High-pressure structures and superconductivity of bismuth hydrides

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Abstract

We have systematically searched for the ground state structures of bismuth hydrides based on evolutionary algorithm method and particle swarm optimization algorithm method. Given only rich-hydrogen region, except for BiH₃, other hydrides (BiH, BiH₂, BiH₄, BiH₅, BiH₆) have been predicted to be stable with pressurization. With the increase of hydrogen content, hydrogen exists in bismuth hydrides with the different forms and presents the characteristics of ionicity. Under high pressure, the remarkable structural feature is the emergence of H₂ units in BiH₂, BiH₄ and BiH₆, and BiH₃ adopts a startling layered structure intercalated by H₂ and the linear H₃ units. Further calculations show these energetically stable hydrides are good metal and their metallic pressures are lower than that of pure solid hydrogen because of the doping impurities. The $T_c$ in the range of 20-119 K has been calculated by the Allen-Dynes modified McMillan equation, which indicates all these stable hydrides are potential high-temperature superconductors. Remarkably, it is the H-Bi-H and Bi atoms vibrations rather than the high-frequency H₂ or H₃ units that dominate the superconductivity. In addition, hydrogen content has a great influence on the superconducting transition temperature.
Introduction

The research on superconductivity in solid state hydrogen can be traced back to 1968 [1]. However, the synthesis of metallic hydrogen as the prerequisite has been far beyond the people's expectation and the accessible experimental pressures [2, 3]. In order to circumvent the problem, it was proposed that metallization pressures could be reduced in hydrogen-rich compounds due to the impurity rendering “chemical precompression” and these hydrides will become high-temperature superconductor after metallization [4]. In the first instances, the focus was concentrated on group-IV hydrides. Explorations on high-pressure structures of silane (SiH₄) [5-9], disilane (Si₂H₆) [10, 11] germane (GeH₄) [12], and stannane (SnH₄) [13, 14] have revealed the possibility of metallic phases with high superconducting transition temperature $T_c$. These researches are not only limited in group-IV hydrides, but also other hydrides (LiH₆, KH₆, CaH₆, and so on) [15-17] have also been extensively explored. More recently, one quite startling report consolidates this reality in both theory and experiment. Remarkably, by using the *ab initio* calculation method, our group predicted the covalent crystal H₃S [18, 19] identified with space group *Im-3m* to be an extraordinarily conventional high-temperature superconductor with a high $T_c$ values of 191 ~ 204 K at 200 GPa, which has been proved by Eremets *et al* through the high-pressure experiment [20].

More exciting, Eremets *et al* also measure a $T_c$ of another covalent hydride “phosphine” [21] (underdetermined structural information) that reaches 103 K at 207 GPa. Later, PH₂ [22] proposed by Andrew Shamp *et al* could be a candidate hydride according to “phosphine”. The observation of superconductivity in “phosphine” activates this “stagnant water” that the superconductivity of group VA hydrides is rarely studied and it may play a guiding role on researching other hydrides in same family. For instances, the semimetal antimony (Sb) element doped into hydrogen has been performed theoretically by us to explore the high-pressure crystal structures and superconductivity. Specially, a nontrivial binding was found in SbH₄ [23] and it was predicted to have a high $T_c$=106 K at 150 GPa. As same family element, bismuth has a larger atomic mass which could yield low energy vibrations. Although the low-frequency vibrations may generate the low phonon frequency logarithmic average ($\omega_{log}$), they also do have the advantages in improving the electron phonon coupling (EPC). Unfortunately, Bismuth hydrides are unstable under normal pressure. As is known, pressurization is an effective way to reduce the chemical potential of the reaction and then overcome the high reaction barrier of hydrogen with some elements to promote the synthesis of hydrides.
In this letter, in order to search low-enthalpy ground-state structures in H-rich regime of Bi-H compounds, we consider enough components of bismuth-rich and hydrogen-rich compounds over a wide range of pressure (50–300 GPa). Our calculations suggest that except for BiH₃, all of the bismuth hydrides become stable with increasing pressure. The H₂ units are discovered in bismuth hydrides BiH₂, BiH₄ and BiH₆ by hydrogenation. A layered structure of BiH₅ containing H₂ and linear H₃ units is uncovered. Moreover, all the stable Bismuth hydrides are good metal containing ionic hydrogen and the superconducting critical temperature $T_c$ values of BiH, BiH₂, BiH₄, BiH₅ and BiH₆ are 24–30 K, 51–59 K, 81–93 K, 92–103 K and 88–100 K at 250, 150, 150, 200 and 200 GPa, respectively. The increasing hydrogen content plays a significant role in enhancement of $T_c$ for different stoichiometries hydrides.

