



First-principles study of the electronic structures of α -rhombohedral boron codoped with lithium and oxygen

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ABSTRACT

α -Rhombohedral (α -rh) boron, which is the most stable of boron's polymorphs at low temperatures, has p -type semiconductive properties. There have been some attempts to dope the interstitial sites with alkali atoms to create metallic or n -type semiconductive α -rh boron, but this has yet to be achieved. In a previous work, we proposed the codoping of α -rh boron with Li and P or As, and revealed from first principles calculations that $B_{12}PLi$ and $B_{12}AsLi$ could be synthesized and become narrow-gap semiconductors. The band structure suggested that the mobility of electrons might be greater than that of holes. In this paper, based on these prospective results, we selected a new combination of dopants, Li and O, and theoretically studied such compounds as $B_{12}OLi$ and $B_{12}O_2Li$. The results showed that both of these materials are metallic, while the reaction energies of the Li insertion into $B_{12}O$ and $B_{12}O_2$ are lower (more unstable) than with $B_{12}PLi$ and $B_{12}AsLi$. It was proved that the differences in the electronic structures are caused by the dangling bonds of the dopant atoms, O, P and As.

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1. Introduction

Elemental boron has four fundamental polymorphs, which are α -rhombohedral (α -rh), β -rhombohedral (β -rh), α -tetragonal (α -t) and β -tetragonal (β -t) [1]. Of these, α -rh is the most stable at temperatures below 1400 K [2]. The structure of these polymorphs consists of icosahedral B_{12} units, triplex icosahedra B_{28} for β -rh, and duplex icosahedra B_{21} for β -t. α -rh boron has a simple structure with a B_{12} icosahedron at each vertex of the unit cell. The structure has some voids that are large enough to accept another atom. The locations of these voids are the center of an icosahedron (I-site), the center of a tetrahedron comprising four icosahedra (T-site), and the center of an octahedron comprising six icosahedra (O-site). The O-site corresponds to the center of a unit cell.

α -rh boron has semiconductive properties with a band gap of about 2 eV, and the carriers are mainly holes (p -type) [3,4]. It would be interesting to be able to synthesize n -type or metallic α -rh boron by doping boron with another atom. If we expect the dopant atom at the interstitial site to work as a donor, it should have lower electronegativity than boron. There have been some attempts to dope boron with Li atoms [5]. It was successful for β -rh boron, but not for α -rh boron although the interstitial sites have sufficient space. According to our theoretical work [6,7], a Li

atom has a negative binding energy (unstable) at the I- and T-sites. At the O-site, the binding energy is positive but very small (0.17 eV). In addition, the diffusion of Li atoms appears to be hindered by the potential barrier between the O-sites. The potential barrier was not exactly calculated because there are many possible paths and geometrical optimization is required at each point in the path. It is at least higher than the difference of the binding energy between the O- and the T-sites, 1.21 eV. For these reasons, it is difficult to dope boron with Li atoms by thermal diffusion. However, since Li atoms can remain at these sites in a metastable state, high-energy doping such as ion implantation may be possible.

The reason for α -rh boron not easily accepting a donor is related to its electronic structure. According to a density of states (DOS) calculation [8], the DOS curve of α -rh boron is not greatly affected by Li atoms, and an electron directly enters the conduction band. The energy difference between the conduction band and the Li 2s state is very small and so the binding energy for Li is also small.

The fact that an n -type semiconductor is more difficult to obtain than a p -type one is similar to the diamond case. For diamond, the simultaneous doping of a donor and an acceptor (codoping) was proposed [9], where the Coulomb interaction between the donor and the acceptor effectively lowers the total energy. We thought this idea would also be applicable to α -rh boron. The meaning of doping is slightly different for diamond and α -rh boron. Diamond doping is carried out by the substitution of atoms, while α -rh boron doping is carried out by the insertion

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of atoms. Despite this difference, we assumed that the mechanism for lowering the total energy by the Coulomb interaction would remain effective in α -rh boron if the donor and acceptor come close to each other.

