

# The investigation of hardness and bonding behavior in $XB_4$ , $X = \{Ce, Th, U, Pa\}$ , tetraborides by first-principles

Sezgin AYDIN and Aynur ÖZCAN

*Department of Physics, Faculty of Arts and Science, Gazi University, Teknikokullar,  
Ankara-TURKEY  
e-mail: sezginaydin@gazi.edu.tr*

Received 03.07.2009

## Abstract

The mechanical and electronic properties of  $XB_4$ ,  $X = \{Ce, Th, U, Pa\}$ , tetraborides have been studied by using first-principles based on density functional theory. The results show that these boron-rich solids are mechanically and thermodynamically stable. From the calculated band structure and density of states, we obtained that they have metallic character. When the calculated parameters related to the crystal structure were considered with the bonding characteristics, the microscopic hardnesses of these boron-rich solids can be theoretically calculated. The obtained hardness values indicate that, these materials are hard, but not superhard. Furthermore, from the detailed hardness analysis, we found that the octahedron structural unit of the structure has an important role on the total hardness of the materials.

**Key Words:** First-principles, tetraboride, hardness, boron-rich solids

## 1. Introduction

Boron-rich solids have received considerable attention for their fascinating characteristics such as high strength, low density, high chemical inertness, neutron capture properties (useful in solid state neutron detectors) [1–4], superconductivity [5–6] and, especially, excellent hardness [7–10]. In addition, these solids possess unique crystal structure and many borides contain boron clusters as structural units which they have different number of atoms. Special among the borides are those with 6- and 12-atom clusters, known for their, respective, octahedral and icosahedral structures [9, 11, 12]. On the other hand, the most important subject in this point is that these structural units play important roles in the electronic and mechanical properties of the boron-rich solids.

It is well known that the hardness characteristics of a material are closely related to its crystal structure and internal chemical bonding [9]. Furthermore, a material will exhibit higher hardness with increasing covalent

bond strength. In general, atoms which form octahedral and icosahedral units in boron-rich solids exhibit highly covalent and partially ionic bonding [9, 13]. Then, it can be expected that a material with these structural units will be hard or superhard.  $\text{ThB}_4$ ,  $\text{UB}_4$  and  $\text{CeB}_4$  tetraborides are such boride materials, and they contain octahedral units in their crystal structures. These tetraborides are important members of hard borides due to the strong covalent B-B bonding within and among the octahedrons [14].

In early work, Zalkin et al. [15–17] reported octahedral and icosahedral structures in  $\text{ThB}_4$ ,  $\text{UB}_4$  and  $\text{CeB}_4$  tetraborides, but to-date there has been no detailed theoretical investigation within the density functional theory framework for mechanical properties such as single-crystal elastic constants and microscopic hardness.

## 2. Calculation method

In the present work, the mechanical and electronic properties of  $\text{XB}_4$ ,  $X = \{\text{Ce, Th, U, Pa}\}$ , tetraborides were calculated by using the CASTEP simulation package [18], based on density functional theory. The Vanderbilt ultrasoft pseudopotential [19] was used. Exchange-correlation effects were treated by using the Generalized Gradient Approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [20]. A plane wave cut-off energy of 460 eV was employed. The valence electrons configuration considered in this study include  $4f^1 5s^2 5p^6 5d^1 6s^2$  for Ce,  $6s^2 6p^6 6d^2 7s^2$  for Th,  $5f^3 6s^2 6p^6 6d^1 7s^2$  for U,  $5f^2 6s^2 6p^6 6d^1 7s^2$  for Pa and  $2s^2 2p^1$  for B. The special k-points of  $4 \times 4 \times 6$  were generated by Monkhorst-Pack scheme [21]. In all calculations in this study, ultra-fine setup of software package was chosen, namely, it was assume that all calculations were converged when the maximum ionic Hellman-Feynman force was below  $0.01 \text{ eV}/\text{\AA}$ , maximum displacement between cycles was below  $5.0 \times 10^{-4} \text{ \AA}$ , maximum energy change was below  $5.0 \times 10^{-6} \text{ eV/atom}$ , and maximum stress was below 0.02 GPa.

The cohesive energies  $E_{coh}$  and formation energies  $\Delta H$  per formula unit of these tetraborides were calculated as [22]

$$E_{coh} = E_{tot}(\text{XB}_4) - (E_{iso}^X + 4E_{iso}^B), \quad (1)$$

$$\Delta H = E_{tot}(\text{XB}_4) - (E_{solid}^X + 4E_{solid}^B), \quad (2)$$

where  $E_{iso}^X$  and  $E_{iso}^B$  are total energies of isolated  $X$  and boron atoms, respectively;  $E_{tot}(\text{XB}_4)$  is total energy of  $\text{XB}_4$  tetraborides per unit cell;  $E_{solid}^X$  is energy per  $X$  atom in its solid phase; and  $E_{solid}^B$  is energy per boron atom in the  $\alpha$ -rhombohedral phase.

