

Обчислювальне матеріалознавство

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***Ab-initio* investigations of icosahedral boron compounds with Al, Mg, C, O, Si atoms**

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The geometry and cohesive energy of isolated clusters - fragments of icosahedral boron compounds — with Al, Mg, C, O, Si substitution atoms have been calculated within the framework of DFT electron density theory using the Gamess software package. Electron density distribution between atoms has been investigated. The bulk modulus of the B₁₂ cluster has been calculated on the basis of quantum chemical calculations and a thermodynamic series of cluster hardness has been constructed: $H_{B_{22}O_2} > H_{B_{22}C_2} > H_{B_{24}} > H_{B_{22}Si_2} > H_{B_{22}Al_2} > H_{B_{22}Mg_2}$. The calculated bulk modulus and hardness values based on the results of the first-principles study of the clusters are in good agreement with the experimental data for compounds with similar chemical compositions. The technique is applicable to the prediction of the choice of substitutional atoms in icosahedral boron groupings.

Keywords: boron, boride, isolated cluster model, bulk modulus, hardness.

Introduction

Computer-aided design plays an important role in the development of the theoretical basis for creating composite materials based on high-boron compounds, the performance characteristics of which will be higher than those of existing ones.

Due to the tendency of boron atoms to form three-center electron-deficient B—B bonds, a stable state of crystalline boron is achieved through the formation of complex structural motifs, including B₁₂ icosahedra [1]. They are the structural blocks of both allotropes of elemental boron [2] and complex boride phases [3], which demonstrate high hardness, low density and thermal endurance, which opens up prospects for the search for new materials based on them [4, 5]. One direction of such a search is higher metal borides [6, 7].

Icosahedrons B₁₂ act as structural elements of high-boron compounds, which are characterized by an increase in hardness with increasing boron content. With increasing boron content, the proportion of B—B covalent bonds

increases and the metal-boron interaction decreases, as a result of which the hardness, melting point, and thermal conductivity increase and the temperature coefficient of linear expansion decreases. The high hardness of AlMgB₁₄ boride ($H_V \sim 32\text{--}35$ GPa) has been established experimentally; even higher hardness has been found in AlMgB₁₄ + Si ($H_V \sim 35\text{--}40$ GPa) and AlMgB₁₄ + TiB₂ ($H_V \sim 40\text{--}46$ GPa) composites [8]. A special group of systems containing B₁₂ icosahedra as structural elements are lower (icosahedral) subcarbides (B₁₂C₃, B₁₃C₂), subnitride (B₁₂N₂) and boron suboxide (B₁₂O₂). Boron suboxide B₁₂O₂ exhibits a Vickers hardness of $H_V \sim 45$ GPa [9].

Computational quantum chemical methods from first principles, along with experimental studies, have gained a significant role in the design of superhard materials. These methods make it possible to calculate the elasticity parameters of crystals, study the features of the electronic structure, the nature of the chemical bond, and, consequently, determine the macro- and operational characteristics of materials. The study of the atomic and electronic structure, energy, cohesive and elastic properties of new predicted materials through the use of first-principles calculations have implemented, in particular, in articles [4, 10], within the framework of the isolated cluster model [11—14].

In this work, the cohesion energy and electron density distribution have been studied within the framework of the isolated cluster model and quantum chemical first-principles calculations, and from there, the physical-mechanical properties of materials based on B₁₂ groups with C, O, Al, Si, Mg atoms have been predicted. This approach has been shown to be useful for predictive studies in the design of new materials.

Research models and methods

The choice of B₁₂ icosahedra and C, O, Al, Si, and Mg atoms as structural elements of the model is due to the fact that they are present in thermally stable and solid high-boron compounds [8, 9]. At the first stage of the study, a model of icosahedral B₁₂ was constructed. Cluster B₁₂ was considered a regular icosahedron with a bond length of 0.16 nm. At the second stage, a basic model based on two B₁₂ clusters (with pre-optimized geometry) was built. The bond length of 0.14 nm was taken as the distance between icosahedra. In the model, in each of the B₁₂ icosahedra, one boron atom is replaced by an substitution atom. The substitution atom was positioned so that boron atom and substitution atoms alternated [4]. The basic model is not a prototype of a real compound; it is used to study the effect of substitutional atoms on the electronic and cohesive characteristics of compounds with icosahedral boron and to predict their physical-mechanical properties. As a result, models B₁₁M + B₁₁M, where M is an substitution atom: Al, Mg, C, O, Si (Fig. 1), were constructed.

