

FULLERENES AND ATOMIC CLUSTERS

Structure and Properties of BeO Nanotubes

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Abstract—The structure of a new non-carbon (beryllium oxide BeO) nanotube consisting of a rolled-up graphene sheet is proposed, and its physical properties are described. *Ab initio* calculations of the binding energy, the electronic band structure, the density of states, the dependence of the strain energy of the nanotube on the nanotube diameter D , and the Young's modulus Y for BeO nanotubes of different diameters are performed in the framework of the density functional theory (DFT). From a comparison of the binding energies calculated for BeO nanotubes and crystalline BeO with a wurtzite structure, it is inferred that BeO nanotubes can be synthesized by a plasma-chemical reaction or through chemical vapor deposition. It is established that BeO nanotubes are polar dielectrics with a band gap of ~ 5.0 eV and a stiffness comparable to that of the carbon nanotubes (the Young's modulus of the BeO nanotubes Y_{BeO} is approximately equal to $0.7Y_{\text{C}}$, where Y_{C} is the Young's modulus of the carbon nanotubes). It is shown that, for a nanotube diameter $D > 1$ nm, the (n, n) armchair nanotubes are energetically more favorable than the $(n, 0)$ zigzag nanotubes.

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1. INTRODUCTION

Since the discovery of single-walled carbon nanotubes in 1991 by Iijima [1], nanotubes have been continuing to attract the attention of researchers owing to their unique combination of electronic and physical properties [1]. A great variety of non-carbon nanotubes composed of different elements, for example, $(\text{Mo}, \text{W})\text{S}_2$, BN, etc. [2], have been synthesized over the past few years. The existence of nanotubes with other compositions, such as $(\text{Mg}, \text{Be}, \text{Zr})\text{B}_2$ diboride nanotubes [2] and B_2O nanotubes [3], has been predicted theoretically. This has opened up fresh opportunities for their use in electronic, optical, and electromechanical devices.

In this paper, we analyze the possibility of forming new non-carbon (beryllium oxide BeO) nanotubes. The compound $\text{Be}^{+2}\text{O}^{-2}$ has a wurtzite-type (B4) structure ($6mm$ symmetry class). In this compound, the beryllium and oxygen atoms are bound together by sp^3 hybridized bonds to form a structure similar to the structure of diamond but with atoms of different types. In 1990, Continenza *et al.* [4] theoretically predicted the existence of a BeO phase in which the beryllium and oxygen atoms are linked together by sp^2 hybridized bonds, thus forming a structure similar to the structure of graphite. On this basis, using the similarity between the allotropic modifications of carbon and BeO and reasoning from the existence of carbon nanotubes, we can consider nanotubular BeO in the form of a rolled-up sheet that consists of alternating beryllium and oxygen

atoms and is isoelectronic with graphite [2]. Beryllium oxide nanotubes, like carbon nanotubes, are conveniently described in terms of two integral indices (n, m) specifying a two-dimensional developed hexagonal lattice: $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$, where the length of the chiral vector \mathbf{C}_h is equal to the circumference of the cylindrical layer consisting of atoms. Beryllium oxide nanotubes can be divided into three classes: (i) armchair nanotubes with $n = m$, (ii) zigzag nanotubes with $n \neq 0$ and $m = 0$, and (iii) chiral nanotubes with $n \neq m$.

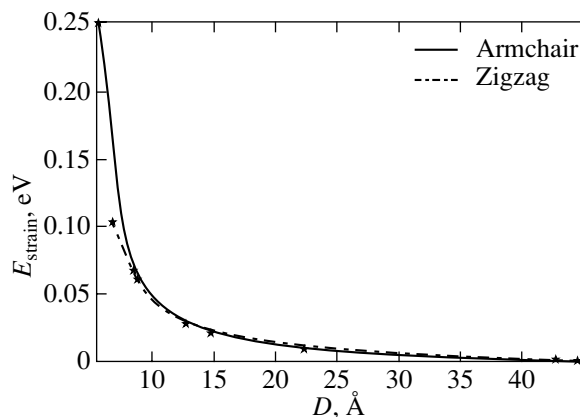


Fig. 1. Dependences of the strain energy E_{strain} on the diameter of the BeO nanotubes.