In our previous work [10], we attempted the codoping of α -rh boron with Li and P or As to form $B_{12}PLi$ and $B_{12}AsLi$, and calculated the electronic structures. We chose P and As because $B_{12}P_2$ and $B_{12}As_2$ are stable compounds with an α -rh boron-like structure. Since P and As have a larger electronegativity than B, they are expected to work as acceptors. The results of the calculations are summarized as follows: (1) $B_{12}PLi$ and $B_{12}AsLi$ can be theoretically synthesized, namely the energy gain for inserting Li and P (As) into B_{12} is positive. (2) They can be decomposed into Li and $B_{12}P_2$ or $B_{12}As_2$, thus making them metastable. (3) They form narrow-gap semiconductors with band gaps of 0.478 and 0.536 eV, respectively. (4) The curvature of the band structure suggests that the mobility of electrons may be greater than that of holes.

It would be interesting if these materials were experimentally synthesized and found to exhibit n -type behavior, because α -rh boron itself is a p -type semiconductor. Since the results for $B_{12}PLi$ and $B_{12}AsLi$ were promising, we selected another dopant combination, Li and O. We chose O for the same reason that we chose P and As, i.e., a stable α -rh boron-like compound $B_{12}O_2$ exists [11–13] and O will probably be an acceptor. Since O has a small atomic radius and large electronegativity, we expected different results from those obtained with P and As. We investigated from first principles the optimized structure and the electronic structures of $B_{12}OLi$ and $B_{12}O_2Li$. The reason for studying $B_{12}O_2Li$ as well as $B_{12}OLi$ is explained in Section 3.

2. Computational details

The calculations were performed in the same manner as in our previous work [10]. First principles calculations were implemented using the CPMD code, version 3.9.1 [14,15], which is based on the density functional theory [16,17] with plane waves and pseudopotentials. Norm-conserving Troullier–Martins-type pseudopotentials [18] in the Kleinman–Bylander form [19] were used. The generalized gradient approximation was included by means of the functional derived by Becke [20] and by Lee, et al. [21]. An energy cutoff of 80 Ry was sufficient to provide a convergence for total energies and geometries. Geometry optimization and total energy calculations were performed using Monkhorst–Pack sampling [22] of a $(4 \times 4 \times 4)$ mesh. The test calculation was compared with that for a $(5 \times 5 \times 5)$ mesh. The difference in total energy per atom was about 4×10^{-4} eV.

$B_{12}OLi$ and $B_{12}O_2Li$ have an odd number of valence electrons in a unit cell, so they should essentially be dealt with using spin-unrestricted calculations. However, since the numbers of valence electrons are sufficiently large (43 and 49) and there are no d -electrons, the effect of spin must be very small. In fact, we compared spin-restricted and unrestricted calculations of the total energy of $B_{12}OLi$ and found that the difference was only 0.15 eV. The lattice parameters were the same. We also calculated the density of states of $B_{12}OLi$, and the difference between the spin-up and spin-down states was almost negligible. Therefore, we adopted spin-restricted calculations for the lattice parameters, DOSs, energy bands, and electron densities, and spin-unrestricted calculations only for the formation energies.

3. Results and discussion

We first substituted a Li atom for one of the O atoms in $B_{12}O_2$ and energetically optimized the whole structure. The result is

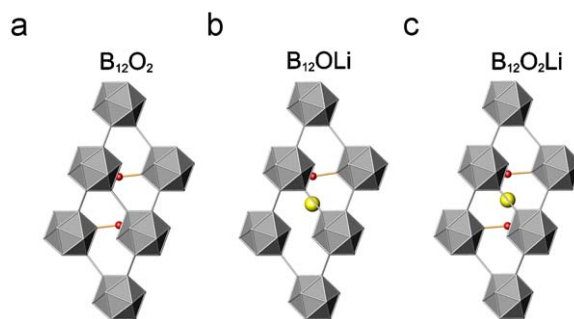


Fig. 1. Structures of $B_{12}O_2$, $B_{12}OLi$ and $B_{12}O_2Li$. Boron atoms are at the vertices of the icosahedra, and O and Li atoms are indicated by red (small) and yellow (large) spheres. (a) $B_{12}O_2$, (b) $B_{12}OLi$ and (c) $B_{12}O_2Li$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 1

Calculated lattice parameters a , interaxial angles α , and some bond lengths of $B_{12}O_2$, $B_{12}OLi$, and $B_{12}O_2Li$ along with the former results of $B_{12}P_2$ and $B_{12}As_2$.