The optimized geometry, total energy, electronic structure, and electron density distribution of the studied clusters has been calculated using the DFT method with the hybrid B3LYP functional and the 6—31d basis set for the isolated B₁₂ cluster and the STO-3G basis set for the B₁₁M+B₁₁M clusters. The geometry of the clusters has been optimised by gradient descent. The cohesive energy per atom is calculated as the difference between the total energy of the cluster and the total energy of non-interacting constituent atoms without taking

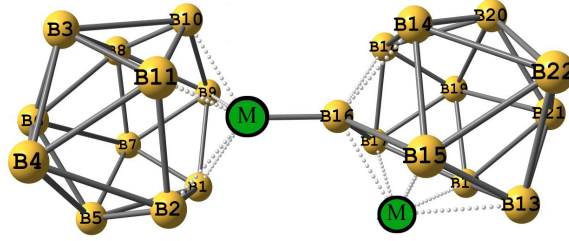


Fig. 1. Location of substitution atom in $B_{11}M + B_{11}M$ clusters, where M: Al, Mg, C, O, Si.

into account the energy of zero-point vibrations, divided by the number of atoms in the cluster. The GAMESS'09 software package [15] and the ChemCraft calculation visualisation software [16] were used to perform the calculations.

Discussion of results of computational experiment

The optimization process of searching for the equilibrium geometry of the B_{12} cluster is accompanied by a deviation from its initial correct geometric shape. The bond lengths in the equilibrium geometry vary from 0,1683 to 0,1729 nm. The cohesive energy in cluster B_{12} is 3,867 eV/at.

The results of the computational experiment for the $B_{11}M + B_{11}M$ clusters, where M are Al, Mg, C, O, Si atoms, are presented in the Table and Fig. 2. Previously calculated equilibrium geometry and cohesive energy of a pair of icosahedral B_{12} boron clusters connected by vertices without substitution atoms were used as a basis. Clusters $B_{11}M + B_{11}M$ in the Table and Fig. 2 are arranged in increasing order of the tetrahedral covalent radius of the M atom (R_M , nm) [17].

The geometry of isolated clusters with substitution atoms is significantly distorted compared to the basis one. As can be seen from the Table and Fig. 2, *a*, the cohesive energy of atoms in the $B_{11}M + B_{11}M$ cluster in comparison with the basis is largely determined by the size of the M atom. For oxygen and carbon atoms, which are smaller than a boron atom, the cohesive energy is greater and for silicon, aluminum and magnesium atoms, which are larger than a boron atom, it is lower than the basis one. The conclusion that the most energetically favorable of the studied clusters are $B_{11}C + B_{11}C$ and $B_{11}Si + B_{11}Si$ coincides with the data of [4].

When performing calculations, it was noticed that the optimization procedure for a cluster with an Al proceeded without oscillations and faster than for clusters with other substitution atoms. This is probably due to the fact that Al is isoelectronic up to B. To clarify the assumption, calculations were carried out for clusters with Mg, C, O, Si atoms, in which the isoelectronic state was simulated by establishing a charge on the clusters. For $B_{11}C + B_{11}C$ and $B_{11}Si + B_{11}Si$ the charge on the cluster was set to $+2e$ (2 electron charges), for $B_{11}Mg + B_{11}Mg$ ($-2e$), and for $B_{11}O + B_{11}O$ ($+6e$). In this case, the optimization procedure proceeded more smoothly and without oscillations of the total energy of the cluster, but the cohesive energy turned out to be somewhat lower than in calculations with zero cluster charge (Fig. 3). The cluster with an oxygen stands apart — it tends to decay.

