Synthesis of molecular metallic barium superhydride: pseudocubic BaH\textsubscript{12}

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Following the discovery of high-temperature superconductivity in the La–H system, we studied the formation of new chemical compounds in the barium-hydrogen system at pressures from 75 to 173 GPa. Using in situ generation of hydrogen from NH\textsubscript{3}BH\textsubscript{3}, we synthesized previously unknown superhydride BaH\textsubscript{12} with a pseudocubic (fcc) Ba sublattice in four independent experiments. Density functional theory calculations indicate close agreement between the theoretical and experimental equations of state. In addition, we identified previously known P\textsubscript{6}/mmm-BaH\textsubscript{2} and possibly BaH\textsubscript{10} and BaH\textsubscript{6} as impurities in the samples. Ab initio calculations show that newly discovered semimetallic BaH\textsubscript{12} contains H\textsubscript{2} and H\textsubscript{3}– molecular units and detached H\textsubscript{12} chains which are formed as a result of a Peierls-type distortion of the cubic cage structure. Barium dodecahydride is a unique molecular hydride with metallic conductivity that demonstrates the superconducting transition around 20 K at 140 GPa.

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In recent years, the search for new hydride superconductors with $T_c$ close to room temperature attracts great attention of researchers in the field of high-pressure materials science. Variation of pressure opens prospects of synthesis of novel functional materials with unexpected properties. For example, according to theoretical models, compression of molecular hydrogen over 500 GPa should lead to the formation of an atomic metallic modification with $T_c$ near room temperature. Pressures of 420–480 GPa were achieved in experiments with toroidal diamond anvil cells; however, for conventional high-pressure cells with a four-electrode electric setup, pressures above 200 GPa remain challenging.

In 2004, Ashcroft suggested an alternative method of searching for high-$T_c$ superconductors that uses other elements, metals or nonmetals, to precompress the hydrogen atoms, which should lead to a dramatic decrease in the metallization pressure. A decade later this idea found its experimental proof. Extraordinarily high superconducting transition temperatures were demonstrated in compressed $Im3m$-H$_6$ (203 K at 150 GPa), $Im3m$-YH$_2$ and $P6_3/mmc$-YH$_3$, respectively, $Fm3n$-ThH$_2$ (161 K at 174 GPa), $P6_3/mmc$-CeH$_4$ ($-100$ K) and lanthanum decahydride $Fm3n$-LaH$_{10}$ ($250$ K at 175 GPa).

The neighbor of lanthanum, barium is a promising element for superhydride synthesis. The calculated maximum $T_c$ is only about 30–38 K for predicted $P4/mmm$-BaH$_4$ stable at 100 GPa, which has a hydrogen sublattice consisting of H$_2$ molecules and H$^-$ anions. Lower barium hydride, BaH$_2$, well-known for its extraordinarily anionic (H$^-$) conductivity, exists in $Pmna$ modification below 2.3 GPa, whereas above 2.3 GPa it undergoes a transition to hexagonal Ni$_2$In-type $P6_3/mmc$ phase. At pressures above 41 GPa, BaH$_2$ transforms into $P6_3/mmm$ modification, which metamorphizes at over 44 GPa, but its superconducting $T_c$ is close to zero. So far, no relevant experiments at pressures above 50 GPa have been reported.

In this work we experimentally and theoretically investigate the chemistry of the barium-hydrogen system at pressures from 75 to 173 GPa filling the gap of previous studies. We discover new pseudocubic BaH$_{12}$ that has molecular structure with H$_2$ and H$_2$–molecular units and detached H$_2$ chains formed due to Peierls-type distortion. These structural features lead to metallic conductivity of unique molecular hydride and to the superconducting transition around 20 K at 140 GPa.

### Results

**Synthesis at 160 GPa and Stability of BaH$_{12}$.** To investigate the formation of new chemical compounds in the Ba–H system at high pressures, we loaded four high-pressure diamond anvil cells (DACs #B0-B3) with sulfimated ammonia borane NH$_3$BH$_3$ (AB), used as both a source of hydrogen and a pressure transmitting medium. A tungsten foil with a thickness of about 20 μm was used as a gasket. Additional parameters of the high-pressure diamond anvil cells are given in Supplementary Table S1.

