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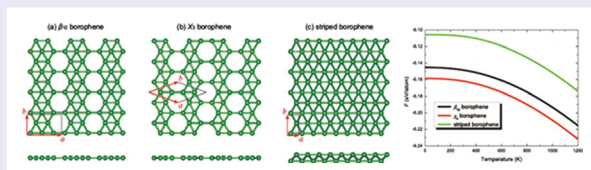
Stability and strength of atomically thin borophene from first principles calculations

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ABSTRACT

A new 2D material, borophene, has been grown successfully recently on single crystal Ag substrates. Three main structures have been proposed (β_{12} , χ_3 and striped borophene). However, the stability of three structures is still in debate. Using first principles calculations, we examine the dynamical, thermodynamical and mechanical stability of β_{12} , χ_3 and striped borophene. Free-standing β_{12} and χ_3 borophene is dynamically, thermodynamically and mechanically stable, while striped borophene is dynamically and thermodynamically unstable due to high stiffness along a direction. The origin of high stiffness and high instability in striped borophene along a direction can both be attributed to strong directional bonding. Our work shows a deep connection between stability and strength, and helps researchers to estimate accurately the mechanical performance of 2D materials.



IMPACT STATEMENT

- A benchmark for examining the relative stability of different structures of borophene is provided.
- Strong directional bonding in striped borophene leads to high stiffness and high brittleness.

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KEYWORDS

Two-dimensional materials; borophene; stability; strength

1. Introduction

Recent years have witnessed many breakthroughs in research on 2D materials due to their potential applications in next-generation electronic and energy conversion devices [1–14]. Recently, a new type of 2D material, borophene (2D boron sheet) [15], has been successfully grown on single crystal Ag(111) substrates by two parallel experiments [16,17]. Although various proposals of stable 2D boron sheets and quasiplanar boron clusters have been made [18–34], three main structures (β_{12} , χ_3 and striped borophene) have been observed by scanning tunnelling microscopy in these two experiments:

β_{12} and χ_3 borophene has planar structure with periodic holes [17], while striped borophene has buckled structure with anisotropic corrugation [16]. The following first principles calculations have predicted that striped borophene possesses remarkable mechanical properties [35,36], which may rival graphene [16]. However, phonon instability in striped borophene is observed [37], which may challenge previous results demonstrating that borophene is stiffer than graphene along a direction [16,35,36].

Theoretical investigation of the formation of boron sheet on Ag(111) surface has demonstrated that stable

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boron sheet should contain $\frac{1}{6}$ vacancies in a striped pattern [38]. This is consistent with previous theoretical studies indicating that planar boron sheets with vacancies are more stable [21,23–25,29–31,39,40]. The ground state of 2D boron is in debate [16,17,21,31,35,36,38–45]. These debates raise several questions: (i) Are these three structures stable? (ii) What is the relative stability of β_{12} , χ_3 and striped borophene? (iii) Could these structures possess high hardness in thermodynamic aspect? In fact, due to the structural complexity of boron, even the relative stability of α - and β -rhombohedral boron has been discussed for over 30 years [46–52]. Thus a systematic investigation is needed to examine the stability and strength of these three structures.

When discussing the stability of crystal structures, it is important to distinguish dynamical, thermodynamical and mechanical stability [53,54]. A material is dynamically stable when no imaginary phonon frequencies exist. Thermodynamical stability can be described by the Helmholtz free energy [55], which demonstrates how phonons determine the relative stability at finite temperatures. Regarding mechanical stability, the Born–Huang criteria for elastic constants must be fulfilled [56,57]. The Born–Huang mechanical stability criteria provide a *necessary* condition for the dynamical stability, but not a *sufficient* one [54]. Therefore, although the mechanical properties of striped borophene have been studied intensively [16,35,36], the questions of stability still remain unanswered. In this work, the dynamical, thermodynamical and mechanical stabilities of β_{12} , χ_3 and striped borophene are evaluated using first principles calculations. We further study for the first time the mechanical properties of β_{12} and χ_3 borophene, and compare the stiffness of all these structures. The bonding characteristics are also examined to understand the stability and strength of striped borophene.