Characteristics of B₁₂ clusters with Al, Mg, C, O, Si atoms and the hardness value for comparable chemical compounds

Cluster	VEC	E_{coh}	E_g	R_M	H	H_{exp} [9, 18, 19]
B ₁₂ + B ₁₂	3	5,911	0,498	0,089	39,9 [11]	42—45
B ₁₁ O + B ₁₁ O	3,25	6,454	2,063	0,066	47,5	38, 45
B ₁₁ C + B ₁₁ C	3,08	6,379	1,858	0,077	46,3	45, 57
B ₁₁ Si + B ₁₁ Si	3,08	5,891	1,717	0,117	39,5	27, 41*
B ₁₁ Al + B ₁₁ Al	3	5,667	0,577	0,126	36,7	37
B ₁₁ Mg + B ₁₁ Mg	2,92	5,588	1,703	0,140	35,5	34*

VEC — the valence electron concentration; E_{coh} — the cohesive energy per atom (eV/at.); E_g — the band gap (eV); H and H_{exp} — the calculated and experimental hardness (GPA); *hardness calculation from [19].

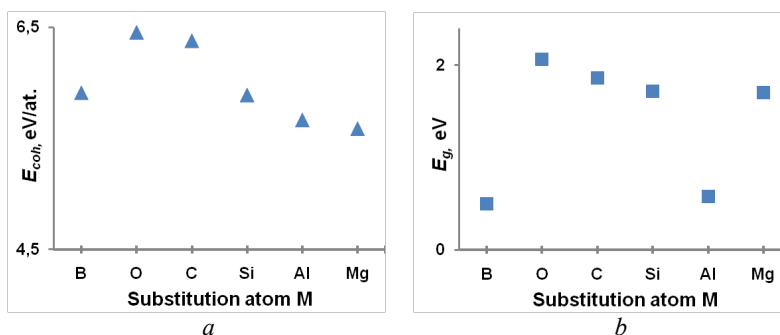


Fig. 2. Dependence of cohesive energy (a) and bandgap energy (b) of B₁₁M + B₁₁M clusters on the type of substitution atoms M.

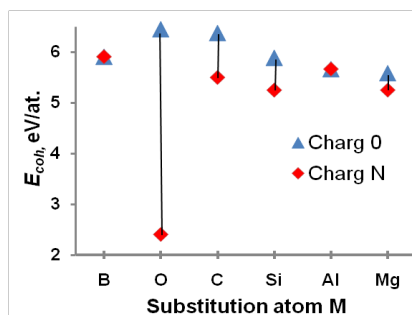


Fig. 3. Effect of charge on a cluster on the cohesive energy of B₁₁M + B₁₁M.

The study of the B₁₂ cluster has shown that the electron density is represented as a superposition of the electron density of the atomic backbone and the accumulation of the electron density of the valence part between the atoms. The density of electrons is distributed over the surface of the cluster. The covalent chemical bond is characterized by the cluster. In a case of covalent bonds between atoms, it is necessary that the molecule has at least $2n$ valence

electrons, where n is the number of formal bonds. There are only 36 valence electrons and 30 bonds in the B₁₂ cluster, which requires 60 electrons to fill. Thus, the B₁₂ cluster belongs to the electron-deficient compounds. A reasonable way to describe such structures is to consider them as systems of delocalized electrons [20].

The research of the electron density of B₁₁M + B₁₁M clusters, where M is B, Al, C, Si, is shown in Fig. 4. The electron density maps in the range of -0,01 to

0.1 relative units [16] pass in the plane of M—B—M bonds. The distribution of electron density in the region of bonding between an substitution and a boron atoms is presented.