The first attempt of the experimental synthesis was made in DAC #B1 heated to 1700 K by an infrared laser pulse with a duration of ~0.5 s at a pressure of 160 GPa. During heating, the Ba particle underwent significant expansion and remained nontransparent. The obtained synchrotron X-ray diffraction pattern (XRD, $\lambda = 0.62$ Å, Fig. 1a) consists of a series of strong reflections specific to cubic crystals. Decreasing the pressure in DAC #B1 to 119 GPa (Fig. 1b) gave a series of diffraction patterns that can mostly be indexed by a slightly distorted face-centered cubic structure (e.g., pseudocubic $Cmc2_1$, Fig. 1a). Recently, similar cubic diffraction patterns have been observed at pressures above 150 GPa for the La–H ($fcc$-LaH$_{10}$) and Th–H ($fcc$-ThH$_{10}$) systems. By analogy with the La–H system, and considering the lack of previously predicted cubic superhydrides BaH$_2$, we used the USPEX code to perform theoretical crystal structure evolutionary searches, both variable- and fixed-composition, for stable Ba–H compounds at pressures of 100–200 GPa and temperatures of 0–2000 K.

According to the USPEX calculations, $P6_3/mmm$-BaH$_{12}$ remains stable up to 150–200 GPa (Fig. 1c, Supplementary Tables S7–S12, Supplementary Figs. S2 and S3). This compound was experimentally detected in DAC #B0 at 173–130 GPa with the cell volume $\sim$3% smaller than theoretically predicted (Supplementary Table S14). At 100–200 GPa, several new barium polyhydrides lying on or near the convex hulls were found: $BaH_6$, $BaH_{11}$ and $BaH_{12}$ with the unit cell $BaH_{38}$ and $BaH_{66}$ (Fig. 1c).

In subsequent experiments at 142 and 154–173 GPa we have detected a series of reflections that can be indexed by $BaH_6$ and $BaH_{10}$ with the unit cells close to the calculated ones (see Supporting Information, p. S25–S27). However, the main phase in almost all diffraction patterns is the pseudocubic barium superhydride which will be described below.

The analysis of the experimental data within space group $Fm3m$ (Fig. 1b and Supplementary Table S3) of Ba-sublattice and its comparison with density functional theory (DFT) calculations show that the stoichiometry of barium hydride synthesized in DAC #B1 is close to BaH$_{12}$. Examining the results of the fixed-composition search, we found that an ideal $Fm3m$-BaH$_{12}$ (similar to $fcc$-YB$_2$) is unstable and cannot exist, while pseudocubic $P2_1$-BaH$_{12}$, whose predicted distortion pattern is similar to the experimental one, lies on the convex hull at 100–150 GPa. There is also pseudocubic $P1$-Ba$_6$H$_{36}$, located very close to the convex hull at 150 GPa, and $Cmc2_1$-BaH$_{12}$ ($= BaH_{48}$) with a similar X-ray diffraction (XRD) pattern, lying a bit farther. Above 190 GPa the $P2_1$-BaH$_{12}$ transforms to other possible candidate, orthorhombic $Immm$-BaH$_{12}$, which stabilizes between 150 and 200 GPa, but does not correspond to the experimental XRD pattern (Fig. 1a, Supplementary Fig. S1) and is not considered further.

The computed equation of state of $Fm3m$-BaH$_{12}$ (Fig. 1d) corresponds well to the experimental volume-pressure dependence above 100 GPa. However, the DFT calculations show that the ideal $Fm3m$ barium sublattice is unstable (it is $\sim 0.19$ eV/atom above the convex hull, Supplementary Fig. S4) both thermodynamically and dynamically, and transforms spontaneously to $Cmc2_1$ or $P2_1$ via distortion (Fig. 2). Studying the temperature dependence of the Gibbs free energy (Fig. 2a), we found that $P2_1$-BaH$_{13}$ is the most stable modification at 0–2000 K and 100–150 GPa. Moreover, high-symmetry cubic phases cannot explain the weak reflections at 8.9–9.4°, 14.5, 16, 19.5, and 20.6° present in many XRD patterns (Fig. 1a, b).