2. Computational details

All the calculations are performed using the Vienna *ab initio* simulation package (VASP) based on density functional theory (DFT) [58,59] under the generalized gradient approximation expressed by the Perdew–Burke–Ernzerhof functional [60]. A plane-wave basis set is employed with kinetic energy cutoff of 700 eV with $15 \times 25 \times 1$, $29 \times 29 \times 1$ and $27 \times 15 \times 1$ $\mathbf{k}$ -mesh for β_{12} , χ_3 and striped borophene respectively during structural relaxation, until the energy differences are converged within 10^{-8} eV, with a Hellman–Feynman force convergence threshold of 10^{-6} eV/Å. The vacuum space is around 15 Å. The harmonic interatomic force constants (IFCs) are obtained using density functional perturbation theory (DFPT) within a supercell approach [61]. A $5 \times 7 \times 1$, $5 \times 5 \times 1$ and $7 \times 5 \times 1$ supercell with $7 \times 7 \times 1$, $5 \times 5 \times 1$ and $7 \times 5 \times 1$ $\mathbf{k}$ -mesh is used for β_{12} , χ_3 and striped borophene, respectively. The phonon dispersion and thermodynamical properties are calculated from the harmonic IFCs using the PHONOPY code [62,63]. We calculate the elastic tensor coefficients including ionic relaxations using the finite differences method [64,65].

3. Results and discussion

3.1. Crystal structure and dynamical stability

Three structures of borophene are shown in Figure 1. For β_{12} (χ_3) borophene, five (four) B atoms in the unit cell are arranged in the same plane. For striped borophene, there is no corrugation along a direction, while a vertical buckling along the b direction is observed. The major difference between striped borophene and the other two structures is the absence of vacancies. The introduction of vacancies leads to lower cohesive energy, as shown in Table 1, which is in good agreement with

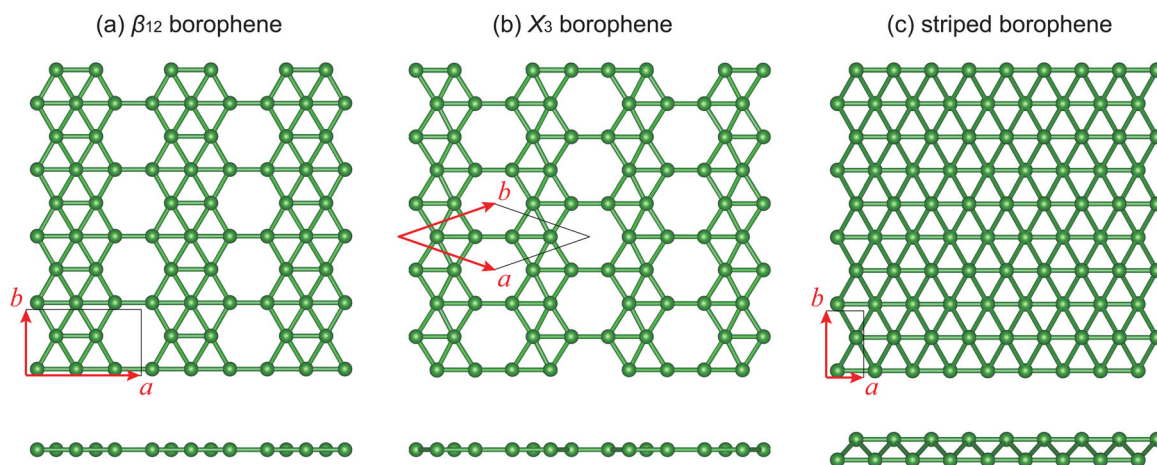
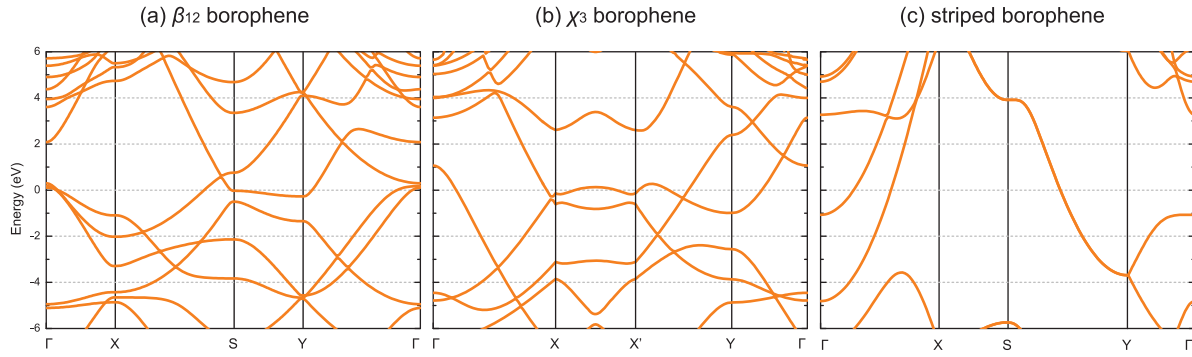


