The mechanical properties of CaX_6 (X=B and C)

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Abstract: The structural, electronic and mechanical properties of CaX_6 (X=B and C) are investigated by using first-principles calculations within density functional theory. Cohesive energies are determined and mechanical stabilities by mean of the calculated elastic constants are tested. Mechanical properties such as bulk, Young and shear modulus are calculated within Reuss-Voigt-Hill approximation. As a special interest, hardnesses of CaX_6 (X=B and C) compounds are calculated.

Keywords: First-principles, graphite intercalation, boron, hardness

1. INTRODUCTION

Graphite intercalation compounds (GIC) are produced by placing foreign atoms between two-dimensional sheets of graphite [1] and due to these sheets they possess interesting two-dimensional properties [2]. Therefore, these compounds have attracted a considerable interest and their physical properties were studied in a wide framework [3-5]. In alkali metal GICs, two dimensional high conductivity is appeared through charge transfer from s-electron of intercalated atoms to carbon 2p π band of the graphene layers [2]. However, some of alkali-metal GICs are superconductor (CaC_6) and generally, their superconducting temperature are low (11.5 K) [6].

In this study, structural, electronic and mechanical properties (such as bulk modulus, shear modulus, Young modulus and hardness) of CaC_6 compound were investigated by using first-principles calculations within density functional theory. Replacing carbon atom to boron atom in the structure, it was studied how change the physical properties of the structure.

Crystal structure of CaX_6 compound is shown in Fig.1 [7]. There is one Ca atom and six carbon atoms in the unit cell. Space group is R-3m (No:166)

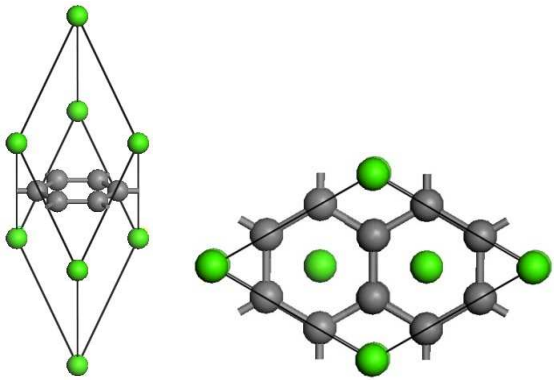


Fig.1. Crystal structure of rhombohedral CaC_6. Green and gray spheres stand for calcium and carbon atoms, respectively

2. COMPUTATIONAL METHOD

Our calculations are based on the first-principles plane-wave calculations. All calculations were performed by using CASTEP simulation package [8] within the density functional theory. In calculations, all the atomic coordinates and unit cell parameters were relaxed for minimization of Broyden, Fletcher, Goldfarb, Shanno (BFGS) scheme. The Vanderbilt ultrasoft pseudopotential [9] was used to model the ion-electron interactions, and exchange-correlation effects were treated within the generalized gradient approximation (GGA) by the Perdew-Burke-Ernzerhopf (PBE) [10-11] exchange correlation functional. The plane wave cut-off energy of 500 eV was employed, and the special k-points were generated by Monkhorst-Pack scheme, and they were chosen as 10×10×10. For the convergence, the ultra-fine setup of software package was chosen, i.e., all calculations were converged in following qualities together (i) when the maximum ionic Hellman-Feynman force was below 0.01 eV/Å, (ii) maximum displacement was below 5.0×10^{-4} Å, (iii) maximum energy change was below 5.0×10^{-6} eV/atom, and (iv) maximum stress was below 0.02 GPa.

After optimization of the unit cell, cohesive energy is calculated, $E_{\text{coh.}} = (E_{Total} - E_{iCa} - 6E_{iX})/n$, which is a key parameter to discuss energetic stability of the structure, where E_{Total} is total energy of the unit cell, E_{iCa} and E_{iX} are energies of an isolated Ca atom and X atom, respectively. *n* is total number of atoms in the unit cell.