To clarify the question of dynamical stability of pseudocubic structures, we calculated a series of phonon densities of states for different modifications of BaH$_{12}$ (Fig. 2b). Within the harmonic approach, symmetric and corresponding to the experimental data $Cmc2_1$-BaH$_{12}$ has a number of imaginary phonon modes. Its distortion to much more stable $P2_1$-BaH$_{12}$ leads to the disappearance of many of the imaginary phonon modes and deepening of the pseudogap (Fig. 2c) in the electronic density of states $N(E)$. The subsequent distortion of $P2_1$ to $P1$ converts BaH$_{12}$ to a semiconductor with a bandgap exceeding 0.5 eV. However, the experimental data show that BaH$_{12}$ remains opaque in the visible range, does not give Raman signals (Supplementary Figs. S39–S40), retains an almost fcc crystal structure, and exhibits metallic properties (see next sections) down to 75 GPa. For this reason, the electronic band structure and parameters of the superconducting state were further investigated only for $Cmc2_1$-BaH$_{12}$, which does not have a bandgap at 100–150 GPa. Stability...
of all considered polymorphic modifications of BaH$_{12}$ at different pressures with respect to other Ba-H phases and with respect to each other are shown in Supplementary Figs. S4 and S5 (see Supporting Information).

The comparative analysis of Cmc$_2$, P$_{21}$, and P$_1$ structures of BaH$_{12}$ shows that semimetallic Cmc$_2$ explains well the experimental results of X-ray diffraction (see Supplementary Fig. S1, Supporting Information) and lies closer to the convex hull than Fm3m or I4/mmm modifications. P$_1$-BaH$_{12}$ shows a complex picture of splitting of the diffraction signals, both P$_1$-BaH$_{12}$ and P$_{21}$-BaH$_{12}$ have a bandgap above 0.5 eV at 100 GPa (Supplementary Fig. S38b) which does not correspond to the experimental data. Therefore, pseudocubic Cmc$_2$-BaH$_{12}$, whose cell volume is near that of the close-packed Fm3m-BaH$_{12}$, is the appropriate explanation of the experimental results despite the presence of a few imaginary phonon modes.

The molecular dynamics simulation of Cmc$_2$-BaH$_{12}$ and P$_{21}$-BaH$_{12}$ at 10–1500 K, after averaging the coordinates, both lead to a distorted pseudocubic P$_1$-BaH$_{12}$ with the similar XRD pattern. However, all structures retrieved by molecular dynamics are less stable both dynamically and thermodynamically than P1-BaH$_{12}$, P$_{21}$-BaH$_{12}$, and Cmc$_2$-BaH$_{12}$ found by USPEX. More accurate analysis accounting for the anharmonic nature of hydrogen oscillations$^{27}$, which is actually beyond the scope of this work, may help to explain the experimental stability of higher-symmetry BaH$_{12}$ modifications compared to lower-symmetry P1-BaH$_{12}$.

Synthesis of BaH$_{12}$ at 146 GPa. Similar X-ray diffraction patterns were obtained in the next experiment (DAC #B2) where the Ba sample was heated at an initial pressure of 146 GPa, which led to a decrease in pressure to 140 GPa. During the heating and subsequent unloading of the cell, the sample remained opaque down to ~40 GPa. Unlike the synthesis at high pressure (cell #B1, 160 GPa, Fig. 1a, b), in this experiment we observed many more side phases and corresponding side reflections than before (Fig. 3 and Supporting Information).
Similar to the experiment with DAC #B1, five reflections from the pseudocubic Ba sublattice dominate in a wide range of pressures (65–140 GPa), whereas side reflections change their intensities and, at some pressures, almost disappear (Fig. 3d and Supplementary Figs. S33 and S35). The diffraction circles corresponding to the ideal cubic barium sublattice have pronounced granularity (Fig. 3e), corresponding to the ideal cubic barium sublattice have pronounced granularity (Fig. 3e), which suggests that all "cubic" reflections belong to the same phase.