Figure 1. Top view and side view of (a) β_{12} , (b) χ_3 and (c) striped borophene.

Table 1. Calculated lattice constant a and b , buckling height h , cohesive energy E_c and ZPE of three structures of borophene.

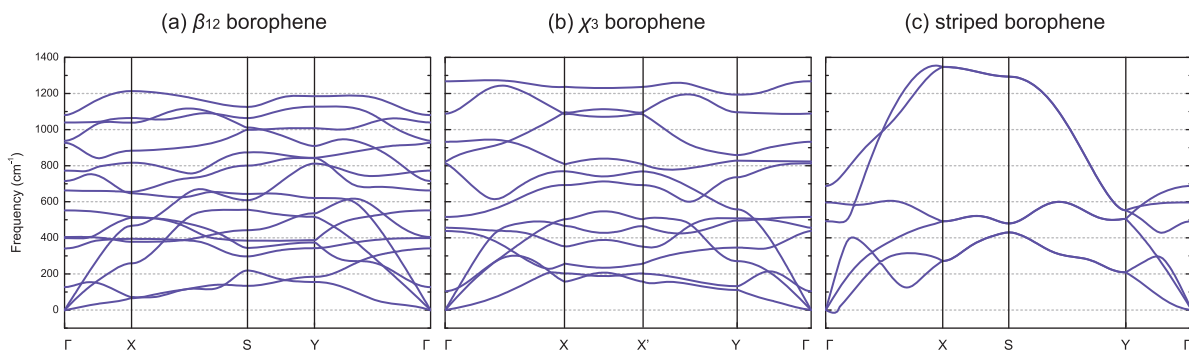
	Space group	a (Å)	b (Å)	h (Å)	E_c (eV/atom)	ZPE (eV/atom)
β_{12} borophene	$Pmm2$	5.07	2.93	0	-6.147	0.116
	–	5.0 [17]	2.9 [17]	–	–	–
χ_3 borophene	$Cmmm$	4.45	4.45	0	-6.159	0.114
	–	4.3 [17]	4.3 [17]	–	–	–
Striped borophene	$Pmmn$	1.613	2.864	0.911	-6.099	0.109
	–	5.1 ± 0.2 [16]	2.9 ± 0.2 [16]	–	–	–

Note: Previous experimental data are also listed for comparison.

**Figure 2.** Calculated band structures of (a) β_{12} borophene and (b) striped borophene along different symmetry lines.

previous results [21,39]. The optimized geometries of three structures are listed in Table 1. The predicted a of striped borophene corresponds to $\frac{1}{3}$ the a observed in the experiment, while the lattice constants of β_{12} and χ_3 borophene is in excellent agreement with experimental results [16,43]. Although a significant difference in the lattice constant a of striped borophene between the first principles calculations and observations in experiment is observed, its simulated scanning tunnel microscope image is in good agreement with the experimental results [16,38]. Thus the reliability of the present calculations is confirmed. Figure 2 presents the calculated band structures of all three phases, which agree well with previous theoretical results [66]. It should be noticed that due to highly anisotropic crystal structure, striped borophene shows anisotropic metallic behaviour.

For newly proposed 2D materials, stability is an important aspect for experimental realization and large-scale production. We investigate the dynamical stability of these three structures in Figure 3. No imaginary vibrating mode is seen for β_{12} and χ_3 borophene, which demonstrates that these structures are kinetically stable at 0 K. However, for striped borophene, the vibrational frequencies become imaginary in the long-wavelength limit along Γ -X direction, showing its dynamical instability for long-wavelength acoustic vibrations [16,37]. The imaginary frequencies remain even when employing a larger supercell with a higher convergence criterion (especially the $\mathbf{k}$ -mesh). In fact, a recent study has found that free-standing striped borophene is dynamically unstable even under high tensile stress [35].