The electron density for the $B_{12} + B_{12}$ cluster of each of the B_{12} icosahedrons is described above. A bond between atoms of the $B_{12} + B_{12}$ cluster is covalent. The study of the electron density on B and M atoms in clusters with substitution atoms suggests a predominantly covalent bond in the clusters. The electron density between the B and C atoms in the $B_{11}C + B_{11}C$ cluster is located in the bonding zone (Fig. 4, *b*). There is a slight transfer of electron density from boron to the carbon atom. The electron population by Mulliken is 6,3 and 4,8 e on carbon and boron atoms, respectively. In the $B_{11}Si + B_{11}Si$ cluster, there is an additional electron density on silicon atoms and neighboring boron atoms due to the electron density of the cluster as a whole. The electron clouds are anisotropic, pear-shaped (Fig. 4, *c*). The Mulliken electron population is 14,07 and 5,05 e on silicon atoms and neighboring boron atoms, respectively. The bond is a covalent-ionic one. Electron clouds on aluminum atoms in the $B_{11}Al + B_{11}Al$ cluster are spherical (Fig. 4, *d*). The Mulliken electron population is 12,8 and 5,02 e on aluminum atoms and neighboring boron atoms, respectively. The electron density is transferred from aluminum to neighboring boron atoms. The bond between the impurity atom and boron is a covalent ionic one.

The examined clusters meet the requirement [21] for the design of superhard materials regarding the covalent type of interatomic bonds and the highest possible density of valence electrons in the desired material (see Table).

Boron groupings with a B—B covalent bond in boride molecules are electron-deficient [20]. To stabilize them, it is necessary to attract electrons from the metal atom. As a result, an intermediate type bond is created between metal and boron. In borides of elements of groups III—VIII (Al, C, Si), which

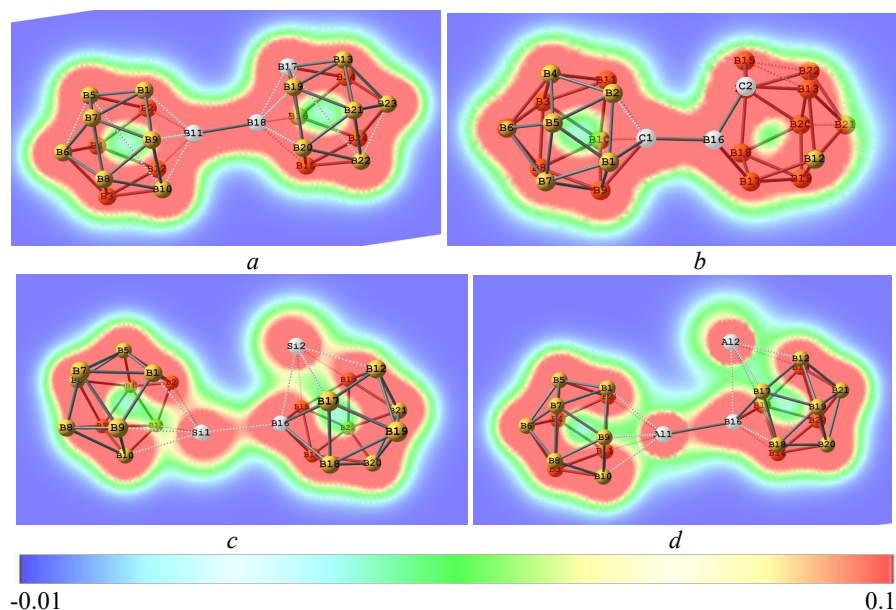


Fig. 4. Electron density maps of $B_{11}M + B_{11}M$ clusters, where M: B (*a*), C (*b*), Si (*c*), Al (*d*).

give up more than two electrons, they are partially metallic, in other cases (Mg) — partially ionic. As the boron content increases, the ratio of B—B covalent bonds increases and the metal-boron interaction decreases, resulting in higher hardness, melting point, and thermal conductivity.

