High-temperature superconductivity of ternary Y–Hf–H compounds under high pressure

Yanqi Wang  
Yangtze University

Yuanyuan Jin  
Yangtze University

Fulong Yang  
Yangtze University

Jinquan Zhang  
Yangtze University

Chuanzhao Zhang  
zcz19870517@163.com

Yangtze University

Fangguang Kuang  
Gannan Normal University

Meng Ju  
Southwest University

Song Li  
Yangtze University

Shubo Cheng  
Yangtze University

Article

Keywords:

Posted Date: March 28th, 2024

DOI: https://doi.org/10.21203/rs.3.rs-4019202/v1

License: ☛ This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License

Additional Declarations: No competing interests reported.
Abstract

Compressed ternary alloy superhydrides are currently considered to be the most promising competitors for high-temperature superconducting materials. Here, the stable stoichiometries in the Y-Hf-H ternary system under pressure are comprehensively explored and four fresh phases are found: \( \text{Pmna-YHfH}_6 \) and \( \text{P4/ mmm-YHfH}_7 \) at 200 GPa, \( \text{P4/ mmm-YHfH}_8 \) at 300 GPa and \( \text{P-6m2-YHfH}_{18} \) at 400 GPa. The four Y-Hf-H ternary phases are thermodynamically and dynamically stable at corresponding pressure. In addition, structural features, bonding characteristics, electronic properties, and superconductivity of the four ternary Y-Hf-H phases are systematically calculated and discussed. Among them, the superconducting transition temperatures \( (T_c) \) are significantly enhanced as the hydrogen content and the contribution of H atoms to the density of states at the Fermi level increase. The \( \text{P-6m2-YHfH}_{18} \) with high hydrogen content exhibits a high \( T_c \) value of 130 K at 400 GPa.

Introduction

In recent years, the searches for superconducting materials have been a hotspot in the field of condensed matter physics, and realizing room-temperature superconductivity at atmospheric pressure is a long-held dream pursued by researchers. Hydrogen ranks first in the periodic table and has the smallest atomic mass in nature, thus exhibiting a substantially high Debye temperature\(^1\). According to the Bardeen–Cooper–Schrieffer (BCS) theory, metallic hydrogen has been a prospective candidate for a room-temperature superconductor\(^1\), which inspired extensive experimental and theoretical studies on the metallization of hydrogen under high pressure\(^2-^5\). However, the metallization of hydrogen requires extreme pressure over 500 GPa experimentally. In 2004, Ashcroft innovatively predicted that the lattice of hydrogen can be chemically “precompressed” to achieve metallization at lower pressures by alloying hydrogen with other elements\(^6\). This idea greatly reduces the pressure conditions required by room-temperature superconductors, which set off an upsurge in the investigation for room-temperature superconductivity of hydrogen-rich materials.

So far, the theoretical and experimental explorations for binary hydrides of almost all elements in the periodic table (except for some radioactive and magnetic elements) have been basically completed and considerable results have been achieved\(^7-^14\). Especially, the Y-H and Hf-H binary systems stand out due to their unusual hydrogen configuration structures and significantly high superconducting transition temperatures under pressures. For hafnium hydrogen compounds, the dense superhydrides HfH\(_{10}\) with a planar “pentagraphenelike” sublattice can exhibit a \( T_c \) up to 234 K at 250 GPa\(^15\). HfH\(_9\) with H\(_{12}\) tube and HfH\(_3\) framework has a predicted \( T_c \) of 110 K at 200 GPa\(^16\). A superconducting critical temperature with \( T_c \sim 83 \text{ K} \) was observed in HfH\(_{14}\) at 243 GPa in the experiment\(^17\). For binary yttrium hydrides, the \( T_c \) of YH\(_6\) with H\(_{24}\) cage-like clathrate structure achieves 251–264 K at 120 GPa\(^18\) and 290 K at 300 GPa\(^19\). YH\(_9\) with H\(_{29}\)-cage structure has a \( T_c \) of 276 K at 150 GPa. YH\(_{10}\) with H\(_{32}\)-cage structure possesses an \( T_c \).
value of 303 K at 400 GPa\textsuperscript{20}. Among them, the high-temperature superconductivity of $\text{YH}_6$ and $\text{YH}_9$ materials have been confirmed in subsequent high-pressure experiments\textsuperscript{21–23}.