	a (Å)	α (deg.)	X–X (Å)	X–Li (Å)	X–B (Å)	Li–B (Å)
$B_{12}O_2$	5.16 (5.150)	63.0 (62.9)	3.048 (3.083)		1.50 (1.424)	
$B_{12}OLi$	5.22	61.9		1.77	1.53	2.13
$B_{12}O_2Li$	5.32	61.7	3.33	1.66	1.53	2.34
$B_{12}P_2$	5.27 (5.256)	69.5 (69.6)	2.27 (2.240)		1.92 (1.911)	
$B_{12}PLi$	5.45	68.0		2.29	1.91	2.28
$B_{12}As_2$	5.34 (5.333)	70.4 (70.5)	2.41 (2.390)		2.01 (2.000)	
$B_{12}AsLi$	5.44	69.7		2.51	2.03	2.26

X represents O, P, As, respectively. Experimental values shown in the parentheses are from Refs. [13] ($B_{12}O_2$) and [23] ($B_{12}P_2$, $B_{12}As_2$).

shown in Fig. 1(b). The Li atom shifts almost to the center of the unit cell on the $\langle 111 \rangle$ diagonal. The B_{12} icosahedra preserve their symmetry. These features are quite different from those of $B_{12}PLi$ and $B_{12}AsLi$, where Li occupied the position of the replaced P or As, and the B_{12} icosahedra were slightly distorted [10]. Noting that the Li atom moved to the center, we thought that it might be possible to insert a Li atom between O atoms, forming $B_{12}O_2Li$. The optimized structure is shown in Fig. 1(c). The Li atom stays at the center of the unit cell without distorting the B_{12} icosahedra. The distance between the O atoms increases slightly by 0.27 Å.

The details of the structures are summarized in Table 1 along with the former results of $B_{12}P_2$ and $B_{12}As_2$ [10]. X in the table represents O, P, and As. $B_{12}O_2$ has a smaller lattice parameter a and a smaller interaxial angle α than those of $B_{12}P_2$ and $B_{12}As_2$. This is probably due to the smaller atomic radius of oxygen. The calculated results agree well with the experimental values shown in the parentheses [13,23], thus guaranteeing the accuracy of the calculations.

When we compare $B_{12}OLi$ with $B_{12}O_2$, we find that the lattice parameter increases by 0.06 Å (1.2%) and the interaxial angle decreases by 1.1°. This tendency is similar to that for $B_{12}PLi$ and $B_{12}AsLi$, but the increase in the lattice parameter is not as large as with $B_{12}PLi$ (0.18 Å, 3.4%) and $B_{12}AsLi$ (0.1 Å, 1.9%). The distance between O and Li, 1.77 Å, is smaller than the sum of each covalent radius, 0.66 Å (O) and 1.23 Å (Li). Therefore, it appears that the Li atom is partially or fully ionized. The O–B distance of 1.53 Å is not very different from that of $B_{12}O_2$ and is close to the sum of each covalent radius, 0.66 Å (O) and 0.81 Å (B). The increase of the lattice parameter cannot be explained simply by the difference of atomic radius between Li and O, suggesting that it is induced by the change of the electronic band structure.

If no atoms are inserted in the α -rh B_{12} lattice, the most stable point for a Li atom is the center of the unit cell (O-site) [6,7]. Therefore, the location of the Li atom is greatly affected by its counterpart atom (O, P or As). Since an O atom has a much smaller covalent radius than P (1.10 Å) and As (1.21 Å), a Li atom could get closer to the O-site.

Compared with $B_{12}O_2$, the lattice parameter of $B_{12}O_2Li$ increases by 0.16 Å (3.1%) and the interaxial angle decreases by 1.3°. The inserted Li atom increases the O–O distance by 0.27 Å (8.9%). This increase appears slightly large, indicating that the insertion of a Li atom between O atoms may not be energetically favorable. This will be confirmed later in the total energy calculations. The O–Li distance of 1.66 Å is shorter than that in $B_{12}OLi$, suggesting again that the Li atom is ionized. The O–B distance is the same as in $B_{12}OLi$ and not greatly affected by the Li atom.