At pressures below 65 GPa, it is no longer possible to refine the cell parameters of pseudocubic BaH12. The parameters of the $Cmc_{21}, BaH_{12}$ unit cell, refined to the experimental data, are presented in Supplementary Table S6. Fitting this pressure-volume data in the pressure range from 75 to 173 GPa by the third-order Birch–Murnaghan equation of state28 gives the cell volume $V_{100} = 45.47 \pm 0.13 \, \text{Å}^3$, bulk modulus $K_{100} = 305 \pm 8.5 \, \text{GPa}$, and its derivative with respect to pressure $K'_{100} = 3.8 \pm 0.48$ (the index 100 designates values at 100 GPa). Fitting the theoretical data yields similar values: $V_{100} = 46.0 \, \text{Å}^3$, $K_{100} = 315.9 \, \text{GPa}$, and $K'_{100} = 2.94$.

**Synthesis of BaH12 at 90 GPa.** In the experiment with DAC #B3, we investigated the possibility to synthesize BaH12 at pressures below 100 GPa. After the laser heating of Ba/AB to 1600 K, the pressure in the cell decreased from 90 to 84 GPa. The observed diffraction pattern is generally similar to those in the previous experiments with DAC #B1, except the presence of the impurity, h-BaH$_{12}$, whose reflections may be indexed by hexagonal space groups $P6_3/mmc$ or $P6_3/mc$ ($a = 3.955(7) \, \text{Å}, c = 7.650(7) \, \text{Å}, V = 51.84 \, \text{Å}^3$ at 78 GPa). For the main set of reflections, slightly distorted cubic BaH12 is the best solution (Fig. 4). The refined cell parameters of BaH12 (Supplementary Table S4) agree well with the results obtained previously with DACs #B1 and B2. When the pressure was reduced to 78 GPa, barium dodecahydride began to decompose, and subsequent diffraction patterns (e.g., at 68 GPa, see Supporting Information) show a complex image of broad reflections that confirms the lower experimental bound of ~75 GPa mentioned above.

**Discussion**

**Electronic properties of BaH12.** BaH12 is the first known metal hydride with such a high hydrogen content that is stable at such low pressures (~75 GPa). We further investigated its electronic structure and the charge state of the hydrogen and barium atoms. The electron localization function (ELF) analysis29 (Fig. 4e–g) shows that hydrogen in BaH12, similar to NaH30, is present in the form of H$_2$ ($d_{H-H} = 0.78 \, \text{Å}$) and almost linear H$_3$ ($d_{H-H} = 0.81$ and 1.07 Å) molecular fragments that form separate flat horseshoe-like H$_2$ chains ($d_{H-H} = 1.27 \, \text{Å}$, Fig. 4).

Bader charge analysis of $Cmc_{21}, BaH_{12}$, performed in accordance with our previous experience31,32 (Supplementary Table S18), shows that the Ba atoms serve as a source of electrons for the hydrogen sublattice. The charge of the barium atoms in BaH12 is +1.15 at 150 GPa, whereas most of the hydrogen atoms have a negative charge. In the H$_3$ fragments, the charge of the end atoms is close to −0.2 and −0.27, whereas the charge of the bridge has a small positive charge of +0.06 (Fig. 4–g). In general, the H$_3^−$ anion, similar to one found in the structure of NaH$_3$, has a total charge of −0.4 $| e |$, whereas molecular fragments H$_2$ ($d_{H-H} = 0.78 \, \text{Å}$) have a charge of only −0.1 $| e |$. Therefore, the Ba–H bonds in BaH$_{12}$ have substantial ionic character, whereas the H–H bonds are mainly covalent.