The general rules of hydrogen-rich superconductors are summarized based on binary hydrides and applied to ternary hydrides with more abundant hydrogen configurations by the diverse chemical compositions\textsuperscript{24–29}. The explorations on ternary hydrogen-rich materials can be mainly divided into two aspects. (i) Add another element to the binary hydride for structural modulation to form a new ternary hydride with better superconductivity. For example, the designed $\text{Li}_2\text{MgH}_{16}$ with remarkably high $T_c$ of 473 K at 250 GPa via doping lithium into the parent $\text{MgH}_{16}$\textsuperscript{30}. (ii) Mix metal binary hydrides proportionally in the form of solid solutions to obtain alloy-type ternary hydrides, in which the metal elements have similar electronegativity and atomic radius. Theoretical predictions show that ternary hydrides such as $(\text{Y}, \text{Sr})\text{H}_{11}$\textsuperscript{31}, $(\text{YCa})\text{H}_{12}$\textsuperscript{32}, and $(\text{YZr})\text{H}_{18}$\textsuperscript{33} through alloying hydrogen-rich binary compounds exhibit good superconductivity under high pressures, and the experimentally observed $T_c$ values of $(\text{La}, \text{Y})\text{H}_{10}$\textsuperscript{34}, $(\text{La}, \text{Y})\text{H}_6$, and $(\text{Y}, \text{Ce})\text{H}_9$\textsuperscript{35} at various pressures are 253 K, 226 K, and 140 K, respectively. Obviously, ternary hydrides have made significant breakthroughs in the discovery of room-temperature superconductors both theoretically and experimentally.

It is widely known that $\text{Y}$ and $\text{Hf}$ elements are located diagonally in the periodic table with close electronegativity, which indicates prominent high-temperature superconductivity potentially exists in $\text{Y-Hf-H}$ system. In this work, we perform an extensive calculation to investigate the ternary $\text{Y-Hf-H}$ system under high pressure and analyze their thermodynamical stability and dynamical stability. Indeed, several new stoichiometries in the ternary $\text{Y-Hf-H}$ system have been found under pressure. The structural features, Bader charges, band structures, density of states (DOS), electron-phonon coupling (EPC) and superconducting transition temperatures of the new ternary $\text{Y-Hf-H}$ phases are systematically studied and they are found to possess the unusual structural features and superconductivity.