**Figure 3.** Phonon dispersion for (a) β_{12} , (b) χ_3 and (c) striped borophene along different symmetry lines.

3.2. Thermodynamical stability

For light elements such as boron, phonons play an important role in determining the thermodynamical stability of crystals both at 0 K and at finite temperatures [55]. Using phonon frequencies in the whole Brillouin zone, we further examine the thermodynamical stability of three structures of borophene by calculating the Helmholtz free energy F [55],

$$F = E_{\text{tot}} + \frac{1}{2} \sum_{\mathbf{qj}} \hbar \omega_{\mathbf{qj}} + k_B T \sum_{\mathbf{qj}} \ln[1 - \exp(-\hbar \omega_{\mathbf{qj}}/k_B T)], \quad (1)$$

where E_{tot} is the total energy of the crystal, and the summation term is the Helmholtz free energy for phonons [62,63]. The first summation term is a temperature-free term corresponding to the zero point energy (ZPE) of phonons; and the second summation term is a temperature-dependent term referring to the thermally induced occupation of the phonon modes. The calculated ZPE of β_{12} , χ_3 and striped borophene are listed in Table 1, which are the Helmholtz free energies of phonons at 0 K. The inclusion of the ZPE brings the F of β_{12} , χ_3 and striped borophene to -6.145 , -6.159 and -6.106 eV/atom, respectively.

Temperature is also an important thermodynamic variable for determining the stability of materials. At higher temperature, the phonon modes are occupied according to Bose–Einstein statistics. The Helmholtz free energies F as a function of temperature are shown in Figure 4. In the temperature range of 0–1000 K, the Helmholtz free energy of χ_3 borophene is lowest, while the F of β_{12} borophene is much lower than that of striped borophene, indicating that β_{12} and χ_3 borophene is more thermodynamically stable than striped borophene over a wide temperature range.

In comparison to striped borophene, the thermodynamical stability of β_{12} and χ_3 borophene is due to the softness of the phonon modes: The phonon frequencies of β_{12} and χ_3 borophene are relatively low, leading to an increase in entropy at high temperatures, thus the structures are more stabilized than that of striped borophene, which is similar to α - and β -boron [67], and α - and β -tin [68].

3.3. Mechanical stability

To investigate the mechanical stability of both structures, we calculate the elastic constants. Due to 3D periodic boundary conditions, the 2D coefficients C_{ij}^{2D} need to be renormalized by the vacuum space between the 2D

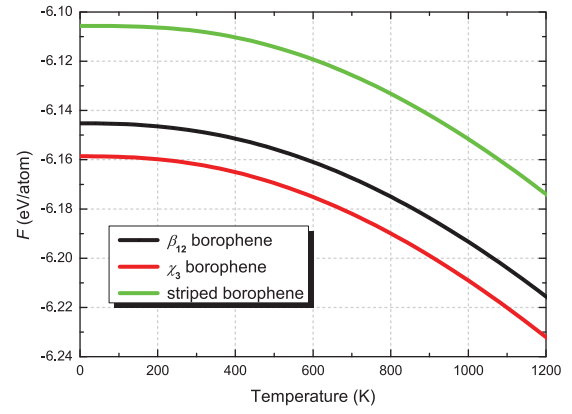


Figure 4. Helmholtz free energy as a function of temperature for (a) β_{12} , (b) χ_3 and (c) striped borophene.

layers [69], i.e. $C_{ij}^{2D} = c C_{ij}^{3D}$. The calculated elastic constants of both β_{12} , χ_3 and striped borophene in Table 2 satisfy the corresponding Born stability criteria according to Born–Huang’s lattice dynamical theory [56,57], indicating both structures are mechanically stable.

Using the elastic tensor, the mechanical properties such as 2D Young’s modulus E^{2D} and the corresponding Poisson’s ratio ν^{2D} can be calculated [70], as shown in Table 2. 2D Young’s modulus is defined as the ratio between stress and strain, and provides a measure of in-plane stiffness of the solid materials; while Poisson’s ratio reflects the stability of the crystal against shear. The calculated E^{2D} and ν^{2D} of striped borophene are in good agreement with other theoretical data [16,35]. Negative Poisson’s ratio is observed in striped borophene, which is due to highly buckled structure [35].

