Sr-Doped Hydrogen Glass: Synthesis and Properties of SrH22

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Recently, several research groups announced reaching the point of metallization of hydrogen above 400 GPa. Despite a notable progress, detecting superconductivity in compressed hydrogen remains an unsolved problem. Following the mainstream of extensive investigations of compressed metal polyhydrides, here we demonstrate that small doping by strontium leads to a dramatic reduction in the metallization pressure of molecular hydrogen to about 200 GPa. Studying the high-pressure chemistry of the Sr–H system, we observed the formation of several new phases: C2/m-Sr₃H₁₃, pseudocubic SrH₆, SrH₉ with cubic $F\overline{4}3m$ Sr sublattice, and pseudo tetragonal P1-SrH₂₂, the metal hydride with the highest hydrogen content (96 at. %) discovered so far. High diffusion coefficients of hydrogen in the latter phase

 $D_{\rm H} = 0.2-2.1 \times 10^{-9} \text{ m}^2/\text{s}$ indicate an amorphous state of the H-sublattice, whereas the strontium sublattice remains solid. Unlike Ca and Y, strontium forms molecular semiconducting polyhydrides, whereas calcium and yttrium polyhydrides are high- $T_{\rm C}$ superconductors with an atomic H sublattice. Discovered SrH₂₂, a kind of hydrogen sponge, opens a new class of materials with ultra-high content of hydrogen.

Reaching the metallic state of pure molecular hydrogen by compression is one of the most spectacular challenges in high-pressure physics and chemistry. Studies of hydrogen metallization¹⁻³ have been in the focus since the 1990s, with the experimental metallization limit moving step by step from 150 GPa⁴ to 430–500 GPa.^{1,5} A consistent increase in pressure leads to a series of phase transitions in solid hydrogen (phases I–V^{1,5}), gradual quenching of the Raman signals, and darkening of the sample down to a complete loss of transparency. Despite a significant progress in achieving ultrahigh pressures in the last five years, detecting superconductivity of metallic hydrogen remains an unsolved problem. Studies of the electrical conductivity at pressures above 400 GPa remain very challenging.

In 2004, N. Ashcroft suggested that the precompression effects from chemical bonding to other atoms may help to convert hydrogen to a metallic state. Fifteen years later, this idea was confirmed in the synthesis of many metallic and superconducting hydrides such as H_3S ,^{6,7} La H_{10} ,^{8,9} YH₆^{10,11} and YH₉,^{11,12} ThH₁₀,¹³ CeH₉,¹⁴ PrH₉,¹⁵ NdH₉,¹⁶ and so forth. It is believed now that the superconducting properties of these compounds are due to the presence of a sublattice of metallic hydrogen, which is formed in pure hydrogen only at pressures of 500–700 GPa.

There must be an intermediate link between these two forms of hydrogen, metallic and superconducting, and a molecular dielectric or semiconducting phase. Moreover, this "bridge", a molecular metal, has been found. In 2015–2017, it has been shown that lithium and sodium form molecular nonconducting hydrides LiH_6^{17} and NaH_7 .¹⁸ Continuing these studies, we have recently synthesized a unique barium superhydride BaH_{12}^{19} which is a molecular metal and a superconductor at moderate pressures of about 120–140 GPa. Pure hydrogen should demonstrate such properties at pressures above 350 GPa during the transition between the semiconducting and metallic modifications due to band overlap. Looking from a different perspective, BaH_{12} is almost pure hydrogen doped by ~8 atom % of barium ($Ba_{0.08}H_{0.92}$). This kind of electron doping brings metallization closer and allows us (at very moderate pressures) to see what happens with pure hydrogen at more extreme conditions.

In this work, we investigated chemical reactions of strontium and strontium dihydride with hydrogen at high pressures (up to 181 GPa) and temperatures. In addition to a series of new molecular polyhydrides with compositions Sr₃H₁₃, SrH₆, and SrH_{~9}, we discovered an amazing compound with a tetragonal strontium sublattice and the chemical formula SrH₂₂, which is hydrogen doped by 4 atom % of Sr. It is a yellow-colored semiconductor at 140 GPa. Together with BaH₁₂, this novel polyhydride, a successful model of hydrogen

metallization via doping, does not require multi-megabar pressures and can be studied using a wide range of physical methods.

Results and discussions

At the first stage of the research, we reexamined the Sr–H system at pressures of 50–200 GPa using the USPEX code.²⁰⁻²² From the chemical point of view, strontium has many of the characteristics of barium, which, as has been shown in our recent work,¹⁹ reacts with hydrogen to form dodecahydride BaH₁₂. One of the goals of this research was to study the possibility of formation of similar strontium polyhydrides with the composition SrH₁₂ or higher.

An evolutionary search using USPEX for thermodynamically stable phases in the Sr – H system (Figure S4, Supporting Information Figures S1–S2) shows that this system is very rich in various compounds. At 150 GPa and 0 K (Figure 1f), there are several strontium hydrides on the convex hull: well-known *P6/mmm*-SrH₂; pseudocubic *P*1-SrH₆ (or Sr₈H₄₈) similar to recently discovered Eu₈H₄₆²³ and Ba₈H₄₆;²⁴ and superhydrides *C2/m*-SrH₁₀ and *P*1-SrH₁₇. At 100 GPa (Figure 1c), lower hydrides *Cmmm*-SrH and *Cmcm*-SrH₄ are stable, as well as Sr₈H₄₈ and superhydride *P*1-SrH₂₂, whose structure is described below. Surprisingly, even at low pressures, there is wide variety of stable or slightly metastable (<30 meV from the convex hull) higher strontium polyhydrides, in agreement with previous studies ²⁵ (Supporting Information Figure S1). This indicates a high probability of discovering new compounds in the strontium–hydrogen system even at low pressures.

We first experimentally investigated chemical reactions of strontium with hydrogen at pressures above 1 Mbar. The analysis of the X-ray diffraction patterns (Figure 1a,b) shows that a mixture of two strontium hydrides is formed after the laser heating of Sr with ammonia borane in DAC Sr2 at 146 GPa, with a predominance of the phase having the *bct* tetragonal

set of reflections (Figure 1a) and a very large unit cell volume. The comparison with USPEX calculations shows that the main phase can be immediately ascribed to pseudotetragonal P1-SrH₂₂ with a unit cell volume of ~65.1 Å³/Sr at 100 GPa. At this pressure, the H sublattice of P1-SrH₂₂ consists of H₂ molecules and H⁻ anions, and the minimum H–H bond length is d(H-H) = 0.76 Å. The best candidate for the second phase, monoclinic C2/m-Sr₃H₁₃, with a unit cell volume of 25.26 Å³/Sr at 100 GPa, was found 60 meV above the convex hull. For both phases, the predicted diffraction patterns, equation of state, and pressure dependence of the unit cell parameters are in very close agreement with the experimental data (Figure 1d,e). A similar situation was observed in DAC Sr1 loaded with SrH₂/AB, where an XRD pattern characteristic for SrH₂₂ was detected at 138 GPa with a minimum amount of impurities (Supporting Information Figure S25). For this reason, DAC Sr1 was used for subsequent optical and Raman measurements.

Molecular polyhydrides are not something entirely new in the chemistry of hydrogen. In 2009, the formation of other molecular van der Waals polyhydride Xe(H₂)₇₋₈ was confirmed using single-crystal X-ray diffraction as well as IR and Raman spectroscopy in a Xe–H₂ mixture at about 5 GPa.²⁶ This discovery had been followed by an investigation of (HI)(H₂)₁₃ obtained as a small impurity in HI(H₂) after laser heating of the H₂ + I₂ mixture above 25 GPa.²⁷ A significant difference of strontium hydrides from xenon and iodine (HI) polydydrides is a strong charge transfer and polarization of the Sr–H bonds. Indeed, Bader charge analysis performed in accordance with our previous experience^{28,29} (Supporting Information Table S9) shows that the Sr atoms are a source of electrons for hydrogen. The charge of the strontium atoms in SrH₂₂ is +1.23|*e*| at 120 GPa, whereas most of the H₂ molecules have a small negative charge (~ -0.1|e|). About 10% of the H atoms are solitary anions H⁻ with a charge of -0.32|e| (Inset in Figure 1d, blue circles). Further theoretical study shows that anharmonic effects stabilize the structure of SrH₂₂ at 100 GPa (Supporting

Information Figures S13). Calculations of the band structure point to a pronounced bandgap of 1.5–1.9 eV in this material at 120 GPa. Increasing pressure above 200 GPa leads to metallization of the molecular H sublattice and emergence of superconductivity with $T_{\rm C}$ about 21 K ($\mu^* = 0.1$, Supporting Information Figure S14).

Optical properties of *P*1-SrH₂₂ were studied in DAC Sr1 at 100–135 GPa. In transmitted light, this superhydride has a yellow or orange color at 100 GPa with the maximum transmission of ~630 nm wavelength. Increasing the pressure to 131 GPa leads to a significant darkening of the sample that corresponds to the gradual closure of the bandgap (Supporting Information Figures S34). The Raman spectra, measured using a 532 nm excitation laser, have the main peak at 4140 cm⁻¹ (123 GPa) whose pressure dependence v(*P*) is very similar to the behavior of the molecular hydrogen vibron, and the intensity of this peak decreases with increasing pressure. The one-phonon resonant Raman calculations for *P*1-SrH₂₂ at 120 GPa (Supporting Information Figures S29) give the main signal at about 4154 cm⁻¹, in close agreement with experiment, whereas the nonresonant calculations predict several signals < 4100 cm⁻¹ which are not observed experimentally. Careful calculations show that all these Raman peaks have practically zero intensity.

Another strontium hydride, metastable Sr₃H₁₃, crystallizes in the monoclinic space group C2/m. A unique property of this compound is the presence of zigzag H₅ molecules with almost constant distance d(H-H) = 0.9-1.0 Å. Calculations of the band structure indicate that this material exhibits metallic properties and should have a superconducting transition temperature $T_{\rm C} \sim 84$ K at 150 GPa ($\mu^* = 0.1$, Supporting Information Figure S9). A decrease in pressure in DAC Sr2 from 146 to 70 GPa demonstrates that monoclinic Sr₃H₁₃ remains stable in this pressure range, whereas SrH₂₂ superhydride decomposes below 100 GPa. At the next stage of the study, we reduced the pressure of synthesis and examined DAC Sr3 with 100 µm culet, loaded with ammonia borane (AB), gold foil (Au) and a strontium

particle. Golden film was placed between AB and Sr to isolate them from each other and prevent the formation of Sr(AB)₂. The sample was heated by a 1 µm IR fiber laser from the AB side at 123 GPa. After decompression to 48 GPa, the sample became transparent and demonstrated the Raman peaks at around 3635 and 735 cm⁻¹ (Supporting Information Figure S27).

The observed X-ray diffraction pattern (Figure 2a,b) with main reflections (200), (210), and (211) corresponds to the $Pm\bar{3}n$ structure found earlier in the studies of europium (Eu₈H₄₆²³) and barium (Ba₈H₄₆²⁴) polyhydrides. However, both the harmonic and anharmonic calculations show dynamical instability at 300 K of structurally similar cubic strontium hydride Sr₈H₄₆, which distorts to $R\bar{3}c$ having a significantly different XRD pattern. For this reason, we performed an additional structural search for stable compounds with fixed Sr:H compositions of 2:12 and 8:48. As a result, we found thermodynamically and dynamically stable (Figure 1c,f) pseudocubic P1-Sr₈H₄₈, denoted as P1-SrH₆, whose Sr sublattice differs from that of $Pm\bar{3}n$ -Sr₈H₄₆ by only a slight distortion and has an almost identical XRD spectrum. Slightly larger calculated cell volume of ~0.5 Å³ (Figure 2c) can be explained by inaccuracy of the DFT methods or nonstoichiometric composition of the hydride (e.g., Sr₈H₄₇). The experiment shows that the obtained $Pm\bar{3}n$ -like phase is stable to at least 74 GPa. In addition to Sr₈H₄₈, this sample probably also contains an admixture of the previously described C2/m-Sr₃H₁₃.

At 100 GPa, Sr₈H₄₈ crystallizes in the triclinic space group *P*1. The Sr–H bond length is 2.04–2.31 Å, the minimum H–H bond length is 0.84–0.87 Å. According to theoretical calculations, *P*1-SrH₆ is a narrow-bandgap semiconductor (Supporting Information Figures S16–S17) whose bandgap increases as pressure lowers. This may explain the fact that at pressures near or above 100 GPa the sample is opaque, whereas transparent regions and several Raman signals appear when pressure decreases (Supporting Information Figure S27).

To study conductivity in P1-SrH₆, we made an electrical DAC E1 described further in the article.

The same pseudocubic P1-SrH₆ with a $Pm\bar{3}n$ -like Sr sublattice was obtained in the experiment in high-pressure DAC Sr165 with a 50 µm culet, in which the loaded Sr/AB sample ($d \sim 15 \,\mu\text{m}$) was heated by a laser to 1500–1800 K at 165 GPa. At this pressure, the synthesized compound is almost opaque, whereas below 56 GPa the sample became translucent (Supporting Information Figure S32). During the subsequent decompression from 181 to 56 GPa, a series of low-intensity XRD patterns was obtained (Figure 2e). The analysis of the XRD patterns points to pseudocubic P1-SrH₆ as the main component. The obtained hydride has a surprisingly high stability: the character of the XRD pattern does not change down to 56 GPa, in agreement with ab initio thermodynamic calculations (Supporting Information Figures S1–S2). In principle, this suggests that polyhydrides can maintain their structure during decompression, as has been recently shown for FeSe.³⁰ Electrical measurements for strontium hydrides are hindered by their low conductivity. The active resistance of samples at low frequencies is about several M Ω ; however, the use of high-frequency current up to 1 MHz makes it possible to obtain high-quality impedance patterns. We studied in detail the electrical DAC E1 with a pseudo-four-contact van der Pauw circuit, loaded with Sr/AB and heated at 126 GPa. According to the XRD study, the opaque sample consists of $Pm\bar{3}n$ -like pseudocubic P1-SrH₆ (Supporting Information Figure S26). Before the experiment, we checked that an impedance of the circuit is equal for any combination of contacts (Figure 3a). On a typical hodograph for the SrH₆ sample, there is a clear first semicircle, the radius of which has a pronounced dependence on the temperature and pressure (Figure 3b,d,e). In some cases, especially at high temperatures and pressures, a part of the second semicircle or, to be correct, half-ellipse, is visible, which continues with an

oblique low-frequency tail. The dimensions of the second half-ellipse also significantly decrease as the temperature and pressure rise.