**Results and Discussion**

*Ternary phase diagrams and phase stability*

In the first step, in order to determine the stable low-energy compounds of $\text{Y-Hf-H}$ ternary system under high pressure, we thoroughly explored the potential stoichiometries of $\text{Y}_x\text{Hf}_y\text{H}_z$ ($x = 1 \sim 3$, $y = 1 \sim 3$, $z = 2 \sim 24$) at pressures of 200, 300 and 400 GPa, respectively, and constructed the ternary phase diagrams of $\text{Y-Hf-H}$ system under selected pressures (see Fig. 1). Its corresponding stable elemental solids ($\text{Y}$, $\text{Hf}$ and $\text{H}$) located at three vertexes of triangle and binary hydrides ($\text{Y-H}$ and $\text{Hf-H}$ systems) on three sides have been systematically investigated experimentally and theoretically. The elemental solids and binary compounds information referenced in the present structural predictions are from previous works\textsuperscript{15–23,36–39}. From Fig. 1(a), $\text{YHfH}_6$ and $\text{YHfH}_7$ are both thermodynamic stable stoichiometries, which are exactly located on the convex hull of 200 GPa. Except for directly compressing $\text{Y}$, $\text{Hf}$, and $\text{H}$, the two red lines exhibit others potential synthetic routes for $\text{YHfH}_6$ ($\text{YH}_3 + \text{HfH}_3 \rightarrow \text{YHfH}_6$) and $\text{YHfH}_7$ ($\text{YH}_4 + \text{HfH}_3 \rightarrow$
YHfH$_7$) based on the “triangle straight-line method” (TSLM)$^{40,41}$. As the pressure increased, YHfH$_6$ gradually becomes thermodynamic unstable while YHfH$_7$ can maintain energy stability up to 300 GPa, and a new stable component YHfH$_8$ has emerged on the convex hull. Similarly, YHfH$_8$ can be synthesized through the route YH$_4$ + HfH$_4$ → YHfH$_8$ shown in the red line of Fig. 1(b). Upon further compression, YHfH$_{18}$ compound with the highest hydrogen content, as the only composition falling into the convex hull, can be stable energetically superior to other stoichiometries at 400 GPa [see Fig. 1(c)]. The above analysis demonstrates that the four ternary hydrides (YHfH$_6$, YHfH$_7$, YHfH$_8$ and YHfH$_{18}$) are thermodynamically stable under high pressures, and provides their potential synthetic routes, which will stimulate the experimental synthesis. Subsequently, we focus on the structural characteristics, electronic properties, and superconductivity of YHfH$_6$ and YHfH$_7$ at 200 GPa, YHfH$_8$ at 300 GPa, and YHfH$_{18}$ at 400 GPa, respectively.

**Structural features, bonding features, and electronic properties**

The crystal structure diagrams of YHfH$_6$ and YHfH$_7$ at 200 GPa, YHfH$_8$ at 300 GPa and YHfH$_{18}$ at 400 GPa are depicted in Fig. 2 and homologous detailed structural parameters are summarized in Table S1 of Supplementary Information (SI). In addition, to better understand the interaction information, we also depict their ELF in Fig. 3. The predicted YHfH$_6$ is found to crystallize in the orthorhombic $Pmna$ phase with the lattice parameters of $a = 10.170$ Å, $b = 8.108$ Å, and $c = 8.209$ Å at 200 GPa. This phase is observed in ternary hydrides for the first time. There are three inequivalent H atoms are located at the Wyckoff sites $4h$ (0.000, 0.360, 1.386), $4h$ (0.000, 0.124, 1.123) and $4g$ (0.250, 0.239, 0.750), respectively, and these H atoms form one-dimensional linear H$_4$ chains with two types H-H separations of 1.626 and 1.669 Å, as shown in Fig. 2(a). Its weak covalence is accurately described by the ELFs in Fig. 3(a) and (b), while the absence of electron localization between metal atoms and H atom reveals the purely ionic of neighboring Hf-H and Y-H connections. For YHfH$_7$ at 200 GPa and YHfH$_8$ at 300 GPa, both are stable with tetragonal $P4/mmm$ phase, which adopts the same symmetry as previously reported YZrH$_8$$^{33}$, YPrH$_8$$^{42}$, YBaH$_8$$^{43}$ and YMgH$_8$$^{44}$ hydrides. In this structure, Hf atoms occupy the center position of the tetragonal lattice while Y atoms are located at eight vertices, and all H atoms form H-clathrate structures around metal Hf atoms. The Hf-centered H$_{14}$ cage in $P4/mmm$-YHfH$_7$ contains eight twisted quadrilateral and four square “H$_4$” units with only two types H-H distances of 1.51 and 1.78 Å [see Fig. 2(b)]. The hydrogen sublattice of $P4/mmm$-YHfH$_8$ is very similar to YHfH$_7$, which can be considered to insert an H atom into each long edges of YHfH$_7$ lattice, forming an H$_{18}$ cage with three types H-H separations of 1.29, 1.40 and 1.42 Å [see Fig. 2(c)]. It is noteworthy that this H atoms insertion facilitates the four squares “H$_4$” of $P4/mmm$-YHfH$_7$ to evolve into four hexagon “H$_6$” units in $P4/mmm$-YHfH$_8$. The shortest H-H distance 1.29 Å in “H$_6$” units are greatly shortened compared to that in “H$_4$” (1.78 Å), which makes it closer to the H-H distance (0.98 Å) in metallic monatomic H at 500 GPa$^{45}$. The decrease in distance between H atoms enhances their mutual interactions, which not only promotes the stability of the hydrogen cage skeleton, but also plays a decisive role in the superconductivity of the system. From Fig. 3(c), (d) and (e), (f), the H atoms are weakly covalently bonded to one another in the cages, which are evident in view of the charge
localizations between the nearest-neighbor H atoms. In the case of YHfH\textsubscript{18} at 400 GPa, it is stable in hexagonal structure with \textit{P}-6\textit{m}2 symmetry, which has the lattice parameters of \(a = b = 3.176\ \text{Å} \) and \(c = 4.770\ \text{Å}\) [see Fig. 2(d)]. It is found that all H atoms form semi-cages with the H-H connections around 1.03-1.46 Å in this phase. The weak covalence between H-H connection is also demonstrated by the ELF diagrams plotted in Fig. 3(h) and (i), as the ELF values between metal atoms and the nearest H atom are smaller than 0.5. In addition, the shortest H-H bond length in \textit{P}-6\textit{m}2-YHfH\textsubscript{18} phase is closest to the atomic H under 500 GPa\textsuperscript{45} and famous ultra-high \(T_c\) hydride Li\textsubscript{2}MgH\textsubscript{16} (1.02 Å, at 300 GPa)\textsuperscript{30}, HfH\textsubscript{10} (1.14 Å, at 200 GPa)\textsuperscript{15}, YH\textsubscript{10} (1.08 Å, at 200 GPa)\textsuperscript{20} and LaH\textsubscript{10} (1.11 Å, at 200 GPa)\textsuperscript{46}, etc.