The low electronic density of states $N(E_F)$ in semimetallic $Cmc_{21}, BaH_{12}$ looks typical for one-dimensional $\ldots H–H–H\ldots$ chains (Fig. 4h, Supplementary Figs. S36 and S38) which are divided into H$_2$, H$_3$ fragments due to the Peierls-type distortion33. In fact, all of the discussed structures of BaH$_{12}$ can be viewed as a result of Peierls-type distortion. The main contribution to $N(E_F)$, 83% at 150 GPa, comes from hydrogen (Fig. 4h), and ¼ of this contribution is related to s orbitals. At 150 GPa, barium in BaH$_{12}$ exhibits the properties of a d-block element, and its bonding orbitals have a significant d-character (Fig. 4i). Electrical conductivity is localized in the H layers consisting of quasi-one-dimensional $\ldots H–H–H\ldots$ chains which are interconnected in non-trivial way (Fig. 4e–g, Supplementary Table S2 for crystal structure). Thus, barium dodecahydride is the first known molecular superhydride with metallic conductivity embedded in layers and one-dimensional chains of molecular hydrogen.
Superconductivity of BaH$_{12}$. On the basis of powder diffraction experiments and thermodynamic calculations alone, we cannot unambiguously determine the structure of the H sublattice in BaH$_{12}$, which is essential for understanding superconductivity. To clarify this, we measured the electrical resistance $R$ of barium hydride samples using the well-known four-probe technique in the temperature range of 2–300 K. At pressures of 90–140 GPa, all five BaH$_{12}$ samples (DACs E#1-5, see Supporting Information) synthesized in electric DACs behave as typical metals with an almost linear decrease of $R(T)$. At low temperatures the resistance of the samples drops sharply, indicating a possible superconducting transition at about 5–7 K below 130 GPa (Supplementary Fig. S41), and ~20 K at 140 GPa (cell #E5, Fig. 5a). This DAC #E5 was assembled with an 80 μm diamond anvil culet, c-BN/epoxy insulating gasket, 45 × 32 μm Ba piece, and sputtered 0.5 μm thick Mo electrodes. After the laser heating at 1600 K and 140 GPa, the Ba/AB sample demonstrated the superconducting transition at around 20 K (Fig. 5a). When we tried to change the pressure, the cell collapsed and pressure dropped to 65 GPa. The obtained data together with the measured Raman spectra and optical microscopy exclude low-symmetry BaH$_{12}$ semiconducting structures, leaving for consideration only metallic and semimetallic modifications (Supplementary Figs. S39 and S40).

The harmonic DFT calculations (Fig. 5b) demonstrate that the low density of electronic states near the Fermi level in Cmc2$_1$-BaH$_{12}$ is associated with a weak electron-phonon coupling, mostly related to low-frequency Ba and H phonon modes (1–10 THz), resulting in relatively low $\lambda = 1.02$, $\omega_{\text{ph}} = 677$ K, $T_C = 39–53$ K, and $\mu_eH_C(0) = 5.1–7$ T at 150 GPa ($\mu^* = 0.15–0.1$). Decreasing pressure leads to a decrease of $\lambda$ and $T_C$ (from 53 to 46 K) at 140 GPa with a slope $dT_C/dP = 0.7$ K/GPa.

One of the roles of metal atoms in superhydrides is to donate electrons to antibonding orbitals of the H$_2$ molecules and weaken the H–H bonds. In BaH$_{12}$, each H atom accepts few electrons, on average 0.16 electrons. As a result, H$_2$ and H$_3$ groups are still present in the structure, and we have a rather low $T_C$. We think that at high pressures, due to dissociation of molecular groups, BaH$_{12}$ may have a network of weak H–H bonds (rather than discrete H$_2$ and H$_3$-groups) and, as a result, a much higher $T_C$. Increasing the pressure will also facilitate further metallization of BaH$_{12}$ and symmetrization of the hydrogen sublattice, increasing $N(E_F)$. To estimate the possible improvement, we calculated at...
120–135 GPa the superconducting parameters of $I_{4}$/mmm-$BaH_{12}$ and $Fm\bar{3}m$-$BaH_{12}$, isostructural to $YB_{12}$, the structures that were considered as possible solutions at the first step of the XRD interpretation. The calculations show that filling of the pseudogap in $N(E)$ makes it possible to reach $T_{C} \sim 200$ K with $\lambda \gtrsim 3$ in these compounds (Supplementary Figs. S42 and S43).

