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The Ge-doped (6,0) *zigzag* single-walled boron phosphide nanotubes: A computational study

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ABSTRACT

Electronic structure properties including bond lengths, bond angles, tip diameters, dipole moments (μ), energies, band gaps, NMR, and NQR parameters were calculated using density functional theory for Ge-doped boron phosphide nanotubes (BPNTs). Geometry optimizations were carried out at the B3LYP/6-31G* level of theory the Gaussian 03 program suites. The isotropic (CS^I) and anisotropic (CS^A) chemical shielding parameters for the sites of various ^{11}B and ^{31}P atoms, and quadrupole coupling constant (C_Q) and asymmetry parameter (η_Q) at the sites of various ^{11}B nuclei were calculated for Ge-doped (6,0) *zigzag* BPNT models. The calculations indicated that average B–P bond lengths of the Ge_B model are larger than average B–P bond lengths of pristine and the Ge_P models. For the Ge_B and Ge_P models, the diameters values changes were almost negligible. The dipole moments of the two Ge-doped BPNT structures show slightly changes due to the Ge-doping with respect to the pristine model. In comparison with the pristine model, band gaps of the two Ge-doped models are reduced and increase their electrical conductance. The changes in the NMR and NQR parameters due to the Ge-doping are more significant for the Ge_B model than for the Ge_P model with respect to the pristine model.

1. Introduction

Synthesis of carbon nanotubes (CNTs) by Ijima [1] caused a burst of activity by their extraordinary structural, mechanical, chemical, physical, and electronic properties [1–3] and applications as novel materials [4,5]. The electronic properties of CNTs depend on their tubular diameter and chirality. Many investigations have been undertaken to investigate non-carbon based nanotubes, which exhibit electronic properties independent of these features. Among these, boron nitride (BN) [6], aluminum nitride (AlN) [7], gallium nitride (GaN) [8], indium nitride (InN) [9], boron phosphide (BP) [10], aluminum phosphide (AlP) [11], gallium phosphide (GaP) [12], and indium phosphide (InP) [13] nanotubes, which are made from the group III and V elements neighboring C in the Periodic Table, are an interesting subject of many studies. These nanotubes are inorganic analogues of carbon nanotubes (CNTs) and have good physical properties for a broad variety of applications and the nanotubes are always semiconductor [14]. Also, the nanotubes are being considered as materials that are more appropriate than CNTs for applications in specific electronic and mechanical devices. However, the properties of nitride compounds have been studied more often than the properties of phosphide compounds [15,16], and further study of the electronic properties of BPNTs is necessary.

Nuclear magnetic resonance (NMR) spectroscopy [17] and nuclear quadrupole resonance (NQR) [18] spectroscopy are the best techniques to study the electronic structure properties of matters. Moreover, doping of BPNTs by Ge atom may be able to yield changes in the interactions between the nanotube and foreign atoms or molecules. Also, the Ge-doped (6,0) *zigzag* BPNT models can using as n- or p-type semiconductor which depends on the substitution of the B or P atoms by the Ge atom; therefore, the electronic structure properties of the BPNTs are important. The objective of the present work is to study the electronic structure properties of Ge-doped BPNTs by performing density functional theory (DFT) calculations of the NMR and NQR parameters of representative (6,0) *zigzag* BPNT models (Fig. 1). The electronic structure properties, including bond lengths, bond angles, tip diameters, dipole moments (μ), energies, band gaps, and NMR and NQR parameters in the two Ge-doped BPNTs structures were investigated by calculations of the chemical shielding (CS) tensors including isotropic and anisotropic chemical shielding parameters at the sites of various ^{11}B and ^{31}P atoms and NQR calculations at the sites of ^{11}B atoms.

