Materials by design at high pressures

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Pressure, a fundamental thermodynamic variable, can generate two essential effects on materials. First, pressure can create new high-pressure phases via modification of the potential energy surface. Second, pressure can produce new compounds with unconventional stoichiometries via modification of the compositional landscape. These new phases or compounds often exhibit exotic physical and chemical properties that are inaccessible at ambient pressure. Recent studies have established a broad scope for developing materials with specific desired properties under high pressure. Crystal structure prediction methods and first-principles calculations can be used to design materials and thus guide subsequent synthesis plans prior to any experimental work. A key example is the recent theory-initiated discovery of the record-breaking high-temperature superhydride superconductors H₃S and LaH₁₀ with critical temperatures of 200 K and 260 K, respectively. This work summarizes and discusses recent progress in the theory-oriented discovery of new materials under high pressure, including hydrogen-rich superconductors, high-energy-density materials, inorganic electrides, and noble gas compounds. The discovery of the considered compounds involved substantial theoretical contributions. We address future challenges facing the design of materials at high pressure and provide perspectives on research directions with significant potential for future discoveries.

1 Introduction

Pressure, a fundamental thermodynamic variable, can dramatically reduce interatomic distances and alter chemical bonds to induce structural transformations and new high-pressure phases. In general, each material is expected to experience several structural transformations when compressed up to a pressure of a million atmospheres. Additionally, new oxidation states appearing under high pressure can stabilize new compounds with unconventional stoichiometries. As an example, we can consider the unconventional Na₃Cl and NaCl₃ stoichiometries of Na and Cl that form under pressure rather than the known chemical species NaCl. These new high-pressure phases and compounds often exhibit exotic physical and chemical properties and are thus potentially functional materials. Pressure is therefore an efficient tool in developing new materials that are inaccessible at ambient pressure.

Since the first achievement of lab pressure at ~10 GPa in a so-called large-volume apparatus obtained by Percy Bridgeman in 1905, many high-pressure generating techniques have been developed. This includes the static-pressure generating equipment such as diamond anvil cells (DAC) and large-volume presses (multiple-anvil system, piston-cylinder devices and sealed vessel systems), and large-scale shock-wave facilities that generate dynamic compression. DAC is the most widely used device to generate steady-state pressure with a record upper pressure of above 1000 GPa (ref. 12) achieved by using nano-diamonds as second-stage anvils in double-stage DAC, much higher than that (~30 GPa (ref. 13)) generated by large-volume presses. Dynamic-compression facilities could generate pressures well above terapascal by using shock waves produced by gas guns, laser-driven compression or hemispherically converging explosives, capable of reaching 5000 GPa on a ~1 mm³ sample for a fraction of a second. The fairly high upper frontiers of pressure expanded tremendously the searching space for new functional materials.

Exploration of new materials often involves experimental trial and error, with a range of possible compounds being synthesized and compared to identify the best. This is a time-consuming and expensive process. A classic example is Edison’s testing of approximately 8000 materials over two years to find a material durable enough to provide electric lighting for 1000 hours. An experimental search for target functional materials among the large number of new phases and unconventional compounds available under high pressure would be challenging. Considering hydrides as an example, little experimental progress in these potential high-temperature superconductors was made before 2014 due to the great variety of hydrides at high pressure. Only when theoretical work explicitly identified highly compressed H₂S as a superconductor, the
H₃S superconductor with a critical temperature (Tc) of 200 K was subsequently developed.¹⁵ This demonstrates the successes possible when theoretical and experimental efforts are applied together to the discovery of new materials at high pressure.