In conclusion, studying the high-pressure chemistry of the $Ba$–$H$ system in four independent DACs we successfully...
synthesized novel barium superhydride BaH$_{12}$ with a pseudocubic crystal structure, stabilized in the pressure range of 75–173 GPa. The compound was obtained by laser-heating metallic barium with an excess of ammonia borane compressed to 173, 160, 146, and 90 GPa. The Ba sublattice structure of BaH$_{12}$ was resolved using the synchrotron XRD, evolutionary structure prediction, and several postprocessing Python scripts, including an XRD matching algorithm. Discovered BaH$_{12}$ has unique metallic conductivity, localized in the layers of molecular hydrogen, and the highest hydrogen content (>92 mol%) among all metal hydrides synthesized so far. The experimentally established lower limit of stability of barium dodecahydride is 75 GPa. The third-order Birch–Murnaghan equation of state and unit cell parameters of BaH$_{12}$ were found in the pressure range of 75–173 GPa: \( V_{100} = 45.47 \pm 0.13 \, \text{Å}^3 \), \( K_{100} = 305 \pm 8.5 \, \text{GPa} \), and \( K''_{100} = 3.8 \pm 0.48 \). The ab initio calculations confirm a small distortion of the ideal fcc-barium sublattice to space group \( \text{Cm}2\text{c} \), or \( \text{P}2_1 \text{C} \), determined by the presence of additional weak reflections in the diffraction patterns. The impurity phase analysis indicates possible presence of BaH$_6$ and BaH$_{10}$. According to the theoretical calculations and experimental measurements, BaH$_{12}$ exhibits metallic and superconducting properties, with \( T_c = 20 \, \text{K} \) at 140 GPa, and its crystal structure contains H$_2$ and H$_3$ groups. The results of these experiments confirm that the comparative stability of superhydrides increases with the increase of the period number of a hydrogen–metal system using the USPEX code, for pressures of 50, 100, 150, 200, and 300 GPa, with a variable-composition evolutionary search from 0 to 24 atoms of each type (Ba, H). The first generation of the search (120 structures) was created using a random symmetric generator, all subsequent generations (100 structures) contained 20% of random structures and 80% of those created using the heredity, soft mutation, and transmutation operators. The results contain the files extended_convex_hull and extended_convex_hull_POSCAR, which were postprocessed using the Python scripts change_pressure.py, split_CIFs.py, and xr_screening.py (see Scripts for XRDP1 Postprocessing with USPEX section). The postprocessing script change_pressure.py performs an isotropic deformation of the unit cell of structures predicted by USPEX, bringing them to approximately the experimental pressure. All three lattice constants of the structures are multiplied by a factor \( k \), calculated under the assumption of validity of the Birch–Murnaghan equation of state\(^{28} \) with the bulk modulus \( k_0 = 300 \, \text{GPa} \) and its first derivative \( k'' = 3 \). This approach is a quick alternative to the script that uses a crude DFT reoptimization of a set of theoretically possible structures, bringing them to the experimental pressure. The script split_CIFs.py converts the set of POSCARs recorded in the extended_convex_hull_POSCAR files into a set of CIF files, simultaneously symmetrizing the unit cells and sorting the files by ascending (the distance from the convex hull). The CIF files created in such a way can be directly analyzed using Dioptas\(^{37} \) and JANA2006\(^{38} \) and other software. Finally, the script xr_screening.py automatically searches for the structures found by USPEX.
and translated to the experimental pressure that exhibit a high similarity between the experimental and predicted XRD patterns (the latter are obtained using pymatgen: Python library). The analysis of complex mixtures consisted of two steps: first, we searched for the main component having the most intense reflections, then the already explained reflections were excluded to analyze the side phases.