A detailed investigation of bonding characteristics is very important to explain the properties of a crystal structure. Therefore, we studied the bonding characteristics of  $\text{XB}_4$ ,  $X = \{\text{Ce, Th, U, Pa}\}$ , tetraborides by using partial/total density of states (DOS) and Mulliken's population analysis [23]. Finally, we calculated the theoretical microscopic hardnesses of these tetraborides with the semi-empirical method proposed by Gao et al. [24]. In this hardness method, which was improved to investigate hardness of covalent or highly covalent crystals, hardness of a  $\mu$ -bond in the structure is calculated via the relation

$$H_v^\mu = 350 (N_e^\mu)^{2/3} e^{-1.191 f_i^\mu} / (d^\mu)^{2.5}, \quad (3)$$

where  $f_i^\mu$  and  $d^\mu$  are the ionicity and length of the  $\mu$ -bond, respectively; and  $N_e^\mu$   $N_e^\mu$  is the valence electron

density and is calculated as

$$N_e^\mu = \left( \frac{Z_X}{N_X} + \frac{Z_Y}{N_Y} \right) \left[ \sum_\mu (d^\mu)^3 N^\mu \right] / \left[ V (d^\mu)^3 \right], \quad (4)$$

where  $Z_X$  and  $Z_Y$  are the valance electron numbers of X and Y atoms forming the  $\mu$ -bond,  $N_X$  and  $N_Y$  are the nearest coordination numbers of the X and Y atoms,  $N^\mu$  is the number of  $\mu$ -bond, and  $V$  is the volume of the unit cell. After individual bond hardnesses of all bonds in the structure is calculated by equation (3), the total Vickers hardness of the crystal structure is found as taking geometric average of these bond hardnesses.

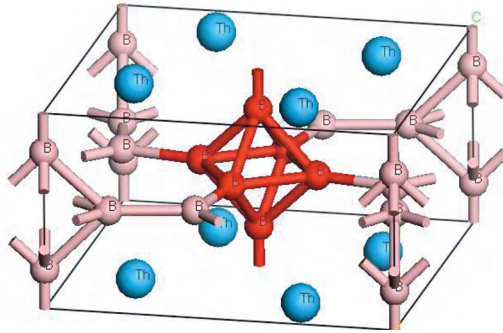
Elastic constants define response to applied stress of a given structure. In order to calculate elastic constants of a structure, a small strain is applied onto the structure, and change in energy is determined. For a crystal with small strain  $\varepsilon$ , total energy can be expressed by a Taylor expansion [25]:

$$E(V, \varepsilon) = E(V_0, 0) + V_0 \sum_{i=1}^6 \sigma_i e_i + \frac{V_0}{2} \sum_{i,j=1}^6 c_{ij} e_i e_j + \dots,$$

where  $V_0$  and  $E(V_0, 0)$  are volume and energy of an undistorted crystal, respectively;  $c_{ij}$  are elastic constants; and strain tensor  $\varepsilon$  is defined as [25]

$$\varepsilon = \begin{pmatrix} e_1 & \frac{1}{2}e_6 & \frac{1}{2}e_5 \\ \frac{1}{2}e_6 & e_2 & \frac{1}{2}e_4 \\ \frac{1}{2}e_5 & \frac{1}{2}e_4 & e_3 \end{pmatrix}.$$

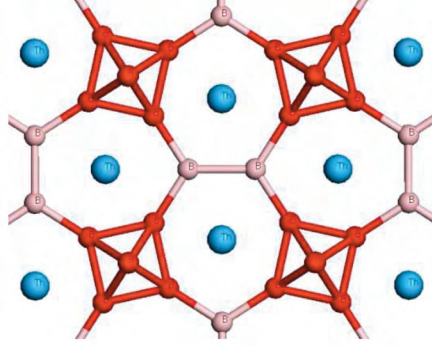
In the present work, the mechanical and electronic properties, bonding behaviors and hardnesses of  $XB_4$ ,  $X = \{\text{Ce}, \text{Th}, \text{U}, \text{Pa}\}$ , tetraborides are investigated using first-principles calculations as detail. Also, we investigated  $\text{PaB}_4$  with the same structure as a new compound. It was suppose that  $XB_4$  tetraborides are crystallized in  $\text{ThB}_4$ -type structure, a structure with four thorium atoms and sixteen boron atoms in the unit cell, with space group  $P4/m\bar{3}m$ . While thorium atoms are localized at the 4(g) Wyckoff site, boron atoms are localized at the 4(e), 4(h) and 8(j) Wyckoff sites. Figure 1 shows the crystal structure of  $\text{ThB}_4$ .



**Figure 1.** The unit cell of  $\text{ThB}_4$ -type crystal structure. Blue spheres denote thorium atoms, and pink spheres for boron atoms. Boron atoms forming the octahedron are shown in red.

The  $\text{ThB}_4$ -type structure is analogous the rhombohedral boron carbide ( $\text{B}_4\text{C}$ ) structure. In the  $\text{B}_4\text{C}$  structure, boron atoms form the icosahedra and bond with the linear carbon chains of three atoms [9]. However,

in the  $\text{ThB}_4$ -type structure, boron atoms form the octahedrons and bond with linear boron chains of two atoms (see Figure 2).



**Figure 2.** Top view of the  $\text{ThB}_4$ -type crystal structure.

### 3. Results and discussion

The calculated equilibrium lattice constants, elastic constants, bulk ( $B$ ) and shear ( $G$ ) modulus,  $B/G$  ratios, cohesive and formation energies are listed in Table 1. Bulk modulus  $B$  and shear modulus  $G$  were calculated by Voigt-Reuss-Hill's approximation from single-crystal elastic constants [26, 27].