**Computational Methods**

We report on our investigations of the high-pressure crystalline structure of Bi-H system by using the evolutionary algorithm, implemented in the USPEX code [24-26] and the particle swarm optimization algorithm as implemented in CALYPSO (crystal structure analysis by particle swarm optimization) code [27, 28]. First of all, variable-composition structural predictions were executed by considering enough bismuth-rich and hydrogen-rich hydrides at 50, 100, 150, 200, 250, 300 GPa. Secondly, these most stable structures in thermodynamics were accurately searched by changing the cell size (1-4 formula units). The most promising candidate structures are further optimized with a higher accuracy by using the projector augmented waves method [29], implemented in the Vienna ab initio simulation package VASP code [30]. H (1s) and Bi (6s²6p³) were treated as valence electrons. The generalized gradient approximation of Perdew-Burke-Ernzerhof [31] was chosen to describe the exchange-correlation potential. The higher accuracy includes a plane-wave basis set cutoff of 800 eV and a Brillouin zone sampling grid of spacing $2\pi \times 0.03$ Å⁻¹, resulting in total energy convergence better than 1 meV/atom. The phonon spectrum and electron phonon coupling (EPC) were obtained from density functional perturbation theory [32], as implemented in the QUANTUMESPRESSO code [33]. The norm-conserving pseudopotentials are used. We tested a suitable 100 Ry kinetic energy cutoff for all hydrides. For $P6_3/mmc$-BiH and $Pmnn$-BiH₆, a $16 \times 16 \times 16$ Monkhorst-Pack (MP) [34] $k$-point sampling mesh is enough for the electronic Brillouin zone (BZ) integration and a $4 \times 4 \times 4$ $q$-mesh used to evaluate both the phonon band structure. A $24 \times 24 \times 18$ MP $k$-point sampling mesh and a $4 \times 4$
× 3 $q$-mesh were employed in $P2_1/m$-BiH$_2$ and $C2/m$-BiH$_5$. A 24 × 24 × 16 MP $k$-point sampling mesh and a 4 × 4 × 2 $q$-mesh were suitable to calculate phonon dispersion curves for $P$-1-BiH$_6$.

**Results and discussion**

**A. Thermodynamic stability of BiH$_n$ under pressure: from enthalpic trends**

To explore which BiH$_n$ species and structures could be synthesized in principle, convex shell is constructed by relaxing the most favorable structures of BiH$_n$, illustrated in Fig 1(a). On the one hand, bismuth-rich hydrides found are unstable. On the other hand, it may be a potential rule that large hydrogen fraction may be an essential condition to produce the high $T_c$ for hydrogen-rich compounds. These bismuth-rich hydrides are not drawn on convex shell. From Fig 1(a), one can deduce which stoichiometries are thermodynamically stable at given pressures. Provided a point (corresponding to a phase) lies on convex hull and does not exhibit any imaginary phonon modes, this phase is stable. If a tie-line connect thermodynamically stable phase A with B and another phase C falls above it, it is expected that C can decompose into A and B structures. That no any unstable mode in the phonon dispersion curves of C implies it is metastable, otherwise it is unstable. The stability and structural character of bismuth hydrides depend on pressure and hydrogen environment. The essential information can be summarized from Fig. 1(a): (1) below 100 GPa, none of BiH$_n$ is stable against elemental dissociation, conforming the fact of nonexistence of Bi hydrides at low pressures; (2) at 150 GPa, both $P2_1/m$-BiH$_2$ and $Pmnn$-BiH$_4$ lie on the convex hulls, but BiH$_2$ has lower average atomic enthalpy, which indicates it could be more likely to be synthesized in experiment; (3) under further compression (when pressure is up to 200 GPa), BiH$_4$ and BiH$_6$ emerge on tie-lines, whereas BiH$_2$ is still the most stable stoichiometry; (4) at 250 GPa, except for BiH$_3$, all stoichiometries fall on the convex shells and BiH becomes the most stable at 300 GPa. With the increasing hydrogen environment, bismuth hydrides are reasonably divided into three groups as depicted in Fig 2: (i) BiH contains hydrogen atoms; (ii) BiH$_2$, BiH$_4$ and BiH$_6$ contains H$_2$ units; (iii) BiH$_5$ contains H$_2$ units and symmetrical linear H$_3$ units.