The Bader charge analysis\textsuperscript{47} was conducted to further gain insight into the chemical bonding features between Y, Hf and H atoms in \textit{Pmna}-YHfH\textsubscript{6}, \textit{P4/mmm}-YHfH\textsubscript{7}, \textit{P4/mmm}-YHfH\textsubscript{8} and \textit{P}-6\textit{m}2-YHfH\textsubscript{18}, as tabulated in Table 1. As the electronegativity of Y (1.2) and Hf (1.3) are much smaller than H (2.2), a large amount of charge should transfer from Y and Hf atoms to H atoms based on the periodic law\textsuperscript{48}. The calculated results show that each Hf atom approximately loses 1.21, 1.25, 1.26 and 1.26 \(e\) electrons in YHfH\textsubscript{6}, YHfH\textsubscript{7}, YHfH\textsubscript{8} and YHfH\textsubscript{18}, respectively, and one Y atom loses 1.23, 1.32, 1.27 and 1.32 \(e\) charges, respectively. For H atoms, per H gains charges of 0.41, 0.37, 0.32 and 0.14 \(e\), respectively. We intuitively observe that the number of electrons accepted by H atoms gradually decreases in these four structures with the rise of pressure. The obtained electrons for H-H unit will reside in the H-H antibonding orbitals, which can elongate the H-H bond length in the high-pressure hydrides\textsuperscript{49,50}. Consequently, the H-H bonds in four phases present a gradually decreasing trend as well. The discussion of Bader charge is consistent with the above ELF analysis, further confirming the strong ionic natures between metal atoms and H atoms in the four stable configurations.