The calculation of the modulus of bulk elasticity [22, 23] of boron K is given by the second derivative of the total energy E_{tot} over the volume V

$$K = V \frac{d^2 E_{tot}}{dV^2}$$

at the equilibrium point. As the studied cluster B_{12} can be considered a nanoscale isotropic body of almost spherical shape, we apply the formula in which the determination of the bulk elasticity modulus K is carried out along the optimisation curve of the B_{12} cluster similarly to that described in [13]:

$$K = V_{opt} \frac{E_{tot} - E_{opt}}{(V - V_{opt})^2},$$

where E_{opt} and V_{opt} are the total energy and volume of the optimised cluster (at the equilibrium point); E_{tot} and V are the total energy and volume of the cluster in the neighbourhood of the equilibrium point; the calculation of the volume values V_{opt} and V is carried out by the diameters (distances between the centres of opposite atoms) of the cluster at the corresponding step of the optimisation curve.

After studying the geometrical and energetic characteristics of the isolated B_{12} cluster, the values of the total energy at the equilibrium point E_{opt} (−297.7776431 a.u.) and near the equilibrium point E_{tot} (−297.7679879 a.u.), as well as the distances between the centres of opposite atoms in the optimised cluster (0.336 nm) and the cluster at the corresponding steps of the optimisation curve (0.323 nm).

Based on the results of the study of the B_{12} cluster, the bulk modulus $K = 177.5$ GPa has been obtained, being in good agreement with the experimental value $K_{exp} = 178$ GPa of the α - B_{12} structure [23].

The thermodynamic series of the hardness of compounds based on $B_{12} + B_{12}$ with substitutional atoms C, O, Si, Al, and Mg has been constructed taking into account that isolated clusters representing fragments of crystalline compounds are macromolecules and there is no concept of direction in the crystal or dispersion for them. Therefore, the method where the hardness is determined by the strength of the bonds between the atoms of the solid has been applied. The method of determining the dependence between the specific total surface energy of a solid and the cohesive energy of atoms in a crystal was proposed in [24—27]. In other words, the connection between the structure and energy of the atomic lattice (covalent, metallic) and mechanical properties is considered. This method makes it possible to relate the above calculated cohesive energies and geometries of isolated $B_{11}M + B_{11}M$ ($M = B, C, O, Al, Si, Mg$) clusters to the relative hardness values H and to construct a thermodynamic hardness series of these compounds: $H_1 : H_2 : H_3$.

According to work [24], the relationship between the crystal cohesive energy E_{coh} and its full specific surface energy ε_{hkl} is defined as follows:

$$\varepsilon_{hkl} = M_{\varepsilon(hkl)} E_{coh} / a^2,$$

where a is the lattice period; $M_{\varepsilon(hkl)}$ is the surface energy structural constant,

$$M_{\varepsilon(hkl)} = 694.34 \delta(c - x)/mnC,$$

where δ — the multiplicity of the elementary parallelogram of the plane hkl ; m — a constant equal to 1 for the face [100] of cubic systems crystals; n — the number of atoms in the compound formula; C — the coordinate number.

Since all the factors, except for the cohesive energy, for calculating the specific total surface energy ε_{hkl} of the studied clusters are practically the same, the thermodynamic series of hardness of the $B_{11}M + B_{11}M$ clusters corresponds to the series of cohesive energy E_{coh} (see Table):

$$H_{B_{22}O_2} \rangle H_{B_{22}C_2} \rangle H_{B_{24}} \rangle H_{B_{22}Si_2} \rangle H_{B_{22}Al_2} \rangle H_{B_{22}Mg_2}.$$

As can be seen from the Table, the obtained series also in general corresponds to the valence electron concentration series of the examined structures. Indeed, according to [19, 21, 28], the valence electron concentration is proportional to the hardness of the material. The hardness values of the compounds $H_{B_{22}M_2}$ (Table) have been estimated by the ratio of the cohesive energy of the cluster of the corresponding composition, $E_{coh}(B_{22}M_2)$, to the cohesive energy in the etalon cluster $E_{coh}(B_{24})$

$$H_{B_{22}M_2} = H_B (E_{coh}(B_{22}M_2)/E_{coh}(B_{24})),$$

where H_B — the hardness value of boron.

