

Nanotubes folded from cubic and orthorhombic SrZrO₃: First-principles study

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Abstract. Hybrid functional of the density functional theory has been applied for investigations of the electronic and atomic structure of nanotubes (NTs) based on cubic and orthorhombic strontium zirconate. The full optimization of all atomic positions in the considered systems has been performed to study the atomic relaxation and to determine the most favourable nanostructures. The stability of the single-walled nanotubes of chiralities $(n, 0)$ and (n, n) for the cubic, and $(n_1, 0)$ and $(0, n_2)$ for the orthorhombic SrZrO₃ has been investigated in dependence on their diameter, the number of layers (2 or 4) in the slab, and the outer surface termination (SrO or ZrO₂). The spontaneous splitting of the SrO-terminated (n, n) 4-layer nanotubes folded from the cubic phase into the two separated NTs has been found. The NTs folded from the orthorhombic phase, generally, preserve the atomic distortions inherent to the bulk SrZrO₃ orthorhombic phases. However, the concrete NT surface structure depends on the chirality, the number of layers and termination type.

1. Introduction

Presently, ABO₃ type perovskites are widely studied objects that exhibit unique electronic, magnetic and optical properties. Perovskite based nanomaterials can significantly improve the performance of a variety of electronic, electro-optical, electrochemical, and electromechanical devices and systems. Nanoscale systems based on SrZrO₃ (hereinafter SZO) and BaZrO₃ exhibit great promise as a solid fuel cells and hydrogen sensors due to their high chemical and mechanical stability and high proton conductivity at high temperatures [1]. Additionally, SZO, having a high dielectric constant, is great for creating high-voltage capacitors [1].

In this work we consider the different types of stoichiometric nanotubes (NTs) folded from the cubic and orthorhombic SZO. SZO undergoes [2] three temperature-dependent phase transitions. It is orthorhombic ($Pbnm$) at room temperature and it becomes cubic ($Pm\bar{3}m$) above 1360 K. In one of our previous works [3] the surface relaxation of SZO has been investigated. The first goal of the present study is to provide the understanding of the relation between the bulk SZO atomic structure and the stability of SZO-based nanotubes. The second goal of this work is to compare properties of the NTs folded from the layers of SZO with those of the NTs folded from the layers of SrTiO₃ studied earlier [4]. For the rolling up of nanotubes we use the relaxed or reconstructed thin slabs obtained by cleaving the perovskite SZO crystals along the nonequivalent atomic planes.

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2. Computational details

All the calculations have been performed within the periodic LCAO method using the CRYSTAL-2009 computer code [5]. A hybrid exchange-correlation functional PBE0 [6] has been applied. All-electron basis set for O atom has been taken from [7]. The CRENBL [8] small-core pseudopotentials and the corresponding basis set has been used for Sr 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 have been removed from the corresponding basis sets. The method chosen provides the good quality of the calculated SZO bulk properties. Thus, optimized lattice constants of cubic and orthorhombic SZO differ from the experimental values by less than 1% (see Table 1).

Stoichiometric nanosheets composed of 2 and 4 alternating (001) SrO and ZrO₂ atomic planes from the cubic phase and (001) or (110) atomic layers from orthorhombic phase have been constructed and studied as nanotube precursors. The lattice parameters and atomic structure of initial slabs have been optimized before folding. It has been proved that the obtained lattice constants of two-dimensional square or rectangular lattices are only slightly decreased compared to the bulk values (see Table 1).

Table 1. Calculated lattice parameters, formation and surface energies of nanosheets cut from SrZrO₃

Value	System	Parent phase and surface index		
		Cubic, $Pm\bar{3}m$	Orthorhombic, $Pbnm$	
		001	001	110
Lattice constants, $a, b, c, \text{\AA}$	Bulk ^a	4.123 (4.154)	5.750, 5.819, 8.173 (5.786, 5.815, 8.196)	
	2 layer slab	4.115	$a=5.782, b=5.867$	$a/\sqrt{2}=5.802, b/\sqrt{2}=5.854$
	4 layer slab	4.104	$a=5.766, b=5.778$	$a/\sqrt{2}=5.704, b/\sqrt{2}=5.813$
Formation energy, kJ/mol	2 layer slab	282.2	276.7	275.6
	4 layer slab	145.7	157.2	156.8
Surface energy, kJ/m ²	2 layer slab	1.221	1.355	1.347
	4 layer slab	1.437	1.568	1.571

^a Bulk values of experimental lattice constants [2] are given in parenthesis.

3. Results and discussion

The stability of the single-walled nanotubes of chiralities $(n, 0)$ and (n, n) for the cubic, and $(n_1, 0)$ and $(0, n_2)$ for the orthorhombic SZO has been investigated in dependence on their diameter, the number of layers in the slab, and the outer surface termination (SrO or ZrO₂). The first (I) type of NTs has been obtained by rolling up of (001) slabs of the cubic phase, the second (II) and the third (III) types were folded from (001) and (110) slabs of the orthorhombic phase, accordingly.

