

Band Gap Engineering and 14 Electron Superatoms in 2D Superoctahedral Boranes B_4X_2 (B, N, P, As, Sb)

- Fedik N.^a,
- Steglenko D.V.^b,
- Muñoz-Castro A.^c,
- Minyaev R.M.^b,
- Minkin V.I.^b

Abstract

Band gap tuning in 2D monolayers is one of the most attractive approaches in design and production of new atomically thin semiconductors. Following our recent computational design of stable two-dimensional octahedral boranes, we present comprehensive computational study of electronic structure, stability and properties of members belonging to family B_4X_2 ($X = B, N, P, As, Sb$). We select 15 group atoms (pnictogens) as apical substituents to stabilize quasi-octahedral units by delocalized bonding and create interlayer "pressure" caused by vertically aligned lone pairs. We first substitute apical B atoms by N and then go down the 15 group to capture electronic structure trends. $B \rightarrow N$ substitution opens band gap, while further substitution consistently narrows band gap. We revealed elegant band gap trend which is inversely proportional to the size of octahedral units. Thus, old as world isoelectronic substitution could be used for band gap engineering in superoctahedral 2D boranes and other monolayers. We also discovered superatomic bonding in B_4As_2 and B_4P_2 octahedra which agrees with their exceptional stability (up to 800 K) and magnetic response properties. Remarkably, both B_4As_2 and B_4P_2 units have 14 valence electrons, making them exceptional examples of stable nonconventional electron count of spherical aromaticity. Alongside with a considerable negative formation energy and phonon stability, B_4As_2 has extremely low exfoliation energy of 0.02 eV/atom implying probability of synthetic route from a putative bulk material. It gives a strong basis to believe in possibility of experimental fabrication of B_4As_2 monolayer which can serve as alternative to MoS_2 and silicon. © 2021 American Chemical Society.