Binding energies for different modifications of the BeO compound

Structure of the BeO compound	Molecule	Wurtzite-type structure	Graphene sheet	(6, 6) nanotube	(10, 0) nanotube
Energy, eV/molecule	-7.466	-14.3692	-14.1909	-14.1298	-14.0412

In this work, we calculated the electronic band structure and physical properties of BeO nanotubes of different diameters and chiralities.

2. COMPUTATIONAL TECHNIQUE

All the calculations were performed with the Vienna *Ab Initio* Simulation Package (VASP) code [5–7]. This program package makes it possible to perform *ab initio* calculations based on the pseudopotential method and expansion in a plane-wave basis set in the framework of the local density functional formalism [8, 9].

It is known that, in this method, the electron wave function can be represented as the sum of a series of plane waves [9]:

$$\psi(\mathbf{r}) = \sum_{\mathbf{G}=0}^{G_c} C_{\mathbf{k}+\mathbf{G}} \exp(i(\mathbf{k} + \mathbf{G})\mathbf{r}), \quad (1)$$

where the sum over the vectors of the reciprocal lattice is cut off at the maximum vector of the reciprocal lattice, i.e., \mathbf{G}_C , which characterizes the cutoff energy

$E_{\text{cutoff}} = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}_C|^2$. The use of the Vanderbilt ultra-soft pseudopotential [10] in our calculations led to a substantial decrease (to 287 eV) in the cutoff energy E_{cutoff} of the plane-wave basis set without a significant loss of accuracy in the calculation of the wave functions and the electronic band structure of the BeO nanotubes. The electron–electron exchange and correlation interactions were described using the density functional theory with the Ceperley–Alder exchange–correlation functional [11], which has worked well in similar calculations.

We calculated the electronic band structures for the (4, 4), (6, 6), (10, 10), and (15, 15) armchair nanotubes and the (8, 0), (10, 0), (12, 0), and (15, 0) zigzag nanotubes. Moreover, the electronic band structures of the (50, 0) and (30, 0) BeO nanotubes with a larger diameter were calculated using the corrugated surface technique proposed in our recent paper [12]. Then, we plotted the dependence of the strain energy of the nanotube surface on the nanotube diameter (see Fig. 1).

3. RESULTS AND DISCUSSION

The calculated binding energies for different possible structures in which beryllium oxide can exist are presented in the table. As can be seen from the table, the binding energy per molecule in the structure of a BeO

nanotube is significantly less (by ~ 6.66 eV) than the binding energy for a single BeO molecule. This indicates that BeO nanotubes are energetically stable and can be synthesized from single molecules in the course of the plasma-chemical reaction or chemical vapor deposition, as is the case with a wurtzite structure or a planar graphite-like structure of beryllium oxide [4]. It should be noted that the binding energy calculated for BeO nanotubes is close to that for the graphite-like solid phase of beryllium oxide (the energy difference is $\Delta E_{\text{hex-NT}} \cong 0.06$ eV), which is in perfect analogy to carbon structures. The results of the calculations demonstrate that the equilibrium distances between the nearest neighbor atoms in all the nanotubes under investigation are very close to ~ 1.54 Å, as well as to those in the structure of the hexagonal surface of beryllium oxide.