To interpret the obtained experimental data, we used a simplified L(C, R)(CPE, R) scheme of five elements, where L reflects the inductance of the lead wires, (C, R) corresponds to ionic conductivity at the grain boundaries of the SrH₆ nanocrystals, and (CPE, R) describes the transport and hydrogen diffusion phenomena at the border of the Mo electrodes.³¹⁻³³ Simple calculations show that in the formula $R(T) = R_0 \times \exp(-E_g/2k_BT)$, the activation energy E_g approximately equals 0.44–0.51 eV at 150 GPa (the average value is 0.475 eV) and increases to 0.64 eV at 126 GPa. This agrees with the optical properties of the sample (its darkening) and the value of the bandgap for P1-SrH₆, predicted to be 0.55 eV at 150 GPa (Supporting Information Figure S17). Moreover, the pressure dependence allows us³⁴ to calculate dE_g/dP . The data from Figure 3b give dln(R)/dP = -0.13 GPa⁻¹ and $dE_g/dP =$ -0.0067 eV/GPa at 300 K. Thus, the expected metallization pressure of $Pm\overline{3}n$ -like pseudocubic P1-SrH₆ is about 220 GPa (Figure 3f).

We calculated the diffusion coefficients of hydrogen for SrH₆ and SrH₂₂ at 150 GPa using machine learning interatomic potentials (MLIP, Supporting Information Table S2 and Figures S37–S38, S45). Extrapolation of the data to 300 K gives $D_{\rm H} = 0.18$ Å²/ns for SrH₆ and a significantly larger $D_{\rm H} = 17$ Å²/ns for SrH₂₂. However, direct simulation at 300 K gives much higher diffusion coefficients: 7.7 and 20 Å²/ns, respectively. A better ordered structure of *P*1-SrH₆, which is close to the cubic prototypes $Pm\bar{3}n$ -Eu₈H₄₆²³ and Ba₈H₄₆,²⁴ is more stable than the disordered molecular hydride SrH₂₂, where individual hydrogen atoms and molecules can migrate to a neighboring unit cell within 1 ns. This surprising fact is confirmed by the radial distribution functions (Supporting Information Figures S39-S45): both strontium hydrides have a glassy H-sublattice and a solid Sr-sublattice, stabilized due to the interaction of coordination shells [SrH₂₄] at 300-600 K and 150 GPa. Calculations of the phonon band structure and elastic moduli in both cases indicate the absence of dispersion and almost complete isotropy of hydrogen sublattices, which exhibit properties of a glass.

The importance of studying strontium polyhydrides stems from Sr being a promising element for the design of ternary and quaternary superconducting hydrides stable below 1 Mbar. Unlike Ca and Y, strontium forms binary superhydrides with a very high hydrogen content at relatively low pressures of ~50–90 GPa. These compounds exhibit semiconducting behavior below 120–150 GPa, whereas calcium and yttrium superhydrides are high- $T_{\rm C}$ superconductors.

Complex and diverse behavior of the Sr–H system under pressure differs significantly from that of Ca–H, where CaH₄ and CaH₆ are present, and is closer to Ba–H in the chemical properties. In the Sr–H system, there is a series of molecular polyhydrides forming at pressures of 25–165 GPa: $Pm\bar{3}n$ -like and $Im\bar{3}m$ -like polymorphs of SrH₆, $F\bar{4}3m$ -like SrH₋₉ (see Supporting Information) and pseudotetragonal P1-SrH₂₂. Using the impedance spectroscopy, we estimated the direct bandgap in the $Pm\bar{3}n$ -like polymorph P1-SrH₆ to be 0.44–0.51 eV at 150 GPa and the metallization pressure of this hydride to be 220 GPa. The most amazing strontium hydride we observed is pseudotetragonal P1-SrH₂₂, the hydride of metal with the highest hydrogen content discovered so far, which can be considered a form of molecular hydrogen glass doped with 4 atom % of Sr. This compound is stable at a relatively low pressure of 100 GPa, and its metallization can be achieved during compression to about 200 GPa. Observing metallization in pure hydrogen is still a very difficult task associated with study of extremely small samples. Therefore, SrH₂₂ can be used as a helpful model of the hydrogen behavior above 300–350 GPa, realized at 1–2 Mbar. In a similar manner, barium hydride BaH_{12} (or $Ba_{0.08}H_{0.92}$) that we have discovered earlier can be used as a model for the emergence of superconductivity in already metallic hydrogen.

Methods

Experimental details: To synthesize the predicted strontium hydrides, we prepared several diamond anvil cells (DACs): Sr1-4, Sr50, Sr90, Sr165, and an electrical cell E1. We used diamond anvils with a 50–100 μ m culet beveled to 250– 300 μ m at 8.5°. Electrical DACs were equipped with four Mo electrodes having a thickness of ~500 nm that were sputtered onto a diamond anvil. Gaskets consisting of a tungsten ring and a c-BN/epoxy mixture were used to isolate the electrical leads. Strontium (>99.9%) particles with a diameter of ~ 15 -30 µm or SrH₂ powder (>99.9%) and sublimated ammonia borane (AB, >99.9%) were loaded into the gasket hole, with a thickness of $10-12 \mu m$ and a diameter of $35-60 \mu m$, in an inert glove box. AB was used as a hydrogen source, following the technique that has shown excellent results in previous studies.¹⁻⁵ In DAC Sr3, the strontium particle was protected from reacting with AB by a thin sputtered layer of gold. Ammonia borane is a weak acid, therefore strontium may react with it upon contact during the DACs' loading. However, the salt Sr(AB)₂ forming on the surface of the Sr particle decomposes with emission of H₂ during laser heating and does not interfere with the synthesis of hydrides. A special test on DACs Sr4 and E1 confirmed a uniform pressure distribution in the sample area (Supporting Information Figure S31), with the accuracy of the pressure determination of ± 6 GPa (4%). The heating of the Sr and SrH₂ samples above 1000 K at pressures of 70–170 GPa was carried out by several 0.1-0.5 s pulses of a Nd:YAG infrared laser (1.07 µm), and led to formation of strontium polyhydrides.

The applied pressure was measured by the edge of diamond Raman signal⁶ using Horiba LabRAM HR800 Ev spectrometer with an exposure time of 10 s at 532 nm. The X-ray diffraction (XRD) patterns from samples in diamond anvil cells (DACs) were recorded on BL15U1 synchrotron beamline at the Shanghai Synchrotron Research Facility (SSRF, China) using a focused ($5 \times 12 \mu m$) monochromatic X-ray beam with a linear polarization (20 keV, 0.6199 Å). Mar165 CCD was used as a detector.

The experimental XRD images were analyzed and integrated using Dioptas software package (version 0.5).⁷ The full profile analysis of the diffraction patterns and the calculations of the unit cell parameters were performed in Materials studio⁸ and JANA2006⁹ using the Le Bail method.¹⁰

To investigate the electrical resistivity of strontium polyhydrides, we performed measurements in Cu-Be DACs E1 using the pseudo-four-probe technique. The tungsten gasket with an initial thickness of 250 µm was precompressed to about 25 GPa. Then a hole with a diameter 20% larger than the culet diameter was drilled in the tungsten gasket using a pulse laser ($\lambda = 532$ nm). The cubic boron nitride (c-BN) powder mixed with epoxy was used as an insulating layer. We filled the chamber with MgO and compressed it to about 5 GPa. Then, in the obtained transparent MgO layer, a hole with a diameter of about 40 µm was drilled by a laser. Ultraviolet lithography was used to prepare four electrodes on the diamond culet. We deposited the 500 nm thick Mo layer by magnetron sputtering (with the field of 200 V at 300 K) and removed excess metal by acid etching. Four deposited Mo electrodes were extended by a platinum foil. The chamber was filled with sublimated ammonia borane (AB) and a small piece of Sr was placed on the culet of the upper diamond with four electrodes. All preparations were made in an argon glove box ($O_2 < 0.1$ ppm, $H_2O < 0.01$ ppm). After that, the DAC was closed and compressed to the required pressure. We used the 1.07 μ m infrared pulse laser (~0.1 s, ~1000 K) to heat the Sr/AB samples. Impedance spectroscopy was performed using Solartron SI 1260 impedance analyzer equipped with Solartron 1296 dielectric interface. A 100 mV sine signal with a sweep frequency from 0.1 to 10⁷ Hz was irradiated on the sample. The symmetric BeCu cell was put on a thermostatic flat-plate heater for higher temperature, which was recorded using a T-type thermocouple inserted into the cell.

A summary of the stability parameters of all studied compounds and DACs is presented in Table S1.

Computational details: The non-self-consistent and self-consistent calculations were performed using the density functional theory (DFT)^{11,12} within the Perdew–Burke–Ernzerhof functional (generalized gradient approximation)¹³ as implemented in the Abinit code.^{14,15} The computations of the total energy and optimization of the geometry of strontium hydrides were carried out using the optimized norm-conserving scalar-relativistic Vanderbilt pseudopotentials (ONCVPSP).¹⁶ The kinetic energy cutoff for plane waves was found through the convergence tests for the total energy and the unit cell parameters performed in the interval from 5 to 80 Ha (ecut). The Brillouin zone was sampled using *k*-points meshes with a resolution found via the convergence tests for the total energy and the unit cell parameters performed in the interval from $1\times1\times1$ to $8\times8\times8$ (ngkpt). The band structure calculations were performed using the Hartwigsen–Goedecker–Hutter nonrelativistic localdensity approximation (LDA) pseudopotentials¹⁷ with the kinetic energy cutoff of 30 Ha and a $4\times4\times4$ *k*-points mesh.

The non-self-consistent and self-consistent calculations of the equations of state and electron and phonon band structure of Sr_3H_{13} and SrH_{22} were performed using the density functional theory (DFT) within the Perdew–Burke–Ernzerhof functional (generalized gradient approximation) as implemented in the Abinit and VASP codes. For comparison of the total enthalpy and optimization of the geometry of SrH_{22} , calculations were also carried out using the optimized norm-conserving scalar-relativistic Vanderbilt pseudopotentials (ONCVPSP). Within the Abinit calculations, the kinetic energy cutoff of 40 Ha for plane waves was found through the convergence tests for the total energy and the unit cell parameters performed in the interval from 5 to 80 Ha. The Brillouin zone was sampled using *k*-points meshes with a resolution of $8\times8\times8$ found via the convergence tests for the total energy and the unit cell parameters performed in the interval from $1\times1\times1$ to $8\times8\times8$ (ngkpt). The LDA band structure calculations were performed using the Hartwigsen–Goedecker–Hutter(HGH) nonrelativistic LDA pseudopotentials with the kinetic energy cutoff of 30 Ha and an $8\times8\times8$ *k*-points mesh. The Bader analysis was performed using Critic2 software.^{18,19}

The dynamic stability and phonon density of states of SrH₂₂ were studied using classical molecular dynamics and the interatomic potential based on machine learning. We used the Moment Tensor Potential (MTP)²⁰ whose applicability in calculations of the phonon properties of materials has been demonstrated previously. Moreover, within this approach we can explicitly take into account the anharmonicity of hydrogen vibrations. To train the potential, we first simulated Sr hydrides in quantum molecular dynamics in an NPT-ensemble at 100 GPa and 10, 100, and 300 K, with a duration of 5 ps using the VASP code.²¹⁻²³ We used the PAW PBE pseudopotentials for the H and Sr atoms, and $2\pi \times 0.06$ Å⁻¹ k-mesh with a cutoff energy of 400 eV. For training the MTP, sets of Sr-H structures were chosen using active learning. We checked the dynamical stability of the studied Sr hydrides with the obtained MTPs via several runs of molecular dynamics calculations at 300 K and 180 GPa. First, the NPT dynamics simulations were performed in a supercell with about 1000 atoms for 40 ps. During the last 20 ps, the cell parameters were averaged. In the second step, the coordinates of the atoms were averaged within the NPT dynamics with a duration of 20 ps and the final structures were symmetrized as implemented in T-USPEX method. Then, for the structures of Sr polyhydrides relaxed at 100 GPa and 10, 100, and 300 K, the phonon density of states (DOS) was calculated within the MTP using the velocity autocorrelator (VACF) separately for each type of atoms:

$$g(\theta) = 4 \int_0^\infty \cos\left(2\pi\theta t\right) \frac{\langle \overline{V(0)V(t)} \rangle}{\langle \overline{V(0)^2 \rangle}} dt$$
(S1)

where θ is the frequency. The calculations were carried out in a 20×20×20 supercell. The velocity autocorrelator was calculated using molecular dynamics, then the phonon DOS was obtained.

All Raman investigations were performed using Abinit v.9.4.1. At 120 GPa, P1-SrH₂₂ is a metal with a band structure where the bands do not intersect with each other (see TB09 band structure). We optimized the crystal structure using the PBE DFT functional with the Fermi-Dirac distribution and a smearing temperature of 0.01 Ha. A Γ -centered *k*-point grid with a 6×6×6 mesh was used. The obtained initial band structure showed no intersection between the valence and conduction bands in the Brillouin zone. Therefore, we can treat SrH₂₂ as a semiconductor in the first approximation, fixing the number of the occupied bands, which allowed us to calculate the Raman spectra using the density functional perturbation theory for semiconductors.²⁴ In this case, we tested two different approaches using the same Γ -centered grid with 6×6×6 *k*-points:

(i) the crystal structure was optimized using the LDA DFT functional with norm-conserving pseudopotentials and its band structure generated using a non-self-consistent approach was compared with the band structure generated using the TB09 meta-GGA DFT functional; (ii) the crystal structure was optimized using the PBE DFT functional with norm-conserving pseudopotentials and its band structure generated using a non-self-consistent approach was compared with the band structure generated using the TB09 meta-GGA DFT functional. In the first and second approaches, SrH₂₂ was considered a semiconductor, maintaining the fixed band occupation. The subsequent one-phonon nonresonant Raman spectra were calculated using PEAD approach²⁴ and compared with the experimental one (Supporting Information Figure S29). Both approaches give rather poor agreement with the experimental data, but the position of one of the groups of signals (about 4200 cm⁻¹) predicted in approach (ii) coincides with the experimental value.