**B. Structural characteristics with hydrogenation in BiH$_n$**

The structural parameters for the BiH$_n$ structures at selected pressures are shown in Table SI (seeing Supplementary Material) and corresponding perspectives are provided in Fig. 2. The direct results from the figures reveal the commensurable impurity forms the $P6_3/mmc$-BiH where H atoms
constitute a hexagonal frame with two Bi atoms occupying on 2c Wyckoff site. With the redundant hydrogen content, a clear structural feature in bismuth hydrides (BiH, BiH₂, BiH₄ and BiH₆) is appearance of H₂ units. For P2₁/m-BiH₂, it is thermodynamically stable (with respect to Bi and H₂) above 117 GPa and contains H₂ units with a H-H distance of 0.804 Å at 150 GPa. Pmmn-BiH₄ is stable from 125 to 300 GPa, where Bi atoms adopt a wrinkled layered and the H₂ units with a H-H distance of 0.838 Å are intercalated in adjacent Bi atoms layer. It is notable that BiH₄ is a unique layered structure which is different from other hydrides like KH₆[17] and PbH₄ [35]. In BiH₄, only Bi atoms array as a layered and all of H₂ units insert into the interval of the layers, whereas the mixed H₂ units or H₃ units and K atoms constitute these layers in C2/m-KH₆. Comparing with PbH₄ (phase VIII), although all H₂ units are insert into the intervals, those H₂ units are coplanar in PbH₄, while these H₂ units in BiH₄ are intercalated intervals keeping a certain angle with XY plane (seeing Fig 2 (c)). Notably, there are two metastable BiH₄ identified with P6₃/mmm and P6₃/mmc symmetry also found in our work. The P6₃/mmc-BiH₄ structure is analogous with the previously predicted SbH₄ by us [23] and SnH₄ [14] proposed by Gao et al. However, it is metastable because of the higher enthalpy. When pressure reaches 200 GPa, an individual layered structure C2/m-BiH$_{5}$ containing H₂ and symmetrical linear H₃ units is uncovered, as depicted in Fig 2 (d) (e). The linear H₃ units are also found in other hydrides, for example CsH₃ [36], RbH₃ [37], KH₅ [38], BaH₆ [39] and Te₂H₅ [40]. Another triangular form of H₃ units is reported in H₅F [41], H₅Cl [41, 42] and OsH₈ [43]. The C2/m-BiH₅ is akin to C2/c-KH₆, however, the major difference is that H₅ units in KH₆ is unequal separation, whereas it is symmetrical (0.914 Å at 200 GPa) in BiH₅. Turning to the richest-H₂ stoichiometry BiH₆ (seeing Fig 2(f)), it has a low P-1 symmetry with a H-H distance of 0.830 Å at 200 GPa.

C. Metallization of BiHₙ and the role of hydrogen

To understand the electronic properties and role of hydrogen, the electronic band structure, density of states (DOS) and Bader charges [44-46] are calculated. The overlap of electronic band near Fermi level (seeing Fig 3) implies that all stable hydrides exhibit metallic feature and the DOS near Fermi level is mainly contributed by Bi-6p (depicted in Fig. S2). Bismuth hydrides have been predicted to have the lower metallic pressure than that in pure solid hydrogen, supporting that impurities can reduce the metallization pressure. Specially, the calculated electron localization function (ELF) (seeing Fig. 3 and Fig. S3) suggests that the ELF value around H hydrogen is close to 0.95, which also proves the existence of H₂ and H₃ units. To explore the role of hydrogen in BiHₙ, we calculate Bader charges
listed in Table S1-S5. The obvious charges are found to transfer from Bi to H. Furthermore, we also analyzed the band structure of a hypothetical system where all Bi atoms are removed and only the H sublattices with a compensating background charge are remained. As is depicted in Fig 3(a), the band structures of BiHₙ and the hydrogen subsystem are qualitatively similar, which hints that Bi atoms mainly donate their electrons to hydrogen and form the ionic H. The homogeneous shape of electronic band usually indicates the ionic bonding features of Bi-H system, similar to AlH₃ [47], GaH₃ [19], TeH₄ [40] and LiHₙ [15]. However, the binding in Bi-H system is quite different from the same group hydride SbH₄. Our previous research on SbH₄ reveals, except for H₂ units, the weak covalent interaction was found between H and Sb. There is no doubt that the discrepancy of binding depends on both crystalline structures and elemental nature. In VA group, nitrogen (N) and phosphorus (P) are nonmetal. Arsenic and antimony are regarded as semimetal, while bismuth is the only real metal. Compared with other elements in group VA, bismuth has the heaviest atomic mass and the weakest electronegativity. In Bi-H system, H atoms may have a stronger ability in attracting electrons than Bi and then causes the ionic bonding form. Besides, energy band structures near the Fermi level for C2/m-BiH₃ is characterized as “flat band (near M point)-steep band”, indicating that it may be a potential high-temperature superconductor [48].

