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Remarkable Thermal Contraction in Small Size Single-Walled Boron Nanotubes

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Abstract. Density functional theory combined with the Grüneisen approximation is used to calculate the thermal properties of single-walled boron nanotubes (BNTs). The specific heat and thermal expansion are investigated. The thermal expansion coefficient of the BNT is found to be significantly correlated with tube size and chirality. A remarkable thermal contraction is found at small tube diameters. These results indicate that BNTs would have potential applications in sensors, actuators, and memory materials.

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1 Introduction

Since the discovery of the carbon nanotube (CNT) by Iijima in 1991 [1], the one-dimensional (1D) tube system has attracted considerable attention, due to its outstanding electronic and mechanical properties [2–4]. Although the CNT demonstrates excellent properties, it suffers from the key problem of controlling tube chirality during preparation [5]. This technical problem restricts many of its potential applications such as electrical conduction and field emission devices [6]. Other materials which are less dependent

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on chirality are therefore sought. Boron, as the neighboring element of carbon in the periodic table, has logically been of interest to scientists interested in this topic. It demonstrates many outstanding properties which are similar to carbon, such as low density and high melting point [7]. The 1D single-walled boron nanotube (BNT) was first fabricated by Ciuparu et al. as early as 2004 [8]. Later, Liu et al. synthesized multi-walled BNTs combined with boron nanowire [6]. There have also been plentiful theoretical studies of BNTs [9–17]. These predict that BNTs will have higher electrical conductivity and more storage capacity for hydrogen and lithium compared to CNTs [13,18,19]. In addition, the electrical properties of single-walled BNT are shown to have less chirality dependence. The single-walled BNT with a buckled triangular shape has been predicted to be metallic regardless of tube size and chirality [9–13]. The most stable single-walled BNTs [14–16] occur in the form of the hexagonal density $\eta=1/9$ ($\eta=$ the number of hexagons/the number of triangles) with two- and three-center bonding, which structures have been found to be metallic at tube diameters larger than $17\mathring{A}$ [15]. The mechanical and electrical properties of this type of tube have been researched by Singh et al., who reported a stiffness of 210N/m [20]. Its electron transport has been researched by Lau et al., who showed that BNTs have lower resistance than single-walled CNTs of comparable length [21]. Because of their low chirality dependence, Liu et al. proposed that BNT would be superior to CNT in some aspects, for instance in field emission applications [6].

Due to these fascinating properties, BNTs are likely to have potential applications in the future development of nanoscale devices. Although their structural and electrical properties have been widely investigated [14–16,20,21], little work has been done on their thermal properties. In this paper, we therefore calculate the thermal properties of the single-walled BNTs, including the specific heat and thermal expansion, with the focus on the latter. We obtain a large negative thermal expansion for small tube diameter, which suggests an application for the BNT in counteracting the thermal expansion of normal materials in a BNT-based nanodevice. Moreover, our results indicate that BNTs would also be useful in sensors, actuators, and memory materials [22].

The rest of this paper is organized as follows. In Section 2 we present the theoretical and computational method. In Section 3 we discuss the thermal properties of BNTs and we summarize our work in Section 4.

2 Theoretical and computational method

In our study, the BNTs are calculated using density functional theory (DFT) [23] implemented in SIESTA code [24, 25] based on the Troullier-Martins pseudopotential. The generalized gradient approximation (GGA) [26] with Perdew-Burke-Ernzerhof (PBE) parameterization is used for the exchange and correlation functional. A basis set of double zeta polarizations (DZP) is employed, together with a plane-wave energy mesh cutoff of 240Ry and an energy shift of 0.02Ry. All systems are relaxed until the atomic forces are smaller than $0.001\text{eV}/\mathring{A}$. These parameters are crucial for structural optimization and