Then, in more advanced one-phonon resonant Raman calculations, the Raman susceptibility was obtained from the derivative of the dielectric function for the incoming laser frequency (532 nm).^{25,26} We considered the optimized crystal structure with the PBE and norm-conserving pseudopotentials for a metal with a Fermi–Dirac distribution and the temperature of smearing equal to 0.01 Ha to calculate the subsequent dynamical matrix(Δ) using the density functional perturbation theory with the LDA DFT functional and norm-conserving pseudopotentials. The right frequencies of metal *P*1-SrH₂₂ were obtained solving the secular equation

$$\Delta Q_{\zeta} = \omega_{\zeta}^2 Q_{\zeta} \quad (S2)$$

where $Q_{\zeta} = (e_{1\zeta}, \dots, e_{N\zeta})$ is the eigenvector (i.e., displacement) of the phonon mode ζ with a frequency ω_{ζ} , which in general consists of 3N components, where N is the number of atoms per unit cell. The intensity I of the Raman spectra at each phonon frequency mode ω_{ζ} for a photon of frequency ω_{laser} is defined as

$$I = \left(\omega_{\text{laser}} - \omega_{\zeta}\right)^4 \left| \boldsymbol{e}_{\text{out}} \cdot \boldsymbol{\alpha}^{\zeta} \cdot \boldsymbol{e}_{\text{in}} \right|^2 \frac{n_{\zeta} + 1}{2\omega_{\zeta}} \qquad (S3)$$

where $n_{\zeta} = \frac{1}{e^{\hbar\omega_{\zeta}/kT}-1}$ is the phonon occupation factor that depends on the temperature *T*. Two ω_{laser} values were considered: 532 nm (green) and 650 nm (red), which can cover the energy of the bandgap seen in the electronic structure of *P*1-SrH₂₂ calculated using the PBE DFT functional. The fundamental bandgap is 0.08 eV, the direct bandgap is 1.39 eV (Supporting Information Figures S10-S12).

The term α^{ζ} in eq. S3 is defined as the Raman susceptibility:²⁴

$$\alpha_{ij}^{\zeta}(\omega) = \sqrt{\Omega_0} \sum_{\tau\beta} \frac{\partial \chi_{ij}(\omega)}{\partial R_{\tau\beta}} u_{\tau\beta}^{\zeta}(S4)$$

where Ω_0 is the unit cell volume, χ_{ij} is the macroscopic dielectric susceptibility, and $u_{\tau\beta}^{\zeta}$ is the eigendisplacement of the phonon mode ζ of atom τ in the direction β . In the case of the Raman spectra of powders, the intensity of a peak at each frequency is the sum of the parallel intensity I_{\parallel}^{powder} and perpendicular intensity I_{\perp}^{powder} , which can be defined as

$$I_{\parallel}^{\text{powder}} = C(10G_0 + 4G_2) \quad (S5)$$
$$I_{\perp}^{\text{powder}} = C(5G_1 + 3G_2) \quad (S6)$$
$$I_{\text{tot}}^{\text{powder}} = I_{\parallel}^{\text{powder}} + I_{\perp}^{\text{powder}} (S7)$$

where

$$G_{0} = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^{2}}{3} \quad (S8)$$

$$G_{1} = \frac{(\alpha_{xy} - \alpha_{yz})^{2} + (\alpha_{yz} - \alpha_{zx})^{2} + (\alpha_{zx} - \alpha_{xy})^{2}}{2} \quad (S9)$$

$$G_{2} = \frac{(\alpha_{xy} + \alpha_{yz})^{2} + (\alpha_{yz} + \alpha_{zx})^{2} + (\alpha_{zx} + \alpha_{xy})^{2}}{2} + \frac{(\alpha_{xx} + \alpha_{yy})^{2} + (\alpha_{yy} + \alpha_{zz})^{2} + (\alpha_{zz} - \alpha_{xx})^{2}}{2} \quad (S10)$$

$$C = (\omega_{\text{laser}} - \omega_{\zeta})^{4} \frac{n_{\zeta} + 1}{2\omega_{\zeta}} \quad (S11)$$

We calculated I_{tot}^{powder} for the previously optimized structure of primitive triclinic SrH₂₂ at 120 GPa using the PBE DFT functional and norm-conserving pseudopotentials. The macroscopic dielectric susceptibility χ_{ij} was calculated using the LDA DFT functional and norm-conserving pseudopotentials with 80 bands for the derivative of energy with respect to k-points within the Brillouin zone, and the Fermi–Dirac distribution of occupation with a smearing temperature of 0.01 Ha. A Γ -centered grid with $16 \times 16 \times 16 k$ -points was used. As a result, the Raman spectrum of SrH₂₂ was significantly simplified: only three signals, ~4000, 4150, and 4300 cm⁻¹, remained in the spectrum, the most intense of which corresponds well to the experimentally observed peak at 4140 cm⁻¹ (123 GPa, 100 K). Another peak, lower than 4000 cm⁻¹ and of much weaker intensity, is also seen in such onephonon resonant Raman computations, but its intensity strongly depends on the match between the theoretical gap value and incoming laser frequency. Because of the absence of a pressure dependence in the cell, we assume that the signals at about 4500 cm⁻¹ and 4800 cm⁻¹ do not belong to the sample.

We estimated the diffusion rate in strontium hydrides using classical molecular dynamics with a machine learning interatomic potential implemented in the MLIP package.^{20,27,28} The interatomic potential was actively trained on the ab initio molecular dynamics trajectories of SrH_6 and SrH_{22} unit cells in the NPT-ensemble (P = 150 GPa, T = 1000 K) with the external electric field of 10⁴ V/m applied in the [100] direction. The reference ab initio data on energies, forces, and stresses were obtained on the DFT level using the VASP code.²¹⁻²³ We used the following VASP settings for training set preparation: the cutoff energy of the plane waves basis set was 450 eV, the first Brillouin zone was sampled by a Gamma-centered grid with $2\pi \times 0.03$ Å⁻¹ resolution, and the partial occupancies of electron states were set using a Gaussian method with 0.05 eV smearing width. The convergence criteria of the Self Consistent Field (SCF) cycle was 10⁻⁵ eV. The resulting actively selected training set had 2012 configurations, and the mean absolute errors (MAE) of the prediction of these configurations' energies and forces were 4.8 meV/atom and 0.27 eV/A (~25%), respectively. Molecular dynamics simulation in VASP for 30 ps shows discontinuous movement of H atoms; from this data, it is impossible to draw a clear conclusion about the diffusion parameters of the system.

The obtained interatomic potential was used to perform a large-scale molecular dynamics run on a $4\times4\times4$ supercell of SrH₂₂ and $3\times3\times3$ supercell of Sr₈H₄₈ at temperatures of 500, 550, and 600 K and a constant pressure of 150 GPa using LAMMPS package.²⁹ Each run lasted within 300 ps with a time step of 0.3 fs. Additionally, the external electric field of 10⁶ V/m was applied to each system. We found that applying this electric field has practically no effect on diffusion in the direction of the field in the MLIP calculations. Thus, the studied compounds SrH₂₂ and SrH₆ have no substantial ionic conductivity. However, estimates of ionic conductivity using the Nernst–Einstein relation give the following results: $\sigma(300 \text{ K}) \sim 10^{-3} \text{ S/cm}$ and $\sigma(500 \text{ K}) \sim 3.5 \times 10^{-2} \text{ S/cm}$ for SrH₆ at 150 GPa. Higher ionic conductivity is expected in SrH₂₂: $\sigma(500 \text{ K}) \sim 0.2 \text{ S/cm}$ at 150 GPa.

The initial atomic charges of the Sr and H atoms were obtained using the Bader charge analysis (Supporting Information Tables S9, S16-S17, Figures S14, S37-38) of the DFT ground state charge distributions of SrH₆ and SrH₂₂ hydrides and kept fixed during the simulation. The Bader analysis of the simulations in VASP after 30 ps indicates that the charges on atoms change insignificantly (Supporting Information Figures S37-S38). Finally, the diffusion coefficients of hydrogen atoms in the [100] direction were calculated using the Einstein formula (projection on *x*): $\overline{x^2} = 2Dt$. An activation formula $D(T) = D_0 \times \exp(-E_a/k_BT)$ was used to extrapolate the temperature dependence of the diffusion coefficients (from 500-600 K to 300 K, Supporting Information Table S2). In the order of magnitude, the obtained diffusion coefficients agree with the results of other works.³⁰

Author Contributions

D.V.S., W.C., and X.H. contributed equally to this work. W.C. performed all experiments with diamond anvil cells. D.V.S. analyzed and interpreted the results of the XRD, impedance, and optical measurements, and wrote the manuscript. X.H., A.R.O. and T.C. directed the research and edited the manuscript. I.A.K. and A.B.M. performed the T-USPEX and anharmonic phonon density of states calculations and MLIP-LAMMPS diffusion simulations. M.G. wrote Python scripts for accelerated USPEX data processing and automatic interpretation of diffraction patterns. A.G.K., D.Z., and A.R.O. prepared the theoretical analysis and calculated the equation of states and electron and phonon band structures for various strontium hydrides. C.T. and X.G. performed the Bader analysis, ABINIT band structure calculations with TB09 and PBE, dielectric function calculations, and nonresonant (PEAD) and resonant Raman spectrum calculations. All the authors provided critical feedback and helped shape the research.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. X-ray diffraction (XRD) study of strontium hydrides in DAC Sr2. (a) Experimental XRD pattern and the Le Bail refinements of the unit cell parameters of pseudotetragonal P1-SrH₂₂ and C2/m-Sr₃H₁₃ at 146 GPa. The experimental data, fit, and residues are shown in blue, red, and gray, respectively. Unidentified reflections are indicated by asterisks. The broadening of the (110) reflection is related to the proximity to the edge of WC seat. Inset shows the 2D diffraction image. (b) XRD patterns obtained during decompression of DAC Sr2 from 146 to 70 GPa. (c, f) Convex hulls of the Sr–H system at 100 and 150 GPa calculated with and without the zero-point energy (ZPE) contribution. (d, e) Experimental and theoretical dependences of the unit cell parameters on the pressure for (d) P1-SrH₂₂ and (e) C2/m-Sr₃H₁₃. Insets: crystal structures of SrH₂₂ (blue circles indicate isolated H atoms) and Sr₃H₁₃₆.



Figure 2. X-ray diffraction study of strontium hydrides in DACs Sr3 and Sr165. (a) Experimental XRD pattern and Le Bail refinements of the unit cell parameters of $Pm\bar{3}n$ -like pseudocubicP1-SrH₆ and C2/m-Sr₃H₁₃ at 110 GPa. The experimental data, fit, and residues are shown in blue, red, and gray, respectively. Inset shows the 2D diffraction image. (b) XRD patterns measured during the decompression of DAC Sr3 from 117 to 74 GPa. During the XRD experiment, the sample was shifted, thus we can see various relative intensities of Au. (c) Experimental and theoretical pressure dependences of the unit cell volume for P1-SrH₆, $Pm\bar{3}n$ -Sr₈H₄₆, and SrH₅. Inset: photo of the sample in DAC Sr165 at 160 GPa after the laser heating in transmitted and reflected light. (d) Crystal structure of P1-SrH₆ at 100 GPa. (e) XRD patterns obtained during the decompression of DAC Sr165 from 181 to 56 GPa. The signals at $2\theta > 18$ deg do not change with pressure and do not belong to the sample.



Figure 3. Impedance spectroscopy (Nyquist diagrams) of the pseudocubic P1-SrH₆ sample (DAC E1) in the frequency range from 0.1 to 10^7 Hz. (a) The active resistance of the sample is about 2.5 MΩ, the capacitance of the circuit is ~0.5 µF with any combination of contacts. (b) Impedance at pressures of 126–147 GPa and 300 K. (c) Calculating the activation energy E_g using the temperature dependence of the electrical resistance. (d) Impedance in the temperature interval of 300–440 K at 126 GPa, and (e) in the range of 300–420 K at 150 GPa. (f) Activation energy E_g compared to the direct bandgap of P1-SrH₆ at 100–150 GPa. See Supporting Information for details.

Under high pressure strontium reacts with hydrogen with the formation of pseudo tetragonal molecular SrH_{22} . This compound, a yellow-orange semiconductor with the bandgap ~1.8 eV, has a glassy hydrogen sublattice stabilized by a solid framework of Sr atoms. The formation of hydrogen glass is a new phenomenon that may have a significant impact not only on high-pressure chemistry, but also on the development of new materials for hydrogen storage.

Keywords: hydrogen, high pressure, superhydrides, superconductivity

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Title SrH₂₂: the metal hydride with the highest hydrogen content discovered so far



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Supporting Information

Sr-Doped Hydrogen Glass: Synthesis and Properties of SrH₂₂

Dmitrii V. Semenok, Wuhao Chen, Xiaoli Huang, Di Zhou, Ivan A. Kruglov, Arslan B. Mazitov, Michele Galasso, Christian Tantardini, Xavier Gonze, Alexander G. Kvashnin, Artem R. Oganov, and Tian Cui

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Experimental details

Discovered phase	DAC	Lowest pressure of synthesis, GPa	Stability range, GPa
c-SrH~9	Sr50, Sr90	62	62–139
P42/mnm-SrH6	Sr90	90	87–139
Cmme-Sr ₂ H ₃	Sr50	62	62–101
<i>C</i> 2/ <i>m</i> -Sr ₃ H ₁₃	Sr3, Sr2	118	70–146
<i>Pm</i> 3 <i>n</i> -like <i>P</i> 1-Sr ₈ H ₄₈	Sr3, Sr165, Sr4, E1	118	56-158
<i>P</i> 1-SrH ₂₂	Sr2, Sr1	146	99–146

Table S1. Studied strontium polyhydrides and regions of their experimental stability.

Computational details

Temperature, K	Diffusion co	Diffusion coefficients, Å ² /ps	
	$Pm\overline{3}n$ -like $P1$ -SrH ₆	P1-SrH ₂₂	
300	0.0077	0.02	
500	0.0103	0.126	
550	0.0186	0.159	
600	0.0282	0.208	
D_0 , Å ² /ps	4.505	2.471	
$E_{\rm a}$, meV	261.5	128.8	

Table S2. Calculated parameters of hydrogen diffusion in SrH₆ and SrH₂₂ at 150 GPa.



Thermodynamic stability of Sr-H compounds

Figure S4. Convex hulls of the Sr–H system at (a) 50, (b) 100, (c) 150 and (d) 200 GPa at 0 K, calculated without the zero-point energy (ZPE) contribution. Stable and metastable phases are shown as filled and hollow squares, respectively. P1-SrH₂₂ and pseudocubic P1-Sr₈H₄₈ are located near the convex hull at 50 GPa. At the same time C2/m-SrH₁₂ is stabilized, whereas it is dynamically unstable at 50–150 GPa in the harmonic approximation and has a different XRD pattern than the experimentally obtained phases. At 100GPa, many strontium hydrides lie on the convex hull or in its immediate vicinity: SrH₂₂, SrH₁₇, SrH₁₂, SrH₁₀, SrH₉, Sr₈H₄₈, Sr₂H₃, and so forth. As the pressure rises to 200 GPa, the most important phases, SrH₂₂ and Sr₈H₄₈, retain their stability and position on the convex hull.