D. Dynamics and superconducting properties in BiHₙ

To explore the dynamics properties of BiHₙ, we calculated the phonon band structure. As is depicted in Fig. 4 and Fig. S4, no imaginary frequency in the phonon band structure suggests that all the researched structures are vibrationally stable. Different forms of hydrogen in Bi-H system determine the phonon band structures. For P6₃/mmc-BiH containing commensurable H atoms, the phonon dispersion curve is divided into two parts and the low-frequency is caused by Bi atoms vibrations whereas high-frequency is related to H atoms vibrations. For H₂ or H₃ units-contained hydrides, the phonon band structures are divided into three parts. The low-frequency and middle frequency are derived by Bi atoms vibrations and H-Bi-H vibrations, respectively, whereas the high-frequency is contributed from H₂ or H₃ units. For BiH₅, the phonon dispersion curve is different from others H₂-contained hydrides (BiH₃, BiH₄ and BiH₆). As is shown in Fig. 4 and Fig. S4, BiH₂, BiH₄ and BiH₆ have a flat moderate-frequency band, whereas for BiH₅, these dips appear at M and Γ, which is helpful to enhance the electron phonon coupling (λₑₚ). Moreover, in whole Brillouin zone, all
phonon modes contribute to superconductivity, which proves BiH₅ is an isotropic three-dimensional system.

To explore the possible superconductivity of Bi-H system at high pressures, the phonon frequency logarithmic average ($\omega_{\text{log}}$), DOS at Fermi level $N(E_f)$ and EPC parameter ($\lambda$) at stable pressures are calculated and listed in Table SII-SVI. The obtained EPC parameter $\lambda$ is 0.75 for BiH (at 250 GPa), 1.34 for BiH₂ (at 150GPa), 1.27 for BiH₄ (at 200 GPa), 1.23 for BiH₅ (at 200GPa) and 1.26 for BiH₆ (at 200 GPa), while the calculated $\omega_{\text{log}}$ from the phonon spectrum reach 699.2, 506.8, 870, 1021.9 and 934.6 K, respectively. The superconducting critical temperature $T_c$ of Bi-H system stable phases can be estimated by using the Allen-Dynes-modified McMillan equation \[ T_c = \frac{f_1 f_2 \omega_{\text{log}}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right] \] where the coulomb pseudopotential $\mu^*$ is often taken as ~ 0.1 and 0.13. As is depicted in Table SII-SVI, with pressure increasing, the $T_c$ decreases in BiH and BiH₄ while increases in BiH₂ and BiH₆. For BiH₅, the superconducting transition temperature first increases and then decreases with increasing pressure. In addition, the $T_c$ of all hydrides increases with the increasing hydrogen-content. It is very obvious the $T_c$ have a weak dependence on pressure.