To calculate the equations of state (EoS) of BaH$_2$, we performed structure relaxations of phases at various pressures using the density functional theory (DFT) functional within the generalized gradient approximation (Perdew–Burke–Ernzerhof functional) and the projector augmented wave method as implemented in the VASP code. The plane wave kinetic energy cutoff was set to 1000 eV, and the Brillouin zone was sampled using the 1-centered k-points meshes with a resolution of 2π/0.05 Å$^{-1}$. The obtained dependences of the unit cell volume on the pressure were fitted by the Birch–Murnaghan equation to determine the main parameters of the EoS—the equilibrium volume $V_0$, bulk modulus $K_0$, and its derivative with respect to pressure $K'$. Using EOSfit software. We also calculated the phonon densities of states for the studied materials using the finite displacement method (VASP and PHONOPY).

The calculations of the phonons, electron-phonon coupling, and superconducting T$_c$ were carried out with QUANTUM ESPRESSO (QE) package using the density functional perturbation theory, employing the plane-wave generalized gradient approximation with Perdew–Burke–Ernzerhof functional. In our ab initio calculations of the electron-phonon coupling (EPC) parameter of Ba$_2$C$_2$–Ba$_2$H$_4$, the first Brillouin zone was sampled by $2 \times 2 \times 2$ q-point mesh and $4 \times 4 \times 4$ or $8 \times 8 \times 8$ k-points meshes with the smearing $\sigma = 0.005–0.05$ Ry that approximates the zero-width limits in the calculation of $\lambda$. The critical temperature $T_c$ was calculated using the Allen–Dynes equations. Badly charged states were calculated using Criti57–58 software with the atomic partition generated using the YT$^59$ method. The electron localization function (ELF) of BaH$_2$ and iso surfaces are shown for an isovalue of 0.12. The lattice planes (100) and (111) are shown at distances from the origin of 0 and 2.289 Å, respectively. We projected the ELF on these planes to show H$_2$ and H$_2$ bonding. The charge structure of BaH$_2$ was analyzed using the ab initio molecular dynamics (AIMD) simulations within the general gradient approximation and using the augmented plane wave method implemented in VASP software. The total number of atoms in the model was 52, including 48 hydrogen atoms and 4 barium atoms. The positions of the barium atoms were fixed during the simulation. The energy cutoff was set to 400 eV. The behavior of the hydrogen atoms in the BaH$_2$ crystal structure was studied upon annealing from 1500 to 10 K using the Nosé–Hoover thermostat. The total simulation time was 10 ps with the time step of 1 fs.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files.

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References

1. Oganov, A. R., Pickard, C. J., Zhu, Q. & Needs, R. J. Structure prediction drives materials discovery. Nat. Rev. Mater. 4, 331–348 (2019).
2. Wigner, E. & Huntington, H. B. On the possibility of a metallic modification of germanium. J. Chem. Phys. 3, 764–770 (1935).
3. McMahon, J. M., Morales, M. A., Pierleoni, C. & Ceperley, D. M. The hydrogen bonding structure of Ba$_2$H$_2$: analysis using the ab initio molecular dynamics (AIMD) simulations within the general gradient approximation and using the augmented plane wave method implemented in VASP software. The total number of atoms in the model was 52, including 48 hydrogen atoms and 4 barium atoms. The positions of the barium atoms were fixed during the simulation. The energy cutoff was set to 400 eV. The behavior of the hydrogen atoms in the BaH$_2$ crystal structure was studied upon annealing from 1500 to 10 K using the Nosé–Hoover thermostat. The total simulation time was 10 ps with the time step of 1 fs.
4. Azadi, S., Monserrat, B., Foulkes, W. M. C. & Needs, R. J. Dissociation of high-pressure hydrogen and helium under extreme conditions. Nat. Rev. Mater. 3, 1653 (2018).
5. McMinis, J., Clay, R. C., Lee, D. & Morales, M. A. Molecular to atomic phase transition in hydrogen under high pressure. Phys. Rev. Lett. 114, 105305 (2015).
6. Eremets, M. I., Drozdov, A. P., Kong, P. P. & Wang, H. Semimetallic molecular hydrogen at pressure above 350 GPa. Nat. Phys. 15, 1264–1269 (2019).
7. Ashcroft, N. W. Hydrogen dominant metallic alloys: high temperature superconductors? Phys. Rev. Lett. 92, 187002 (2004).
8. Duan, D. et al. Pressure-induced metallization of dense (H$_2$Si)$_2$H$_4$ with high-Tc superconductivity. Sci. Rep. 4, 6966 (2014).
9. Drozdov, A. P., Eremets, M. I., Troyan, I. A., Ksenofontov, V. & Shlyin, S. I. Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system. Nature 525, 73–76 (2015).
10. Troyan, I. et al. Observation of superconductivity in hydrogen sulfide from nuclear resonant scattering. Science 351, 1303–1306 (2016).
44. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).