Elastic constants are determined by using stress-strain method [12], and mechanical properties such as Bulk modulus, shear modulus and Young modulus are calculated as functions of elastic constants within Reuss-Voigt-Hill approximation [13]. For hexagonal/rhombohedral crystals, there are five independent elastic constants; c_{11}, c_{33}, c_{44}, c_{12} and c_{13}. Reuss (R) and Voigt (V) bulk modulus and shear modulus are given as,

$$B_V = \frac{1}{9}[2(c_{11} + c_{12}) + 4c_{13} + c_{33}] ,$$

$G_V = \frac{1}{30}[M + 12c_{44} + 12c_{66}]$,
$B_R = C^2/M$,
$G_R = \frac{5}{2}(C^2 c_{44} c_{66})/[3B_V c_{44} c_{66} + C^2(c_{44}+c_{66})]$.

where, the abbreviations are $C^2 = (c_{11} + c_{12})c_{33} - 2c_{13}^2$, $M = c_{11} + c_{12} + 2c_{33} - 4c_{13}$ and $c_{66} = (c_{11} - c_{12})/2$. While Reuss value is minimum limit, Voigt value is maximum limit for quantity. And, mechanical stability criteria are
$c_{44} > 0, c_{11} > |c_{12}|, (c_{11} + 2c_{12})c_{33} > 2c_{13}^2$.

Other hand, hardness is one of important mechanical properties of a material, and can be calculated by Simunek's method [14]. In this method, hardness of a material is defined as

$$H = \frac{C}{\Omega} n\left[\prod_{i,j=1}^{n} N_{ij} S_{ij}\right]^{1/n} e^{-\sigma f_e},$$
$$f_e = 1 - \left[k\left(\prod_{i=1}^{k} e_i\right)^{1/k} / \sum_{i=1}^{k} e_i\right]^2.$$

where, C and σ are constants, Ω is volume of unit cell, n is denoted the number of different bond type, k corresponds to the number of atoms in the system, and the number N_{ij} counts inter-atomic bonds in unit cell. S_{ij} is bond strength of individual bonds (d_{ij}) between atoms i and j defined as, $S_{ij} = \sqrt{e_i e_j}/(n_i n_j d_{ij})$; and $e_i = Z_i/R_i$, where Z_i is the valance electron number and R_i is atomic radius of the atom i. In calculation, $C = 1450$ and $\sigma = 2.8$ values are used and the atomic radii for different elements are taken from Pearson text book [15].

3. RESULTS AND DISCUSSION

Table 1. Calculated structural parameters, elastic constants (c_{ij}), bulk modulus (B), shear modulus (G) and Young modulus

	CaC_6	CaB_6
a (Å)	5.142 5.170 [7]	5.333
α (°)	49.40 49.55 [7]	56.00
V (Å^3)	71.939	97.354
E_{coh} (eV/atom)	-8.512	-5.763
c_{11}	645	184
c_{33}	84	88
c_{44}	78	42
c_{12}	88	132
c_{13}	87	49
c_{66}	278	26
B	147 103 [16]	90
G	122	35
E	287	93

The calculated structural parameters, elastic constants (c_{ij}), bulk modulus (B), shear modulus (G) and Young modulus (E) are listed in Table 1. Cohesive energies of both compounds are negative, thus, they are energetically stable. Cohesive energy of CaC_6 is smaller than that of CaB_6. Therefore, we can expect that CaC_6 is more stable than CaB_6. The calculated structural parameters for CaC_6 agrees well with the literature, but calculated bulk modulus in this study is higher than value of 103 GPa in Ref.[16].

However, all mechanical properties of CaC_6 listed in Table 1 are higher than those of CaB_6. This is an expected result, because of CaC_6 is more stable than CaB_6. From calculated elastic constants, it was shown that, CaC_6 and CaB_6 are mechanically stable. Other words, CaB_6 can be crystallized in CaC_6-type structure with lower mechanical properties.

Calculated band structure and density of states for CaX_6 compounds are shown in Fig.2 and Fig.3, respectively. It is shown from Fig.2 and Fig.3 that CaC_6 and CaB_6 have metallic character. From Fig.3, X atoms are dominant on DOS. B p-orbitals possess more density of states than C p-orbitals. The hybridization between Ca s-orbitals and C p-orbitals is stronger than that of B-p orbitals.