The electronic band structures and DOS of \textit{Pmna}-YHfH\textsubscript{6}, \textit{P4/mmm}-YHfH\textsubscript{7}, \textit{P4/mmm}-YHfH\textsubscript{8} and \textit{P}-6\textit{m}2-YHfH\textsubscript{18} at high pressure were calculated to reveal their electronic properties, as exhibited in Fig. 4. As a result, these four structures possess metallic properties due to the overlapping of the conduction and valence bands, and a large total density of states (TDOS) at the Fermi level also confirms this conclusion. Furthermore, it is found that the electronic density of states at Fermi level is obviously dominated by metal Y and Hf atoms in YHfH\textsubscript{n} \((n = 6, 7 \text{ and } 8)\) phases, so the metallic properties of the above three phases are contributed by metal atoms. Due to their less hydrogen content, the H atoms provide low total H-DOS with 0.21, 0.11 and 0.16 \((\text{states/eV})/\text{f.u.}\), respectively, and H-DOS merely account for 11\%, 15\% and 23\% of the total density of states, respectively. Interestingly, the electronic band structures of YHfH\textsubscript{7} and YHfH\textsubscript{8} are quite similar, which is attributed to their similar crystal structures. As for \textit{P}-6\textit{m}2-YHfH\textsubscript{18} phase with the highest H content at 400 GPa, more electrons participate in the formation of Cooper pairs and there is a steep large electron pocket passing through the Fermi level at G point, which increases the TDOS at Fermi level. In this structure, the total H-DOS at Fermi level significantly enhances to 0.67 \((\text{states/eV})/\text{f.u.}\), which is comparable to HfH\textsubscript{9}\textsuperscript{16}, YH\textsubscript{6}\textsuperscript{18}, YCa\textsubscript{2}H\textsubscript{18}\textsuperscript{51}, YCaH\textsubscript{20}\textsuperscript{51}, CaHfH\textsubscript{18}\textsuperscript{52}, YLuH\textsubscript{12}\textsuperscript{53} and Rb\textsubscript{2}MgH\textsubscript{18}\textsuperscript{54}, and the proportion of H-DOS in TDOS increases to 47\% as well. In fact, the H-
Dynamical properties and electron–phonon coupling

The computed phonon dispersion curves, projected phonon density of states (PHDOS), Eliashberg spectral function $\alpha^2 F(\omega)$ and the integral EPC parameters $\lambda(\omega)$ of YHfH$_6$, YHfH$_7$, YHfH$_8$ and YHfH$_{18}$ are plotted in Fig. 5. The phonon dispersion curves can effectively confirm their dynamic stability because of the absence of any imaginary phonon frequencies throughout the whole Brillouin zone. In the PHDOS, the low-frequency phonon bands are mainly originated from the vibrations of Hf and Y atoms, while the middle-frequency and high-frequency phonon modes regions are associated with H atoms due to the Hf and Y atomic masses are much heavier than H atoms.

Based on the discussion of electronic properties of four stable phases, their excellent metallic properties under pressures prompt us to explore their potential superconductivity. Therefore, the electron-phonon coupling parameters $\lambda$, the logarithmic average phonon frequency $\omega_{\text{log}}$ and electron density of states at Fermi level $N(E_f)$ were calculated in Table 2. Moreover, based on the Eliashberg spectral function $\alpha^2 F(\omega)$ and the integral EPC parameters $\lambda(\omega)$ of Pmna-YHfH$_6$ at 200 GPa, P4/mmm-YHfH$_7$ at 200 GPa, P4/mmm-YHfH$_8$ at 300 GPa and P-6m2-YHfH$_{18}$ at 400 GPa in Fig. 5, the superconducting critical temperature values are evaluated through solving the Allen–Dynes modified McMillan equation:

$$T_c = \frac{\omega_{\text{log}}}{1.2} \exp \left[ \frac{\ln \left( \frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62 \lambda)} \right)}{\lambda \cdot \mu^* (1 + 0.62 \lambda)} \right]$$

For the hydrides with $\lambda < 1.5$, this equation can estimate highly accurate $T_c$ values. Among them, the Coulomb pseudopotential constants $m^*$ are set to typical 0.10 and 0.13, respectively. It is found that the $T_c$ values slightly decrease when $m^* = 0.13$.