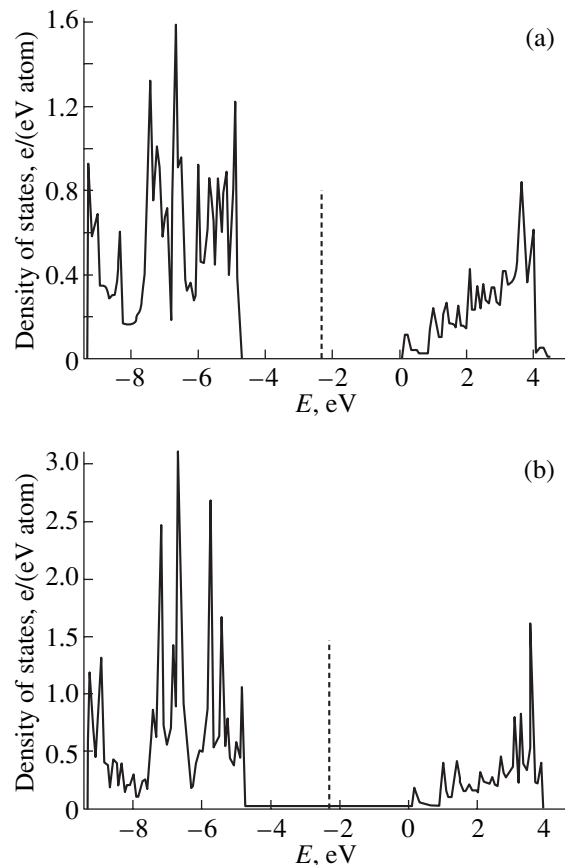


Fig. 2. Densities of states for (a) the (6, 6) BeO nanotubes and (b) the (10, 0) BeO nanotubes. The vertical line indicates the Fermi energy.

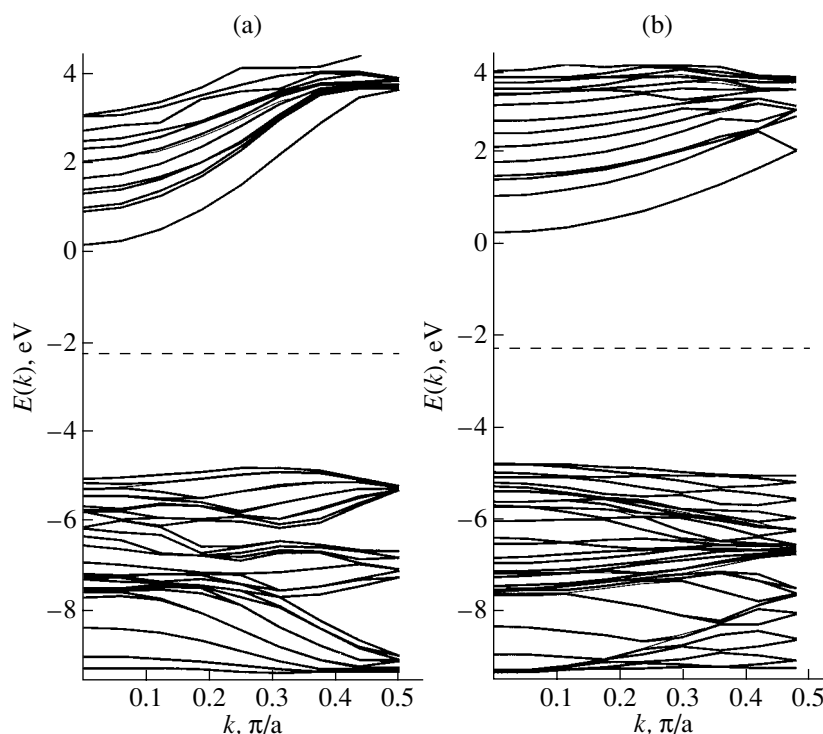


Fig. 3. Band structure for (a) the (6, 6) BeO nanotubes and (b) the (10, 0) BeO nanotubes. The horizontal line indicates the Fermi energy.

The electronic band structure was also calculated for all the nanotubes under investigation. Judging from the densities of states (Fig. 2), all the studied (armchair and zigzag) nanotubes are dielectrics with a band gap of ~ 5.0 eV. According to the results presented in Fig. 3, which shows the electronic band structures for BeO

nanotubes, the dielectric gap at the wave vector $\mathbf{k} = 0$ is indirect for the (6, 6) armchair nanotube and direct for the (10, 0) zigzag nanotube.

