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YB₆: A ‘Ductile’ and Soft Ceramic with Strong Heterogeneous Chemical Bonding for Ultrahigh-Temperature Applications

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Transition metal borides have contributed to the success of ultrahigh-temperature materials (UHTM) development. Current ZrB₂- and HfB₂-based UHTMs exhibit high-temperature environmental stability, high strength and modulus but inevitable brittleness due to strong covalent bonding. In contrast but interestingly, YB₆ is predicted as a ‘ductile’ and soft ceramic for ultrahigh-temperature applications, through density functional theory investigations on its electronic structure and bonding properties. The ‘ductility’ is underpinned by chemical bonding anisotropy, that is, a strong σ bond connecting the B₆ octahedra and a weak banana bond formed by overlapping the lobes of two perpendicular p orbitals (τ bond).

Keywords: Ultrahigh-Temperature Ceramics, YB₆, Ductile Ceramics, DFT, Heterogeneous Chemical Bonding

Ultrahigh-temperature ceramics based on metal borides are regarded as the materials of choice for nose and sharp leading edges of hypersonic vehicles, hot structure components for scramjet engines,[1–3] matrix and/or surface coatings for ultrahigh-temperature ceramic matrix composites.[4,5] ZrB₂- and HfB₂-based materials are the most investigated UHTMs at present owing to their high melting point and chemical inertness. However, the intrinsic brittleness, poor thermal shock resistance and difficulty in machining into sharp or complex shapes have blocked their applications in hypersonic vehicles. In order to stimulate the applications of metal borides for ultrahigh-temperature applications, new advances in understanding structure–property relations and improving ductility and machinability becomes emergent.

In the ZrB₂ and HfB₂ scenarios, the high Young’s modulus is underpinned by the strong covalent bonds between B atoms in the crystal structure.[6,7] It is well established that, in addition to chemical composition, chemical bonding plays an important role in dictating the structure and properties of a material. Therefore, comparing to chemical composition modification of ZrB₂ (or HfB₂), modification of the nature of chemical bonding in transition metal borides is more effective in

overcoming the intrinsic brittleness, poor thermal shock resistance (due to high Young’s modulus) and machinability (due to high hardness). Especially, if weak bonds exist together with the strong covalent bonds in transition metal borides, tailoring the properties will become feasible.

A typical example of chemical bonding dictating structure and defining properties is the interplay of crystal structure, chemical bonding and properties of carbon allotropes. For diamond, the strong covalent C sp^3 –C sp^3 bond within the tetrahedra makes diamond the strongest material. For graphite, the overlapping of C sp^2 –C sp^2 orbitals (σ bond) and C p_z –C p_z orbitals (π bond) makes graphene the strongest in two dimensions, while the alternative stacking of the graphene layers linked by Van de Waals’ force makes graphite soft and machinable. The coexistence of both strong $\sigma + \pi$ bonds in graphene layers and weak Van de Waals’ force in between layers is an extreme example of bonding anisotropy within a crystal structure. Comparing to carbon, boron has three valence electrons, being one less than carbon, such that the chemical bonding in boron allotropes and borides is more diverse and complex. In boron clusters, the bonding is contributed by the two-center two-electron (2c–2e) peripheral B–B bonds, the globally

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delocalized σ -bonds (radial σ -bonds) and the globally π -bonds.[7] In borides, except the layered hexagonal sheet in AB_2 -type compounds, B atoms form B_6 octahedron, B_{12} cuboctahedron and B_{12} icosahedron.[8–10] The B-polyhedra lack two valence electrons per polyhedron to complete the polyhedra-based framework and thus metals donate electrons to B-polyhedra in metal borides, so that boron compounds are often electron-deficient solids.[11–13] The diversity of structures and bonding properties of borides makes it possible to tailor the properties of boride-based ultrahigh-temperature ceramics. In this work, we report our theoretical prediction on the electronic structure, chemical bonding and mechanical properties of a ‘ductile’ and soft ultrahigh-temperature ceramic: YB_6 , which has a low density of 3.70 g/cm^3 and a melting point of 2600°C .[14] Moreover, its oxidation product Y_2O_3 also has a high melting point of 2435°C and a relative low density of 5.03 g/cm^3 .