**Table 1.** The calculated structural parameters, single crystal elastic constants, shear and bulk modulus, cohesive and formation energies of  $\text{XB}_4$ ,  $\{X = \text{Ce}, \text{Th}, \text{U}, \text{Pa}\}$ .

Parameters	$\text{CeB}_4$	$\text{ThB}_4$	$\text{UB}_4$	$\text{PaB}_4$
a ( $\text{\AA}$ )	7.108	7.189	6.942	6.994
	7.205 <sup>a</sup>	7.256 <sup>a</sup>	7.075 <sup>a</sup>	
c ( $\text{\AA}$ )	4.021	4.077	3.902	3.937
	4.090 <sup>a</sup>	4.113 <sup>a</sup>	3.979 <sup>a</sup>	
			3.978 <sup>b</sup>	
V ( $\text{\AA}^3$ )	203.167	210.697	188.080	192.582
$C_{11}$ (GPa)	463.3	528.0	546.9	568.1
$C_{33}$	478.9	594.7	543.5	577.3
$C_{44}$	159.6	198.9	205.3	203.7
$C_{66}$	175.0	202.4	226.0	223.9
$C_{12}$	59.8	87.0	98.1	96.5
$C_{13}$	41.5	79.9	66.0	75.2
B (GPa)	187.9	238.0	232.9	245.2
G (GPa)	181.6	212.8	220.6	223.2
B / G	1.03	1.12	1.06	1.10
Final Energy (eV)	-5524.97	-5219.34	-6892.54	-6002.02
Cohesive Energy, $E_{coh}$ (eV)	-37.294	-38.354	-39.946	-40.896
Formation Energy, $\Delta H$ (eV)	-2.96	-2.83	-2.43	-2.78

<sup>a</sup>Ref. [16], <sup>b</sup>Ref. [28]

One can see in Table 1 that our calculated lattice parameters are in good agreement with experimental results. Considering the  $a$ -lattice parameter, the calculated values deviate from experimental values by 1.36% for  $\text{CeB}_4$ , 0.93% for  $\text{ThB}_4$ , and 1.92% for  $\text{UB}_4$ . Similarly, for the  $c$ -lattice parameter, the calculated values deviate from the experimental values by 1.72% for  $\text{CeB}_4$ , 0.88% for  $\text{ThB}_4$ , 1.97% for  $\text{UB}_4$ .

For  $\text{PaB}_4$  with  $\text{ThB}_4$ -type crystal structure, there is no experimental or theoretical data to which we can compare. It is thus hoped the present results may be useful for future theoretical studies.

The stability of a crystal is determined by its cohesive energy, which is defined as released total energy when isolated atoms combine into crystal form [22]. Thus, the crystal structure is more stable with increasing absolute value of the cohesive energy. The total energies of isolated Ce, Th, U and Pa atoms in a sufficiently large box were calculated as -1060.834 eV, -983.367 eV, -1400.074 eV and -1176.496 eV, respectively. The cohesive and formation energies of  $\text{XB}_4$  tetraborides were calculated from equations (1) and (2); the results are given in Table 1 along with other structural parameters. From Table 1, the stability ranking is  $\text{PaB}_4 > \text{UB}_4 > \text{ThB}_4 > \text{CeB}_4$ ;  $\text{PaB}_4$ , the proposed new compound, has the highest stability, and  $\text{CeB}_4$  has the least stability.

The mechanical stability of  $\text{XB}_4$  tetraborides can be calculated using the single-crystal elastic constants. For tetragonal crystals, there are six independent elastic constants ( $C_{11}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{66}$ ,  $C_{12}$  and  $C_{13}$ ) and mechanical stability requires the following conditions [27]:

**Table 2.** The numbers ( $n^\mu$ ), lengths ( $d^\mu$ , in Å) and Mulliken bond populations ( $P^\mu$ ) of the bonds in the  $\text{XB}_4$  tetraborides.