Developments in crystal structure prediction (CSP) and first-principles calculations have improved the accuracy of the prediction of the structures and properties of new phases and unconventional compounds formed at high pressure, thus prompting the discovery of new materials by design.¹⁵–²⁰ Unbiased CSP methods without any experimental input can predict the energetically most stable or metastable structures at a given pressure, leading to the construction of the phase diagram of a considered system. First-principles calculations can simulate the mechanical, thermal, optical, electronic, and magnetic properties of these high-pressure unconventional compounds and the pressure and temperature conditions for their synthesis, thus allowing theoretical findings to guide the choice of experiments attempted. In 2011, the U.S.A., Japan, and China successively announced the Materials Genome Projects, aiming to combine theory and experiment to accelerate the development of new materials.

Theoretical design for high-pressure synthesis has aided several major experimental discoveries of new materials. A milestone example is the theory-initiated discovery of the record-breaking high-temperature superconductors H₃S¹⁴,¹⁵,²¹ and LaH₁₀ (ref. 6, 7, 22 and 23) with Tc values of 200 K and 260 K, respectively. Other discoveries include high-density-energy materials (e.g., cg-N²⁴,²⁵ layered Pb₂H₂ polymeric nitrogen,²⁶ and LiN₅ (ref. 27)), inorganic electrides (e.g., Na₆⁴ Ca,N₇,²⁸ and Sr₃P₃ (ref. 29)), and noble gas compounds (e.g., XeFe₅,⁴ XeNi₃,⁴ Na₂He,³ and XeO₂ (ref. 30)).

This review surveys these materials, with particular emphasis on their theory-oriented discovery at high pressure. First, we highlight the effect of pressure on materials and discuss the stabilization of new materials. Second, the theoretical methods for material design, especially CSP methods, are discussed. Third, we summarize and discuss recent discoveries of materials at high pressure initiated by theoretical design. We particularly focus on hydrogen-rich superconductors, high-energy-density materials, inorganic electrides, and noble gas compounds. Our work concludes with descriptions of the main drawbacks of high-pressure materials and a discussion of the possible solutions and future research directions. Actually, these available reviews²⁴,²⁵ either focus on new materials with a given function such as superconductivity, or summarize all designed materials at high pressure. Here, our review intends to summarize those materials discovery initiated by theoretical design at high pressure, with a purpose to highlight the leading role of structure prediction in material discovery.

2 Effect of pressure on materials

High pressure provides two main routes to stabilize new materials. First, the decrease in the interatomic distance under compression redistributes valence electrons and alters bonding patterns, thereby effectively modulating the relative energetic stability of possible structures on the potential energy surface and generating new high-pressure phases via structural transformations. A typical example is the pressure-induced phase transformation of sp²-hybrid graphite to sp³-hybrid diamond.¹⁴ Pressure helps overcome the energy barrier for the conversion between the two carbon phases, making diamond the global energy minimum. Each element or compound undergoes several structural transformations at high pressure. For example, at least six phase transformations have been observed or predicted for the alkali metal Na (bcc → fcc [65 GPa] → ct16 [103 GPa] → t19 [156 GPa] → hP4 [200 GPa] → aP8 [1.75 TPa] → c124 (>15.5 TPa)),¹⁶ among which the transformation into the transparent hP4 phase is particularly interesting as it characterizes a so-called anti-Wilson transition, i.e., transformation of a good metal into an insulator, that violates the traditional wisdom of Wilson transition.¹⁵ Many high-pressure phases with exotic properties have been discovered with potential applications, including superconducting phases (e.g., H₃S¹⁴ and AlH₃ (ref. 36)), polymeric nitrogen (e.g., cg-N²⁴,²⁵ LP-Pb₂ (ref. 26) and LP-N²⁷), and electrides (e.g., Li²⁸ and Na¹⁶,³⁵).