When the total energy of an atom or molecule X is written as $E(X)$, the formation energy of the system is expressed as

$$E(B_{12}) + E(O) + E(Li) = E(B_{12}OLi) + 7.85 \text{ eV.} \quad (1)$$

The positive energy means that the synthesis of $B_{12}OLi$ is theoretically possible. The value is larger than those for $B_{12}PLi$ and $B_{12}AsLi$. The energies of various reactions are summarized in Table 2. When a Li atom is inserted into the O defect in $B_{12}O_2$ we obtain

$$E(B_{12}O) + E(Li) = E(B_{12}OLi) + 0.39 \text{ eV,} \quad (2)$$

suggesting that this reaction is also possible. However, in contrast to $B_{12}PLi$ and $B_{12}AsLi$, the reaction energy is very small. (Table 2 (2)). This is explained later from the electronic structures.

The direct substitution of Li for O in $B_{12}O_2$ is expressed as

$$E(B_{12}O_2) + E(Li) = E(B_{12}OLi) + E(O) - 7.92 \text{ eV.} \quad (3)$$

The energy is largely negative and the reaction does not seem to occur. The difficulty of direct substitution is also a feature of $B_{12}PLi$ and $B_{12}AsLi$ (Table 2 (3)). Considering the decomposition reaction, we obtain

$$2E(B_{12}OLi) = E(B_{12}O_2) + E(B_{12}) + E(Li_2) + 0.99 \text{ eV.} \quad (4)$$

Table 2

Calculated energies of reactions in eV corresponding to Eqs. (1)–(4) in the text.

	(1) Total	(2) Insertion	(3) Substitution	(4) Decomposition
$B_{12}OLi$	7.85	0.39	–7.92	0.99
$B_{12}PLi$	3.32	1.89	–7.13	4.66
$B_{12}AsLi$	2.22	1.77	–5.80	4.43

Therefore, as with $B_{12}PLi$ and $B_{12}AsLi$, $B_{12}OLi$ could be decomposed into $B_{12}O_2$, B_{12} , and Li_2 . The decomposition energy is smaller than those for $B_{12}PLi$ and $B_{12}AsLi$ (Table 2 (4)). Judging from the reactions (1)–(4), $B_{12}OLi$ is in a metastable state and might be more difficult to synthesize because the insertion energy for Li (Eq. (2)) is smaller than those for $B_{12}PLi$ and $B_{12}AsLi$.

With $B_{12}O_2Li$, the total reaction energy is expressed as

$$E(B_{12}) + E(O_2) + E(Li) = E(B_{12}O_2Li) + 14.5 \text{ eV,} \quad (5)$$

which indicates that the synthesis of $B_{12}O_2Li$ is theoretically possible. However, unlike $B_{12}OLi$, the direct insertion of Li into $B_{12}O_2$,

$$E(B_{12}O_2) + E(Li) = E(B_{12}O_2Li) - 1.30 \text{ eV,} \quad (6)$$

has a negative reaction energy, suggesting that it will be difficult to dope Li by thermal diffusion.

Fig. 2 shows the electronic band structures of $B_{12}O_2$, $B_{12}OLi$, and $B_{12}O_2Li$. The Brillouin zone and the notation of the symmetrical points are the same as in our previous work [10]. The result for $B_{12}O_2$ is similar to that reported by Lee et al. [24]. The top of the valence band is at the Z point with the B point having nearly the same value. The bottom of the conduction band is also at the Z point, making a direct band gap of 2.439 eV. By contrast, with $B_{12}P_2$ and $B_{12}As_2$, the top of the valence band is at the Z point and the bottom of the conduction band is at the A point, making the gap indirect (Table 3). The calculated gap of $B_{12}O_2$ is slightly wider than that reported by Lee et al. (2.03 eV) [24], which is probably because their calculation was performed within the local density approximation (LDA) and our calculation includes the generalized gradient approximation (GGA). It is well known that the LDA method underestimates band gaps. The gap of 2.40 eV reported by Li et al. [25] is close to ours and the features appear similar although there is a minor difference in the energy at the D point (U point in our work). The gap value has yet to be determined experimentally, but our calculations may still

Table 3

Calculated band gaps with the k -points of the valence-band top and the conduction-band bottom.