45. Blochl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).

46. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999).

47. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).

48. Andrade, N. & Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558–561 (1993).

49. Andrade, N. & Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal amorphous-semiconductor transition in germanium. Phys. Rev. B 49, 14251–14269 (1994).

50. Angel, R. J., Alvaro, M. & Gonzalez-Platas, J. EosFit7c and a Fortran module (library) for equation of state calculations. Z. Für. Krist. - Cryst. Mater. 229, 405–419 (2014).

51. Togo, A. & Tanaka, I. First principles phonon calculations in materials science. Scr. Mater. 108, 1–5 (2015).

52. Togo, A., Oba, F. & Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaC2-type SO2 at high pressures. Phys. Rev. B 78, 134106 (2008).

53. Giannozzi, P. et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys. Condens. Matter 21, 395502 (2009).

54. Giannozzi, P. et al. Advanced capabilities for materials modelling with quantum ESPRESSO. J. Phys. Condens. Matter 29, 465901 (2017).

55. Baroni, S., de Gironcoli, S., Dal Corso, A. & Giannozzi, P. Phonons and related crystal properties from density-functional perturbation theory. Rev. Mod. Phys. 73, 515–562 (2001).

56. Allen, P. B. & Dynes, R. C. Transition temperature of strong-coupled superconductors reanalyzed. Phys. Rev. B 12, 905–922 (1975).

57. Otero-de-la-Roza, A. & Zunger, A. M. & Luana, V. Cric: a new program for the topological analysis of solid-state electron densities. Comput. Phys. Commun. 180, 157–166 (2009).

58. Otero-de-la-Roza, A., Johnson, E. R. & Luana, V. Cric2: A program for real-space analysis of quantum chemical interactions in solids. Comput. Phys. Commun. 185, 1007–1018 (2014).

59. Yu, M. & Trinkle, D. R. Accurate and efficient algorithm for Bader charge integration. J. Chem. Phys. 134, 064111 (2011).

60. Nosé, S. A unified formulation of the constant temperature molecular dynamics methods. J. Chem. Phys. 81, 511–519 (1984).

61. Hoover, W. G. Canonical dynamics: equilibrium phase-space distributions. Phys. Rev. A 31, 1695–1697 (1985).

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Author contributions

X.H., W.C., D.V.S., A.G.K., A.R.O. and T.C. conceived this project. W.C., D.V.S., X.H. performed the experiment, D.V.S., A.G.K., I.A.K., H.S., D.D., A.R.O., M.G. and T.C. prepared the theoretical calculations and analysis. W.C., X.H., A.F.G. and V.B.P. performed X-ray measurements of synthesized samples. W.C., D.V.S., A.G.K., A.R.O., X.H. and T.C. wrote and revised the paper. All the authors discussed the results and offered useful inputs.

Competing interests

The authors declare no competing interests.

Additional information

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