The Gibbs free energy was calculated as $G(T) = E_0 + PV + k_{\rm B}T \int g(\omega) \ln \left[1 - \exp\left(-\frac{\hbar\omega}{k_{\rm B}}T\right)\right] d\omega + \frac{1}{2} \int g(\omega)\hbar\omega d\omega,$ (S12)

where $E_0 + PV$ is the total energy from the DFT calculations, $g(\omega)$ is the phonon density of states at a given pressure calculated using the finite displacements method as implemented in PHONOPY^{31,32} with forces computed using VASP.²¹⁻²³



Figure S2. Convex hulls of the Sr–H system at (a) 100 GPa and (b) 150 GPa calculated with the zero-point energy (ZPE) and entropy (-TS) contributions at temperatures of 0, 500, 1000, and 2000 K. Two phase modifications of SrH₂ (*P6/mmm* and *P6₃/mmc*) occupy almost the same position on the convex hull. Considering the ZPE makes *P6/mmm* preferable at 100 GPa.

Compound	Enthalpy <i>H</i> , eV	<i>H</i> per Sr, eV	$\Delta H_{\text{form}},$ eV/atom	ZPE, eV/cell	Δ (<i>H</i> +ZPE) _{form} , eV/atom	ΔG_{form} , 500K	$\Delta G_{\rm form}$, 1000 K	$\Delta G_{\text{form}}, 2000$ K
P6 ₃ /mmc-Sr	300.50892	12.52121	0	0.76855	0	0	0	0
Cmmm-Sr ₆ H ₆	58.16262	9.69377	-0.81045	1.86997	-0.80109	-1.00689	-1.15781	-1.62108
Cmma-Sr ₈ H ₁₂	66.60027	8.32503	-0.95455	3.70136	-0.93884	-1.15878	-1.28866	-1.69947
Amm2-Sr ₉ H ₁₅	70.38155	7.82017	-1.00881	4.56287	-0.99377	-1.21444	-1.33519	-1.72528
P6/mmm-SrH2	6.92977	6.92977	-1.05946	0.50048	-1.07725	-1.31286	-1.44516	-1.86287
Cmcm-Sr ₂ H ₈	7.70518	3.85259	-0.7685	2.13489	-0.77015	-1.01214	-1.09795	-1.40646
C2/m-Sr ₆ H ₂₆	22.08117	3.68019	-0.67739	6.98828	-0.677	-0.92214	-1.00813	-1.32144
P1-SrH ₆	8.86737	1.10842	-0.59623	11.70365	-0.61545	-0.86626	-0.94386	-1.23114
R-3m-SrH ₆	1.3041	1.3041	-0.56827	1.37014	-0.60076	-0.84985	-0.92716	-1.21982
$P4_2/mnm$ -Sr ₂ H ₁₂	2.88729	1.44365	-0.54834	3.15383	-0.55128	-0.80062	-0.87522	-1.15834
P1-SrH9	-9.36689	-2.34172	-0.40042	9.32768	-0.40525	-0.66336	-0.73784	-1.02039
C2/m-Sr ₂ H ₂₀	-7.79019	-3.89509	-0.39555	6.85252	-0.32417	-0.58334	-0.65497	-0.94037
P1-Sr ₂ H ₃₄	-24.99765	-12.49882	-0.2505	9.62845	-0.23124	-0.49652	-0.56883	-0.85088
P1-SrH ₂₂	-18.73969	-18.73969	-0.2051	4.81316	-0.24679	-0.51748	-0.59651	-0.88911
С2/с-Н	-28.95672	-1.20653	0	6.26195	0	0	0	0

Table S3. Enthalpy, ZPE and Gibbs free energy of formation for various Sr–H phases at 100 GPa and 0, 500, 1000, and 2000 K.

Table S4. Enthalpy, ZPE and Gibbs free energy of formation for various Sr–H phases at 150 GPa and 0, 500, 1000, and 2000 K.

Compound	Enthalpy H,	H per Sr,	ΔH_{form} ,	ZPE,	$\Delta(H+ZPE)_{\text{form}},$	ΔG_{form} ,	ΔG_{form} ,	$\Delta G_{\rm form}, 2000$
Compound	eV	eV	eV/atom	eV/cell	eV/atom	500K	1000 K	K
P6 ₃ /mmc-Sr	403.77031	16.82376	0	0.94392	0	0	0	0
Cmmm-Sr ₆ H ₆	88.75235	14.79206	-0.73927	1.98652	-0.7272	-0.72253	-0.71337	-0.70515
Cmma-Sr ₈ H ₁₂	110.90891	13.86361	-0.85217	3.72533	-0.8422	-0.83132	-0.80578	-0.75075
Amm2-Sr9H15	120.9014	13.43349	-0.92563	5.23784	-0.88939	-0.88118	-0.86231	-0.83391
P6/mmm-SrH2	12.6907	12.6907	-1.00892	0.58811	-1.0044	-0.9902	-0.95592	-0.87885
Cmcm-Sr ₂ H ₈	21.84666	10.92333	-0.73756	2.28638	-0.73088	-0.72308	-0.70739	-0.68601
C2/m-Sr ₆ H ₂₆	66.48349	11.08058	-0.62741	7.74212	-0.61028	-0.60217	-0.5851	-0.56494
P1-SrH ₆	75.30214	9.41277	-0.58458	13.01941	-0.58709	-0.58009	-0.5649	-0.5446
R-3m-SrH ₆	9.51012	9.51012	-0.57067	1.66278	-0.56813	-0.55817	-0.54044	-0.52378
$P4_2/mnm$ -Sr ₂ H ₁₂	19.61206	9.80603	-0.5284	3.30839	-0.52709	-0.52036	-0.50525	-0.48666
P1-SrH9	31.75144	7.93786	-0.39075	10.27908	-0.37856	-0.37315	-0.36203	-0.35171
C2/m-Sr ₂ H ₂₀	13.93573	6.96787	-0.39312	5.38182	-0.39535	-0.39026	-0.3778	-0.35905
P1-Sr ₂ H ₃₄	5.77364	2.88682	-0.25185	9.10114	-0.25397	-0.25037	-0.2446	-0.24348
P1-SrH ₂₂	-0.00129	-0.00129	-0.20242	6.34131	150	-0.18503	-0.18798	-0.20438
С2/с-Н	-13.27573	-0.55316	0	6.42274	0	0	0	0

To determine the crystal structure of three phases with expected stoichiometries SrH_5 , SrH_6 , and SrH_9 , we ran the USPEX code with a multiobjective optimization of stability and agreement with a given experimental XRD pattern. In these calculations, USPEX reads an XRD spectrum file that contains the minimum and maximum diffraction angles 20 of the pattern, the wavelength of the X-ray radiation in Å, the parameter *match_tol* (the maximum distance in degrees at which the calculated and experimental peaks are considered matching), and all major peaks of the pattern in the form of "angle–intensity" doublets on separate lines (the peak intensities are automatically normalized to 100). The disagreement (fitness) *F* between the given diffraction pattern and the calculated pattern of each structure is expressed as

$$F = \sum_{i,j}^{match} \left(\frac{h_i^{exp} - h_j^{th}}{100}\right)^2 \left(\frac{h_i^{exp}}{100}\right)^2 + \sum_i^{exp \ rest} \left(\frac{h_i^{exp}}{100}\right)^2 + \sum_i^{th \ rest} \left(\frac{h_i^{th}}{100}\right)^2$$
(S13)

where h^{exp} and h^{th} are the intensities of the peaks in the experimental and calculated XRD patterns, respectively. The first sum in eq. S13 runs over the matching peaks, the second sum runs over the unmatched experimental peaks, and the third sum runs over the unmatched calculated peaks. In our calculations, we used *match_tol* = 0.3° because the experimental peaks are quite broad. As a rule of thumb, this parameter should be equal to the half of the full width at half maximum (FWHM/2) of the broadest peak in the experimental XRD pattern.

For SrH₅, we did a single USPEX calculation with the stoichiometry Sr₄H₂₀ at 150 GPa. In this and the following USPEX runs, the following parameters were used: a population size of 60 structures, a maximum number of 250 generations, and a stopping criterion of the evolutionary algorithm, which was always set equal to the total number of atoms in the unit cell. For Sr₄H₂₀, we got a single good match with the experimental spectrum (Figure S3) that lies 0.05 eV/atom above the best structure found during this run.



Figure S3. Crystal structure search of Sr₄H₂₀ at 150 GPa with a multiobjective optimization. (a) Enthalpy–fitness Pareto diagram with three first Pareto fronts. The circle marks one of the good matches with the experimental spectrum. (b) Comparison of the experimental (153 GPa, $\lambda = 0.62$ Å, see main text Figure 2e) and theoretical XRD patterns of the Sr₄H₂₀ structure circled in panel (a). The structure, which is lower in energy (42.2 eV/f.u.) than the one highlighted by the circle, has a XRD pattern without reflection at 15.5°.

For SrH₆, we did three USPEX calculations with the stoichiometries Sr_2H_{12} , Sr_4H_{23} (or $SrH_{5.75}$), and Sr_4H_{24} at 100 GPa. During the first run, three good matches were found, all lying less than 0.05 eV/atom above the most stable structure found with USPEX (Figure S4). The second run did not bring any good matches, and the enthalpy–fitness plot shows that the structures tend to group around two different minima of the potential energy surface. The third run resulted in several good matches (Figure S5).



Figure S4. Crystal structure search of Sr₂H₁₂ at 100 GPa with a multiobjective optimization. (a) Enthalpy–fitness Pareto diagram with three first Pareto fronts. Good structures are marked with a rectangle. (b, c, d) Comparison of the experimental (100 GPa, $\lambda = 0.62$ Å, see Figure S19e) and theoretical XRD patterns of three best structures of Sr₂H₁₂ found in the search. Structure (b) is almost ideal $Im\bar{3}m$ -SrH₆, whereas structure (d) can be symmetrized to $P4_2/mnm$ -SrH₆.



Figure S5. Crystal structure search of Sr₄H₂₃ and Sr₄H₂₄ at 100 GPa with a multiobjective optimization. (a) Enthalpy–fitness Pareto diagram with three first Pareto fronts for Sr₄H₂₃. No good candidates were found. (b) Enthalpy–fitness Pareto diagram with three first Pareto fronts for Sr₄H₂₄. Two good structures are indicated by blue circles. (c, d) Comparison of the experimental (100 GPa, $\lambda = 0.62$ Å, see Figure S19e) and theoretical XRD patterns for two best structures of Sr₄H₂₄ found in the search. Structure (c) is almost ideal *Im*3*m*-SrH₆.

For SrH₉, we did two USPEX runs with the stoichiometries Sr_4H_{36} at 100 GPa and Sr_4H_{35} (or $SrH_{8.75}$). In both cases, several good matches were found (Figure S6).



Figure S6. Crystal structure search of Sr₄H₃₅ and Sr₄H₃₆ at 100 GPa with a multiobjective optimization. Enthalpy– fitness Pareto diagram with three first Pareto fronts for (a) Sr₄H₃₅ and (b) Sr₄H₃₆. Good structures are indicated by blue circles. (c, d) Comparison of the experimental (101 GPa, $\lambda = 0.62$ Å, see Figure S19a) and theoretical XRD patterns for two best structures of Sr₄H₃₅ and Sr₄H₃₆ found in the search. Structure (d) is *F*43*m*-like *P*1-SrH₉ described in the main text.

Description of individual Sr-H phases

1. SrH_2



Figure S7. Band structure and the density of electron states for SrH_2 . (a) Band structure and the density of electron states of *Pnma*-SrH₂ at 0 GPa calculated using the GGA–PBE exchange–correlation functional (VASP code). The bandgap is 3.12 eV (indirect). (b) Band structure and the density of electron states of *P*6₃/*mmc*-SrH₂ at 100 GPa calculated using the GGA–PBE functional (VASP code). The bandgap is 1.21 eV (indirect). (c) Band structure of *Pnma*-SrH₂ at 0 GPa calculated using the TB09 exchange–correlation functional (Abinit code). The bandgap is 2.72 eV (indirect). (d) Density of electron states of *P*6₃/*mmc*-SrH₂ at 150 GPa calculated using the GGA–PBE functional (VASP code). The bandgap decreases to ~0.4 eV.

2. *C*2/*m*-Sr₃H₁₃

Pressure, GPa	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	V, Å ³
		DAC Sr2		
146	6.25	2.98	7.92	23.07
142	6.25	2.96	7.955	23.02
138	6.284	2.9819	7.9797	23.38
134	6.2982	2.9886	7.9881	23.52
129	6.3134	2.9953	8.0136	23.70
125	6.465	3.0548	8.128	24.20
110	6.379	3.03	8.11	24.52
99	6.4407	3.05	8.18	25.26
87	6.47	3.08	8.19	25.53
78	6.62	3.098	8.25	26.47
70	6.67	3.1	8.34	26.96
		DAC Sr3		
117	6.39	3.015	8.15	24.57
113	6.45	3.035	8.02	24.55
110	6.40146	3.0435	8.14436	24.82
107	6.44	3.042	8.15	24.97
103	6.46	3.044	8.165	25.12
96	6.5	3.075	8.3	25.95
90	6.52	3.085	8.4237	26.50
83	6.48	3.1048	8.256	26.10
74	6.75	3.15	8.25	27.40
		Theory		
160	6.456	2.833	7.331	21.74
140	6.487	2.897	7.465	22.76
120	6.518	2.974	7.63	23.98
100	6.559	3.06	7.814	25.44
80	6.604	3.162	8.035	27.26
60	6.663	3.286	8.308	29.67
40	6.747	3.445	8.665	33.07

Table S5. Experimental and calculated unit cell parameters of *C2/m*-Sr₃H₁₃ synthesized in DACs Sr2 and Sr3.

Table S6. Crystal structure of the discovered C2/m-Sr₃H₁₃ phase at 100 GPa.

Phase	Pressure, GPa	Lattice parameters		Coordin	ates	
C2/m-Sr ₃ H ₁₃	100	<i>a</i> = 6.559 Å	Sr1(4i)	-0.34408	0.0	0.16684
		b = 3.060 Å	Sr2(2c)	0.0	0.0	0.5
		c = 7.814 Å	H1(4i)	0.02193	0.0	-0.2372
		$\alpha = 90^{\circ}$	H2(4i)	0.05862	0.0	-0.11121
		$R = 102.2^{\circ}$	H3(4i)	-0.3624	0.0	-0.29667
		p = 103.3	H4(4i)	-0.33268	0.0	-0.10272
		$\gamma = 90^{\circ}$	H5(4i)	-0.32295	0.0	0.43516
			H6(4i)	-0.28826	0.0	-0.38035
			H7(2a)	0.0	0.0	0.0



Figure S8. Band structure and the density of electron states of C2/m-Sr₃H₁₃ at 100 GPa calculated using the PBE–GGA exchange–correlation functional (VASP code).