	Gap (eV)	v-band top	c-band bottom	Direct/indirect
$B_{12}O_2$	2.439	Z	Z	d
$B_{12}P_2$	2.788	Z	A	i
$B_{12}As_2$	2.947	Z	A	i
$B_{12}OLi$	0	A	B	Metallic
$B_{12}O_2Li$	0	Z	Z	Metallic
$B_{12}PLi$	0.478	A	A	d
$B_{12}AsLi$	0.536	A	A	d

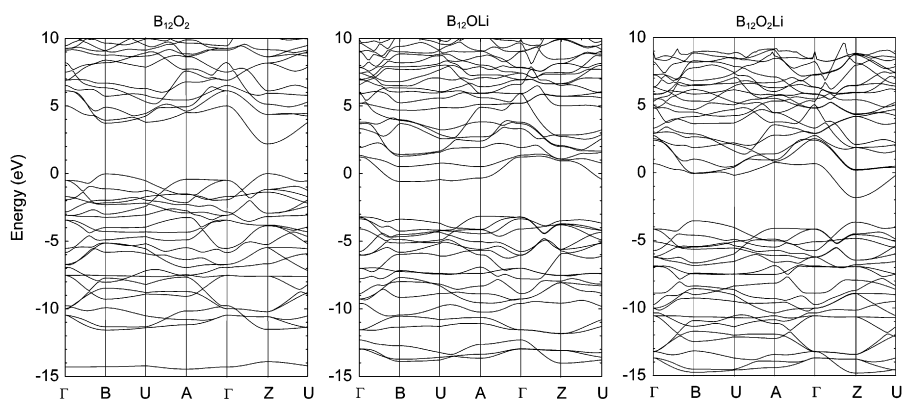


Fig. 2. Band structures of $B_{12}O_2$, $B_{12}OLi$ and $B_{12}O_2Li$. The Fermi energy is set at zero.

underestimate it, as found with the calculations of $B_{12}P_2$ and $B_{12}As_2$.

The band structure of $B_{12}OLi$ is quite different from that of $B_{12}O_2$. An electron enters the conduction band and makes it metallic. The energy at the Z point increases and the bottom of the conduction band shifts to the B point. The top of the valence band is at the A point. This structure is also different from $B_{12}PLi$ and $B_{12}AsLi$ where there are narrow direct gaps (Table 3) with both the valence-band top and the conduction-band bottom at the A point. The bottom of the conduction band is rather flat from the B point through the A point, which will make the density of states of the conduction band rise sharply.

Having a metallic property is very interesting in terms of application, but unfortunately, in this case it also obstructs the synthesis itself. There still remains a gap in $B_{12}OLi$ from about -3.5 to 0.5 eV. Based on the molecular orbital scheme, the conduction band mainly consists of states with an anti-bonding nature, and so an electron entering the conduction band would weaken the bonds between atoms and reduce the cohesive energy. Consequently, the energy gain for Li insertion, as seen in Eq. (2), is less than that for $B_{12}PLi$ and $B_{12}AsLi$ (Table 2 (2)). This is similar to the results for doping α -rh B_{12} with Li, and is also clearly seen in $B_{12}O_2Li$.