We plot the 2D Young’s modulus and Poisson’s ratio of borophene in comparison with other 2D materials in Figure 5. The mechanical properties of β_{12} and χ_3 borophene are similar due to similar in-plane bonding and atomic mass density. The stiffness of β_{12} and χ_3 borophene is lower than that of graphene and monolayer BN, but higher than that of silicene [70].

Most interestingly, the stiffness for striped borophene along a direction is much higher than that along b direction, and even rivals graphene (342.2 N/m) [70]. In fact, although striped borophene is much stiffer than β_{12} and χ_3 borophene, thermodynamically, high stiffness means unstability due to increasing Helmholtz free energy via the increase in vibration frequency [67]. Both the high stiffness and high instability of striped borophene along a direction can be attributed to strong directional bonding.

3.4. Bonding characteristics

To understand the chemical bonding of striped borophene, we calculate its electron localization function

Table 2. Calculated elastic coefficients C_{ij}^{2D} for three structures of borophene, as well as 2D Young's modulus E^{2D} , Poisson's ratio ν^{2D} along the a and b direction.

	C_{11}^{2D} (N/m)	C_{12}^{2D} (N/m)	C_{22}^{2D} (N/m)	C_{66}^{2D} (N/m)	E_a^{2D} (N/m)	E_b^{2D} (N/m)	ν_a^{2D}	ν_b^{2D}
β_{12} borophene	188.1	36.0	214.3	63.5	182.0	207.5	0.17	0.19
χ_3 borophene	194.8	36.2	187.6	70.7	187.8	180.8	0.19	0.19
Striped borophene	382.5	-5.8	154.2	76.4	382.3	154.1	-0.04	-0.02
	-	-	-	-	398 [16]	170 [16]	-0.04 [16]	-0.02 [16]
	-	-	-	-	389 [35]	166 [35]	-	-

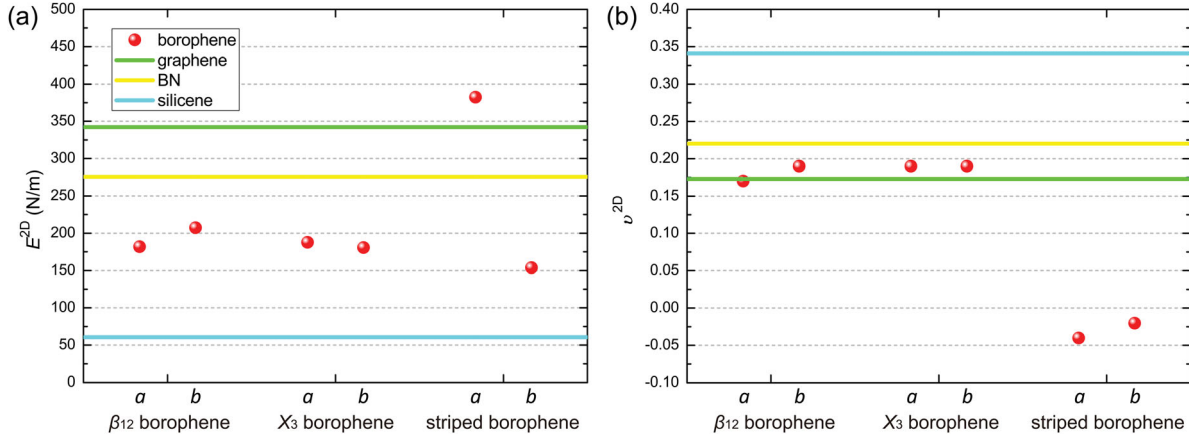


Figure 5. Calculated (a) 2D Young's modulus E^{2D} and (b) Poisson's ratio ν^{2D} along the a and b direction for three structures of borophene in comparison with graphene, monolayer BN and silicene.

(ELF) [71–74] in comparison with β_{12} borophene, which has similar 2D orthorhombic structure. A higher value of ELF corresponds to higher electron localization. As shown in Figure 6, ELF profiles of striped borophene is more anisotropic than that of β_{12} borophene. Strong directional bonding may prevent dislocations from forming to accommodate strains and thereby cause the material to be brittle [75,76]. This is consistent with previous theoretical studies showing that striped borophene is dynamically unstable even under high tensile stress [35,36]. As for β_{12} borophene, strong B–B bonds along different directions in the 2D plane of β_{12} borophene stabilize the structure. Thus β_{12} borophene is more stable than striped borophene considering the bonding characteristics.