Figure S9. Density of electron states of C2/m-Sr₃H₁₃ at (a) 50 and (b) 150 GPa calculated using the PBE GGA exchange–correlation functional (VASP code). The contributions from hydrogen and strontium are approximately equal at the Fermi level. (c) Phonon band structure and the density of states of C2/m-Sr₃H₁₃ at 150 GPa calculated within the harmonic approximation. (d) Ab initio calculated harmonic Eliashberg function $\alpha^2 F(\omega)$ and the electron–phonon coupling (EPC, red curve) parameter at 150 GPa for C2/m-Sr₃H₁₃.

3. *P*1-SrH₂₂

Pressure, GPa	<i>a</i> , Å	b, Å	<i>c</i> , Å	<i>V</i> , Å ³		
DAC Sr2						
146	4.4157	4.4045	3.348	56.6		
142	4.4585	4.4371	3.3308	57.3		
138	4.451	4.4337	3.3784	58.0		
134	4.4603	4.4459	3.3858	58.4		
129	4.4756	4.4576	3.3923	58.9		
125	4.52	4.46	3.3965	59.4		
110	4.583	4.5462	3.4525	62.5		
99	4.627	4.611	3.5156	65.1		
87	4.7393	4.6496	3.5498	67.7		
78	4.8051	4.6919	3.6017	70.2		
70	4.872	4.758	3.627	72.8		
	·	DAC Sr1	·	·		
138	4.457	4.437	3.369	58.15		
		Theory		·		
200	4.269	4.243	3.215	50.438		
180	4.33	4.285	3.256	52.4921		
160	4.396	4.345	3.302	54.8482		
140	4.472	4.409	3.357	57.5752		
120	4.561	4.485	3.419	60.7747		
90	4.724	4.631	3.531	67.0454		
70	4.872	4.758	3.627	72.8096		

 Table S7. Experimental and calculated unit cell parameters of pseudocubic P1-SrH₂₂ synthesized in DACs Sr1 and Sr2.

Table S8. Crystal structure of the discovered pseudocubic *P*1-SrH₂₂ at 100 GPa.

Phase	Pressure, GPa	Lattice parameters		Coord	linates		
			Sr1(4a)	-0.33906	-0.16093	0.43474	
			H1(4a)	0.42825	-0.03638	-0.01041	
			H2(4a)	0.4416	0.13656	-0.10975	
			H3(4a)	0.01787	0.19755	0.21107	
			H4(4a)	0.20074	-0.23729	0.41284	
		<i>a</i> = 4.663Å	H5(4a)	-0.26366	0.27274	-0.12205	
		<i>b</i> = 4.578 Å	H6(4a)	0.21803	-0.24499	-0.01764	
P1-SrHaa	100	c = 3.490 Å	H7(4a)	0.03253	0.19286	-0.00745	
1 1-511122	100	100	$\alpha = 68.38^{\circ}$	H8(4a)	-0.38882	0.38617	0.38085
		$\beta = 69.11^{\circ}$ $\gamma = 82.29^{\circ}$	H9(4a)	0.25424	0.15117	-0.4687	
			H10(4a)	0.03201	0.49453	0.31907	
			H11(4a)	0.34898	0.26444	0.3225	
			H12(4a)	0.12802	-0.08907	0.44684	
			H13(4a)	-0.27421	0.28439	0.48285	
			H14(4a)	0.31581	0.47923	-0.35829	
			H15(4a)	0.00551	0.46212	-0.44802	

H16(4a)	0.12502	-0.1001	-0.10473
H17(4a)	-0.12189	0.05326	-0.27026
H18(4a)	-0.38648	0.38415	-0.02934
H19(4a)	-0.12661	-0.45177	-0.02902
H20(4a)	-0.09512	-0.27865	-0.12742
H21(4a)	0.45099	-0.38208	0.1379
H22(4a)	0.30301	0.47229	-0.13433



Figure S10. Band structure and the density of electron states of P1-SrH₂₂: (a) at 120 GPa, calculated using the LDA norm conserving (NC) exchange–correlation functional, Abinit code; (b) at 150 GPa, calculated using the PBE-GGA, VASP code.



Figure S11. Band structure and the density of electron states of P1-SrH₂₂: (a) at 120 GPa, calculated using the PBE–GGA exchange–correlation functional, Abinit code; (b) at 180 GPa, calculated using the PBE-GGA, VASP code.



Figure S12. Band structure and the density of electron states of P1-SrH₂₂: (a) at 120 GPa, calculated using the TB09-HGH exchange–correlation functional, Abinit code; (b) at 200 GPa, calculated using the PBE-GGA, VASP code.



Figure S13. Phonon spectra of P1-SrH₂₂ at different pressures. (a) Harmonic phonon band structure of P1-SrH₂₂ at 150 GPa (VASP code). The phonon branches show very limited dispersion. (b) Phonon density of states of P1-SrH₂₂ calculated using the DFPT PBE at 100 and 150 GPa within the harmonic approximation (VASP). There are several imaginary acoustic modes. (c) Anharmonic phonon density of states of P1-SrH₂₂ calculated at 100 GPa using molecular dynamics with the MTP and MLIP at 300 K.



Figure S14. (a) Electron density at the isovalue of 0.01 of P1-SrH₂₂ at 120 GPa. The electron density was calculated using the LDA functional. Hydrogen mostly forms slightly charged (~ -0.1|e|) H₂ molecules with a bond length d(H-H) = 0.8 Å, and the charge density ρ at the bond critical point is 2.8|e|/bohr³. The hydrogen molecules form stronger bonds with the Sr atoms with $\rho = 4.7|e|$ /bohr³. (b) Ab initio-calculated harmonic Eliashberg functions $\alpha^2 F(\omega)$ and the electron–phonon coupling (EPC) parameter at 200 GPa for P1-SrH₂₂.

Element	Bader charge	Coordinate X	Coordinate Y	Coordinate Z
Sr	1.2383	0.5766593	0.1630336	0.3344873
Н	-0.0342	0.0143542	0.0478963	0.5734584
Н	-0.0581	0.0120759	0.7964527	0.9605628

Table S9. Bader charge analysis of P1-SrH₂₂ at 120 GPa.

Н	-0.0311	0.0147627	0.2304206	0.8058419
Н	-0.0905	0.0305188	0.6335676	0.373611
Н	-0.0174	0.034599	0.455148	0.1262341
Н	-0.0274	0.1208795	0.0742438	0.8817379
Н	-0.0178	0.1184602	0.8709192	0.5427404
Н	0.0117	0.1491269	0.7362817	0.2457107
Н	-0.0344	0.138188	0.2781709	0.0955161
Н	-0.0080	0.0791917	0.5138391	0.6712897
Н	-0.3276	0.2959499	0.9461376	0.1192135
Н	-0.0569	0.2715705	0.5296145	0.7084117
Н	-0.0150	0.467839	0.5280785	0.9656285
Н	-0.0155	0.4640251	0.7979888	0.703346
Н	-0.0888	0.5401766	0.6924997	0.2953635
Н	-0.0322	0.5535044	0.0956467	0.8631326
Н	-0.0243	0.5793404	0.2518234	0.7872366
Н	0.0119	0.6335984	0.5897855	0.4232638
Н	-0.0247	0.677696	0.5213226	0.9842153
Н	-0.0238	0.685713	0.8047447	0.6847592
Н	-0.0057	0.7667996	0.8122281	0.9976848
Н	-0.3285	0.8637802	0.3799296	0.549761
Total	0.0000			

4. Possible formation of barium polyhydrides BaH₂₁₋₂₃

Studying the Ba–H system,³ we have found that BaH₁₂ is not the highest hydride lying on the convex hull: superhydride C2/m-BaH₂₃ with a pseudotetragonal (*I4/mmm*) structure is also thermodynamically stable at 150 GPa. In that research, we have also predicted the stability of BaH₂₁ and BaH₂₂ at lower pressures, though it was difficult to imagine compounds with such a high hydrogen content. The retrospective analysis shows that the previously unidentified reflections at 8.5–9° and 12.5–12.8° (Supporting Information Figure S15) observed in the diffraction patterns of BaH₁₂ at 119–160 GPa may be explained by the presence of an impurity of thermodynamically stable molecular superhydride C2/m-BaH_{21–23} (Table S10) similar to *P*1-SrH₂₂ we discovered in the Sr–H system. Therefore, there is a high probability that superhydrides with extremely high hydrogen content, XH_{21–23}, exist in both Ba–H and Sr–H systems at 100–150 GPa.



Figure S15. Experimental X-ray diffraction patterns from (a) DAC B1 and (b) DAC B2³ and the Le Bail refinement of the pseudotetragonal phase C2/m-BaH₂₁₋₂₃. Low content of this phase in the sample does not permit to determine the exact Ba:H ratio. Unidentified reflections are indicated by asterisks. Insets show the diffraction image ("cake") and projection of the C2/m-BaH₂₃ structure to the (*ab*) plane. The hydrogen network is shown by light blue lines.

23.						
Crystal structure	Pressure, GPa	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	β, °	Cell volume, Å ³ /Ba
						atom
	126	3.583	8.060	4.399	67.74	58.80
	132	3.502	8.053	4.390	67.84	57.35
	135	3.522	7.996	4.367	67.57	56.85
	145	3.538	7.953	4.338	67.70	56.49
	154	3.471	7.904	4.304	67.60	54.59
	160	3.473	7.886	4.294	67.60	54.38

Table S10. Experimental parameters of the unit cell of the previously unknown barium superhydride C2/m-BaH₂₁₋

5. P1-SrH₆ (Sr₈H₄₈) and proposed $Pm\overline{3}n$ -Sr₈H₄₆

Table S11. Experimental and calculated unit cell parameters of $Pm\bar{3}n$ -like pseudocubic P1-SrH₆ synthesized in DACs Sr3, Sr165, E1, and Sr4.

Pressure, GPa	$a, Å (as Pm\overline{3}n)$	V , Å ³ per Sr atom (as $Pm\overline{3}n$)
	DAC Sr3	
117	5.989	26.86
113	5.999	27.0
110	5.994	26.925
107	6.030	27.4125
103	6.050	27.6875
96	6.102	28.41
90	6.129	28.7875
83	6.103	28.425
74	6.265	30.75
	DAC Sr165	
181.0	5.677	22.875
177.0	5.690	22.9125
171.0	5.688	23.0125
166.0	5.735	23.5875
157.0	5.766	23.975
153.0	5.707	24.35
148.0	5.823	24.675
146.0	5.828	24.75
135.0	5.860	25.15
131.0	5.888	25.5125
95.0	6.076	28.05
78.0	6.170	29.3625
56.0	6.350	32.0
	DAC E1	
122	5.970	26.6
	DAC Sr4	
157	5.796	24.35
	Theory (as $Pm\overline{3}n$)	
50	6.533	34.860
70	6.328	31.687
90	6.173	29.412
100	6.107	28.480
110	6.047	27.647
130	5.942	26.226
150	5.852	25.052

Table S12. P	Pressure de	ependence	of the calcu	lated unit co	ell parameters	of <i>Pm</i> 3 <i>n</i> -like	pseudocubic <i>F</i>	P1-SrH ₆
$(Sr_8H_{48}, Z = 8)$	8).							

Pressure, GPa	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	α, °	β, °	γ, °	<i>V</i> , Å ³
50	6.529	6.514	6.558	90.85	89.96	90.25	278.88
70	6.312	6.307	6.368	90.73	90.14	90.31	253.5
90	6.152	6.148	6.222	90.57	90.19	90.31	235.3
100	6.084	6.080	6.160	90.48	90.21	90.30	227.84
110	6.024	6.016	6.103	90.40	90.23	90.25	221.18
130	5.912	5.912	6.003	90.25	90.25	90.52	209.81
150	5.821	5.821	5.915	90.13	90.14	90.28	200.42

Dhase	Pressure CDo	Lattice		Coord	inates	
1 11050	11035010, UFa	parameters	Coordinates			
			Sr1(1a)	0.12251	0.62481	0.87321
			Sr2(1a)	0.86195	0.13111	0.62262
			Sr3(1a)	0.63559	0.86933	0.1373
			$\frac{Sr4(1a)}{Sr5(1a)}$	0.37682	0.11185	0.63943
			$\frac{SrS(1a)}{Sr6(1a)}$	0.13328	0.55257	0.12320
			Sr7(1a)	0.62007	0.6192	0.6537
			Sr8(1a)	0.12384	0.11843	0.1535
			H1(1a)	0.83108	0.10887	0.97125
			$H_2(1a)$	0 9734	0.81083	0 12742
			$H_3(1a)$	0.12569	0.96391	0.83565
			H4(1a)	0.62632	0.60953	0.33588
			$H_{5}(1a)$	0.30726	0.45652	0.62636
			H6(1a)	0.61939	0.32533	0.47245
			H7(1a)	0.26967	0.32333	0.17216
			H8(1a)	0.12572	0.28312	0.46802
P1_SrH			H9(1a)	0.45582	0.11496	0.30449
1 1-51116			H10(1a)	0.62604	0.95054	0.80334
Sr			H11(1a)	0.77602	0.61062	0.95804
			H12(1a)	0.95377	0.78727	0.62779
		a = 6.084 Å	H13(1a)	0.42108	0.11143	0.98695
		b = 6.080 Å	H14(1a)	0.96016	0.45059	0.12861
HO REAL		c = 6.160 Å	H15(1a)	0.11818	0.96836	0.45703
	100	c = 0.100 A	H16(1a)	0.4607	0.61632	0.96987
	100	$\alpha = 90.48^{\circ}$	H17(1a)	0.93158	0.47973	0.62245
		$\beta = 90.21^{\circ}$	H18(1a)	0.61829	0.91833	0.48649
		$\gamma = 90.30^{\circ}$	H19(1a)	0.33135	0.35301	0.94544
			H20(1a)	0.91214	0.32993	0.34409
			H21(1a)	0.34042	0.9089	0.34199
			H22(1a)	0.41952	0.8247	0.85143
			H23(1a)	0.83306	0.41253	0.85688
			H24(1a)	0.83811	0.83144	0.43647
			H25(1a)	0.41825	0.8435	0.43171
			H26(1a)	0.41229	0.4035	0.84926
			H27(1a)	0.85631	0.41406	0.43398
			H28(1a)	0.91205	0.33316	0.93143
			H29(1a)	0.91975	0.90726	0.36027
			H30(1a)	0.34651	0.89223	0.95227
			H31(1a)	0.77755	0.61264	0.33374
			H32(1a)	0.31471	0.76685	0.6236
			H33(1a)	0.62302	0.30606	0.78698
			H34(1a)	0.81068	0.11671	0.28645
			H35(1a)	0.28222	0.81498	0.11848
			H36(1a)	0.12372	0.2724	0.82894
			H37(1a)	0.63129	0.07832	0.86913
			H38(1a)	0.88945	0.57795	0.11076
			H39(1a)	0.07988	0.85877	0.61495

Table S13. Crystal structure of discovered $Pm\bar{3}n$ -like pseudocubic P1-SrH₆ at 100 GPa.