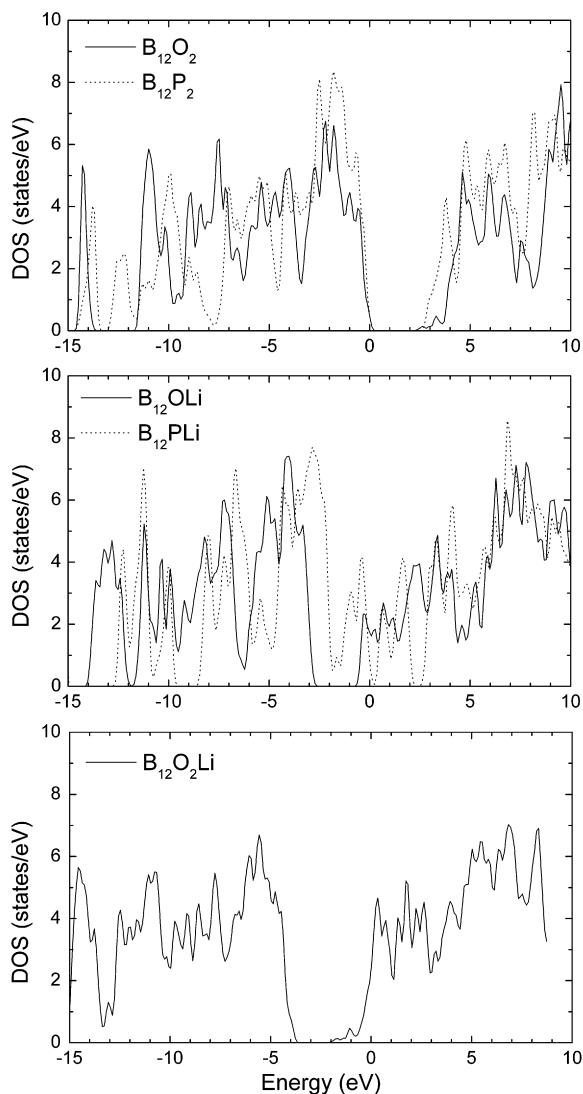


Fig. 3. Densities of states of $B_{12}O_2$, $B_{12}OLi$, $B_{12}O_2Li$ (solid line) and $B_{12}P_2$, $B_{12}PLi$ (dotted line). The Fermi energy is set at zero.

The band structure of $B_{12}O_2Li$ appears very similar to that of $B_{12}O_2$ except that the whole structure shifts downward by about 3.5 eV, and so it can be explained by the rigid band model. This is because the frame of $B_{12}O_2$ hardly changes in $B_{12}O_2Li$, as shown in Fig. 1. A Li atom, without changing the band structure, provides the conduction band of $B_{12}O_2$ with its electron and this produces metallic properties. As a result, for the same reason as that given for $B_{12}OLi$ and α -rh B_{12} , the energy gain for inserting Li into $B_{12}O_2$ is very small (in fact it is negative) (Eq. (6)).

Fig. 3 shows the DOSs of $B_{12}O_2$, $B_{12}OLi$, and $B_{12}O_2Li$ along with those of $B_{12}P_2$ and $B_{12}PLi$. The DOSs of $B_{12}As_2$ and $B_{12}AsLi$ are not shown but they are similar to those of $B_{12}P_2$ and $B_{12}PLi$ [10]. In $B_{12}O_2$, the band gap is slightly narrower than in $B_{12}P_2$, and $B_{12}As_2$ (Table 3), but the DOS at the bottom of the conduction band rises slowly. This is because the energy of the conduction band at the Z point is especially low, as seen in the band structure (Fig. 2), and there is no contribution to the DOS from other k -points around this energy. The DOS of $B_{12}O_2$ is similar to that described by Li et al. [25]. The work by Lee et al. [24] did not provide the DOS explicitly, but it must be almost the same as ours because the band structure is very similar.

In $B_{12}OLi$, although the band structure is quite different from that of $B_{12}O_2$, the DOS is similar to that of $B_{12}O_2$, as though it could be interpreted by the rigid band model. The DOS of $B_{12}OLi$ still has a wide gap below the conduction band. By contrast, in $B_{12}PLi$, and $B_{12}AsLi$, new states were generated in the gap, creating narrow-gap semiconductors. These in-gap states accept an electron and help lower the total energy of the system. In $B_{12}OLi$, these states are not available and an electron enters the conduction band directly, which increases the total energy. This situation is clearer in $B_{12}O_2Li$, where the DOS has almost the same pattern as that of