The surface of constant electron density (isosurface) for the (6, 6) nanotube (at an electron density $\rho = 475 \text{ e}/\text{\AA}^3$) is shown in Fig. 4. This value of the electron density was chosen in order to ensure clearly distinguishable differences in the electron density distributions around atoms of two types. It can be seen that the Be–O bond has the donor–acceptor nature and that the electron density is shifted toward the oxygen atoms. Obviously, the asymmetry of the electron density distribution with respect to the nanotube axis should result in a nonzero dipole moment of the unit cell. In turn, this should lead to a dielectric polarity of the structure and to a manifestation of the piezoelectric properties, as is the case with boron nitride nanotubes [13, 14].

Apart from the electronic band structure, we investigated the elastic properties of BeO nanotubes. The Young's moduli Y_s for the (6, 6) and (8, 0) nanotubes were determined by calculating the energies of the strained nanotubes. In these calculations, the Young's modulus Y_s was determined from the formula modified

in [15]: $Y_s = \frac{1}{S_0} \frac{\partial^2 E}{\partial \varepsilon^2}$, where ε is the strain of the nano-

tube along the nanotube axis and $S_0 = 2\pi LR$ (here, L is the length of the nanotube fragment under investigation and R is the nanotube radius). This formula does not

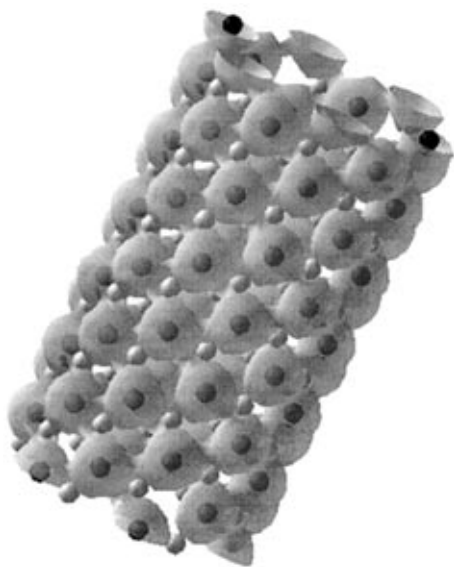


Fig. 4. Surface of constant electron density (isosurface) for the (6, 6) BeO nanotube.

contain the thickness of the nanotube wall (because it is hard to determine unambiguously).

The calculated Young's moduli for the (6, 6) and (8, 0) nanotubes, respectively, are as follows: $Y_s(6, 6) = 0.283 \times 10^{12}$ Pa nm and $Y_s(8, 0) = 0.319 \times 10^{12}$ Pa nm, which amounts to approximately 70% of the Young's modulus for the corresponding carbon nanotube [15] and indicates that the BeO nanotubes are characterized by a sufficiently high strength.

We also calculated the strain energy E_{strain} related to the curvature of the nanotube surface. This energy was determined as the difference between the energies of the planar graphene sheet and the sheet rolled into a nanotube. Figure 1 shows the dependence of the strain energy E_{strain} on the diameter of nanotubes of different chiralities. As can be seen from this figure, the obtained dependence is described by the standard relationship $E_{\text{strain}} \sim 1/D^2$ [2], where D is the nanotube diameter. It can also be seen from the table and Fig. 1 that the zigzag nanotubes are energetically more favorable than the armchair nanotubes for a nanotube diameter smaller than 10 Å and are energetically less favorable than those for a nanotube diameter larger than 10 Å. This can determine the preferred growth of the nanotubes in the course of the plasma-chemical reaction or chemical vapor deposition.

4. CONCLUSIONS

Thus, we theoretically predicted the structures of new single-walled BeO nanotubes. It was shown that these nanotubes are thermodynamically stable and have a binding energy close to the binding energy observed for beryllium oxide with a wurtzite structure. All the studied nanotubes, irrespective of their chirality, are dielectrics with a band gap of ~5.0 eV. The calculated Young's moduli for different BeO nanotubes amount to ~70% of the Young's moduli for the corresponding carbon nanotubes. It was also established that the strain energy related to the curvature of the nanotube surface satisfies the standard relationship between the strain energy and the nanotube diameter: $E_{\text{strain}} \sim 1/D^2$.

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