To estimate the NT stability we use the strain energy E_{str} per formula unit:

$$E_{\text{str}}(\text{NT}) = E_t(\text{NT})/l - E_m(\text{slab})/m, \quad (1)$$

where $E_t(\text{NT})$ – total energy of NT unit cell consisting of l bulk formula units, and $E_m(\text{slab})$ – total energy of slab unit cell containing m bulk formula units.

The atomic positions on the boundary NT surfaces exhibit a noticeable relaxation. Type I NTs folded from 2-layer slabs, generally, keep the initial structure while maintaining the original symmetry during the optimization procedure. However, if the symmetry decreases due to removing of the screw rotations, the nanotube structure exhibits considerable reconstruction with splitting of ZrO₂ shells into two atomic (O and Zr) subshells, thus resembling the surface of SZO orthorhombic phases. Strain energy of those NTs is significantly less than that of the tubes with a full set of symmetry operations. The NTs generated from the layers of cubic SrTiO₃ in ref. [4] do not exhibit such behavior.

It has also been observed a spontaneous splitting of the SrO-terminated (n, n) 4-layer nanotubes into two separated NTs. The resulted double-walled nanotubes are energetically more favorable than

the two isolated single-walled nanotubes (see Figure.1), consisting of ZrO_2 (L_1) and $\text{SrO-ZrO}_2\text{-SrO}$ (L_2) shells, correspondingly. The atomic positions in every one of these two single-walled nanotubes were optimized (see Table 2).

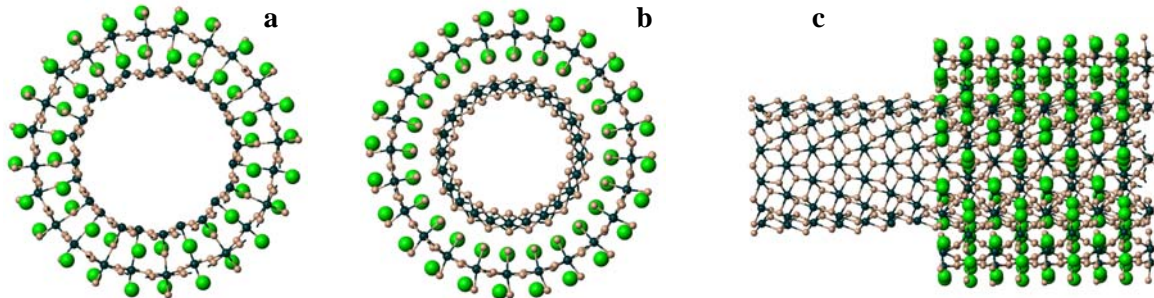


Figure 1. Spontaneous splitting of the type I 4-layer SrO-terminated (n, n) nanotubes into two separated NTs. Cross-section view before optimization (a), cross-section view after optimization (b), and side view after the optimization (c). Legend: Sr – large light balls, Zr – small dark balls, O – small light balls.

Table 2. Binding energy (ΔE) of two SWNTs into DWNT and corresponding NTs dimensions^a.

Chirality	ΔE , kJ/mol (per formula unit)	DWNT				After the optimization	
		Before the optimization		After the optimization		SWNT L_1	SWNT L_2
		R_{\min} , Å	R_{\max} , Å	R_{\min} , Å	R_{\max} , Å	R_{\min} , Å	R_{\max} , Å
(12, 12)	−58.7	8.10	14.21	5.65	13.42	5.35	13.42
(14, 14)	−49.3	9.95	16.06	6.89	14.88	6.37	15.18
(16, 16)	−33.2	11.80	17.90	8.20	16.33	7.39	16.96

^a Radii R_{\min} and R_{\max} of NTs are estimated as the distances from NT axis to the nearest and the most remote atom, correspondingly.

The NTs folded from the orthorhombic SZO phase (of types II and III), generally, preserve the atomic distortions inherent to the orthorhombic structure. However, the concrete NT surface structure depends on the chirality, the number of layers and the termination type. The reconstruction of ZrO_2 -terminated outmost surfaces due to break of the Zr–O bonds has been found in all types of NTs simulated from 4-layer slabs.

In Figure 2 we depict the dependence of the NT strain energy on its average diameter calculated as sum of R_{\min} and R_{\max} . Figure 2 shows that strain energy of SrO-terminated NTs decreases with increasing the size of NTs but that strain energy of ZrO_2 -terminated NTs increases. In the latter case the negative strain energy is a consequence of the large positive formation energy of the initial slabs. On the other hand, the SrO-terminated 2-layer NTs have the positive or zero strain energies because of the unfavorable interaction between the O atoms in the internal ZrO_2 surface due to its shrinking. In both cases the strain energy tends to zero with increasing of the NT size, since the total energy of the NT converges to the total energy of the slab. The final relaxed structure of ZrO_2 -terminated NTs folded from the two layers of both the cubic and orthorhombic phases is very similar and corresponds to the latter phase, which is more stable. Raising the diameter of the (n, n) SrO-terminated SZO NTs above the 50 Å promotes the transition from the cubic-like to the orthorhombic-like NT shell structure, which results in drastic fall of the strain energies (see Figure 2a). Figure 2b effectively demonstrates that the strain energy of ($n_1, 0$) and ($0, n_2$) 2-layer NTs coincides for the both terminations. It means that there is no difference between relaxed ($n_1, 0$) and ($0, n_2$) type II NTs. The same can be seen on Figure 2c for ($n_1, 0$) and ($0, n_2$) ZrO_2 -terminated 2-layer type III NTs.