H40(1a)	0.38572	0.61711	0.09097
H41(1a)	0.15492	0.37096	0.58984
H42(1a)	0.58367	0.12309	0.37057
H43(1a)	0.32822	0.32415	0.35251
H44(1a)	0.41893	0.38965	0.43476
H45(1a)	0.4712	0.6145	0.33036
H46(1a)	0.12	0.12949	0.83601
H47(1a)	0.83019	0.82987	0.84235
H48(1a)	0.8978	0.92451	0.92017

Table S14.	Crystal	structure	of pro	posed P	$m\bar{3}n-S$	r8H46 at	120	GPa
	Crystur	Structure	or pro	posedi	mon D.	131140 ut	120	OI u

Phase	Pressure, GPa	Lattice parameters	Coordinates			
			Sr1	0	0	0
			Sr2	0.25	0	0.5
$Pm\overline{3}n$ -Sr ₈ H ₄₆	120	<i>a</i> = 5.930 Å	H1	0	0.15833	0.31308
			H2	0.25	0.5	0
			H3	0.20572	0.20572	0.20572

Table S15. Calculated unit cell parameters of cubic $Pm\bar{3}n$ -SrH₅ (Sr₈H₄₀). Isostructural $Pm\bar{3}n$ -EuH₅ has been previously proposed to explain the formation of new phases in the Eu–H system.³³ However, ab initio calculations show that the ideal $Pm\bar{3}n$ -SrH₅ structure is completely dynamically unstable and therefore cannot be used to interpret the experimental data.

Pressure, GPa	a , Å (as $Pm\overline{3}n$, $Z = 8$)	V , Å ³ per Sr atom (as $Pm\overline{3}n$)
40	6.413	32.977
60	6.220	30.081
80	6.072	27.99
100	5.952	26.36
120	5.852	25.059
140	5.765	23.96
160	5.689	23.026

Table S16. Bader charge analysis of $Pm\bar{3}n$ -like pseudocubic P1-SrH₆ at 100 GPa.

Element	Bader charge	Coordinate X	Coordinate Y	Coordinate Z
Sr	1,124	0,870808	0,6227229	0,8749857
Sr	1,148	0,6251439	0,1269839	0,1393409
Sr	1,151	0,1387032	0,869925	0,3666065
Sr	1,148	0,6400509	0,1157757	0,6227973
Sr	1,147	0,127004	0,3532591	0,3766161
Sr	1,122	0,3700049	0,6252475	0,8674192
Sr	1,065	0,6535769	0,6199615	0,3768713
Sr	1,065	0,153609	0,1199978	0,8761696
Н	-0,349	0,973023	0,1099248	0,1701267
Н	-0,414	0,1248227	0,8119182	0,0253724
Н	-0,291	0,8344744	0,9633547	0,8752897
Н	0,031	0,3366999	0,6092284	0,3712572
Н	-0,338	0,6212006	0,4625102	0,6830264
Н	-0,376	0,4735865	0,32395	0,3804787
Н	-0,350	0,1200279	0,4307898	0,7278987
Н	-0,212	0,4687275	0,2824226	0,875339
Н	-0,217	0,3041117	0,1157773	0,5445022
Н	-0,218	0,8040751	0,9499099	0,3754673
Н	-0,324	0,9620443	0,6124613	0,2207319

Н	-0,238	0,6259821	0,7844539	0,0455015
Н	-0,409	0,9869781	0,1124019	0,5776545
Н	-0,256	0,1265185	0,4475407	0,0375389
Н	-0,337	0,460331	0,9686129	0.8808238
Н	-0,211	0,9682716	0.6166244	0.5363793
Н	-0,370	0,6197945	0,4756087	0.0664667
Н	-0,390	0,4859749	0,9187875	0,382016
Н	-0,040	0,9459562	0,3520889	0,6678609
Н	-0,149	0,3462164	0,3289077	0,0862806
Н	-0,159	0,3415474	0,90997	0,661004
Н	-0,182	0,8485356	0,8260172	0,5821452
Н	-0,085	0,8535336	0,4110209	0,1677138
Н	-0,093	0,4372868	0,8302066	0,1584418
Н	-0,004	0,4373558	0,8408169	0,5887506
Н	-0,124	0,8474416	0,4049217	0,5865531
Н	-0,011	0,4418416	0,4140313	0,1395418
Н	-0,076	0,9323183	0,3350721	0,0874485
Н	-0,068	0,3562624	0,9084872	0,0821558
Н	0,008	0,9529067	0,8918327	0,6557067
Н	-0,246	0,3320068	0,6123312	0,2207249
Н	-0,396	0,6212498	0,7700113	0,6831097
Н	-0,409	0,7884712	0,3056371	0,3775097
Н	-0,416	0,2879164	0,1171889	0,1894833
Н	-0,332	0,1173372	0,8153535	0,7183523
Н	-0,240	0,8290418	0,2720012	0,876988
Н	-0,018	0,8717853	0,0799804	0,3701721
Н	0,000	0,1037027	0,5828141	0,115619
Н	-0,007	0,6088659	0,8619859	0,9132206
Н	-0,031	0,0915592	0,6161131	0,6135648
H	-0,026	0,5895225	0,3641036	0,8663512
Н	-0,014	0,3724567	0,1237747	0,4152746
Н	-0,176	0,3477018	0,3248401	0,669414
H	0,009	0,4422296	0,3968609	0,5928269
Н	-0,287	0,3308854	0,6147967	0,5284857
Н	0,032	0,8364467	0,1246422	0,880615
H	-0,179	0,8431626	0,8285789	0,1688118
H	0,019	0,9264109	0,9175624	0,099606
Total	0,000			

 Stable S17. Bader charge analysis of $Pm\overline{3}n$ -like pseudocubic P1-SrH₆ at 150 GPa.

Element	Bader charge	Coordinate X	Coordinate Y	Coordinate Z
Sr	1,038	0,1216972	6,23E-01	0,8643163
Sr	1,074	0,8609518	1,22E-01	0,6303453
Sr	1,076	0,622266	8,77E-01	0,1382668
Sr	1,076	0,3768387	1,22E-01	0,6382668
Sr	1,074	0,6223045	3,61E-01	0,1303453
Sr	1,038	0,1233579	6,22E-01	0,3643163
Sr	0,977	0,6225154	6,22E-01	0,6567168
Sr	0,977	0,1220142	1,23E-01	0,1567168
Н	-0,333	0,8249147	1,19E-01	0,9746721
Н	-0,311	0,9682427	8,14E-01	0,1168925
Н	-0,255	0,1201653	9,64E-01	0,8306556
Н	0,029	0,6227485	6,18E-01	0,3406195
Н	-0,311	0,3143441	4,68E-01	0,6168925
Н	-0,333	0,6186704	3,25E-01	0,4746721

Н	-0,291	0,2759871	4,33E-01	0,1159938
Н	-0,229	0,1205407	2,82E-01	0,4639115
Н	-0,244	0,4491025	1,21E-01	0,3052344
Н	-0,244	0,6210622	9,49E-01	0,8052344
Н	-0.229	0.7824073	6.21E-01	0.9639115
Н	-0.291	0.9330509	7.76E-01	0.6159938
Н	-0.359	0.4182123	1 19E-01	0.9804885
 Ц	0.207	0.9673734	1,19E-01	0.1171524
 	-0,297	0,9073734	4,55E-01	0,1171324
 Ц	-0,224	0,1205212	9,01E-01	0,4031023
П	-0,224	0,4000402	0,21E-01	0,9031023
П	-0,297	0,9320443	4,0/E-01	0,01/1324
П	-0,339	0,0180/95	9,18E-01	0,4804883
Н	-0,028	0,3282104	3,4/E-01	0,94/281/
H	-0,136	0,9095175	3,2/E-01	0,3451277
H	-0,167	0,3314/33	9,16E-01	0,3448325
H	-0,16/	0,4162157	8,31E-01	0,8448325
H	-0,136	0,8265974	4,10E-01	0,8451277
H	-0,028	0,8469436	8,28E-01	0,4472817
H	0,000	0,4003662	8,33E-01	0,4498928
H	-0,135	0,4154069	4,11E-01	0,8458325
H	-0,023	0,8455518	4,14E-01	0,4458395
Н	-0,023	0,9141696	3,46E-01	0,9458395
Н	-0,135	0,9114189	9,15E-01	0,3458325
Н	0,000	0,3327845	9,00E-01	0,9498928
Н	-0,242	0,7789434	6,20E-01	0,3293645
Н	-0,304	0,3149984	7,75E-01	0,6146242
Н	-0,339	0,6211853	3,04E-01	0,7942044
Н	-0,339	0,8038242	1,21E-01	0,2942044
Н	-0,304	0,2746191	8,15E-01	0,1146242
Н	-0,242	0,1196015	2,79E-01	0,8293645
Н	-0,028	0,6270762	1,01E-01	0,8786761
Н	-0,039	0,8692059	6,19E-01	0,0968528
Н	-0,046	0,1174326	8,76E-01	0,5969566
Н	-0,046	0,375621	6,17E-01	0,0969566
Н	-0,039	0,1191597	3,69E-01	0,5968528
Н	-0,028	0,6005894	1,27E-01	0,3786761
Н	-0,164	0,3323698	3,26E-01	0,3447297
Н	0,002	0,4047915	4,09E-01	0,4461622
Н	-0,255	0,4641598	6,20E-01	0,3306556
Н	0,029	0,1175383	1,23E-01	0,8406195
Н	-0,164	0,8261942	8,32E-01	0,8447297
Н	0,002	0,9086104	9,05E-01	0,9461622
Total	0.000			



Figure S16. Band structure of P1-SrH₆ (Sr₈H₄₈, $Pm\bar{3}n$ -like) calculated using different methods at 100 GPa. Band structure and the density of electron states of P1-SrH₆ per Sr atom calculated using the PBE–GGA exchange–correlation functional (VASP code). (b) Band structure of P1-SrH₆ at 100 GPa calculated using the TB09-HGH functional (Abinit code).



Figure S17. Band structure of P1-SrH₆ (Sr₈H₄₈, $Pm\bar{3}n$ -like) calculated using different methods at 150 GPa. (a) Band structure and the density of electron states of P1-SrH₆ per Sr atom at 150 GPa calculated using the PBE–GGA exchange–correlation functional (VASP code). (b) Band structure of P1-SrH₆ at 150 GPa calculated using the TB09-HGH functional (Abinit code). An accurate estimation of the direct bandgap gives 0.55 eV.



Figure S18. Phonon band structure and the density of states of P1-SrH₆ at 100 GPa calculated within the harmonic approximation.

6. Synthesis of SrH₉ below 1 Mbar

To further investigate the stability of strontium superhydrides at low pressures, we loaded DAC Sr50 with Sr and ammonia borane and compressed it to 54 GPa. The opaque Sr particle showed metallic luster before being heated by a laser. After the laser heating at about 1000–1500 K, the pressure dropped to 50 GPa and the particle became heterogeneous and translucent, indicating an occurrence of a chemical reaction with generated hydrogen (Supporting Information Figure S32). The XRD study showed that the sample consists of two main components (Supporting Information Figures S19a,d). At about 100 GPa, the cubic phase is the main product, marked quite clearly, whereas the amount of impurity (second phase) is much smaller. Because Sr is a neighbor of Y, for simplicity this cubic set of reflections was

preliminarily indexed using the $F\overline{4}3m$ -SrH₉ structure common among metal polyhydrides (e.g., PrH₉⁵ and EuH₉³³). Despite $F\overline{4}3m$ -SrH₉ (a = 5.316 Å, V = 37.55 Å³ at 62 GPa) being dynamically unstable, its equation of state is in satisfactory agreement with the experimental data (Figure S19g). Molecular dynamics "annealing" of $F\overline{4}3m$ -SrH₉ leads to a better candidate — $F\overline{4}3m$ -like pseudocubic P1-SrH₉, or Sr₄H₃₆, with a molecular H sublattice which is almost stable within the harmonic approximation and lies near (25 meV/atom above) the convex hull at 100 GPa. The comparison of the calculated structure with experimental XRD patterns indicates that this solution is not ideal: the experimental structure is more symmetric and closer to $F\overline{4}3m$ than the predicted P1. Because of some uncertainty about the H content (Sr:H ratio is between 1:9 and 1:8, see also the results from DAC Sr90) and the structure of the compound, in this work the phase is denoted c-SrH_{~9}.



Figure S19. X-ray diffraction study of strontium hydrides in DACs Sr50 and Sr90. (a) Experimental XRD pattern and the Le Bail refinement of the unit cell parameters of cubic SrH₉ and *Cmme*-Sr₂H₃ at 101 GPa in DAC Sr50. Inset shows the 2D diffraction image. (b) Experimental XRD pattern and the Le Bail refinement of the unit cell parameters of cubic SrH₉ and SrH₆ at 87 GPa in DAC Sr90. The experimental data, fit, and residues are shown in red, black, and green, respectively. Unidentified reflections are indicated by asterisks. (c) Diffraction image ("cake") of the sample at 87 GPa, DAC Sr90. (d) XRD patterns obtained during the compression of DAC Sr50 from 63 to 101 GPa. (e) XRD patterns obtained during the compression of DAC Sr90 from 90–94 to 139 GPa. (f) Crystal structure of *P4*₂/*mnm*-SrH₆, which can also be considered as distorted *Im*3m-SrH₆. (g) Experimental and theoretical pressure dependences of the unit cell volume of cubic SrH₋₉, SrH₆, and *Cmme*-Sr₂H₃.

The structure of the impurity phase cannot be determined unambiguously because of a superposition of reflections. One of the simplest possibilities is *Cmme*-Sr₂H₃ (a = 5.62 Å, b = 5.84 Å, c = 5.03 Å, V = 20.7 Å³ at 62 GPa), which lies about 13 meV/atom above the convex hull at 100 GPa and is dynamically stable. During the compression from 62 to 93 GPa, the relative intensity of the XRD peaks of c-SrH₋₉ and *Cmme*-Sr₂H₃ changed greatly. This possibly indicates that c-SrH₋₉ is formed via a chemical reaction of the impurity phase Sr₂H₃ with excess hydrogen detected using the Raman spectroscopy (Supporting Information Figure S30). The sample, semitransparent at 62 GPa, darkens as pressure increases and becomes opaque above 100 GPa (Figure S19d). This indicates the semiconducting nature of

the obtained molecular hydrides and their metallization in DAC Sr50 with increasing pressure. The experiment shows that hydrogen-rich polyhydrides such as $c-SrH_{\sim9}$ can be synthesized at a relatively low pressure of about 50 GPa, which makes strontium a very attractive platform for the design of ternary hydride superconductors that are stable at pressures below 1 Mbar.