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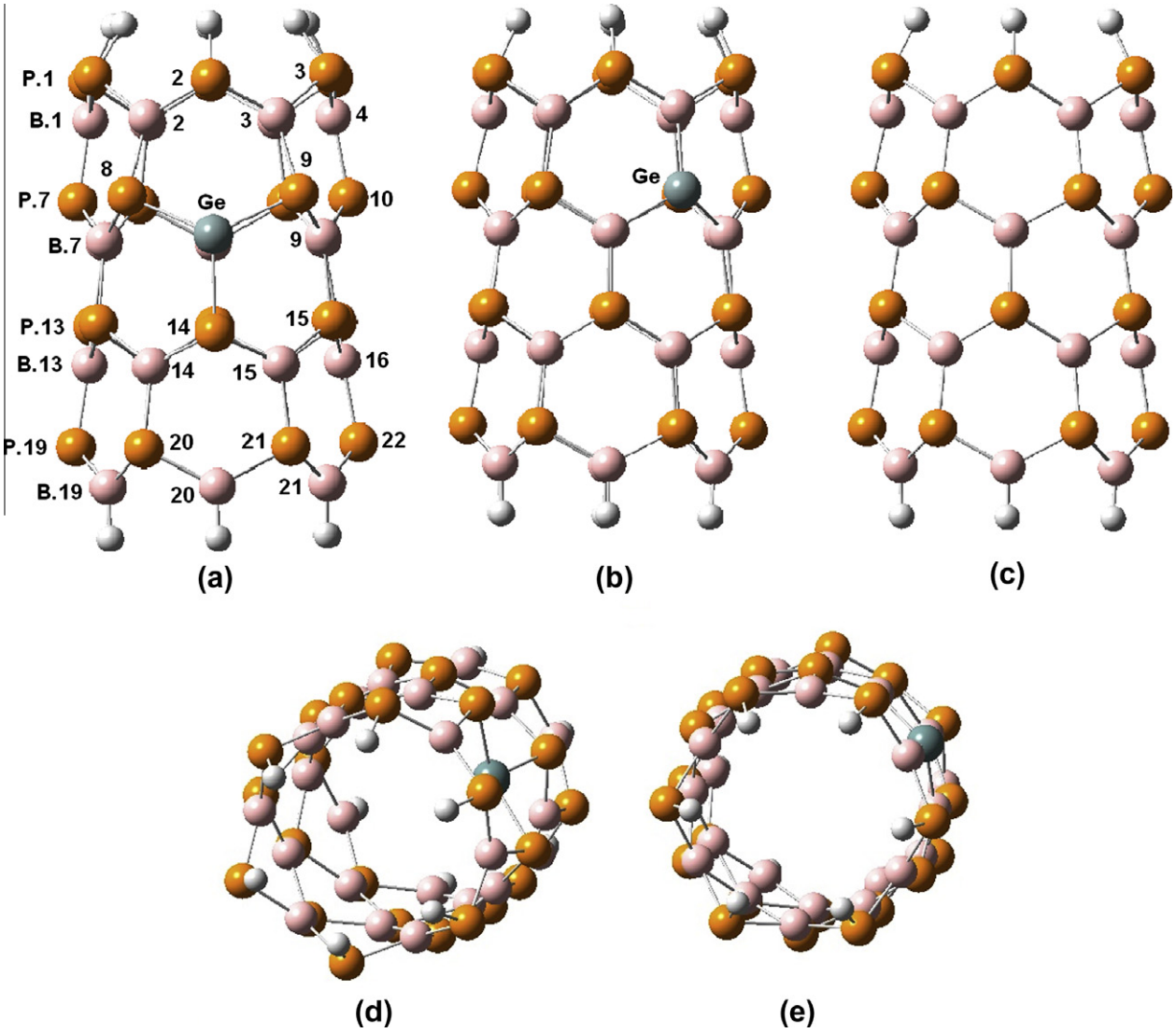

Fig. 1. (a and b) Two-dimensional (2D) views of the Ge-doped (6,0) *zigzag* BPNTs in the Ge_B and Ge_P models, (c) 2D views of the pristine (6,0) zigzag BPNTs, and (d and e) 3D views of the Ge-doped (6,0) zigzag BPNTs in the Ge_B and Ge_P models.

2. Computational methods

In the present work, the electronic structure properties of BPNTs were studied by using representative models of (6,0) *zigzag* BPNTs in which the ends of nanotubes were saturated by hydrogen atoms. Each of the representative models has three forms (Fig. 1), namely pristine (Fig. 1c) , or with a B atom doped by a Ge atom, i.e., the Ge_B model (Fig. 1a), or with a P atom doped by a Ge atom, i.e., the Ge_P model (Fig. 1b). We investigated the influence of the Ge-doping on the properties of the (6,0) *zigzag* BPNT. The hydrogenated models of the pristine (6,0) *zigzag* BPNT and the two Ge-doped models of BPNT consisted of 60 atoms with formulas of $B_{24}P_{24}H_{12}$ (pristine), Ge $B_{23}P_{24}H_{12}$ (Ge_B model), and Ge $B_{24}P_{23}H_{12}$ (Ge_P model). In the first step, the structures were allowed to relax by all atomic geometrical parameters in the optimization at the DFT level of B3LYP exchange-functional and 6-31G* standard basis set. Then, the CS tensors were calculated in the optimized structures by using B3LYP/6-31G* for the sites of various ^{11}B and ^{31}P atoms and NQR parameters of ^{11}B. It is noted that, in DFT methods, B3LYP usually gives more reliable results in comparison with experiments [19,20]. Moreover, in a previous study, it has been found that the NMR parameters calculated at the B3LYP and B3PW91 levels are in good agreement [19]. The calculated CS tensors in the principal axis system (PAS) with the order of $\sigma_{33} > \sigma_{22} > \sigma_{11}$ [21] were converted into measurable NMR parameters (isotropic chemical shielding (CS^I) and anisotropic chemical shielding (CS^A) parameters) using Eqs. (1) and (2) [7] and the NMR parameters of ^{11}B and ^{31}P atoms for the investigated models of the (6,0) *zigzag* BPNT are summarized in Table 2.

$$CS^I(\text{ppm}) = 1/3(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (1)$$

$$CS^A(\text{ppm}) = \sigma_{33} - 1/2(\sigma_{11} + \sigma_{22}) \quad (2)$$

For NQR parameters, computational calculations do not directly detect experimentally measurable NQR parameters, nuclear quadrupole coupling constant (C_Q), and asymmetry parameter (η_Q). Therefore, Eqs. (3) and (4) are used to calculated EFG tensors (electric field gradient) to their proportional experimental parameters; C_Q is the interaction energy of nuclear electric quadrupole moment (eQ) with the EFG tensors at the sites of quadrupole nuclei, but the asymmetry parameter (η_Q) is a quantity of the EFG tensors, which describes the deviation from tubular symmetry at the sites of quadrupole nuclei. Nuclei with $I > 1/2$ (I = nuclear spin angular