In YHfH$_6$ and YHfH$_7$ phases at 200 GPa, their calculated EPC integral coefficients $\lambda$ are close (~ 0.38), which results in their similar predicted $T_c$ values around 3 K (see Table 2). Although YHfH$_6$ has a large electronic density of states at the Fermi level [$N(E_f) = 11.983$ states/spin/Ry/Unit Cell], even the largest among the four stable structures, this large $N(E_f)$ value is mainly provided by metal Hf and Y atoms, which suppresses the superconductivity of YHfH$_6$. From Fig. 5, the low-frequency heavy Hf and Y atomic vibrations below 6 THz contribute 51% of the total $\lambda$, while the high-frequency region above 20 THz associated with light H atom vibration accounts for 49% in YHfH$_6$. As for YHfH$_7$ structure, its phonon modes can be divided into three main regions. The low frequency phonon modes below 10 THz provided by metal atoms account for 39%, while H atoms drive 10% and 51% in the middle (23-27 THz) and upper (> 40 THz) parts, respectively. In this situation, the contribution of the H-phonon band begins to increase.
For YHfH$_8$ at 300 GPa, the dominance of H atom in electron-phonon coupling is further clarified and the contribution of the H-phonon band enhances to 68%. In addition, the significant difference in superconductivity between $P4/mmm$-YHfH$_7$ and $P4/mmm$-YHfH$_8$ with highly similar structures can be further attributed to the fact that the H$_{18}$ cage of YHfH$_8$ bonds more tightly than the H$_{14}$ cage in YHfH$_7$. Based on these reasons, the $T_c$ value of $P4/mmm$-YHfH$_8$ has been effectively enhanced to 47 K. Notably, in YHfH$_{18}$ phases at 400 GPa, metal atoms motions in the lowest part of the phonon bands (< 10 THz) only occupy 18% of the total $\lambda$, while all other vibrational modes up to 82% (> 25 THz) are dominated by H atoms. Obviously, YHfH$_{18}$ possess the highest predicted $T_c$ value 130 K among the four stable structures, which is close to other H-rich materials such as YZrH$_{18}$ (156 K)$^{33}$ and LiP$_2$H$_{14}$ (169 K)$^{56}$, but higher than MgH$_{12}$ (60 K)$^{57}$, YCH$_{12}$ (112 K)$^{58}$, YSH$_6$ (91 K)$^{59}$, Ca$_2$B$_2$H$_{13}$ (89 K)$^{60}$ and Mg(ScH$_4$)$_3$ (10 K)$^{61}$. This result highlights that the high-frequency H atom vibration exhibits a significant contribution to the electron-phonon coupling in YHfH$_{18}$ structure, which is coincide with the analysis result of large H-DOS proportion at the Fermi level. Thus, we have certificated that H-derived DOS at the Fermi level can effectively improve the $T_c$ value of Y-Hf-H ternary hydrides under high pressure.

**Conclusions**

In conclusion, we conducted comprehensive structural searches of the Y-Hf-H ternary system under high pressure by applying unbiased CALYPSO method and first-principles calculations to reveal the phase stability. As a result, we have discovered four thermodynamically stable ternary hydrogen-rich compounds at selected pressures, namely $Pmna$-YHfH$_6$, $P4/mmm$-YHfH$_7$, $P4/mmm$-YHfH$_8$ and $P6m2$-YHfH$_{18}$. YHfH$_6$ contains linear H$_4$ chains, while YHfH$_7$ and YHfH$_8$ adopt clathrate structures of H$_{14}$ and H$_{18}$ cages, respectively. Additionally, YHfH$_{18}$ forms intriguing H semi-cages lattices. In these four stable structures, ionic bonds are formed between the metal and H atoms, and the two nearest H atoms are connected by weak covalent bonds. According to their metallic properties, the superconducting transition temperatures of YHfH$_8$ and YHfH$_{18}$ are 47 K at 300 GPa and 130 K at 400 GPa, respectively. We believe that the density of states at the Fermi level dominated by H atoms are closely associated with the high-temperature superconductivity of the Y-Hf-H system.