We further consider the nature of the electronic bonding by calculating the projected density of states (DOS) for three structures of borophene with separated in-plane (s , p_x and p_y) and out-of-plane (p_z) projections in Figure 7. Generally, in-plane sp^2 bonds (σ bonds) are stronger than sp^3 bonds (π bonds) derived from p_z orbitals. For striped borophene, the p_z projected DOS vanishes from -3.5 to 2.5 eV. As a result, localized σ bonds along a direction are observed in ELF profiles. However, these strong σ bonds will be destabilized by any flattening of the boron sheet, leading to highly metastable structure [77]. Thus striped borophene becomes unstable

under tension along a direction [35]. In addition, some of the strong in-plane sp^2 bonding states are unoccupied in Figure 7(c), and subsequently striped borophene tends to accepting electrons to increase its stability [21]. Indeed, fully hydrogenated borophene has been recently proposed [78].

It should also be noticed that, although the strain effect on borophene has been investigated in detail [35,79], surface tension may also induce instability and even transform a monolayer to a nanotube without applying any external load [80]. In fact, surface tension can be viewed as the driving force for the phase transformation [81], and has two profound effects during the transformation: (i) it induces a large internal stress that triggers the transformation and (ii) maintains the integrity of the surface during the transformation [80]. For covalently bonded materials with directional bonds, surface tension usually leads to the generation of dangling bonds and even surface reconfiguration [82]. In previous study using *ab initio* molecular dynamics calculations, despite considerable deformation due to thermal fluctuations at high temperatures, the chemical bonds of borophene are intact, confirming the stability of the structures [79]. Therefore it is worth investigating the energy barrier for surface reconstruction at different temperatures, and particularly, whether the surface tension can overcome the

