First-principles calculations of thermodynamic properties of superhard orthorhombic β-BC$_2$N

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Abstract. We investigate the thermodynamic properties of the potential superhard orthorhombic structure boron-carbonitride β-BC$_2$N by using *ab initio* plane-wave pseudopotential density functional theory method within both local density approximation (LDA) and generalized gradient approximation (GGA). The lattice parameters (a, b and c), equilibrium volume V, bulk modulus B_0 and its pressure derivative B_0' have been calculated, and compared with those of diamond and cubic boron nitride (c-BN). The obtained results are in excellent agreement with the available experimental data and other theoretical results. Through the quasi-harmonic Debye model, we also investigate the thermodynamic properties of β-BC$_2$N. The variation of the thermal expansion α, the heat capacity C_V and the Grüneisen parameter γ with pressure P and temperature T, as well as the pressure-normalized volume (P-V_n) and the pressure-bulk modulus (P-B) relationship of β-BC$_2$N are obtained systematically.

1 Introduction

Superhard materials are of important in modern high-pressure science and technology due to their outstanding properties, such as ultra-incompressible, high elastic modulus and hardness, scratch resistance, and so on. It is well-known that diamond and cubic boron nitride (c-BN) are considered to rank first and second among the known superhard materials, respectively. By mixing diamond with c-BN, one may create a new pseudo-diamond BC$_2$N alloy compound, which is harder than c-BN. Such a kind of alloys are expected to be thermally and chemically more stable than diamond and harder than c-BN.

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The ternary boron-carbonitride systems, which are isoelectronic with diamond and c-BN, have been attracted more attention because the theoretical prediction that β-C_3N_4 compound should have a hardness comparable to diamond [1]. However, most of the synthesized B-C-N compounds have the turbostratic or amorphous structures so far. A majority of the previous experimental studies on this topic originated from the isoelectronic carbon and c-BN viewed should have the similar crystal structures to diamond and c-BN. The theoretically studied structures are all focus on high dense phases, such as cubic BC_2N [2–9], hexagonal BC_2N [10–14], and chalcopyrite BC_2N [15].

The ternary B-C-N compound, BC_2N, as a new ultra-hard material also known as diamond and c-BN, has an orthorhombic crystal structure belongs to space group *Pmm*2. Therefore, it likely supersede the expensive diamond in various potential applications. Recently, the lattice dynamics and thermodynamics of orthorhombic β-BC_2N have been investigated by Cheng *et al.* [16]. To our knowledge, there are no report on the thermodynamic properties of orthorhombic β-BC_2N under high pressure and temperature.

In this work, we investigate the structure and thermodynamic properties of β-BC_2N through the Cambridge Serial Total Energy Package (CASTEP) program [17,18] and the quasi-harmonic Debye model [19]. The results obtained are well consistent with the available experimental data and other theoretical results. The paper is organized as follows: In Section 2, we make a brief review of the theoretical method. The results and some discussion are presented in Section 3. Finally, the conclusions derived from our calculations are summarized in Section 4.

2   Theoretical method

2.1   Total energy electronic structure calculations

In our electronic structure calculations, we adopt the non-local ultrasoft pseudopotential (USPP) introduced by Vanderbilt [20] for the interactions of the electrons with the ion cores. The exchange and correlation terms are described by both the local density approximation (LDA-CAPZ) proposed by Vosko *et al.* [21] and the generalized gradient approximation (GGA-PBE) proposed by Perdew *et al.* [22]. The electronic wave functions are expanded in a plane wave basis set with energy cut-off of 550 eV. Pseudo-atom calculations are performed for B ($2s^22p^1$), C ($2s^22p^2$) and N ($2s^22p^3$). For the Brillouin-zone k-point sampling, we use the Monkhorst-Pack mesh with $10 \times 10 \times 7$ k-points for both LDA and GGA calculations, where the self-consistent convergence of the total energy is 5.0×10^{-7} eV/atom. These parameters are sufficient in leading to well converged total energy and geometrical configurations. All total energy electronic structure calculations are implemented through the CASTEP code [17,18].