To get to the bottom of physical mechanism for superconductivity, we also analyzed phonon density of states, Eliashberg phonon spectral function $\alpha^2 F(\omega)$ and the partial electron-phonon integral $\lambda$, as shown in Fig. 4 and Fig. S4. For BiH at 250 GPa (Fig. 3S (a)), the low-frequency modes (below 18 THz) vibrations contribute 47% of the total $\lambda$, while high frequency modes above 35 THz provide a contribution 53% in total EPC parameter. For the $P2_1/m$ of BiH₂ at 200GPa (Fig. 3S (b)), approximately 43% of total $\lambda$ is ascribed to Bi atoms vibrations (below 8.6 THz) and the 53% is from the moderate vibrations, the remaining only 4% from the H₂ vibrations (80-83THz). For BiH₄ at 150 GPa (Fig. 3S(c)), the condition is akin to $P2_1/m$-BiH₂. Bi atoms vibrations devote 27% to the total $\lambda$ and 66% mainly comes from H-Bi-H vibrations, whereas only 7% is from H₂ units. For BiH₅ at 200 GPa (Fig. 3), vibrations between 83 and 90 THz produced by the H₃ and H₂ units provide merely 2% to total $\lambda$, while the $\lambda$ from middle region contributes about 73% and Bi atoms contribute about 25%. For BiH₆, it is found that the Bi, H-Bi-H and H₂ units vibration modes account for 22%, 71% and 7% of $\lambda$ at 200 GPa (Figure 3S (d)). This law can be summarized that it is the H-Bi-H vibrations and low-frequency Bi atoms vibrations rather than the high-frequency H₂ or H₃ units that dominate the strength of electron-phonon coupling and superconductivity.
Conclusion

In summary, we explore high-pressure phase and superconductivity of bismuth hydrides by using \textit{ab initio} calculations. The bismuth hydrides (except for BiH$_3$) become thermodynamically stable with respect to decomposition into the Bi and H with increasing pressure. Except $P6_3/mmc$-BiH, a remarkable feature of the predicted stable structures is the presence of H$_2$ units or H$_3$ units. All hydrides are predicted to be potential high temperature superconductors with $T_c$ in the range of 20-119 K. The hydrogen content in bismuth hydrides plays a crucial role on impacting the $T_c$. The Superconducting transition temperature increases with the increasing hydrogen content. Our results suggest in Bi-H system the H-Bi-H and low-frequency Bi atoms vibrations contribute most significantly to the EPC. We expect our finding will open a door for studying experimental synthesis of Bi hydrides and exploring their high-pressure superconductivity.

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Captions

Fig.1. (Color online) (a), Enthalpies of formation (with respect to Bi and H\textsubscript{2}) of BiH\textsubscript{n} (n=1~6). Completely filled symbols denote the structures are on the convex shells, but for half filled represents that are not on tie-lines.

Fig.2. (Color online) (a), \textit{P}6\textsubscript{3}/\textit{mmc}-BiH at 250 GPa. (b), (c), (d) and (f) are the YZ planes of supercells (2 × 2 × 2) for the stable structures. (b), \textit{P}2\textsubscript{1}/\textit{m}-BiH\textsubscript{2} at 150 GPa. (c), \textit{Pmmn}-BiH\textsubscript{4} at 150 GPa. (d), \textit{C}2/\textit{m}-BiH\textsubscript{5} at 200 GPa. (e), the XY plane maps of \textit{C}2/\textit{m}-BiH\textsubscript{5}. (f), \textit{P}-1-BiH\textsubscript{6} at 200 GPa.

Fig.3. (Color online) Calculated electronic band structure and XY plane of electron localization function (ELF) for BiH\textsubscript{5} at 200 GPa. The full black line denotes real electronic band structure and dashed red line represents the hypothetical system composed of the hydrogen sublattice with compensating background charge.

Fig.4. (Color online) (a), calculated phonon dispersion relation for \textit{C}2/\textit{m}-BiH\textsubscript{5} at 200 GPa. These cardinal circles overlapping with the phonon dispersion are proportional to the strength of EPC (\(\lambda_{qp}\)). (b), the phonon DOS projected on H and Bi atoms. (c) The Eliashberg phonon spectral function \(\alpha^2F(\omega)\) and the partial electron-phonon integral \(\lambda(\omega)\).
Fig. 3

Fig. 4
Supplementary Material

High-pressure structures and superconductivity of Bismuth hydrides

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Fig. S1 (Color online) The electronic band structure for BiH at 250, BiH$_2$ at 150, BiH$_4$ at 150 and BiH$_6$ at 200 GPa, respectively. The full black line denotes real electronic band structure and dashed red line represents the hypothetical system composed of the hydrogen sublattice with compensating background charge.
**Fig. S2** (Color online) The density of states (DOS) for BiH at 250, BiH$_2$ at 150, BiH$_4$ at 150 and BiH$_6$ at 200 GPa, respectively.