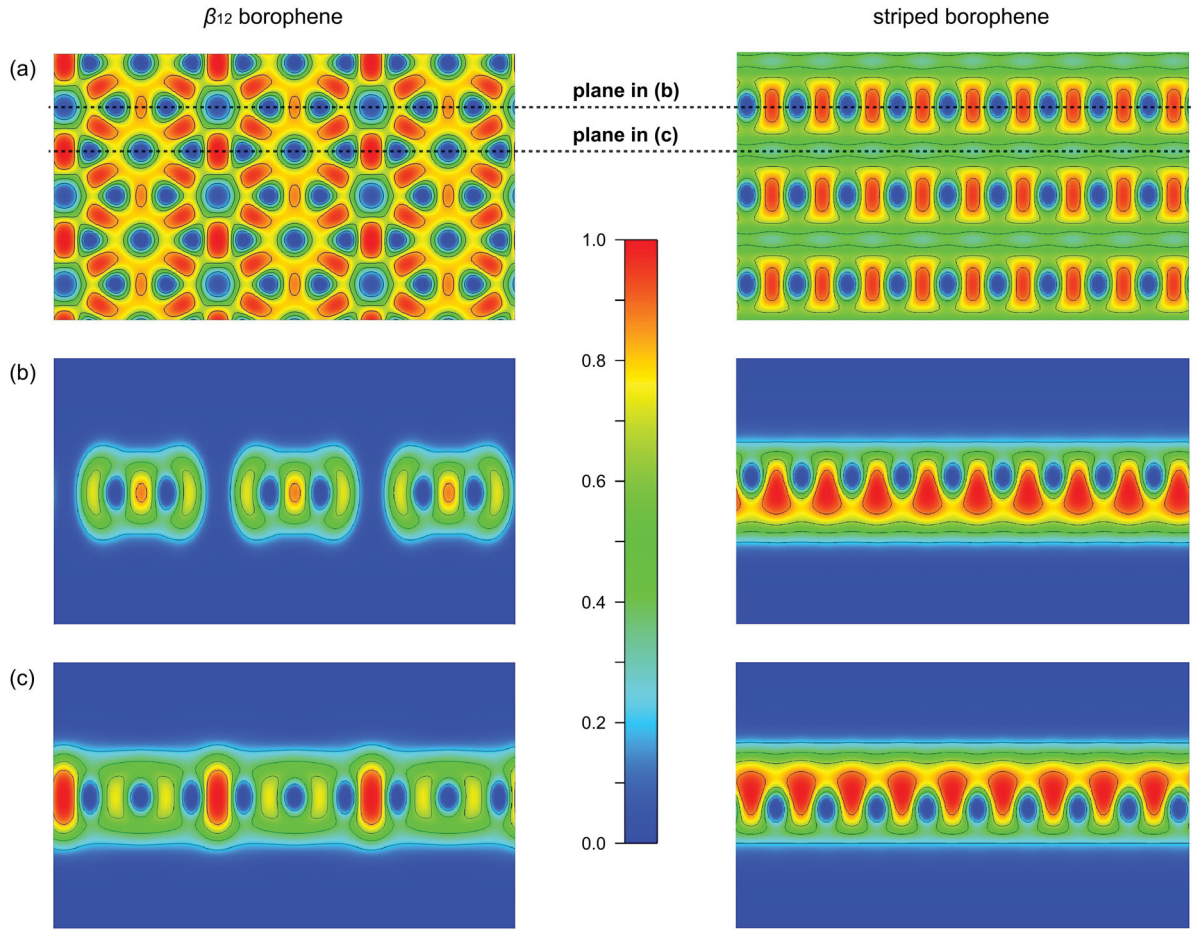


Figure 6. (a) Top view of 2D ELF profiles of β_{12} and striped borophene, as well as side view in the [010] plane with distance of (b) 1.75 Å (1.72 Å) and (c) 3.22 Å (3.15 Å) from origin for β_{12} (striped) borophene.

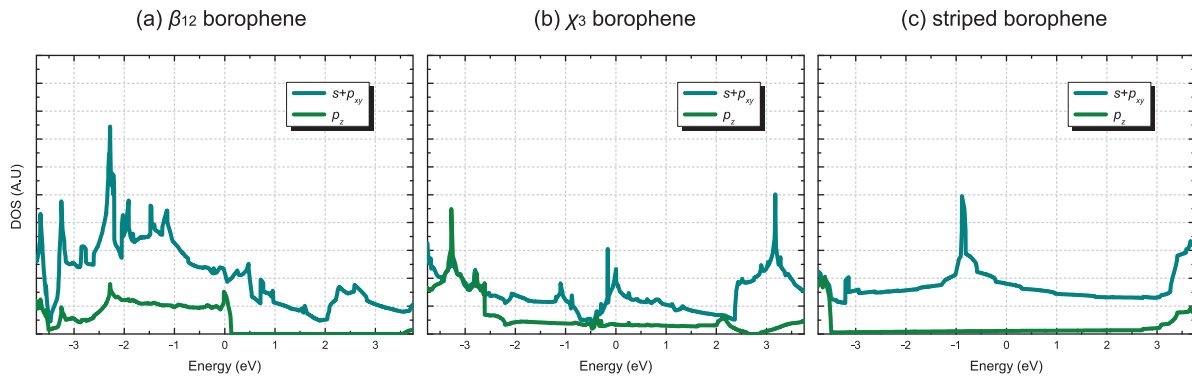


Figure 7. Projected DOS for (a) β_{12} , (b) χ_3 and (c) striped borophene.

energy barrier for phase transformation with the help of thermal vibrations.

4. Conclusion

In conclusion, first principles calculations are performed on 2D borophene sheet to evaluate the dynamical, thermodynamical and mechanical stability of two

distinguished structures. Our results show that the free-standing β_{12} and χ_3 borophene is thermodynamically, mechanically and dynamically stable, while striped borophene is thermodynamically and dynamically unstable due to high stiffness along a direction. The 2D Young's modulus E^{2D} for striped borophene along a direction is 382.3 N/m, even higher than that of graphene (342.2 N/m), while the E^{2D} of β_{12} and χ_3 borophene

are in the range of 180–210 N/m along both *a* and *b* directions. Our calculated ELF shows that the bonding characteristic of striped borophene leads to high stiffness and high instability at the same time. It is worth investigating the stability and strength of oxidized or hydrogenated borophene, as well as the energy barrier for surface reconstruction and phase transformation at different temperatures.

Disclosure statement

No potential conflict of interest was reported by the authors.

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