The hardness value β - B_{12} , calculated in [11] based on the results of a first-principles study of an isolated cluster constructed from boron icosahedrons, according to the following relation, was taken as H_B

$$H = \alpha \frac{VEC}{C} \frac{2E_{coh}}{V^*C},$$

where α — the coefficient of relative (as compared to diamond) plasticity, for the elementary substances and compounds of second period elements α equals 1 [21]; V^* — the molar (atomic) volume obtained by first principles within the cluster model.

The estimated hardness values based on the cluster characteristics are in good agreement with the experimental values for compounds with similar chemical constituents (see Table).

Conclusions

The size of the substituent atom M is crucial for the cohesion energy of isolated $B_{11}M + B_{11}M$ clusters, which is higher than the size of the atom M is smaller. In terms of energy advantage, the most promising of the studied clusters are $B_{11}C + B_{11}C$ and $B_{11}Si + B_{11}Si$.

Analysis of the calculation of the electron density in the $B_{11}M + B_{11}M$ clusters suggests a predominantly covalent bond in the clusters. The electron transfer between the substituent and boron atoms is no more than 0.3 e.

The bulk modulus of boron, calculated on the basis of the results of the first-principles study of the B_{12} cluster, equals 177.5 GPa, which demonstrates a high agreement with its experimental value (178 GPa).

A value of the cohesive energy of atoms in isolated clusters is one of the determining factors for predicting the hardness of compounds whose chemical composition is close to that of these clusters. The thermodynamic series of hardness of $B_{11}M+B_{11}M$ clusters, where M — B, O, C, Si, Al, Mg, corresponds

to the series of the cohesive energy of atoms in these clusters:
 $H_{B_{22}O_2} \rangle H_{B_{22}C_2} \rangle H_{B_{24}} \rangle H_{B_{22}Si_2} \rangle H_{B_{22}Al_2} \rangle H_{B_{22}Mg_2}$.

The calculated hardness values based on the results of the first-principles study of the clusters are in good agreement with the experimental data for compounds with similar chemical compositions. The technique is applicable to the prediction of the choice of substitutional atoms in icosahedral boron groupings.

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***Ab-initio* дослідження сполук ікосаедричного бору
з атомами Al, Mg, C, O, Si**

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У розвиток теоретичної бази створення композитних матеріалів на основі високобористих сполук, експлуатаційні характеристики яких будуть більш високими, ніж у існуючих, виконано ab-initio дослідження ізольованих кластерів з ікосаедричного бору з атомами заміщення Al, Mg, C, O, Si. У рамках теорії електронної густини DFT із застосуванням пакету Gamess розраховано геометричні та енергетичні параметри ізольованих кластерів $V_{11}M + V_{11}M$, де M — атом заміщення Al, Mg, C, O, Si. Досліджено енергію когезії, заряд на атомах, розподіл електронної густини між атомами у кластерах. Зроблено висновок, що розмір атому заміщення має обумовлююче значення для енергії зчеплення кластерів $V_{11}M + V_{11}M$. Найбільш перспективними з точки зору енергетичної вигідності досліджених кластерів є $V_{11}C + V_{11}C$ та $V_{11}Si + V_{11}Si$. На основі даних квантово-хімічних розрахунків обчислено модуль об'ємної пружності кластера V_{12} , який становить 177,5 ГПа, що демонструє високий збіг із його експериментальним значенням (178 ГПа). Побудовано термодинамічний ряд твердості кластерів, який відповідає ряду енергії зчеплення атомів: $H_{V_{22}O_2} \rangle H_{V_{22}C_2} \rangle H_{V_{24}} \rangle H_{V_{22}Si_2} \rangle H_{V_{22}Al_2} \rangle H_{V_{22}Mg_2}$. Значення твердості, розраховані за результатами першопринципного дослідження кластерів, добре узгоджуються з експериментальними даними для сполук з подібним хімічним складом. Методика може бути використана для прогнозу вибору атомів заміщення в угрупованнях ікосаедричного бору.

Ключові слова: бор, бориди, модель ізольованого кластера, модуль об'ємної пружності, твердість.