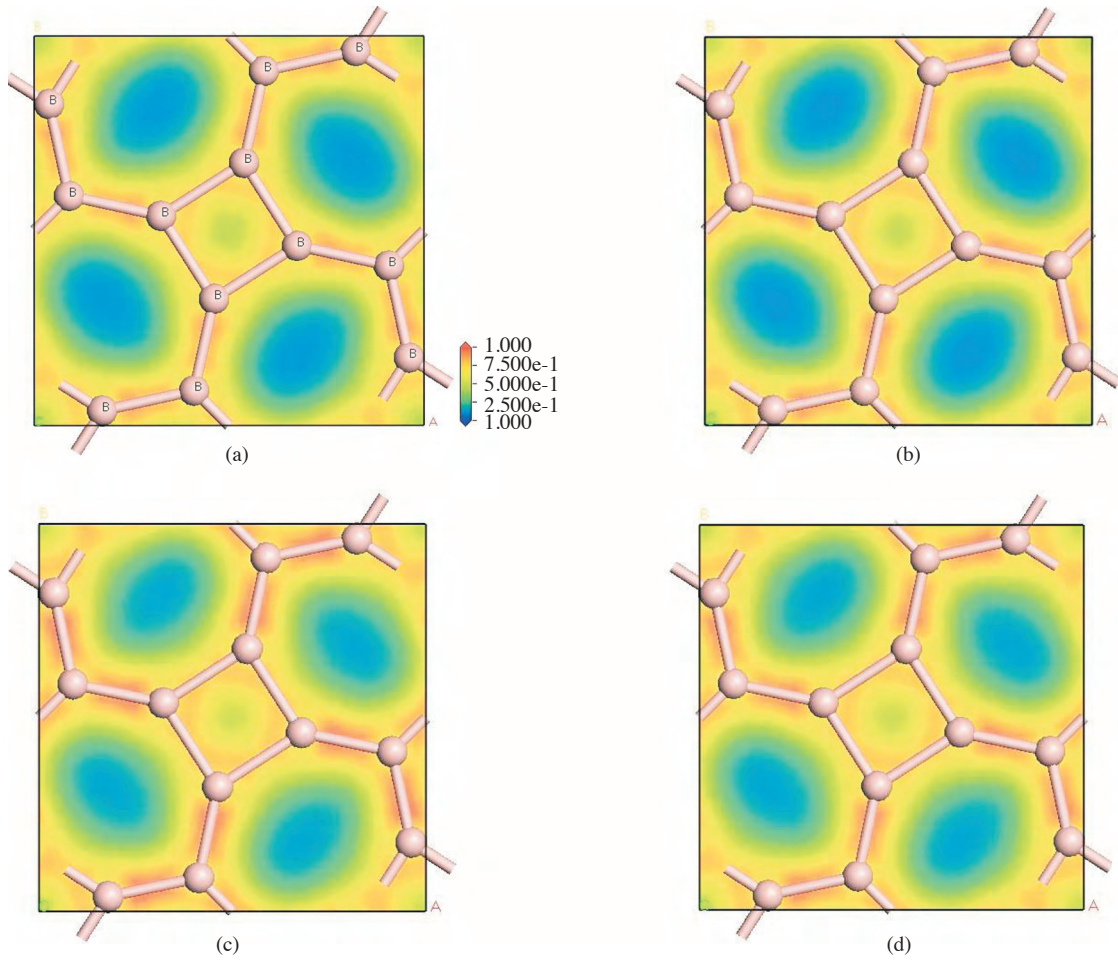
	Bond	$n^\mu$	$d^\mu$	$P^\mu$		Bond	$n^\mu$	$d^\mu$	$P^\mu$
$\text{CeB}_4$	B - B	2	1.623	0.61	$\text{ThB}_4$	B - B	2	1.642	0.62
	B - B	8	1.715	1.03		B - B	8	1.734	1.00
	B - B	16	1.752	0.49		B - B	16	1.770	0.45
	B - B	2	1.778	0.97		B - B	2	1.826	0.90
	B - B	8	1.806	0.52		B - B	8	1.816	0.51
	B - B	4	2.554	-0.38		B - B	4	2.569	-0.35
	B - Ce	16	2.714	-0.19		B - Th	16	2.743	-0.17
	B - Ce	8	2.752	-0.57		B - Th	8	2.791	-0.45
	B - Ce	8	2.799	-0.48		B - Th	8	2.831	-0.38
	B - B	4	2.876	-0.10		B - B	4	2.918	-0.11
B - Ce	8	2.898	-0.06	B - Th	8	2.944	0.00		
	Bond	$n^\mu$	$d^\mu$	$P^\mu$		Bond	$n^\mu$	$d^\mu$	$P^\mu$
$\text{UB}_4$	B - B	2	1.562	0.59	$\text{PaB}_4$	B - B	2	1.571	0.59
	B - B	8	1.661	0.99		B - B	8	1.673	0.98
	B - B	16	1.725	0.45		B - B	16	1.738	0.44
	B - B	2	1.713	0.94		B - B	2	1.739	0.91
	B - B	8	1.793	0.47		B - B	8	1.801	0.48
	B - B	4	2.535	-0.33		B - B	4	2.547	-0.33
	B - U	16	2.642	-0.18		B - Pa	16	2.664	-0.16
	B - U	8	2.675	-0.55		B - Pa	8	2.697	-0.51
	B - U	8	2.714	-0.46		B - Pa	8	2.741	-0.42
	B - B	4	2.779	-0.10		B - B	4	2.805	-0.10
B - U	8	2.833	-0.04	B - Pa	8	2.851	-0.02		

$$C_{11} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0,$$

$$(C_{11} - C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0, [2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0$$

All of  $XB_4$ ,  $X = \{\text{Ce, Th, U, Pa}\}$ , tetraborides satisfy these conditions, and thus are mechanically stable.