Pressure can also stabilize compounds and phases by reordering the energies of outer atomic orbitals, causing charge transfer between different orbitals, thus modifying the chemical identity of atoms via the appearance of new oxidation states and leading to the formation of unconventional compounds that are inaccessible at ambient pressure. For example, the alkali metal Cs shows oxidation states of +3 and +5 at high pressure rather than the +1 state observed at ambient pressure, as evidenced by the unconventional CsF₃ and CsF₅ compounds predicted at high pressure in addition to the typical CsF²⁹ known at ambient pressure. Another example is the formation of compounds of the inert element Xe. Its fully occupied 5p valence states can be partially excited to unoccupied orbitals at high pressure, activating the Xe 5p electrons to form compounds such as XeFe₅.⁴ Advanced structure prediction methods have predicted various unconventional compounds formed at high pressure that have since been experimentally confirmed, including high-Tc superconducting hydrides (e.g., H₃S¹⁴,¹⁵,²¹ LaH₁₀,⁶⁷ YH₆,⁴⁸ and C–S–H⁴¹,⁴³), high-energy-density nitrogen-rich compounds (e.g., LiN₅ (ref. 27) and CsN₂ (ref. 43)), electrides (e.g., Sr₃P₃ (ref. 29) and Na₂He,³), and noble gas compounds (e.g., XeFe₅,⁴ XeNi₃,⁴ and Na₂He,³).

3 Theoretical methods for material design

The crystal structure is one of the most fundamental pieces of information needed to characterize a material. Its prediction for a given compound at high pressures without any prior information is therefore a primary task in material design. This is now possible due to the development of CSP methods such as Crystal structure AnalYsis by Particle Swarm Optimization (CALYPSO) (based on particle swarm optimization⁴⁴,⁴⁵), ab initio random structure searching (AIRSS) (based on random sampling⁴⁶), Universal Structure Predictor: Evolutionary Xtallography (USPEX) (based on a genetic algorithm⁴⁷), Xtallography.
Optimization (XtalOpt),\textsuperscript{48} Global Space-Group Optimization (GSGO),\textsuperscript{49} and Evolutionary Algorithm (EVO).\textsuperscript{50}

These methods have been proven efficient in identifying the global energy minimum among the vast number of local minima on the potential energy surface, making them powerful tools for materials by design.\textsuperscript{51–61} Consider, for example, a binary system formed by elements A and B; material-by-design research requires construction of a convex hull map of composition vs. formation enthalpy to screen the thermodynamically most stable stoichiometries. This can be achieved via systematic structure predictions of candidate A\textsubscript{x}B\textsubscript{y} stoichiometries at selected pressures through the combination of CSP and first-principles calculations. Once the most stable structure of each A\textsubscript{x}B\textsubscript{y} is obtained, a formation enthalpy vs. composition convex hull can be constructed to screen out the thermodynamically stable compounds. The convex hull presents also the possible precursors to synthesize the candidate stable compounds, providing essential information to guide the subsequent experiments. Finally, the useful properties (e.g., electronic band structure, phonons, and electron-phonon coupling parameters, etc.) of the stable compound can be simulated by performing first-principle calculations.

4 Theory-oriented discovery of pressure-induced materials

Here, we summarize and discuss recent accomplishments in material discovery at high pressure initiated by theoretical design. These materials include hydrogen-rich superconductors, high-energy-density materials, inorganic electrides, and noble gas compounds.

4.1 Hydrogen-rich superconductors

Room-temperature superconductivity is the holy grail of condensed-matter physics. Before 2014, there is no report on

