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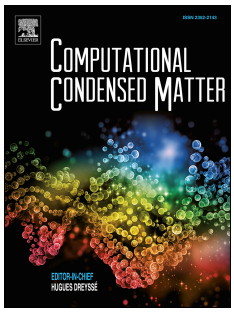

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M. Nuruzzaman, M.A. Alam, M.A.H. Shah, F. Parvin, M.A.K. Zilani

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INVESTIGATION OF THERMODYNAMIC STABILITY, MECHANICAL AND ELECTRONIC PROPERTIES OF SUPERHARD TETRAGONAL B_4CO_4 COMPOUND: *AB INITIO* CALCULATIONS

M. NURUZZAMAN [a,*], M. A. ALAM [a], M. A. H. SHAH [a], F. PARVIN [b], M. A. K. ZILANI [a]

[a] *Department of Physics, Rajshahi University of Engineering and Technology, Rajshahi-6204, Bangladesh*

[b] *Department of Physics, University of Rajshahi, Rajshahi-6205, Bangladesh*

ABSTRACT

The density functional theory (DFT) is employed to systematically investigate the structural, elastic, thermal properties, electronic structure and chemical bonding nature of the predicted superhard tetragonal B_4CO_4 (*t*-B_4CO_4). The estimated values of the elastic constants yield mechanical stability of this compound. The large values of bulk modulus (*B*), shear modulus (*G*), Young's modulus (*E*), Vickers hardness (H_v), small Pugh's modulus and Poisson's ratio identify this compound as a possible candidate for superhard material. The thermodynamic properties of *t*-B_4CO_4 are predicted for the first time through the quasi-harmonic Debye model where the lattice vibrations are taken into account. The variations of bulk modulus, Debye temperature, specific heats, and volume thermal expansion coefficient with temperature and pressure are successfully achieved for the first time. Predicted large values of Debye and melting temperatures anticipate the possibility of the strong microhardness of this compound. The analysis of electronic density of states and Mulliken populations emphasize the strong covalent bonding of B-C (B-O) atoms which can be attributed to the mechanism of superhardness of *t*-B_4CO_4.

Keywords: *ab initio*; crystal structure; elastic moduli; superhard; thermodynamic properties.

1. Introduction

The growing uses of superhard materials (materials with Vickers hardness exceeding 40 GPa) in industrial uses stimulated the scientific community to synthesize and design new superhard materials that are more mechanically, thermally and chemically stable than pure diamond [1]. Even though diamond is the hardest known natural material with a measured hardness within 60 ~ 120 GPa in single crystal form [2], the practical applications of it are limited due to its tendency to react with ferrous materials, and oxidization in air at high temperature. A significant progress for searches of superhard materials by experiment involves diamond [3], *c*-BN [4], BC_5 [5], B_6O [6], BC_2N [7-11] etc. and first principles predictions include *bct*-BN [12], *pct*-BN [13], *Z*-BN [14], *P*-BN [15], *T*-BN [16], cT_8-BN [17], *I*-BN [18], *O*-BN [19,20], *Pbca*-BN [21], B_4N_4 [22], *M*-BN [23], Z'-BN [23], BC_8-BN [23] and NB_2 [24]. Superhardness of materials formed by these light elements (B, C, N and O) is believed due to their relatively short bond lengths and strong covalent bonds. Vickers hardness of BN polymorphs ranges between 47 and 66.8 GPa. Ultra-incompressible phases (Bulk modulus with 350 ~ 430 GPa comparable to that of Diamond of ~440 GPa) are also observed in the partially covalent heavy-transition-metal borides OsB_2 [25], nitrides IrN_2 and OsN_2 [26], carbides OsC [27] and dioxides TiO_2, ZrO_2 and HfO_2 [28] etc. In an attempt to search for new superhard materials in contrast to the above mentioned systems, the ternary B-C-O compounds renewed attention during the last decade. Several materials such as $B_6C_{1.1}O_{0.33}$ and $B_6C_{1.28}O_{0.31}$ [29] under high pressure and high temperature, and single crystals of interstitial phases $B(C,O)_{0.155}$ [30] belonging to the B–C–O system have been synthesized. Li *et al.* predicted a potential superhard ternary material B_2CO with estimated hardness of 50 GPa [31]. Recently, Wang *et al*. found one stable ternary compound *t*-B_4CO_4 in the B-C-O system with Vickers hardness of 39 GPa [32]. Therefore, B-C-O materials can also be categorized into a new class of superhard materials.