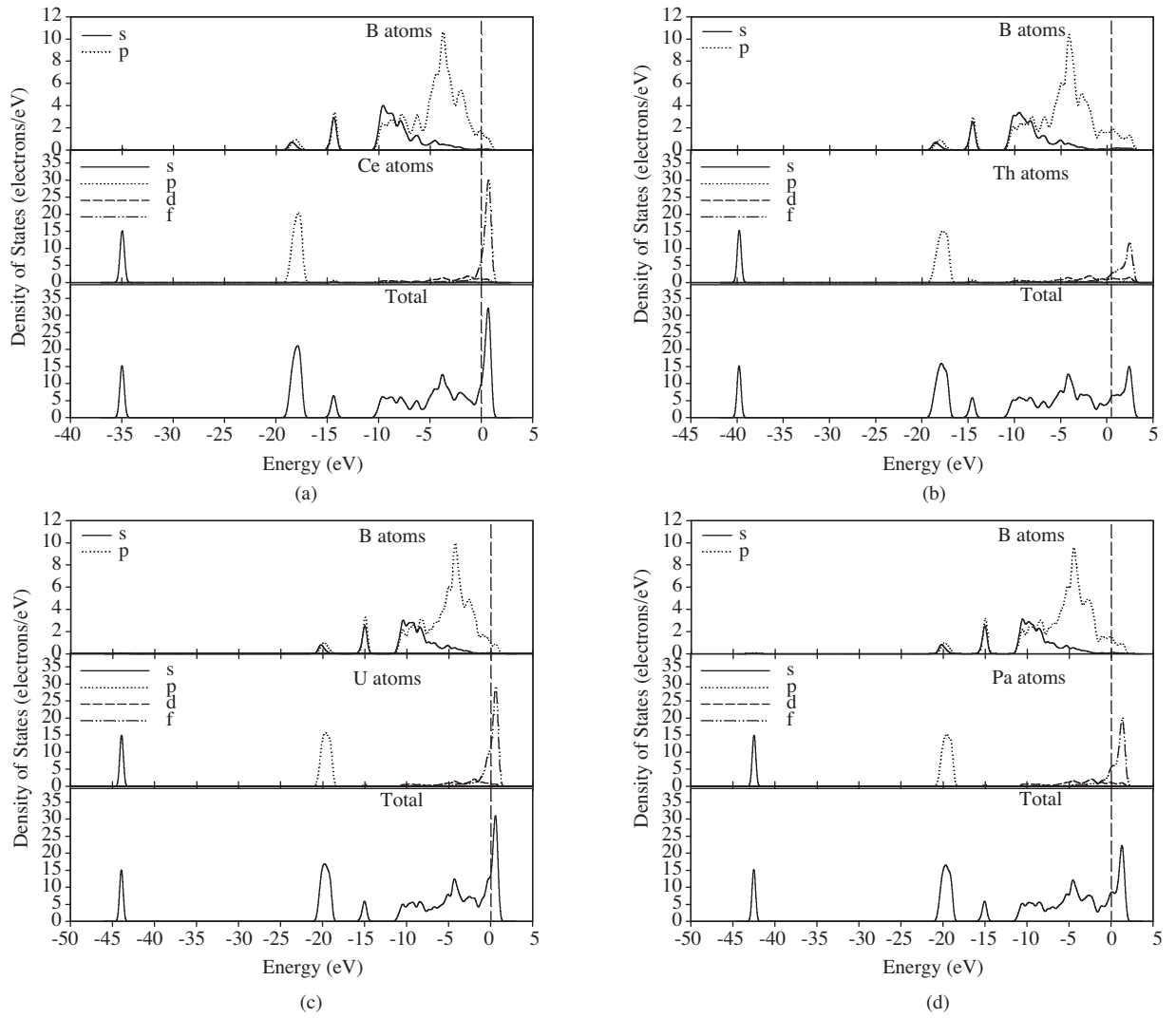
It is known that the  $B/G$  ratio can be used to determine ductility or brittleness of a material. The critical value is 1.75 [29], above which if  $B/G$  is higher (smaller) than this value the material is characterized as ductile (brittle). From calculated  $B/G$  ratios in Table 1, we conclude that all of  $XB_4$  tetraborides are brittle. Additionally, the  $B/G$  values are very close to one another and the ranking is  $\text{ThB}_4 > \text{PaB}_4 > \text{UB}_4 > \text{CeB}_4$ .



**Figure 3.** Charge density distribution map in the boron plane of (a)  $\text{ThB}_4$ , (b)  $\text{CeB}_4$ , (c)  $\text{UB}_4$  and (d)  $\text{PaB}_4$ . Electron density is high in the red regions and is low in the blue regions.