**Computational method**

The extensive variable-composition structure searches of Y-Hf-H ternary system under high pressures were implemented via swarm intelligence-based CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) code$^{62,63}$ including 1-2 formula units (f.u.) at 200, 300 and 400 GPa. A similar method has successfully predicted the high-pressure structures of various systems$^{64-69}$ and provides effective guidance for experimental synthesis. We have performed the structural relaxations, energetic and electronic structures in the VASP (Vienna ab initio simulation package) code$^{70}$ through density functional
theory (DFT) within the Perdew-Burke-Ernzerhof (PBE) exchange correlation function of generalized gradient approximation (GGA)\textsuperscript{71,72}. The Projector-Augmented Wave (PAW)\textsuperscript{73} method with valence electron configurations $4s^24p^64d^15s^2$ for Y, $6s^25d^2$ for Hf and $1s^1$ for H was adopted with 800 eV cutoff energy for the plane-wave basis expansion of the electronic wave functions and appropriate Monkhorst-Pack scheme with a $k$-point grid of 2p $\cdot$ 0.03 Å$^{-1}$ for sampling in the Brillouin zone to ensure that all the enthalpy calculations were well converged to less than 1 meV/atom\textsuperscript{74}. The descriptions of electronic properties and bonding characteristics have been conducted through Bader charge analysis\textsuperscript{47} and electron localization functions (ELF) method\textsuperscript{75,76}. Additionally, the phonon and electron-phonon coupling matrix elements were calculated within density functional perturbation theory (DFPT) as implemented in the QUANTUM ESPRESSO package\textsuperscript{77} with a kinetic cutoff energy of 80 Ry. In the first Brillouin zone, we have selected $k$-point meshes of 12 $\cdot$ 12 $\cdot$ 12, 20 $\cdot$ 20 $\cdot$ 12, 16 $\cdot$ 16 $\cdot$ 16 and 20 $\cdot$ 20 $\cdot$ 16 for $Pmna$-YHfH$_6$, $P4/mmm$-YHfH$_7$, $P4/mmm$-YHfH$_8$ and $P-6m2$-YHfH$_{18}$, respectively, and $q$-point meshes of 3 $\cdot$ 3 $\cdot$ 3, 5 $\cdot$ 5 $\cdot$ 3, 4 $\cdot$ 4 $\cdot$ 4 and 5 $\cdot$ 5 $\cdot$ 4 for $Pmna$-YHfH$_6$, $P4/mmm$-YHfH$_7$, $P4/mmm$-YHfH$_8$ and $P-6m2$-YHfH$_{18}$, respectively.

**Declarations**

**Data availability**

The datasets used and/or analyzed during the current study available from the corresponding author on reasonable request.

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (Nos. 11804031, 11904297 and 11964001), the Fundamental Research Funds for the Central Universities (No. SWU-KT22049) and the Chongqing Talent Plan for Young Top Notch Talents (202005007).

**Author Contributions**

Y.Q.W., Y.Y.J. and C.Z.Z. conceived the idea. Y.Q.W., F.L.Y., J.Q.Z., S.L. and S.B.C. performed the calculations. Y.Q.W., Y.Y.J. and C.Z.Z. wrote the manuscript and all authors contributed to revisions.