Fig.2. Calculated band structure for (a) CaC_6 and (b) CaB_6

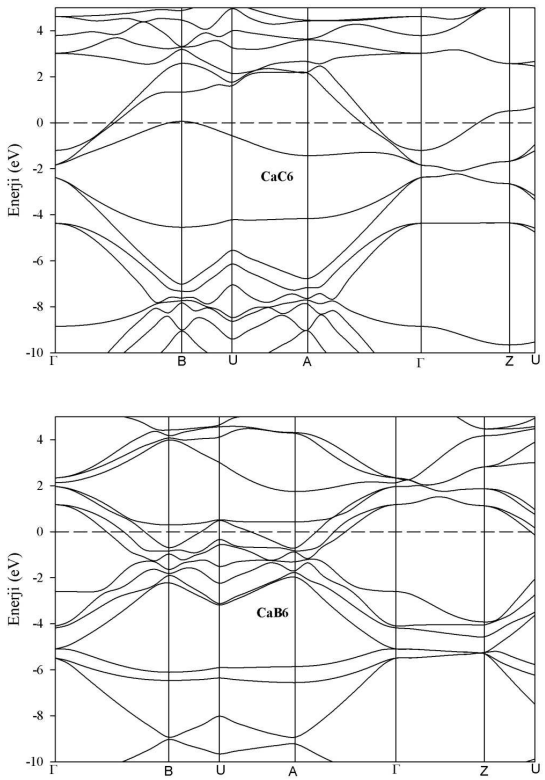
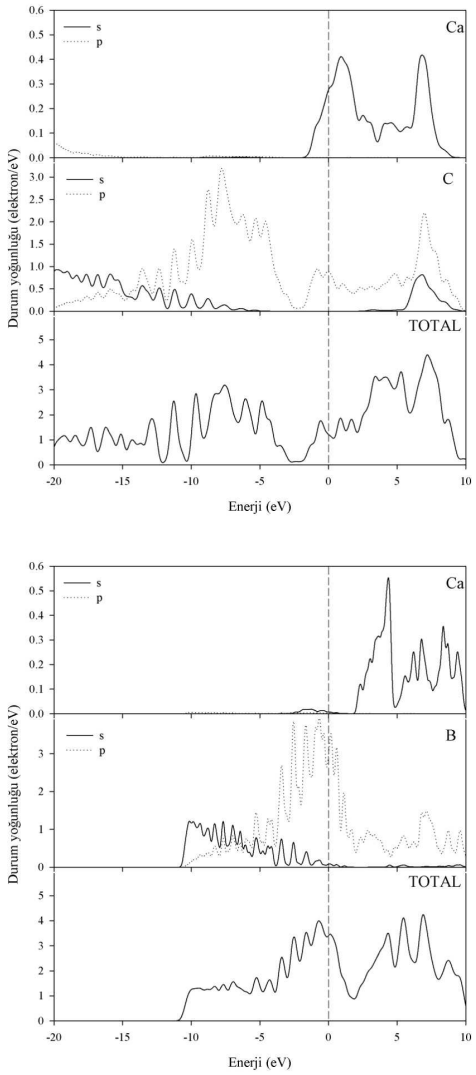


Fig.3. Calculated partial density of states for (a) CaC_6 and (b) CaB_6



Finally, hardness which is one of the important mechanical properties, is investigated. Micro-hardness for CaC_6 and CaB_6 are calculated as 13.4 GPa and 8.8 GPa, respectively. CaC_6 is harder than CaB_6. For CaX_6 compounds, it was shown that X-X bonds are stronger than Ca-X bonds. It is concluded that, graphene layer in the structures plays important role on the mechanical properties.

In conclusion, the structural, electronic and mechanical properties of CaX_6 (X=B and C) were investigated by using first-principles calculations. From calculated cohesive energies and elastic constants, both compounds are energetically and mechanically stable. Our calculations showed that, CaB_6 can be crystallized in CaC_6-type structure. However, graphene layer in the structures plays important role on the electronic and mechanical properties. From hardness analysis, CaX_6 compounds are hard material (not superhard).

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