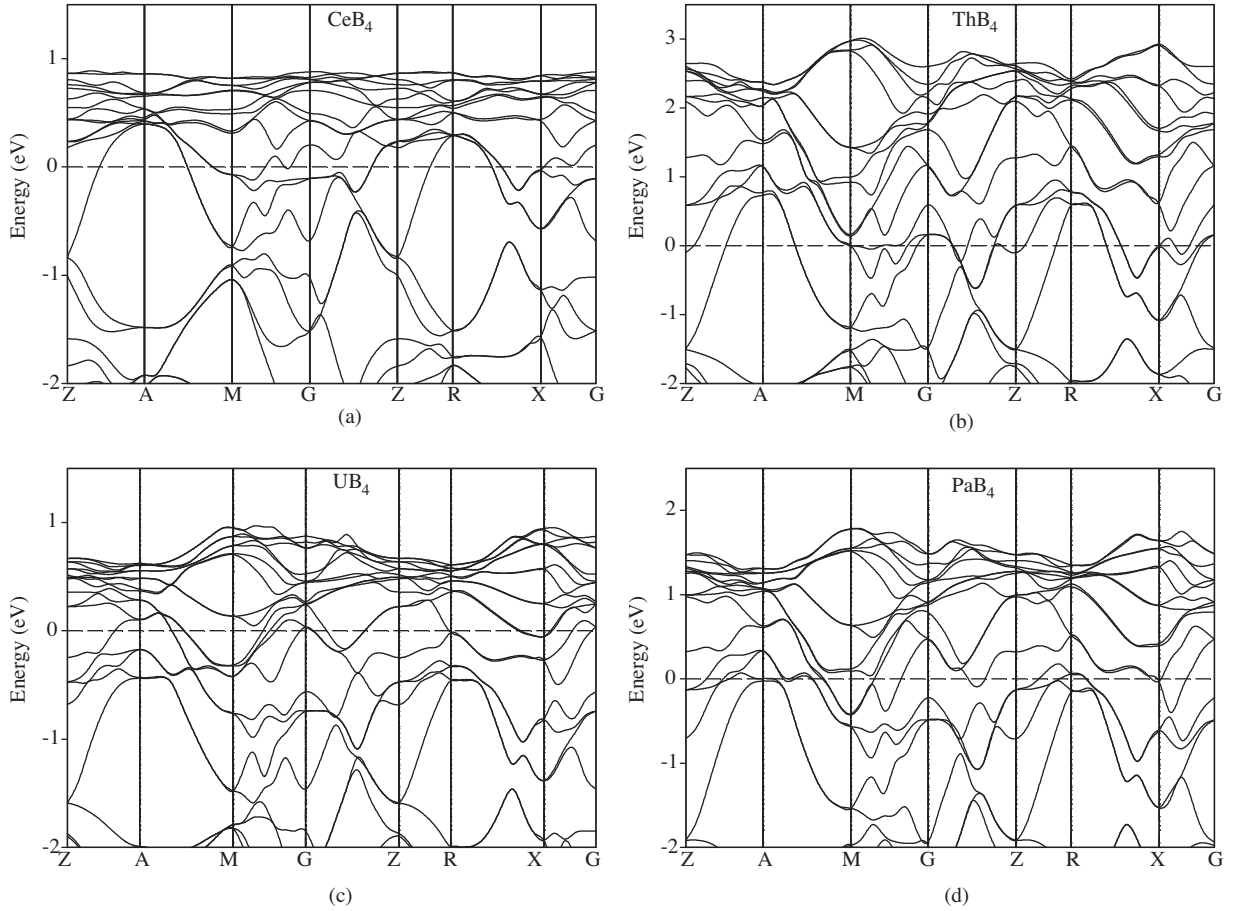
To investigate bonding nature, we performed a Mulliken bond population analysis and draw charge density distribution maps for  $XB_4$  tetraborides. We give the Mulliken bond population analysis results in Table 2.

Positive Mulliken bond population values denote bonding character, and negative values denote antibonding between any two atoms. As population values approach zero, ionic character of the bond increases, and higher positive population values indicate higher covalent character in the bond. Bonds which combine the octahedrons into linear chains in the boron plane have the highest covalent character with population values of 1.03 in  $\text{CeB}_4$ , 1.00 in  $\text{ThB}_4$ , 0.99 in  $\text{UB}_4$  and 0.98 in  $\text{PaB}_4$ . To show this, we give charge density distribution maps of the boron plane in Figures 3(a-d). The electron density along the bond indicates covalent character. When all  $\text{XB}_4$  tetraborides are considered, the bonds which are binding the octahedrons to linear chains and octahedrons, and the bonds which are binding linear chain atoms, are higher covalent than the other bonds. Thus, these bonds are very massive on the physical properties of  $\text{ThB}_4$ -type structures, especially on the hardness.



**Figure 4.** The calculated total and partial density of states of  $\text{XB}_4$  tetraborides: for (a)  $\text{CeB}_4$ , (b)  $\text{ThB}_4$ , (c)  $\text{UB}_4$ , and (d)  $\text{PaB}_4$ .

We show the calculated total and partial density of states for  $XB_4$  tetraborides in Figures 4(a–d). As seen from Figure 4, all  $XB_4$  tetraborides have finite density of states in the Fermi energy level. Therefore, they are metallic, a result controlled by the band structure shown in Figures 5 (a–d). The energy region in DOS pattern can be divided into regions as follows: (1) From -45 to -13 eV, (2) from -13 eV to the Fermi level and (3) above from the Fermi level. In region (1), the peaks around -40 eV and -20 eV are attributed to X s-orbitals and p-orbitals, respectively. The peak around -15 eV occurs through boron s- and p-orbitals. In region (2), the DOS is contributed mainly from the boron p orbitals, the contribution of X atoms is very low and d-orbitals have the highest DOS between its orbitals. Otherwise, boron 2p-orbitals have a strong hybridization with X d-orbitals, indicating the covalent bonding. Finally, above the Fermi energy level, the DOS is contributed mainly from f-orbitals of X atoms and there is a strong hybridization between boron p-orbitals and X f-orbitals.



**Figure 5.** The calculated band structures of  $XB_4$  tetraborides along the high symmetry points in the Brillouin zone: for (a)  $CeB_4$ , (b)  $ThB_4$ , (c)  $UB_4$ , and (d)  $PaB_4$ .