In DAC Sr90, we discovered a compound similar to $c-SrH_{\sim9}$ but with a lower H content. In this cell, strontium metal and ammonia borane were used for the synthesis at a slightly higher pressure of ~90 GPa. After laser heating, the pressure increased from 90 to 94 GPa and the sample obviously expanded (Supporting Information Figure S32). The obtained compound was almost opaque. There are no peaks from 500 cm⁻¹ to 4500 cm⁻¹ in the Raman spectrum of the sample at 94 GPa except for the molecular hydrogen vibron at 4200 cm⁻¹, which can correspond to both free and bound H₂ (Supporting Information Figure S30b). The XRD data (Supporting Information Figures S19a,c) indicates the presence of two phases with cubic structures. The main cubic phase can be indexed using c-SrH₉ (a = 5.141 Å, V = 33.96 Å³/Sr at 87 GPa) previously found in DAC Sr50, but with a 3% lower unit cell volume corresponding to the Sr:H ratio near 1:8.

To interpret the rest of the XRD reflections, we analyzed the diffraction rings at 87 GPa (Figures S19b,c). The reflections at 12.5° and 16° are diffuse, corresponding to a finecrystalline phase of an unknown impurity (marked *), whereas cubic reflections "1–5" (c-SrH₋₉) and "a–c" (Figure S19c) correspond to coarse-crystalline phases and have a granular structure. The "a–c" series can be approximately indexed using the structure of recently discovered $Im\bar{3}m$ -CaH₆³⁴ and $Im\bar{3}m$ -YH₆² with the lattice parameter a = 3.86 Å and V = 28.73 Å³/Sr at 87 GPa. The theoretical cell parameters for this phase at 90 GPa — a = 3.851 Å and V = 28.55 Å³/Sr — are very close to the experimental data. Here the story with SrH₉ repeats: a highly symmetric $Im\bar{3}m$ structure with an atomic hydrogen sublattice is dynamically unstable in the case of SrH₆, whereas its distorted and molecular "isomer" turns out to be a much better candidate. Accurate DFT calculations show that $P4_2/mnm$ -SrH₆ (Sr₂H₁₂), a tetragonally distorted $Im\bar{3}m$ -SrH₆ with molecular hydrogen in the H sublattice, can also explain the experimental XRD pattern. This tetragonal SrH₆ is dynamically stable and lies near (50 meV/atom above) the convex hull (Figure 1c, Supporting Information Figures S1-S2).

Thus, both compounds found in DAC Sr90, c-SrH_{~9} and SrH₆, can be considered molecular semiconducting "isomers" of known superhydrides such as $F\overline{4}3m$ -XH₉ and $Im\overline{3}m$ -XH₆, that is compounds with a similar composition, unit cell parameters, and X-ray diffraction patterns (metal sublattice) but significantly different structure of the hydrogen sublattice. This series of experiments also shows that although SrH_{~9} can be synthesized at a relatively low pressure of about 62 GPa, the synthesis of hexahydride SrH₆ requires a higher pressure of ~90 GPa.

7. $F\overline{4}$ 3*m*-like pseudocubic *P*1-SrH₉ and *P*4₂/*mnm*-SrH₆

Table S18. Crystal structure of $P4_2/mnm$ -SrH₆ (Sr₂H₁₂) at 150 GPa. This structure can be considered tetragonally distorted $Im\bar{3}m$ -SrH₆ similar to $Im\bar{3}m$ -YH₆.

Phase Pressure, GPa Lattice parameters Coordinates	Phase	Pressure, GPa	Lattice parameters	Coordinates
----------------------------------------------------	-------	---------------	--------------------	-------------

		a = 3.672 Å	Sr1	0	0	0.5
P4 ₂ /mnm-SrH ₆	150	c = 3.747 Å	H1	-0.22659	0.05509	0.0000
		c = 5.747 A	H2	0.0000	0.5	0.25

Table S19. Experimental and calculated unit cell parameters of *P*4₂/*mnm*-SrH₆ (Sr₂H₁₂), proposed to explain the results of the synthesis in DAC Sr90.

Pressure, GPa	<i>a</i> , Å	<i>c</i> , Å	V, Å ³ per Sr atom							
	DAC Sr90									
82.0	3.962	3.863	29.57							
87.0	3.946	3.860	29.40							
90.0	3.942	3.854	29.28							
100.0	3.923	3.824	28.68							
121.0	3.882	3.771	27.61							
131.0	3.866	3.757	27.29							
139.0	3.862	3.743	27.06							
	Theory (PBE GC	βA)								
80.0	3.911	4.040	30.89							
90.0	3.868	3.986	29.82							
100.0	3.829	3.935	28.84							
110.0	3.793	3.891	27.99							
130.0	3.729	3.813	26.51							
150.0	3.670	3.747	25.26							

Table S20. Experimental and calculated unit cell parameters of $Im\bar{3}m$ -SrH₆ (Sr₂H₁₂), isostructural to YH₆, which can also be used to explain the results of the synthesis in DAC Sr90.

Pressure, GPa	<i>a</i> , Å	V, Å ³ per Sr atom
	DAC Sr90	
82	3.8659	28.88
87	3.8599	28.75
90	3.8539	28.62
94	3.8619	28.79
100	3.8219	27.91
112	3.7939	27.30
121	3.7759	26.91
131	3.7589	26.55
139	3.7439	26.23
· · ·	Theory (PBE GGA)	
70	3.934	30.44
90	3.851	28.55
100	3.814	27.74
120	3.751	26.38
140	3.696	25.24
150	3.670	24.71

Table S21. Crystal structure of discovered $F\overline{4}3m$ -like pseudocubic P1-SrH₉ at 100 GPa (PBE GGA, VASP).

Phase	Pressure, GPa	Lattice parameters		Coord	linates	
P1-SrH9	100	a = 10.487 Å	Sr1(1a)	0.47972	-0.48646	-0.43961
	100	h = 2.626 Å	Sr2(1a)	0.24665	0.02859	0.08032
		v = 3.020 A	Sr3(1a)	-0.25475	0.04565	-0.03816

	<i>c</i> = 3.713 Å	Sr4(1a)	-0.01671	-0.44344	0.44443
Sr	$\alpha = 89.74^{\circ}$	Hl(la)	0.05993	-0.19215	-0.09202
	$\beta = 89.74^{\circ}$	$H_2(1a)$ $H_3(1a)$	0.29038	-0.29703	-0.4102/
	$\gamma = 91.13^{\circ}$	$H_{1}(1a)$	-0.19394	-0.46020	-0.55521
	y 91.15	$H_{1}(1a)$	0.3032	-0.46927	0.09003
		$H_{5}(1a)$	-0.1044	0.15110	0.10107
		$H_{7}(1_{a})$	0.10550	-0.13116	-0.59005
		$\frac{11}{(1a)}$	-0.24085	-0.20211	0.43121
		$H_0(1a)$	0.10103	0.46037	-0.20372
		$H_{10(1a)}$	0.03091	0.0759	0.29900
		U11(1a)	-0.20722	0.33221	0.43729
		$\Pi \Pi (\Pi a)$ $\Pi \Pi 2(\Pi a)$	0.13703	-0.40434	0.11233
		$\Pi 12(1a)$ $\Pi 12(1a)$	-0.01912	0.27171	-0.04004
		$\Pi 13(1a)$ $\Pi 14(1a)$	-0.43394	0.35216	0.00200
		$\Pi 14(1a)$ $\Pi 15(1a)$	0.03479	0.29/40	-0.06112
		$\Pi I J (1a)$ $\Pi I J (1a)$	0.43134	-0.00024	-0.10095
		$\Pi 10(1a)$ $\Pi 17(1a)$	-0.45502	0.00304	-0.303
		HI/(Ia)	-0.45592	-0.22074	0.10290
		H18(1a)	0.1031/	0.01014	0.4794
		H19(1a)	-0.39081	-2.5E-4	-0.4/80
		H20(1a)	0.29142	0.27035	-0.43/81
		$H_{21}(1a)$	-0.3246/	-0.39039	0.34932
		H22(1a)	-0.01353	-0.15813	-0.04492
		H23(1a)	-0.36331	-0.4251/	-0.0/634
		H24(1a)	0.42874	-0.00554	0.3255
		H25(1a)	-0.11955	0.04//9	-0.48823
		H26(1a)	-0.31863	-0.46483	-0.24704
		H2/(1a)	0.18898	-0.48//4	0.33226
		H28(1a)	-0.08282	0.04282	-0.29448
		H29(1a)	0.43856	-0.06203	0.07688
		H30(1a)	-0.14928	-0.44826	-0.04547
		H31(1a)	0.17071	0.35013	-0.3979
		H32(1a)	-0.44385	0.13201	0.13254
		H33(1a)	0.34135	0.11014	-0.42028
		H34(1a)	-0.07801	0.04967	0.18258
		H35(1a)	0.30736	-0.39937	-0.2113
		H36(1a)	-0.33151	0.37592	0.37801

H

Table S22	. Experimental	and calculated up	nit cell paramete	rs of cubic ($F\overline{4}3$)	m) SrH9, pro	posed to explain	n the results
of the synt	hesis in DACs	Sr50 and Sr90.					

Pressure, GPa	<i>V</i> , Å ³ per Sr	Pressure, GPa	<i>V</i> , Å ³ per Sr	Pressure, GPa	<i>V</i> , Å ³ per Sr
	atom		atom		atom
DAC Sr50		DAC Sr90		Theory	$(F\bar{4}3m)$
101	34.12	139	29.67	60	38.28
93	34.90	131	29.77	80	35.68
83	36.20	121	30.32	100	33.65
75	36.82	100	32.75	120	31.98
68	37.47	94	33.17	140	30.59
62	37.72	90	33.57		
Table S23. Expe	rimental and calcul	ated unit cell parar	neters of Cmme-Sr	₂ H ₃ , proposed to ex	plain the results of

Table 520: Experimental and calculated and cen parameters of comme 51213, proposed to explain the results ofthe synthesis in DAC Sr50.Pressure, GPaa, Åb, Åc, Å $V, Å^3$ per Sr atom

		DAC Sr50		
62	5.62	5.83	5.04	20.7
75	5.57	5.74	5.02	20.13
83	5.53	5.70	4.95	19.56
93	5.48	5.63	4.95	19.11
101	5.45	5.63	4.89	18.82
		Theory		
60	5.485	6.111	5.281	22.13
80	5.401	5.907	5.096	20.32
100	5.337	5.747	4.949	18.97
120	5.282	5.620	4.830	17.92



Figure S20. Phonon band structure and the density of states calculated within the harmonic approximation: (a) *Cmma*-Sr₂H₃ at 100 GPa. (b) $P4_2/mnm$ -SrH₆ (Sr₂H₁₂) at 150 GPa.



Figure S21. (a) Band structure and the density of electron states of $P4_2/mnm$ -SrH₆ (Sr₂H₁₂) at 150 GPa per Sr atom calculated using the PBE–GGA exchange–correlation functional (VASP code). (b) Band structure of $P4_2/mnm$ -SrH₆ (Sr₂H₁₂) at 150 GPa calculated using the TB09-HGH functional (Abinit code). The compound should demonstrate metallic properties at this pressure.



Figure S22. (a) Band structure $P4_2/mnm$ -SrH₆ (Sr₂H₁₂) at 150 GPa calculated using the PBE–GGA exchange–correlation functional (Abinit code). This compound should demonstrate metallic properties at this pressure. (b) Band structure of P1-SrH₉ (c-SrH_{~9}) at 100 GPa calculated using the PBE–GGA exchange–correlation functional (Abinit code).



Figure S23. (a) Phonon band structure and the density of states of $F\overline{4}3m$ -like pseudocubic *P*1-SrH₉ (Sr₄H₃₆) at 150 GPa calculated within the harmonic approximation. (b) Anharmonic phonon density of states of *P*1-SrH₉ calculated at 100 GPa using molecular dynamics with the MTP and MLIP at 10 K. In the harmonic approximation, this structure is unstable at 100 GPa.



Figure S24. (a) Band structure and the density of electron states of $F\overline{4}3m$ -like pseudocubic P1-SrH₉ (Sr₄H₃₆) per Sr atom at 150 GPa calculated using the PBE–GGA exchange–correlation functional (VASP code). (b) Band structure of P1-SrH₉ (c-SrH_{~9}) at 100 GPa calculated using the TB09 HGH functional (Abinit code).

Experiment. Additional X-ray diffraction data



Figure S25. X-ray diffraction study of strontium hydrides in DAC Sr1. (a) Experimental diffraction pattern and the Le Bail refinement of the unit cell parameters of pseudotetragonal P1-SrH₂₂ at 138 GPa. The experimental data, fit, and residues are shown in red, black, and green, respectively. Unidentified reflections are indicated by asterisks. (b) Comparison of the experimental and predicted XRD patterns of DFT relaxed (PBE GGA) P1-SrH₂₂.



Figure S26. X-ray diffraction study of strontium hydrides in (a) DAC Sr4 and (b) the electrical DAC E1. Experimental diffraction pattern and the Le Bail refinement of the unit cell parameters of $Pm\bar{3}n$ -like pseudocubic P1-SrH₆ (Sr₈H₄₈) at (a) 158 GPa and (b) 122 GPa. The experimental data, fit, and residues are shown in red, black, and green, respectively.

Raman measurements



Figure S27. (a) Raman spectra from the back and front sides of DAC Sr3 after the laser heating (the laser wavelength was 532 nm). There is a very strong signal corresponding to the H₂ vibron. (b) Raman spectra of DAC Sr3 during decompression from 48 to 0 GPa. Comparison of the Raman spectra from the sample, AB, and gasket shows that the peaks at 3635 and 735 cm⁻¹ belong to lower Sr hydrides — the products of decomposition. Hydrogen was expected to be one of the decomposition products as the pressure decreased; however, no Raman signals of hydrogen were detected. (c) The sample after a pressure drop to 48 GPa (upper panel). Expansion of the loaded material during decompression (middle and bottom panels). (d) Raman spectra of strontium hydrides synthesized from SrH₂ loaded with H₂ in DAC S1 before and after the laser heating (the laser wavelength was 532 nm). Spectra at 0–131 GPa recorded before the laser heating show the presence of the SrH₂ and H₂ peaks, in accordance with the previous study.³⁵ After the double laser heating at 131–133 GPa, the sample became opaque without an obvious volume change, the SrH₂ peaks disappeared, and no additional Raman signals were detected except a signal at ~4140–4150 cm⁻¹. This peak can be due to both excess of hydrogen not reacted with Sr and to the resulting molecular strontium superhydride.