| Materials | Brief description | Year | References |
|-----------|------------------|------|------------|
| H–S       | The first theoretical prediction of H\textsubscript{3}S with 80 K superconductivity at 160 GPa | 2014 (September) | 14 |
|           | Theoretical prediction of H\textsubscript{3}S with ~200 K superconductivity at 200 GPa | 2014 (November) | 21 |
|           | Experimental confirmation of the superconductivity in compressed H\textsubscript{2}S and the observation of the record 203 K superconductivity | 2015 | 15 |
|           | Experimental confirmation of the pressure-driven disproportionation of H\textsubscript{2}S to H\textsubscript{3}S, contributing the 203 K superconductivity | 2016 | 66 and 69 |
| C–S–H     | Theoretical prediction of a metastable CSH\textsubscript{7} with 190 K superconductivity at 150 GPa | 2021 (April) | 42 |
|           | Theoretical prediction of a metastable CSH\textsubscript{7} with 181 K superconductivity at 100 GPa | 2021 (May) | 41 |
|           | Experimental synthesis of CSH\textsubscript{7} with 288 K superconductivity at 267 GPa | 2021 (October) | 20 |
| LaH\textsubscript{10} | Theoretical prediction of LaH\textsubscript{10} with 255–288 K superconductivity at 250 GPa | 2017 | 6 and 7 |
|           | Experimental observation of superconductivity at 260 K in LaH\textsubscript{10} by compressing La and hydrogen at 200 GPa | 2019 (January) | 22 |
|           | Experimental observation of superconductivity at 250 K in LaH\textsubscript{10} by compressing NH\textsubscript{3}BH\textsubscript{3} and La at 170 GPa | 2019 (May) | 23 |
| CaH\textsubscript{6} | The first predicted clathrate hydride with superconductivity of 235 K at 150 GPa | 2012 | 79 |
|           | Experimental synthesis of CaH\textsubscript{6} with 215 K superconductivity at 172 GPa | 2021 | 81 |
the $T_c$ values that have ever exceeded 40 K for conventional superconductors. Hydrogen-rich compounds at high pressure have long been sought as high $T_c$ superconductors. However, the large amount of unknown hydrogen-containing compounds that can possibly exist under high pressure poses a great challenge to experimentalists seeking candidate hydrides to test. Little progress was initially made experimentally, but theoretical designs of hydrogen-rich superconductors by the aid of CSP methods have led to a series of experimental breakthroughs. The two main categories of superconducting hydrides discovered thus far are the covalent $\text{H}_3\text{S}$ and the ionic clathrate structured, the superconductivity of which arises mainly through $\text{S}–\text{H}$ covalent bonds and caged $\text{H}$ sublattices with encaged metals, respectively (Table 1).

4.1.1 Covalent hydrides. The first breakthrough in this field was the observation by Drozdov et al. of remarkable high-temperature superconductivity ($T_c = 203$ K) in compressed $\text{H}_2\text{S}$. This was inspired by a theoretical prediction that $\text{H}_2\text{S}$ transforms at 160 GPa to new metallic high-pressure phases with potential superconductivity (maximum estimated $T_c = 80$ K), which contrasts with a previous supposition that $\text{H}_2\text{S}$ decomposes into its constituent elements before metallization and suggests that new $\text{H}–\text{S}$ compounds could exist at high pressure. The superconductivities measured by Drozdov et al. for samples prepared at low temperature agree well with the estimates for $\text{H}_2\text{S}$ (Fig. 1a). An accidental finding was that a sample prepared at high temperature exhibited superconductivity at temperatures as high as 203 K under 155 GPa, which originated from the pressure-driven disproportionation of $\text{H}_2\text{S}$ to $\text{H}_3\text{S}$, as confirmed by subsequent theoretical and experimental studies (Fig. 1b).

Notably, van der Waals compound $\text{(H}_3\text{S)}_2\text{H}_2$ (i.e., $2\text{H}_2\text{S}$) was synthesized in 2011 (ref. 70) and $\text{H}_3\text{S}$ was later predicted to adopt a highly symmetric cubic structure showing a potential of high temperature superconductivity with an estimated $T_c \approx 200$ K at 200 GPa.