After the bonding characteristics were clarified by means of Mulliken bond population analysis and DOS analysis, we can calculate the hardnesses of  $XB_4$  tetraborides by using proposed method by Gao [24]. Due to the bonds in the boron plane are dominant and have higher covalent character between the bonds in the  $XB_4$  crystals, we can use this method for hardness characterization of this-type structure. To get the total hardness



$H_v$  from individual bond hardnesses, we used following equation and classified the bonds in the structure as CL1, CL2, CL3, CL4 and CL5 (see Figure 6):

$$H_v = \left[ (H_v^{CL1})^2 (H_v^{CL2})^{16} (H_v^{CL3})^8 (H_v^{CL4})^8 (H_v^{CL5})^2 \right]^{1/36}. \quad (5)$$

The calculated individual bond hardnesses and total hardnesses are given in Table 3. It can be seen that  $UB_4$  has the highest hardness (29.47 GPa), and the hardnesses for  $XB_4$  tetraborides can be ranked  $UB_4 > CeB_4 > PaB_4 > ThB_4$ . Considering the individual bond hardnesses in all tetraborides, we conclude that CL1 bonds have the highest hardness in each compound, and CL3 bonds follow them. If we want to express the individual bond hardnesses, we get a rank sequence such as  $CL1 > CL3 > CL5 > CL2 > CL4$ . But, this sequence is not valid for  $ThB_4$  because of CL4 bond hardness is higher than that of CL2 bond with very little difference. Furthermore, the hardnesses of  $XB_4$  tetraborides are smaller than superhard material limit, 40 GPa. In other words, these tetraborides are hard but not superhard.

**Table 3.** The calculated individual bond hardnesses, total hardnesses and octahedral hardnesses of the  $XB_4$  tetraborides in GPa.

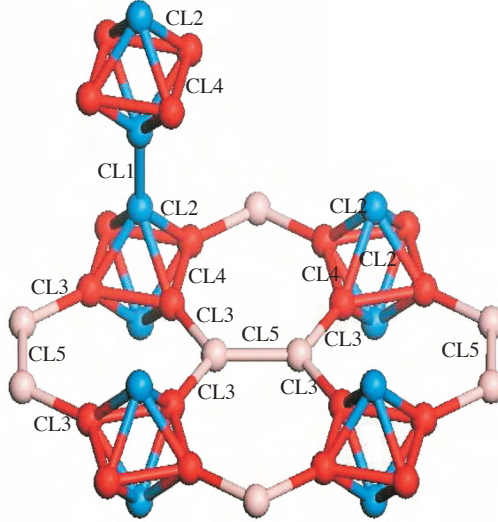
				$P^\mu$	$d^\mu$	$n^\mu$	$N_e^\mu$	$H_v^\mu$	$H_{oct}$	$H_v$
ThB <sub>4</sub>	CL1	B	B	0.62	1.642	2	0.257	40.941	21.33	25.99
	CL2	B	B	0.45	1.770	16	0.205	20.290		
	CL3	B	B	1.00	1.734	8	0.290	38.721		
	CL4	B	B	0.51	1.816	8	0.190	21.735		
	CL5	B	B	0.90	1.826	2	0.311	35.666		
UB <sub>4</sub>	CL1	B	B	0.59	1.562	2	0.298	51.179	23.36	29.47
	CL2	B	B	0.45	1.725	16	0.221	22.784		
	CL3	B	B	0.99	1.661	8	0.331	47.071		
	CL4	B	B	0.47	1.793	8	0.197	18.021		
	CL5	B	B	0.94	1.713	2	0.377	42.423		
CeB <sub>4</sub>	CL1	B	B	0.61	1.623	2	0.267	43.310	24.51	29.14
	CL2	B	B	0.49	1.752	16	0.212	24.046		
	CL3	B	B	1.03	1.715	8	0.302	40.843		
	CL4	B	B	0.52	1.806	8	0.194	23.189		
	CL5	B	B	0.97	1.778	2	0.339	40.375		
PaB <sub>4</sub>	CL1	B	B	0.59	1.571	2	0.294	50.056	22.32	28.29
	CL2	B	B	0.44	1.738	16	0.217	21.434		
	CL3	B	B	0.98	1.673	8	0.325	45.623		
	CL4	B	B	0.48	1.801	8	0.195	17.498		
	CL5	B	B	0.91	1.739	2	0.361	40.789		

We also examined how the octahedron structural unit affected hardness of the tetraborides. We calculated the hardness of octahedrons in the structures in Table 3 using the expression

$$H_{oct} = \left[ (H_v^{CL2})^{16} (H_v^{CL4})^8 \right]^{1/24}. \quad (6)$$

Clearly, B<sub>6</sub> octahedron makes a dominant contribution to the hardness of  $XB_4$  tetraborides. Total hardness originates from the octahedron with value of 82.1% for ThB<sub>4</sub>, 79.3% for UB<sub>4</sub>, 84.1% for CeB<sub>4</sub> and 78.9%

for  $\text{PaB}_4$ . However, CL2 bonds are shorter than CL4 bonds in octahedron, and thus considering general relationships between bond length and hardness, we expect that they are harder than CL4 bonds. This expectation is valid for all tetraborides except  $\text{ThB}_4$ .



**Figure 6.** The classification of bonds in the  $\text{ThB}_4$ -type structure. For atoms on the octahedron, equatorial and polar boron atoms are represented with red and blue colored spheres, respectively. CL1, CL3 and CL5 bonds connect octahedrons to octahedrons, chains to octahedrons, and chain atoms to chain atoms, respectively. CL2 and CL4 bonds form the octahedron. CL2 bonds connect equatorial boron atoms with polar boron atoms. CL4 bonds connect equatorial atoms to each other and remain in the boron plane.