**Additional Information**

**Competing Interests:** The authors declare no competing financial interests.

**References**


**Tables**

**Table 1.** Calculated Bader charges of Hf, Y and H atoms in four stable phases. \( \delta \) represents the amount of charge transferred from Hf and Y atoms to H atom.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Space group</th>
<th>Atom</th>
<th>Charge value (e)</th>
<th>( \delta ) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 GPa</td>
<td>( Pmna ) -YHfH(_6)</td>
<td>Hf</td>
<td>2.79</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y</td>
<td>9.77</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>1.41</td>
<td>-0.41</td>
</tr>
<tr>
<td>200 GPa</td>
<td>( P4/ mmm ) -YHfH(_7)</td>
<td>Hf</td>
<td>2.75</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y</td>
<td>9.68</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>1.37</td>
<td>-0.37</td>
</tr>
<tr>
<td>300 GPa</td>
<td>( P4/ mmm ) -YHfH(_8)</td>
<td>Hf</td>
<td>2.74</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y</td>
<td>9.73</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>1.32</td>
<td>-0.32</td>
</tr>
<tr>
<td>400 GPa</td>
<td>( P-6m2 ) -YHfH(_{18})</td>
<td>Hf</td>
<td>2.74</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y</td>
<td>9.68</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>1.14</td>
<td>-0.14</td>
</tr>
</tbody>
</table>
Table 2. Calculated electron-phonon coupling parameters $\lambda$, electronic density of states at the Fermi level $N(E_f)$ (states/spin/Ry/Unit Cell), logarithmic average phonon frequency $\omega_{\text{log}}$ (K), and superconducting transition temperatures $T_c$ (K) of $\text{Pmna-}\text{YHfH}_6$ at 200 GPa, $\text{P}4/\text{mmm-}\text{YHfH}_7$ at 200 GPa, $\text{P}4/\text{mmm-}\text{YHfH}_8$ at 300 GPa and $\text{P}6m2-\text{YHfH}_{18}$ at 400 GPa.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Pressure</th>
<th>$\omega_{\text{log}}$</th>
<th>$N(E_f)$</th>
<th>$\lambda$</th>
<th>$T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pmna-}\text{YHfH}_6$</td>
<td>200 GPa</td>
<td>849.375</td>
<td>11.983</td>
<td>0.380</td>
<td>2.613</td>
</tr>
<tr>
<td>$\text{P}4/\text{mmm-}\text{YHfH}_7$</td>
<td>200 GPa</td>
<td>944.812</td>
<td>4.189</td>
<td>0.381</td>
<td>2.995</td>
</tr>
<tr>
<td>$\text{P}4/\text{mmm-}\text{YHfH}_8$</td>
<td>300 GPa</td>
<td>1116.317</td>
<td>5.233</td>
<td>0.760</td>
<td>46.668</td>
</tr>
<tr>
<td>$\text{P}6m2-\text{YHfH}_{18}$</td>
<td>400 GPa</td>
<td>1463.220</td>
<td>6.538</td>
<td>1.196</td>
<td>130.465</td>
</tr>
</tbody>
</table>

Figures

Figure 1
Convex hulls of Y–Hf–H system at (a) 200 GPa, (b) 300 GPa, and (c) 400 GPa. Red and blue dots represent stable and unstable structures, respectively.
Figure 2

Crystal structures of (a) *Pmna*-YHfH$_6$ at 200 GPa, (b) *P4/mmm*-YHfH$_7$ at 200 GPa, (c) *P4/mmm*-YHfH$_8$ at 300 GPa and (d) *P6m2*-YHfH$_{18}$ at 400 GPa. The blue, green and pink spheres represent Hf, Y and H atoms, respectively.
Electronic localization functions (ELF) of (a), (b) $\textit{Pmna}$-YHf$_6$ at 200 GPa, (c), (d) $\textit{P4/mmm}$-YHf$_7$ at 200 GPa, (e), (f) $\textit{P4/mmm}$-YHf$_8$ at 300 GPa and (h), (i) $\textit{P-6m2}$-YHf$_{18}$ at 400 GPa. The blue, green and pink spheres represent Hf, Y and H atoms, respectively.
Figure 4

Electronic band structures and density of states (DOS) of (a) $Pmna$-$YHfH_6$ at 200 GPa, (b) $P4/mmm$-$YHfH_7$ at 200 GPa, (c) $P4/mmm$-$YHfH_8$ at 300 GPa and (d) $P-6m2$-$YHfH_{18}$ at 400 GPa.
Figure 5

The phonon dispersion curves, the projected phonon density of states and Eliashberg spectral function $\alpha^2 F(\omega)$ together with the electron-phonon integral $\lambda(\omega)$ of (a) Pmna-YHfH$_6$ at 200 GPa, (b) P4/mmm-YHfH$_7$ at 200 GPa, (c) P4/mmm-YHfH$_8$ at 300 GPa and (d) P-6m2-YHfH$_{18}$ at 400 GPa.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SupplementaryInformation.pdf