To elucidate the chemical bonding and mechanical properties of YB_6 , first-principles calculations based on density functional theory (DFT) were performed using the Cambridge Serial Total Energy Package (CASTEP) code,[15] wherein the Vanderbilt-type ultrasoft pseudopotential [16] and generalized gradient approximation based on the Perdew–Burke–Ernzerhof scheme [17] for the exchange–correlation function were used. The plane-wave basis set cutoff was 450 eV and the special points sampling integration over the Brillouin zone was employed using the Monkhorst–Pack method with $6 \times 6 \times 6$ special k -points mesh.[18] Lattice parameters were modified to minimize the enthalpy and interatomic forces. The Broyden–Fletcher–Goldfarb–Shanno minimization scheme [19] was used in geometry optimization. The tolerance for geometry optimization are difference in total energy within $5 \times 10^{-6} \text{ eV/atom}$, maximum ionic Hellmann–Feynman force within $0.01 \text{ eV/\AA}$, maximum ionic displacement within $5 \times 10^{-4} \text{ \AA}$ and maximum stress within 0.02 GPa. The density of states is calculated using the Vienna ab initio simulation package.[20,21] In this method, the Kohn–Sham equations of DFT were solved within a plane-wave basis set with electron–ion interactions described by the projector augmented wave method.[20] The exchange and correlation, the plane-wave basis set cutoff, the special k -points mesh were selected the same as the calculations used in CASTEP. The elastic stiffness was determined from a linear fit of the calculated stress as a function of strain. The polycrystalline bulk modulus B , shear modulus G , Young’s modulus E were calculated from the second-order elastic constants, c_{ij} , according to the Voigt,[22] Reuss,[23] and Hill [24] approximations.

YB_6 crystallizes in CaB_6 -type structure with a space group of $Pm\bar{3}m$ (No. 221) and Y at $1a$ (0, 0, 0) and B at $6f$ (z , $1/2$, $1/2$) Wyckoff positions. Figure 1 shows a $2 \times 1 \times 1$ supercell of YB_6 . Within the unit cell, six B atoms form an octahedron, and the octahedra in adjacent

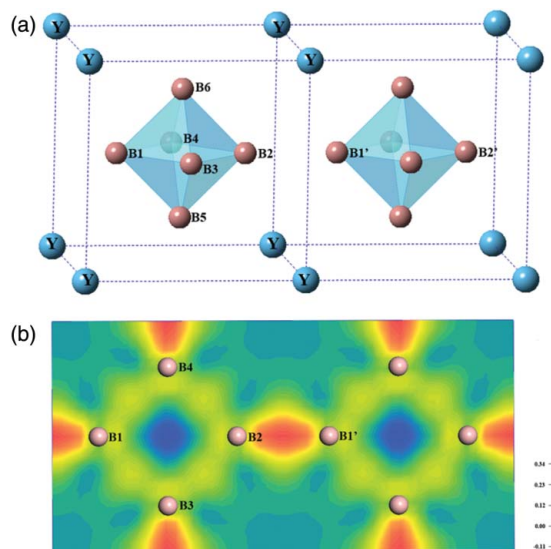


Figure 1. Crystal structure and electron density map on the (002) plane. (a) A $2 \times 1 \times 1$ cell of MB_6 showing octahedron within the unit cell and the inter-octahedral B–B bonds connecting the B_6 octahedra into the three-dimensional network. (b) Electron density difference map on the (002) plane across the B atoms, the B_6 octahedron is cut into a two-dimensional B_4 square. The unit is $\text{electron} \cdot \text{\AA}^{-3}$.

unit cells are connected by the two nearest corner B atoms along three main axis directions, forming a three-dimensional B_6 octahedral network. The fully relaxed structural parameters of YB_6 are listed in Table 1. The consistency is good with both the experimental [14,25] and the previous calculated data.[26–28] As demonstrated in the previous work of Massidda et al.,[28] there are two different B–B bond lengths in YB_6 , that is, the inter-octahedra bond length (e.g. $B1'-B2$ in Figure 1(a)) is shorter than the intra-octahedron bond length (e.g. $B1-B3$ in Figure 1(a)), which is an obvious indication of anisotropic chemical bonding.

To visually illustrate the anisotropic bonding nature, the electron density difference map on the (002) plane of YB_6 is shown in Figure 1(b), wherein the four-corner B atoms in B_6 octahedron are cut into a two-dimensional square. In Figure 1(b), the electron localization in the inter-octahedra bond (e.g. $B1'-B2$) is stronger than that in the intra-octahedron bonds (e.g. $B1-B3$). The inter-octahedra bond is a head on overlapping, which is a typical σ bond. However, the non-uniform redistribution of charges between adjacent B atoms within B_6 octahedron is neither a σ -type nor a π -type bond but somewhat reminiscent of a banana bond. Generally, a banana bond or a bent bond is a general representation of electron density or configuration resembling a similar ‘bent’ structure within small ring molecules or as a representation of double or triple bonds within a compound that is as alternative to the σ and π bond models.[29–31] As we will demonstrate in the later part of this paper, here the

Table 1. The DFT calculated and experimental lattice constants, atomic positions, inter-octahedral (d_{inter}) and intra-octahedral (d_{intra}) B–B bond lengths, second-order elastic constants c_{ij} , bulk, shear and Young's modulus of YB_6 .