## 4. Conclusions

$XB_4$ ,  $X = \{\text{Ce}, \text{Th}, \text{U}, \text{Pa}\}$  tetraborides were investigated by using first-principles calculations. The bonding characteristics and hardness were studied in detail. The results show that these boron-rich solids are mechanically and thermodynamically stable. The calculated electronic properties indicate that they have metallic character. The calculated structural parameters are in good agreement with experimental data. From cohesive energies, it is seen that  $\text{PaB}_4$  which is proposed as new compound in this work has the highest stability between  $XB_4$  tetraborides.

The  $B/G$  ratios calculated from single crystal elastic constants say that all of  $XB_4$  tetraborides are brittleness. From Mulliken bond population analysis, we show that the bonds which are binding the octahedrons to linear chains and octahedrons, and the bonds which are binding linear chain atoms are higher covalent than the other bonds. As a result of this bonding nature, octahedron to octahedron (CL1) and octahedron to chain (CL3) bonds are high individual bond hardness with respect to other bonds. Furthermore,  $B_6$  octahedron makes a dominant contribution to the hardness of  $XB_4$  tetraborides.

## Acknowledgements

This work is supported by the State Planning Organization (Devlet Planlama Teşkilatı Müsteşarlığı) of Turkey, under Grant No. 2001K120590.

## References

- [1] R. Lazzari, N. Vast, J. M. Besson, S. Baroni, and A. Dal Corso, *Phys. Rev. Lett.*, **83**, (1999), 3230.
- [2] F. Mauri, N. Vast, and C. J. Pickard, *Phys. Rev. Lett.*, **87**, (2001), 085506.
- [3] N. Vast, S. Baroni, G. Zerah, J. M. Besson, A. Polian, M. Grimsditch, and J. C. Chervin, *Phys. Rev. Lett.*, **78**, (1997), 693.
- [4] B. W. Robertson, S. Adenwalla, A. Harken, P. Welsch, J. I. Brand, and P. A. Dowben, *Appl. Phys. Lett.*, **80**, (2002), 3644.
- [5] M. Calandra, N. Vast, F. Mauri, *Phys. Rev. B*, **69**, (2004), 224505.
- [6] H. Hyodo, S. Araake, S. Hosoi, K. Soga, Y. Sato, M. Terauchi, and K. Kimura<sup>1</sup>, *Phys. Rev. B*, **77**, (2008), 024515.
- [7] Duanwei He, Yusheng Zhao, L. Daemen, J. Qian, and T. D. Shen, *Appl. Phys. Lett.*, **81**, (2002), 643.
- [8] A. R. Oganov , J. Chen, C. Gatti, Y. Ma, Y. Ma, C. W. Glass, Z. Liu, T. Yu, O. O. Kurakevych and V. L. Solozhenko, *Nature*, **457**, (2009), 863.
- [9] X. Guo, J. He, Z. Liu, Y. Tian, J. Sun and Hui - Tian Wang, *Phys. Rev. B*, **73**, (2006), 104115.
- [10] S. Aydin, M. Simsek, *Physica Status Solidi B*, **246**, (2009), 62.
- [11] M. Carrad, D. Emin, L. Zuppiroli, *Physical Review B*, **51**, (1995), 11270.
- [12] R. Schmitt, B. Blaschkowski, K. Eichele, and H.- Jürgen Meyer, *Inorg. Chem.*, **45**, (2006), 3067.
- [13] J. He, Erdong Wu, H. Wang, R. Liu, and Y. Tian, *Phys. Rev. Lett.*, **94**, (2005), 015504.
- [14] T. Konrad, W. Jeitschko, M. E. Danebrock, C. B. H. Evers, *Journal of Alloys and Compounds*, **234**, (1996), 56.
- [15] A. Zalkin and D. H. Templeton, *J. Chem. Phys.*, **18**, (1950), 391.
- [16] A. Zalkin and D. H. Templeton, *Acta Cryst.*, **6**, (1953), 269.
- [17] P. P. Blum, E. F. Bertaut, *Acta Cryst.*, **7**, (1954), 81.
- [18] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickart, P. J. Hasnip, S. J. Clark, M. C. Payne, *J. Phys.: Condens.Matter*, **14**, (2002), 2717.
- [19] D. Vanderbilt, *Physical Review B*, **41**, (1990), 7892.
- [20] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **77**, (1996), 3865.
- [21] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B*, **13**, (1976), 5188.

- [22] J. Feng, B. Xiao, J. C. Chen, C. T. Zhou, *Solid State Sci.*, **11**, (2009), 259.
- [23] M. D. Segall, R. Shah, C. J. Pickard, M. C. Payne, *Physical Rev. B*, **54**, (1996), 16317.
- [24] F. Gao, J. He, E. Wu, S. Liu, D. Yu, D. Li, S. Zhang, and Y. Tian, *Phys. Rev. Lett.*, **91**, (2003), 015502.
- [25] S. Q. Wu, Z. F. Hou, Z. Z. Zhu, *Solid State Comm.*, **143**, (2007), 425.
- [26] R. Hill, *Proc. Phys. Soc. London*, **65**, (1952), 349.
- [27] Z. Wu, E. Zhao, H. Xiang, X. Hao, X. Liu, and J. Meng, *Phys. Rev. B*, **76**, (2007), 054115.
- [28] S. F. Matar, J. Etourneau, *Inter. J. Inorganic Mater.*, **2**, (2000), 43.
- [29] Z. Wu, E. Zhao, *J. Phys. and Chem. Solids*, **69**, (2008), 2723.