**Fig. S3** (Color online) The 3D-electron localization function (ELF) with isosurface value of 0.75. (a) $P2_1/m$-BiH$_2$ at 150 GPa, (b) $Pmnn$-BiH$_4$ at 150 GPa, (c) $P$-1-BiH$_6$ at 200 GPa.
Fig. S4. (Color online) The phonon band structure, phonon density of states, Eliashberg phonon spectral function $\alpha^2 F(\omega)$ and the partial electron-phonon integral $\lambda$ for BiH at 250, BiH$_2$ at 150, BiH$_4$ at 150 and BiH$_6$ at 200 GPa, respectively.
Table S1. The lattice parameters and atomic positions of \( P6_3/mmc \)-BiH at 250 GPa, \( P2_1/m \)-BiH\(_2\) at 150 GPa, \( Pmmn \)-BiH\(_4\) at 150 GPa, \( C2/m \)-BiH\(_5\) at 200 GPa and \( P-1 \)-BiH\(_6\) at 200 GPa.

| Structure | Parameters | Atom | x   | y   | z   |
|-----------|------------|------|-----|-----|-----|
| BiH       | \( a=2.8355 \) | H    | 0.00000 | 0.00000 | 0.50000 |
|           | \( b=2.8355 \) |      |       |      |      |
|           | \( c=4.5234 \) | Bi   | 0.33333 | 0.66667 | 0.25000 |
| BiH\(_2\) | \( a=4.5029 \) | H    | 0.80375 | 0.25000 | 0.15578 |
|           | \( b=3.0751 \) |      | 0.03102 | 0.75000 | 0.03594 |
|           | \( c=3.0145 \) | Bi   | 0.28727 | 0.25000 | 0.33760 |
| BiH\(_4\) | \( a=3.0607 \) | H    | 0.00000 | 0.14251 | 0.13921 |
|           | \( b=5.2513 \) |      | 0.50000 | 0.30853 | 0.13066 |
|           | \( c=2.9380 \) | Bi   | 0.00000 | 0.50000 | 0.45569 |
| BiH\(_5\) | \( a=2.7849 \) | H    | -0.37224 | -0.37224 | -0.59884 |
|           | \( b=2.7849 \) |      | -0.10423 | -0.10423 | -0.57462 |
|           | \( c=4.1785 \) | H    | -0.50000 | -0.50000 | -0.50000 |
|           | \( \alpha=\beta=119.9594 \) | Bi | 0.00000 | 0.00000 | 0.00000 |
| BiH\(_6\) | \( a=2.8017 \) | H    | 0.17087 | 0.74618 | 0.19468 |
|           | \( b=2.8732 \) |      | 0.24640 | 0.43069 | 0.00802 |
|           | \( c=6.2900 \) | H    | 0.87768 | 0.75018 | 0.46282 |
|           | \( \alpha=89.3171 \) | H | 0.21712 | 0.81684 | 0.06420 |
|           | \( \beta=79.5108 \) | H | 0.73956 | 0.84885 | 0.01119 |
|           | \( \gamma=89.8771 \) | H | 0.17570 | 0.75131 | 0.42965 |
|           | Bi | 0.63408 | 0.25293 | 0.27794 |

Table SII. The phonon frequency logarithmic average (\( \omega_{log} \)), EPC parameter (\( \lambda \)), the electronic DOS at Fermi level \( N(E_f) \), \( f_{f_{2}} \) (\( \mu^* = 0.1 \) and \( 0.13 \)) and critical temperature \( T_c \) (\( \mu^* = 0.1 \) and \( 0.13 \)) for \( P6_3/mmc \)-BiH at 250 and 300 GPa.

| Pressure (GPa) | Lambda(\( \lambda \)) | \( \omega_{log} (K) \) | \( N(E_f) \) states/Spin/Ry/cell | \( f_{f_{2}} (\mu^* = 0.1) \) | \( f_{f_{2}} (\mu^* = 0.13) \) | \( T_c (K) (\mu^* = 0.1) \) | \( T_c (K) (\mu^* = 0.13) \) |
|---------------|------------------------|------------------------|----------------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|
| 250           | 0.76                   | 699.17                 | 5.14                             | 1.05                        | 1.04                        | 30                         | 24                         |
| 300           | 0.61                   | 792.43                 | 5.03                             | 1.04                        | 1.03                        | 20                         | 13                         |
Table SIII. The phonon frequency logarithmic average ($\omega_{\text{log}}$), EPC parameter ($\lambda$), the electronic DOS at Fermi level $N(E_f)$, $f/f_2$ ($\mu^* = 0.1$ and 0.13) and critical temperature $T_c$ ($\mu^* = 0.1$ and 0.13) for $P2_1/m\text{-BiH}_2$ at 150, 200, 250 and 300GPa.

