^{IV}O₂ layer. The cubic phase provides (001) slabs with a 2D-periodic group of $P4mm$. According to the results by Damnjanović et al. [20], after the rolling procedure this layer can generate $(n, 0)$ and (n, n) SWNTs with the line symmetry group belonging to family 11 (point symmetry D_{nh}) and to family 13 (point symmetry D_{2nh}), respectively. The presence of the helical axis $(2n)_n$ distinguishes the latter chirality from the former. The slabs obtained from the orthorhombic SZO crystal have a rectangular cell with a 2D symmetry of $Pb11$ and can be folded with two different types of chirality depending on the direction of the rolling vector. The NTs with $(n_1, 0)$ chirality belong to the line group family 2 (S_{2n}), and NTs with $(0, n_2)$ chirality belong to family 7 (C_{nv}) [20]. We can note that symmetry of NTs may be reduced during structure optimization.

Line symmetry group of DWNT can be found as an intersection of symmetry groups of its SW constituents [21]. Let (n_1, n_2) and (n'_1, n'_2) define the chiral vectors of SW constituents of DWNT. The DWNT axial point group C_N is the principal axis subgroup of DWNT line group with $N = G(n, n') = G(n_1, n_2, n'_1, n'_2)$ where G is the greatest common divisor of n_1, n_2, n'_1 and n'_2 . Only NTs composed exclusively of either (n, n) or $(n, 0)$ SW constituents may have additional mirror and glide planes, as well as two-fold axes perpendicular to the tube axis. The SZO and BZO DWNTs $(n_1, 0)@(n_2, 0)$, $(0, n_1)@(0, n_2)$ and $(n_1, n_1)@(n_2, n_2)$ are commensurate, and the minimal

translation period for such DWNTs is the same as for the constituents. The symmetry group of $(n_1, 0)@(n_2, 0)$ or $(0, n_1)@(0, n_2)$ DWNTs belongs to the same family as its SW constituents. The two possibilities [21] arise for DWNTs $(n_1, n_1)@(n_2, n_2)$ generated from the cubic phase: (a) both n_1/N and n_2/N are odd; (b) one or both n_1/N and n_2/N are even. In the case (a), the line symmetry groups are the same as for their SW constituents and belong to family 13 (the order of screw axis is $2N$). In the case (b), the rotations around the screw axis of order $2N$ are replaced by rotations around the pure rotation axis of order N and the DWNT line symmetry group belongs to family 11. As in the case of SWNT, the final symmetry of DWNT may be lower than the initial one.

3. Computational details

All the calculations were performed within the periodic DFT method implemented in CRYSTAL-2009 computer code [22] using a hybrid exchange–correlation functional PBE0 [23]. This code utilizes localized Gaussian-type functions as a basis set for expansion of crystalline orbitals as linear combinations of atomic orbitals (LCAO). All-electron basis set [24] was chosen for O atom, while the CRENBL [25,26] small-core pseudopotentials and the corresponding basis set were used for Sr, Ba and Zr atoms. To exclude the basis set linear dependence in LCAO crystal calculations, the diffuse s -, p -, d -, and f -Gaussian-type orbitals with exponents less than 0.1 were removed from the corresponding basis sets. The used basis sets and pseudopotential parameters are given in the [Supplementary Data](#).

The Brillouin zone was sampled by means of a $12 \times 12 \times 12$ Monkhorst–Pack [27] grid for cubic bulk crystals. A number of k -points in each periodic dimension were reduced inversely to the corresponding cell constant to provide approximately uniform Brillouin zone sampling for the orthorhombic SZO, all the slabs, and NTs. The full structural optimization of the considered systems was performed. The method chosen provides good quality of the calculated SZO and BZO bulk properties. Thus, the optimized lattice constants of cubic SZO and BZO and orthorhombic SZO differ from the experimental values by less than 1% (see [Table 1](#)).

4. Results and discussion

4.1. Slab calculations

Stoichiometric slabs composed of 2 and 4 alternating (001) SrO or BaO and ZrO₂ atomic layers were constructed from cubic and orthorhombic phases of a bulk crystal and studied as NT precursors ([Fig. 1a](#) and [b](#)). The lattice parameters and the atomic structure of precursor slabs were optimized before NT folding. The slab formation and surface energies were calculated using the equations:

$$E_{\text{form}} = (E_{\text{slab}}/n - E_{\text{bulk}}), \quad (1)$$

$$E_{\text{surf}} = (E_{\text{slab}} - nE_{\text{bulk}})/2S_{\text{slab}}, \quad (2)$$

where E_{slab} is the slab total energy per 2D unit cell, E_{bulk} is the bulk crystal total energy per formula unit, n is the number of formula units in the slab 2D unit cell, and the multiplier 2 before S_{slab} (which is 2D unit cell surface area) corresponds to formation of two faces upon crystal cleaving.

The obtained lattice constants of two-dimensional square or rectangular lattices of the slabs are close to the bulk lattice constants in [100] and [010] directions (see [Table 1](#)). Slab surface energies agree with our previous results calculated for SZO [32] and BZO [33] slabs of different thickness.

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