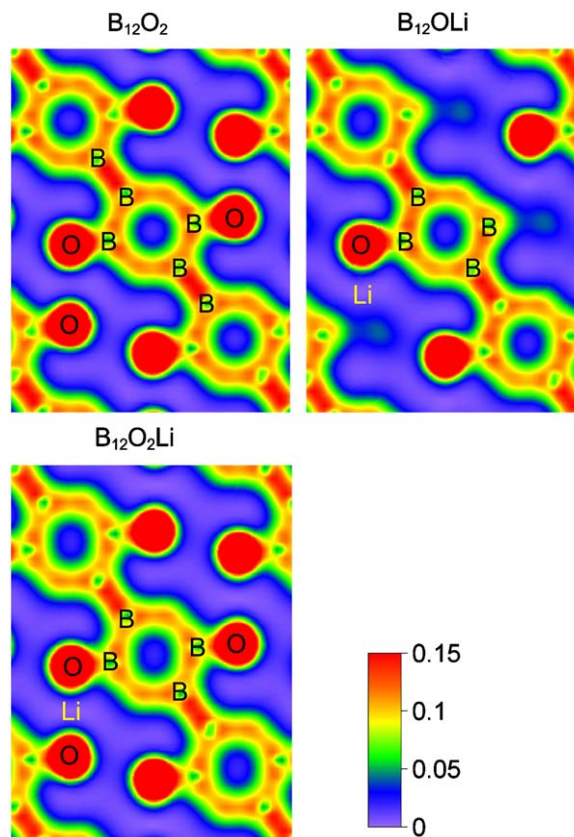


Fig. 4. Density of electrons of $B_{12}O_2$, $B_{12}OLi$ and $B_{12}O_2Li$. The unit is electron/(a.u.)³.

$B_{12}O_2$, and the reaction energy for Li insertion is negative, as mentioned above.

The spatial distributions of electrons are shown in Fig. 4. In all cases, it is seen that a large proportion of the electrons gathers around the O atoms. In $B_{12}O_2$, no covalent bonds are formed between O atoms, which was also pointed out by Lee et al. [24]. As in $B_{12}P_2$ and $B_{12}As_2$, the inter-icosahedron B–B bonds are stronger than the intra-icosahedron B–B bonds. The electron density of the former is about 1.5–2.0 times that of the latter.

In $B_{12}OLi$, no electrons are observed around the Li atoms, indicating that they are almost perfectly ionized. The density in the $B_{12}O$ frame shows few changes, which is probably because $B_{12}O$ has a total of 42 valence electrons, so that an electron from a Li atom does not affect the density very much. Since there are no covalent bonds between the O atoms in $B_{12}O_2$, no dangling bonds appear when an O atom is removed, which explains why $B_{12}OLi$ maintains its gap (Fig. 3). By contrast, in $B_{12}PLi$ and $B_{12}AsLi$, covalent bonds between P (As) atoms are broken when a P (As) atom is removed from $B_{12}P_2$ ($B_{12}As_2$), generating dangling bonds in the band gap. Then, an electron from a Li atom enters this in-gap state, which produces a relatively large binding energy. In $B_{12}OLi$, since such in-gap states are not available, an electron from Li is forced to enter the higher conduction band, producing a lower binding energy than in $B_{12}PLi$ and $B_{12}AsLi$.

In $B_{12}O_2Li$, as in $B_{12}OLi$, the Li atoms appear to be completely ionized and the $B_{12}O_2$ frame exhibits little change except that the O–O distance is slightly elongated. As in the discussion related to the band structure and the DOS, the distribution of electrons is well explained by the rigid band model. The electrons that enter the conduction band are responsible for the negative insertion energy of Li.

4. Conclusions

The possibility of the synthesis of $B_{12}OLi$ and $B_{12}O_2Li$, which are α -rh boron codoped with lithium and oxygen, has been theoretically investigated from first principles. The optimized structure of $B_{12}OLi$ has a Li atom near the center of its unit cell, which is unlike $B_{12}PLi$ and $B_{12}AsLi$. The electronic band structures of $B_{12}OLi$ and $B_{12}O_2Li$ show that they are metallic, while $B_{12}PLi$ and $B_{12}AsLi$ are semiconductive. On the other hand, since the energy gain for inserting a Li atom into $B_{12}O$ or $B_{12}O_2$ is less than in $B_{12}P$ (As), the syntheses of $B_{12}OLi$ and $B_{12}O_2Li$ are expected to be more difficult. In particular, the insertion energy for $B_{12}O_2Li$ is negative and the reaction will not proceed via thermal diffusion.

Since $B_{12}O_2$ has no covalent bonds between its O atoms, when an O atom is replaced, the remaining O atom has no dangling bonds in the band gap. Therefore, an electron provided by a Li atom inevitably enters the conduction band, which lies at a higher energy. This is why $B_{12}OLi$ is metallic and the energy gain for Li insertion is low. By contrast, in $B_{12}PLi$ and $B_{12}AsLi$, there are dangling bonds of P and As in the band gap and they accept an electron from a Li atom, thus forming narrow-gap semiconductors.

As for $B_{12}O_2Li$, the band structure is very similar to that of $B_{12}O_2$, and well explained by the rigid band model. Since the valence band of $B_{12}O_2$ is full, an electron from a Li atom again enters the higher conduction band, which makes the material metallic and the energy gain negative.

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