Figure S28. (a) Raman spectra of strontium hydrides synthesized using SrH_2/AB in DAC Sr1 at different temperatures (40–200 K) and pressures (105–126 GPa, the laser wavelength was 532 nm). The XRD pattern (Figure S25) shows *P*1-SrH₂₂ as the main component of the sample. (b) Pressure dependence of the hydrogen signal of the sample compared with the literature data.³⁶



Figure S29. Calculated and experimental Raman spectra of P1-SrH₂₂ (DAC Sr1) at 120 and 123 GPa. (a) Nonresonant Raman spectra of SrH₂₂ calculated within the LDA NC (1st approach) and PBE NC (2nd approach) functionals. (b) Experimental Raman spectra of strontium hydrides synthesized from SrH₂/AB in DAC Sr1 at different temperatures (60–200 K) and pressures (105–125 GPa, the laser wavelength was 532 nm). Inset: Raman shift measured near the gasket (at the point marked by a bright green dot in the picture) shows that the signal at ~4513 cm⁻¹ does not belong to the sample. (c, d) Comparison of the experimental and calculated resonant Raman spectra for the excitation wavelengths of (c) 532 nm and (d) 650 nm. Inset: photo of the SrH₂₂ sample in transmitted light.



Figure S30. Raman spectra of strontium hydrides synthesized after the laser heating (the laser wavelength was 532 nm). In (a) DAC Sr50 at 63 GPa, the XRD analysis shows that the sample consists mainly of c-SrH₉ and Sr₂H₃. Besides the hydrogen vibron at 4245 cm⁻¹, there are peaks at 340 cm⁻¹, 580 cm⁻¹, 870 cm⁻¹, and 3110 cm⁻¹. The inset shows the Raman shift of the edge of the diamond during compression from 63 to 101 GPa. (b) Raman spectra of strontium hydrides synthesized after the laser heating in DAC Sr90 at 94 GPa.



Figure S31. Raman spectra (633 nm excitation laser) of strontium hydrides in DAC Sr4 at 190 GPa (a, b) and in the electrical DAC E1 at ~148 GPa (c, d). (a) Pressure gradient in the sample area. (b) Full Raman spectra from the back (B) and front (F) sides of the DAC. (c) Pressure gradient in the sample area, ± 6 GPa. (d) Full Raman spectra from the back (B) and front (F) sides of the DAC.

Optical properties



Figure S32. Photographs of samples (Sr/AB) before/after laser heating observed with reflected and transmitted light. (a) The sample in DAC Sr50. (b) The sample in DAC Sr90. (c) The sample in DAC Sr165. Below 56 GPa the sample becomes translucent, which speaks in favor of its semiconducting properties. (d) The sample in DAC W2. A significant increase in the volume of the particle after the laser heating and a change in its color and transparency were observed.



Figure S33. Sample photos in reflected and transmitted light in cells before and after the laser heating. (a) DAC Sr4 was loaded with SrH₂/AB at 152 GPa. According to ab initio calculations (PBE GGA), the bandgap in $P6_3/mmc$ -SrH₂ narrows with increasing pressure: 3.12 eV at 0 GPa, 1.2 eV at 100 GPa, and 0.4 eV at 150 GPa. The observed change in the color and transparency of the sample is in qualitative

agreement with the calculation results. A better quantitative agreement can be achieved in calculations using the TB09 functional. No additional Raman signals other than that of diamond were detected in the spectra of the sample. (b) The sample in DAC Sr3, loaded with Sr/Au/AB, before and after the laser heating, photographed in reflected and transmitted light.



Figure S34. (a) Imaginary and (b) real parts of the dielectric function of strontium superhydride P1-SrH₂₂ calculated at 120 GPa. (c) A sample of SrH₂₂ in DAC Sr1 at various pressures (100–131 GPa). As the pressure increases, the sample becomes darker, which corresponds to the closure of the bandgap in this semiconductor. (d) Calculated transmission spectrum of the SrH₂₂ at 120 GPa. The color of the sample in DAC Sr1 observed in transmitted light corresponds to the calculated values.

Impedance spectroscopy

Table S24. Parameters of the equivalent electrical circuit used to approximate the experimental behavior of the sample in DAC E1 at different pressures and a fixed temperature of 300 K. C1 and R1 correspond to the first semicircle, R2 and CPE1 — to the second half-ellipse and low-frequency tail.

^{L1}				-				
Pressure, GPa	Temperature, K	Inductance, (<i>L</i> 1), μH	$R1, M\Omega$	<i>C</i> 1, pF	<i>R</i> 2, MΩ	CPE-T (Q), 10 ⁻⁶	CPE-P (n)	χ^2
147	300	86.373	0.344	2.13	1.081	0.910	0.477	0.04
144	300	73.199	0.604	2.47	3.1105	0.607	0.482	0.035
139	300	90.65	1.239	2.09	9.3872	0.344	0.500	0.046
136	300	83.881	1.669	2.24	11.665	0.255	0.508	0.046
130	300	67.121	3.120	2.73	13.091	0.108	0.553	0.04
126	300	284.16	3.244	0.80	00	0.140	0.413	0.13

Table S25. Parameters of the equivalent electrical circuit used to approximate the experimental behavior of the sample in DAC E1 at different temperatures and a fixed pressure of 150 GPa. C1 and R1 correspond to the first semicircle, R2 and CPE1 — to the second half-ellipse and low-frequency tail.

^{L1}				-				
Pressure, GPa	Temperature, K	Inductance, (<i>L</i> 1), μH	R 1, k Ω	<i>C</i> 1, pF	<i>R</i> 2, kΩ	CPE-T (Q), 10 ⁻⁶	CPE-P (n)	χ^2
150	300	48.43	251.2	3.385	672	1.174	0.489	0.03
150	320	40.53	117.9	3.827	411	1.889	0.470	0.024
150	340	39.42	67.82	3.997	276	2.354	0.470	0.024
150	360	38.52	42.27	4.005	179	2.699	0.486	0.027
150	380	35.81	27.58	4.072	120	3.134	0.501	0.028
150	400	33.67	20.09	4.056	86.5	3.510	0.519	0.03
150	420	28.03	14.24	4.181	58.8	3.953	0.536	0.03

Table S26. Parameters of the equivalent electrical circuit used to approximate the experimental behavior of the sample in DAC E1 at different temperatures and a fixed pressure of 126 GPa. C1 and R1 correspond to the first semicircle, R2 and CPE1 — to the second half-ellipse and low-frequency tail.

Pressure, GPa	Temperature, K	Inductance, (L1), μH	<i>R</i> 1, kΩ	<i>C</i> 1, pF	<i>R</i> 2, MΩ	CPE-T (Q), 10 ⁻⁶	CPE-P (n)	χ^2
126	300	415.52	3263	0.755	12.95	0.083	0.526	0.176
126	320	38.0	1242	4.03	19.65	0234	0.412	0.084
126	340	233	604.8	0.917	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	0.449	0.416	0.1
126	360	210	308.6	0.979	00	0.686	0.421	0.1
126	380	191	175.4	1.02	~	1.00	0.436	0.1
126	400	150	112.1	1.236	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	1.278	0.445	0.085
126	420	127	80.18	1.36	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	1.676	0.455	0.083
126	440	120	65.95	1.33	×	2.38	0.465	0.083



Figure S35. Impedance spectroscopy (Nyquist diagram) of the P1-SrH₆ sample (DAC E1) in the frequency range of $0.1-10^7$ Hz at 121 GPa in the (a) heating and (b) cooling cycles. Impedance spectroscopy (Nyquist diagram) of the P1-SrH₆ sample in DAC E1 with (red, green, violet) and without (black) illumination by a 532 nm laser (power 0-1.2 W) at 300 K. Illumination from the (c) back and (d) front sides of the DAC leads to a significant increase in the size of the half-ellipse.

The illumination of the sample with a green laser (532 nm, power 0–1.2 W) practically does not change the parameters of the first semicircle in the hodograph but increases the size of the subsequent half-ellipse corresponding to the electrode processes. This suggests that the sample does not heat up during irradiation, whereas the resistance R2 and pseudocapacitance CPE-P increase. Irradiation significantly reduces the electrical resistance of the bulk SrH₆ phase because of photoconductivity. However, this change ($\sim 10^2-10^3 \Omega$) cannot be seen probably because the contribution of bulk resistance to the total resistance of the sample is very small.

Table S27. Parameters of the equivalent electrical circuit used to approximate the experimental behavior of the sample in DAC E1 at different powers of the light source (532 nm laser) and fixed pressure (148 GPa) and temperature (300 K). *C*1 and *R*1 correspond to the first semicircle, *R*2 and CPE1 — to the second half-ellipse and low-frequency tail.



Figure S36. Impedance spectroscopy (Nyquist diagram) of the *P*1-SrH₆ sample in DAC E1 (a) before and (b) after the laser reheating. Strong laser heating at 148–149 GPa neutralizes the electrode part (the half-ellipse and low-frequency spike) of the hodograph. At the same time, the active resistance of the sample is reduced 20 times to 10 k Ω , which speaks in favor of the reordering of grain boundaries and the change in the nature of conductivity to predominantly electronic.

Hydrogen diffusion



Figure S37. Thermal diffusion in P1-SrH₆ at 150 GPa and 600 K in an external electric field E(z) of 10^6 V/m (VASP, PBE GGA). (a, b) The structure of SrH₆ (a) before and (b) after the simulation. (c) Comparison histogram of the Bader charges of the Sr and H atoms before and after the molecular dynamics simulation shows that the charges do not change significantly. (d) Mean-square displacement (MSD) of the hydrogen atoms in different directions (*x*, *y*, *z*), averaged over all hydrogen atoms, calculated considering the shift of the center of gravity of the unit cell. Thermal diffusion in (e, f) P1-SrH₆ at 150 GPa in an external electric field E(z) of 10^4 V/m (MLIP, LAMMPS). (e) Diffusion coefficients obtained at 500, 550, and 600 K using the Einstein equation (mean-square displacement (MSD)-time) from the results of the molecular modeling with a duration of 300 ps. (f) Temperature dependence of the diffusion coefficients interpolated using the Arrhenius formula.



Figure S38. Thermal diffusion in P1-SrH₂₂ at 150 GPa and 600 K in an external electric field E(z) of 10^6 V/m (VASP, PBE GGA). (a, b) The structure of SrH₂₂ (a) before and (b) after the simulation. (c) Comparison histogram of the Bader charges of the H atoms before and after the molecular dynamics simulation shows that the charges do not change significantly. (d) Mean-square displacement (MSD) of the hydrogen atoms in different directions (x, y, z), averaged over all hydrogen atoms, calculated considering the shift of the center of gravity of the unit cell. Thermal diffusion in (e, f) SrH₂₂ at 150 GPa in an external electric field E(z) of 10^4 V/m (MLIP, LAMMPS). (e) Diffusion coefficients obtained at 500, 550, and 600 K using the Einstein equation (mean-square displacement (MSD)-time) from the results of the molecular modeling with a duration of 300 ps. (f) Temperature dependence of the diffusion coefficients interpolated using the Arrhenius formula.



Figure S39. Radial distribution functions g(r) for hydrogen sublattice in $Pm\bar{3}n$ -like P1-SrH₆ at 150 GPa and 600 K calculated after a) 0 ps, b) 10 ps, c) 20 ps and d) 30 ps of molecular dynamics simulation in VASP. At a given temperature and pressure, the hydrogen sublattice is a liquid and demonstrates only a short-range order. Pair separation distance (r) is in Å.



Figure S40. Radial distribution functions g(r) for strontium sublattice in $Pm\overline{3}n$ -like P1-SrH₆ at 150 GPa and 600 K calculated after a) 0 ps, b) 10 ps, c) 30 ps and d) 40 ps of molecular dynamics simulation in VASP. At a given temperature and pressure, the strontium sublattice is a solid and plays the role of a "sponge" for the glassy hydrogen. Pair separation distance (r) is in Å.



Figure S41. Radial distribution functions g(r) for hydrogen sublattice in $Pm\bar{3}n$ -like P1-SrH₆ at 150 GPa and 300 K calculated after a) 0 ps, b) 10 ps, c) 30 ps and d) 50 ps of molecular dynamics simulation in VASP. At a given temperature and pressure, the hydrogen sublattice is a liquid and demonstrates only a short-range order. Pair separation distance (r) is in Å.



Figure S42. Radial distribution functions g(r) for hydrogen sublattice in P1-SrH₂₂ at 150 GPa and 600 K calculated after a) 0 ps, b) 10 ps, c) 20 ps and d) 30 ps of molecular dynamics simulation in VASP. At a given temperature and pressure, the hydrogen sublattice is a molecular liquid and demonstrates only a short-range order. Pair separation distance (r) is in Å. The pronounced maximum of g(r) at 0.7-0.8 Å corresponds to molecular hydrogen.



Figure S43. Radial distribution functions g(r) for strontium sublattice in P1-SrH₂₂ at 150 GPa and 600 K calculated after a) 0 ps, b) 10 ps, c) 20 ps and d) 30 ps of molecular dynamics simulation in VASP. At a given temperature and pressure, the strontium sublattice is a solid and plays the role of a "sponge" for the glassy hydrogen. Pair separation distance (r) is in Å.



Figure S44. Radial distribution functions g(r) for hydrogen sublattice in *P*1-SrH₂₂ at 150 GPa and 300 K calculated after a) 0 ps, b) 20 ps, c) 40 ps and d) 80 ps of molecular dynamics simulation in VASP. At a given temperature and pressure, the hydrogen sublattice is a molecular liquid. Pair separation distance (r) is in Å. The pronounced maximum of g(r) at 0.7-0.8 Å corresponds to molecular hydrogen.



Figure S45. (a, c) Mean-square displacement (MSD) of the hydrogen atoms in different directions (x, y, z), averaged over all hydrogen atoms, calculated considering the shift of the center of gravity of the unit cell of $Pm\overline{3}n$ -like P1-SrH₆ (a) and P1-SrH₂₂ at 150 GPa and 300 K (c, d). Comparison of radial distribution functions g(r) for H-H, Sr-H and Sr-Sr distances in P1-SrH₂₂ at 150 GPa and 300 K. Pair separation distance (r) is in Å. Stabilization of Sr-sublattice is achieved through the interaction of Sr-H coordination spheres, which interact through hydrogen (inset in figure d).

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