| Pressure (GPa) | Lambda($\lambda$) | $\omega_{\text{log}}$(K) | N($E_f$) states/Spin/Ry/cell | $f/f_2$ ($\mu^*=0.1$) | $f/f_2$ ($\mu^*=0.13$) | Tc(K) ($\mu^*=0.1$) | Tc(K) ($\mu^*=0.13$) |
|---------------|-------------------|--------------------------|-----------------------------|-------------------------|-------------------------|----------------------|----------------------|
| 150           | 1.34              | 506.80                   | 6.74                        | 1.13                    | 1.11                    | 59                   | 51                   |
| 200           | 1.07              | 706.70                   | 6.53                        | 1.09                    | 1.08                    | 60                   | 52                   |
| 250           | 0.99              | 841.53                   | 6.45                        | 1.08                    | 1.07                    | 63                   | 52                   |
| 300           | 0.96              | 917.48                   | 6.41                        | 1.07                    | 1.06                    | 65                   | 55                   |

Table SIV. The phonon frequency logarithmic average ($\omega_{\text{log}}$), EPC parameter ($\lambda$), the electronic DOS at Fermi level $N(E_f)$, $f/f_2$ ($\mu^* = 0.1$ and 0.13) and critical temperature $T_c$ ($\mu^* = 0.1$ and 0.13) for $Pmmn\text{-BiH}_4$ at 150, 200, 250 and 300GPa.

| Pressure (GPa) | Lambda($\lambda$) | $\omega_{\text{log}}$(K) | N($E_f$) states/Spin/Ry/cell | $f/f_2$ ($\mu^*=0.1$) | $f/f_2$ ($\mu^*=0.13$) | Tc(K) ($\mu^*=0.1$) | Tc(K) ($\mu^*=0.13$) |
|---------------|-------------------|--------------------------|-----------------------------|-------------------------|-------------------------|----------------------|----------------------|
| 150           | 1.27              | 864.72                   | 8.01                        | 1.17                    | 1.10                    | 93                   | 81                   |
| 200           | 1.10              | 1008.85                  | 6.77                        | 1.09                    | 1.08                    | 88                   | 77                   |
| 250           | 0.97              | 1101.09                  | 5.62                        | 1.08                    | 1.06                    | 77                   | 66                   |
| 300           | 0.92              | 1150.38                  | 5.33                        | 1.07                    | 1.06                    | 75                   | 63                   |

Table SV. The phonon frequency logarithmic average ($\omega_{\text{log}}$), EPC parameter ($\lambda$), the electronic DOS at Fermi level $N(E_f)$, $f/f_2$ ($\mu^* = 0.1$ and 0.13) and critical temperature $T_c$ ($\mu^* = 0.1$ and 0.13) for C2/m-BiH$_5$ at 200, 250 and 300GPa.

| Pressure (GPa) | Lambda($\lambda$) | $\omega_{\text{log}}$(K) | N($E_f$) states/Spin/Ry/cell | $f/f_2$ ($\mu^*=0.1$) | $f/f_2$ ($\mu^*=0.13$) | Tc(K) ($\mu^*=0.1$) | Tc(K) ($\mu^*=0.13$) |
|---------------|-------------------|--------------------------|-----------------------------|-------------------------|-------------------------|----------------------|----------------------|
| 200           | 1.23              | 1021.90                  | 4.23                        | 1.11                    | 1.10                    | 103K                 | 92K                  |
| 250           | 1.45              | 801.68                   | 4.18                        | 1.15                    | 1.13                    | 101K                 | 90K                  |
| 300           | 1.20              | 1220.96                  | 4.05                        | 1.10                    | 1.09                    | 119K                 | 105K                 |

Table SVI. The phonon frequency logarithmic average ($\omega_{\text{log}}$), EPC parameter ($\lambda$), the electronic DOS at Fermi level $N(E_f)$, $f/f_2$ ($\mu^* = 0.1$ and 0.13) and critical temperature $T_c$ ($\mu^* = 0.1$ and 0.13) for P-1-BiH$_6$ at 200, 250 and 300GPa.