Space group and lattice constant			
Space group	Lattice parameter, a_{exp} (Å)	Lattice parameter, a_{cal} (Å)	
$Pm\bar{3}m$ (No. 221)	4.1016	4.1124	
Atomic coordinates			
Y	B ($z, 1/2, 1/2$), z_{exp}	B ($z, 1/2, 1/2$), z_{cal}	
(0,0,0)	0.1988	0.1995	
Inter-octahedra and intra-octahedron B–B bond lengths			
Inter-Oct _{exp} (Å)	Inter-Oct _{cal} (Å)	Intra-Oct _{exp} (Å)	Intra-Oct _{cal} (Å)
1.630	1.6409	1.746	1.7479
Second-order elastic constants (GPa)			
c_{11}	c_{44}	c_{12}	
451	14	32	
Elastic constants of polycrystalline bulk YB_6 (GPa)			
B	G	E	ν
172	58	156	0.348
Cauchy pressure, Pugh's modulus ratio and shear anisotropic factor			
Cauchy pressure ($c_{12}-c_{44}$)	Pugh's modulus ratio (G/B)	Shear anisotropic factor $A = \frac{2c_{44}}{(c_{11}-c_{12})}$	
18 (GPa)	0.296	0.067	

Note: Cauchy pressure $c_{12}-c_{44}$, Pugh's modulus ratio G/B and shear anisotropic factor are also given.

banana bond is resulted from a weak bond formed by overlapping of perpendicular p orbitals.

To give a clear view on the inter-octahedra and intra-octahedra B–B bonding, total density of states (TDOS), projected density of states (PDOS) and the decomposed distribution of charge density from different covalent bonding peaks in the TDOS of YB_6 are investigated. Figure 2(a) shows the TDOS and PDOS of YB_6 . Three features are observed: the first is the hybridization between B $2s$ and B $2p$ orbitals (sp hybridization); the second is the presence of a pseudo-gap, and the third is the finite states at a Fermi level. Strong sp hybridization is evident because the B $2s$ orbitals are extended and overlapped with B $2p$ orbitals in a large energy range. The creation of the pseudo-gap may be attributed to, on the one hand, the ionization because of the charge transferring from Y to B, and on the other hand, the

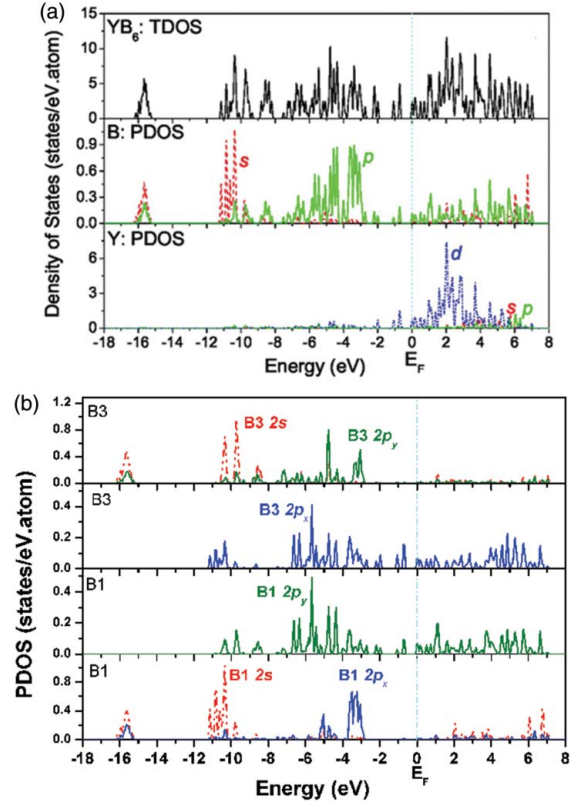


Figure 2. (a) TDOS and PDOS of YB_6 . (b) Projected electronic density of states of B1 and B3 atoms on the (002) plane of YB_6 , the states of B1 $2s2p_x$, B1 $2p_y$, B3 $2s2p_y$, B3 $2p_x$ orbitals are plotted separately to give a clear view on the inter-octahedra and intra-octahedron B–B bonds.

hybridization effect in YB_6 . In short, the Y–B bond is ionic-covalent in nature. The finite states at a Fermi level are from both Y $3d$ and B $2p$ states, indicating the presence of the metallic bond in YB_6 and it is electrically conductive. In short, metallic, ionic and covalent bonding all have contributions to the chemical bonding in YB_6 .