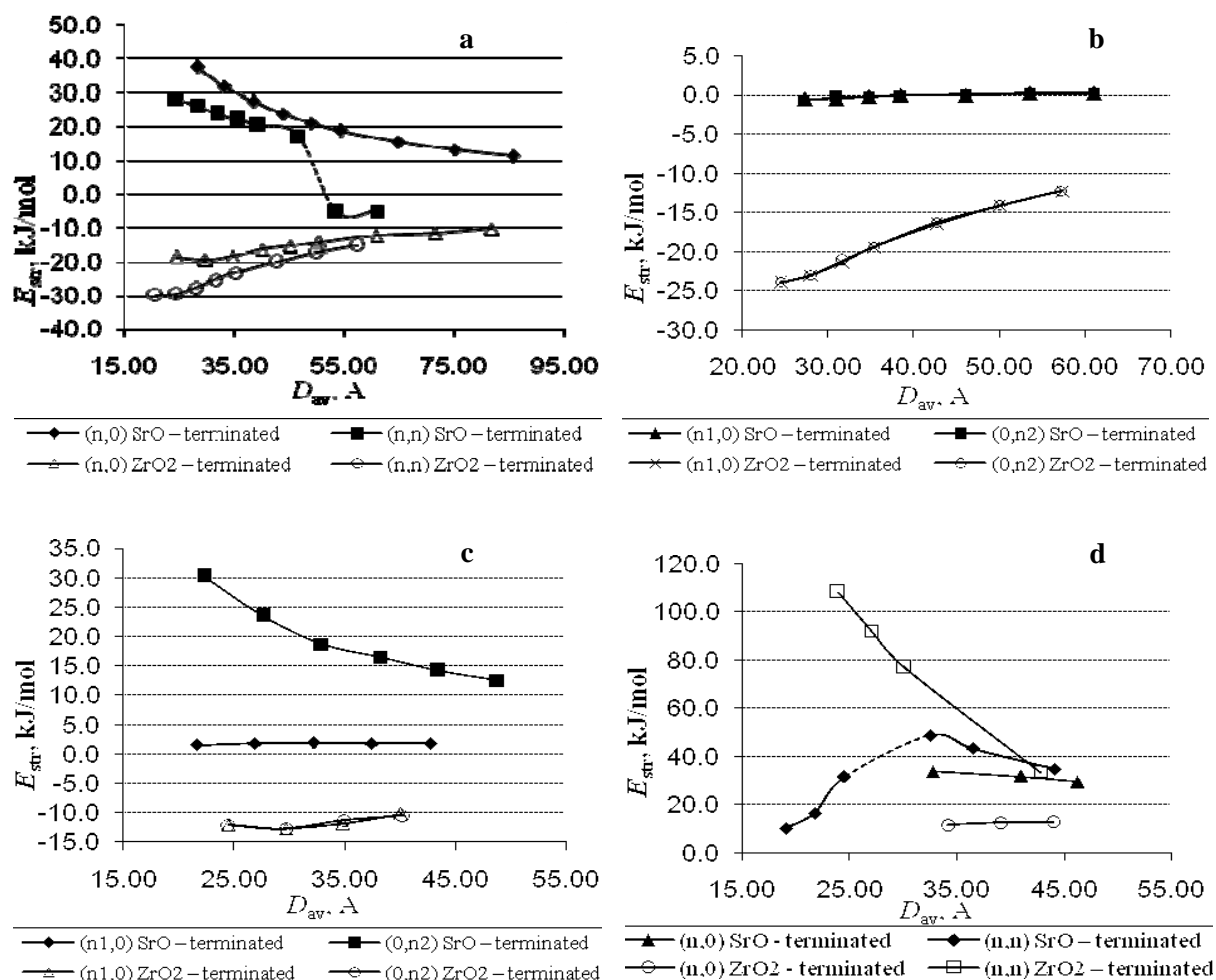


Figure 2. Dependence of strain energy E_{str} on average tube diameter D_{av} for 2-layer type I NTs (a), 2-layer type II NTs (b), 2-layer type III NTs (c), and 4-layer type I (d) NTs.

In the Figure 2d we can see the region where the E_{str} increases with increasing the diameter of SrO-terminated type I NTs. This just is the case for spontaneous splitting of 4 layer nanotubes into two separated NTs that was discussed above.

Acknowledgments

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