| Pressure (GPa) | Lambda($\lambda$) | $\omega_{\text{log}}$(K) | N($E_f$) states/Spin/Ry/cell | $f/f_2$ ($\mu^*=0.1$) | $f/f_2$ ($\mu^*=0.13$) | Tc(K) ($\mu^*=0.1$) | Tc(K) ($\mu^*=0.13$) |
|---------------|-------------------|--------------------------|-----------------------------|-------------------------|-------------------------|----------------------|----------------------|
| 200           | 1.26              | 934.62                   | 7.54                        | 1.12                    | 1.10                    | 100                  | 88                   |
| 250           | 1.24              | 1035.33                  | 7.32                        | 1.11                    | 1.07                    | 107                  | 92                   |
| 300           | 1.23              | 1102.82                  | 6.76                        | 1.11                    | 1.09                    | 113                  | 100                  |
Table S1. Calculated Bader charges of H and Bi atoms in BiH ($P6_3/mmc$) at 250 GPa.

| Pressure | Atom | Charge  | $\sigma$(e) |
|----------|------|---------|-------------|
| 250 GPa  | H1   | 1.4650  | -0.4650     |
|          | H2   | 1.4650  | -0.4650     |
|          | Bi1  | 4.5339  | 0.4661      |
|          | Bi2  | 4.5339  | 0.4661      |

Table S2. Calculated Bader charges of H and Bi atoms in BiH$_2$ ($P2_1/m$) at 150 GPa.

| Pressure | Atom | Charge  | $\sigma$(e) |
|----------|------|---------|-------------|
| 150 GPa  | H1   | 1.1731  | -0.1731     |
|          | H2   | 1.1731  | -0.1731     |
|          | H3   | 1.1591  | -0.1591     |
|          | H4   | 1.1591  | -0.1591     |
|          | Bi1  | 4.6670  | 0.3330      |
|          | Bi2  | 4.6687  | 0.3313      |

Table S3. Calculated Bader charges of H and Bi atoms in BiH$_4$ ($Pmmn$) at 150 GPa.

| Pressure | Atom | Charge  | $\sigma$(e) |
|----------|------|---------|-------------|
| 150 GPa  | H1   | 1.1490  | -0.1490     |
|          | H2   | 1.1691  | -0.1691     |
|          | H3   | 1.1490  | -0.1490     |
|          | H4   | 1.1691  | -0.1691     |
|          | H5   | 1.1789  | -0.1789     |
|          | H6   | 1.1789  | -0.1789     |
|          | H7   | 1.1789  | -0.1789     |
|          | H8   | 1.1789  | -0.1789     |
|          | Bi1  | 4.3241  | 0.6759      |
|          | Bi2  | 4.3241  | 0.6759      |

Table S4. Calculated Bader charges of H and Bi atoms in BiH$_5$ ($C2/m$) at 200 GPa.

| Pressure | Atom | Charge  | $\sigma$(e) |
|----------|------|---------|-------------|
| 200 GPa  | H1   | 1.3573  | -0.3573     |
|          | H2   | 1.2573  | -0.2573     |
|          | H3   | 1.0973  | -0.0973     |
|          | H4   | 1.1131  | -0.1131     |
|          | H5   | 1.0139  | -0.0139     |
|          | Bi   | 4.2612  | 0.7388      |
| Pressure | Atom | Charge  | σ(e)  |
|----------|------|---------|-------|
| 200 GPa  | H1   | 1.2092  | -0.2092 |
|          | H2   | 1.2092  | -0.2092 |
|          | H3   | 1.0951  | -0.0951 |
|          | H4   | 1.0950  | -0.0950 |
|          | H5   | 1.1705  | -0.1705 |
|          | H6   | 1.1705  | -0.1705 |
|          | H7   | 1.0372  | -0.0372 |
|          | H8   | 1.0372  | -0.0372 |
|          | H9   | 1.0952  | -0.0952 |
|          | H10  | 1.0952  | -0.0952 |
|          | H11  | 1.1871  | -0.1871 |
|          | H12  | 1.1871  | -0.1871 |
|          | Bi1  | 4.2058  | 0.7942 |
|          | Bi2  | 4.2058  | 0.7942 |

Table S5. Calculated Bader charges of H and Bi atoms in BiH$_6$ (P-1) at 200 GPa.