To distinguish the different covalent bonds between B_6 octahedra and within B_6 octahedron, PDOS of B1 and B3 atoms of s , p_x and p_y orbitals are given in Figure 2(b) and decomposed charge density distributions on the (002) plane are shown in Figure 3. The lowest lying states from -16.1 to -15.2 eV in Figure 2(a) are quasi-core sp band of B atoms.[32] The states from -11.2 to -8.1 eV are mainly from hybridized B1 $2s2p_x$ (B2 $2s2p_x$) and B3 $2s2p_y$ (B4 $2s2p_y$) orbitals. For B1, sp hybridization is realized through recombination of B1 $2s$ and B1 $2p_x$ orbitals; for B3, sp hybridization is realized through recombination of B3 $2s$ and B3 $2p_y$ orbitals. As shown in Figure 3(a), overlapping of B1' $2s2p_x$ –B2 $2s2p_x$ forms a strong σ -type inter-octahedra covalent bond in the x direction; similarly, overlapping of B3 $2s2p_y$ –B4 $2s2p_y$ forms a strong σ -type inter-octahedra covalent bond in the y direction. In the states from -7.8

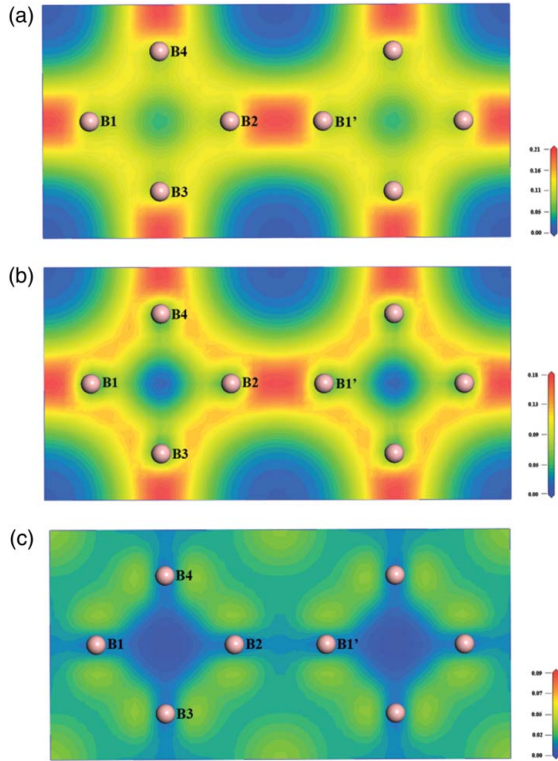


Figure 3. Decomposed distribution of charge density from different covalent bonding peaks in the TDOS of YB₆. (a) Distribution of charge density on the (002) plane across B atoms in the energy range from -11.2 to -8.1 eV, inter-octahedral B sp -B sp overlapping forms a strong σ -type double bond. (b) Distribution of charge density on the (002) plane across B atoms in the energy range from -7.8 to -1.9 eV, inter-octahedral B sp -B sp overlapping forms strong σ -type covalent bonds, intra-octahedral B p_x -B p_y overlapping forms weak τ -bonds. (c) Distribution of charge density on the x - y plane across B atoms in the energy range from -1.9 eV to the Fermi level, intra-octahedral overlapping the lobes of perpendicular B1 $2p_y$ -B3 $2p_x$ -B2 $2p_y$ -B4 $2p_x$ orbitals predominates. The unit for all distributions is electron $\cdot \text{\AA}^{-3}$.

to -1.9 eV, besides the overlapping of hybridized B sp -B sp orbitals, characters of B1 $2p_y$ and B2 $2p_y$, B3 $2p_x$ and B4 $2p_x$ orbitals (Figure 3(b)) are also observed. Considering the characteristics of B1 $2p_y$ and B3 $2p_x$ peaks in the PDOS curves of Figure 2(b) and the orbital characters in Figure 3(b), we conclude that the intra-octahedron B-B bonds are formed by overlapping the lobes of perpendicular B $2p$ orbitals, for example, B1 $2p_y$ -B3 $2p_x$ -B2 $2p_y$ -B4 $2p_x$ on the (002) plane. From -1.9 eV to the Fermi level, overlapping between perpendicular B $2p$ orbitals, for example, B1 $2p_y$ -B3 $2p_x$ -B2 $2p_y$ -B4 $2p_x$ becomes predominate (Figure 3(c)). In short, the banana bond within the B₆ octahedron is formed by overlapping the lobes of perpendicular B- $2p$ orbitals (e.g. $2p_y$ for B1 and B2, $2p_x$ for B3 and B4). According to Wade, a *clos*o-cluster with n vertices needs $2n + 2$ electrons to stabilize the polycentric bonding system. For B₆ octahedron, 14 electrons are needed to stabilize the polycentric

bonding system, and 6 electrons are used to form the $2e-2c$ bond between the octahedra. The strong σ bond is the $2e-2c$ bond, and the banana bond is the HOMO of the polycentric bonding system. We must emphasize that unlike the banana bond in organic compounds,[29–31] the banana bond formed by overlapping the lobes of perpendicular B- $2p$ orbitals is much weaker (we name it τ bond, since it is a Greek letter τ , meaning perpendicular).

The coexistence of strong σ bond and weak banana bond makes the mechanical properties of YB₆ tunable. For example, strong anisotropy in elastic stiffness is observed from the second-order elastic constants c_{ij} , bulk modulus B and shear modulus G for YB₆ as tabulated in Table 1 (which are consistent with previous experimental and theoretical results [27,33]). c_{11} that represents stiffness against principle tensile/compression strain (451 GPa) is much higher than c_{44} that represents shear deformation resistance against $\{100\}\langle 001\rangle$ shear strain (14 GPa). For cubic crystals, the shear anisotropic factor is calculated by $A = 2c_{44}/(c_{11} - c_{12})$. The shear anisotropic factor for YB₆ is 0.067, demonstrating huge shear anisotropy. Pettifor's Cauchy pressure $c_{12}-c_{44}$ and Pugh's modulus ratio G/B are often used to distinguish intrinsic ductile materials from brittle ones.[34,35] Positive Pettifor's Cauchy pressure and low Pugh's modulus ratio ($G/B < 0.571$) are criteria for intrinsic ductile materials. Pettifor's Cauchy pressure ($c_{12}-c_{44}$) and Pugh's modulus ratio G/B of YB₆ are 18 GPa and 0.296, respectively, indicating the intrinsic ductility and damage tolerance of YB₆. It is intriguing that Pugh's modulus ratio of YB₆ is much lower than the experimentally confirmed quasi-ductile and damage tolerant ceramics such as Ti₃SiC₂ (0.759),[36] Ti₃AlC₂ (0.706),[37] Cr₂AlC (0.513),[38] γ -Y₂Si₂O₇ (0.545),[39] Y₂SiO₅ (0.435),[40] β -Yb₂Si₂O₇ (0.448) [41] and LaPO₄ (0.535).[42] Thus, YB₆ is predicted a 'ductile' ultrahigh-temperature ceramic.

Besides damage tolerance, easy machining into sharp edge and complex shape components is also important for ultrahigh-temperature applications. Low hardness is a necessary parameter to ensure the easy machinability. Using the model proposed by Chen et al. [43,44], $H_v = 2(k^2 G)^{0.585} - 3$, where k is Pugh's modulus ratio, the Vickers hardness of YB₆ is calculated to be 3.02 GPa, which is in good agreement with the experimental microhardness (H_K) of 2.69 GPa determined under a load of 20 g.[45] Both the intrinsic ductility and the low hardness are resulted from the anisotropic elastic properties which originate from the anisotropic chemical bonding and the presence of weak bond formed by overlapping the lobes of perpendicular B- $2p$ orbitals. In addition, YB₆ has Young's modulus of 156 GPa, which is much lower than those of ZrB₂ and HfB₂ (523 and 535 GPa, respectively).[46] Low Young's modulus indicates better thermal shock resistance for YB₆.

In summary, we have predicted an intrinsic ‘ductile’ and soft machinable ultrahigh-temperature ceramic YB_6 through DFT investigations. The ‘ductility’ is underpinned by the anisotropic chemical bonding within the crystal structure of YB_6 , that is, the coexistence of strong σ bond connecting the B_6 octahedra and the weak banana bond within the B_6 octahedron. Unlike the banana bonds in organic compounds, the banana bond in YB_6 is formed by overlapping the lobes of two perpendicular $\text{B}-2p$ orbitals (τ bond). This kind of weak covalent bond not only exists in metal hexaborides but also in metal tetraborides, which can be described by alternating sheets of metal atoms and B_6 octahedra linked together laterally by B_2 units. The disclosure of this new type of covalent bond not only enriches the diversity of covalent bonds in ceramics but also opens the door to design next-generation UHTMs for applications in hypersonic reentry vehicles. The YB_6 -based composites are expected to the solution of tailoring ‘ductility’ of UHTMs.

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