Theoretical studies have demonstrated that strong covalent bonding is a key determinant of the high superconductivity in $\text{H}_3\text{S}$, thus providing a new route to design superconducting hydrides. Many attempts have been made to design covalent superconducting hydrides, including $\text{H}_3\text{Se}$, $\text{PH}_2$, $\text{PH}_3$, $\text{TeH}_4$, $\text{H}_2\text{Cl}/\text{Br}/\text{I}$, $\text{H}_6\text{SSe}$, and $\text{C}–\text{S}–\text{H}_2$ as summarized in Fig. 2. Two independent theoretical studies in early 2020 proposed that the intercalation of methane (CH$_4$) into the $\text{H}_3\text{S}$ framework forms a new candidate superconductor, $\text{CSH}_7$, with an estimated $T_c$ of 100–190 K. This proposal stimulated subsequent experimental synthesis of $\text{CSH}_x$ by compressing elemental C, S, and $\text{H}_2$ above 4 GPa, where a maximum $T_c$ of ~288 K at ~267 GPa (ref. 20) was claimed. However, the undetermined value of $x$ and lack of structural information prevent elucidation of the origin of the superconductivity. We expect future experimental confirmation from an independent group for the record high superconductivity observed in $\text{CSH}_x$ and theoretical studies, especially those using CSP, may help provide further details on the structures.

4.1.2 Clathrate hydrides. Another breakthrough was the observation of 260 K superconductivity in the clathrate superhydride $\text{LaH}_{10}$ under pressure (Fig. 3a). The experimental work investigated two independent theoretical predictions of pressure-stabilized $\text{LaH}_{10}$ containing $\text{H}_32$ cages with high superconductivity (257–288 K at 250 GPa). $\text{CaH}_6$ containing sodalite-like $\text{H}_{24}$ cages was the first predicted clathrate hydride (in 2012); it shows a high $T_c$ of 235 K at 150 GPa. The same sodalite-like $\text{H}_{24}$ cage was later predicted in $\text{YH}_6$ (ref. 40) and $\text{MgH}_{61}$ which show high $T_c$ values of 264 K and 260 K at 120 GPa. Notably, the predicted high superconductivities of

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**Fig. 1** (a) Comparison of the calculated and measured $T_c$ for $\text{H}_2\text{S}$ pressurized at low temperature. Insets show two predicted structures. (b) Comparison of the calculated and measured $T_c$ for $\text{H}_2\text{S}$ pressurized at high temperature. The inset shows the predicted structure.
both CaH$_6$ and YH$_6$ have been experimentally confirmed, with $T_c$ values of 215 K (at 172 GPa)$^{81}$ and 260 K (at 120 GPa)$^{82,83}$ respectively.

Theoretical studies have established the crucial contribution of hydrogen cages to the high superconductivity of the above clathrate hydrides. The cages represent another pathway to the design of high-$T_c$ superconductors, namely, pressure-stabilized clathrate superhydrides. Ref. 11 proposed that there is common rule for the formation of clathrate structures in rare-earth (RE) superhydrides with appearing three different H$_{24}$, H$_{29}$, and H$_{32}$ cages in stoichiometric superhydrides of REH$_6$, REH$_9$, and REH$_{10}$, respectively. Subsequent theoretical attempts have further confirmed hydrogen cages as common species at high pressure.$^6,7,82–94$ Fig. 4a summarizes the cage-structured hydrides predicted at high pressure, most of which show high superconductivity, such as $T_c$ at 473 K in H$_{18} +$ H$_{28}$ cage-structured Li$_2$MgH$_{16}$,$^{88} T_c$ at $\sim$146–243 K in H$_{29}$ cage-structured Y(Ce, Th)H$_{29}$,$^6,83,94$ $T_c$ at 150–303 K in H$_{32}$ cage-structured Y(Th, Ac)H$_{10}$,$^6,7,83,93$ and $T_c$ at 173 K in H$_{10}$ cage-structured Ach$_{12}$.$^{93}$ Besides the above mentioned experimental confirmation on the theoretical prediction of high superconductivity in CaH$_6$ and YH$_6$, subsequent experimental studies have also confirmed high superconductivity in, for example, YH$_{10}^{95}$ CeH$_{11}^{91}$ ThH$_{8}^{92}$ and ThH$_{10}$ (ref. 92) with measured $T_c$ values at $\sim$262, 110, 146 and 160 K, respectively. These successful examples on the theory-orientated finding of high $T_c$ superconductors among pressure-stabilized superhydrides demonstrate that the leading role of theoretical methods.

4.1.1 Challenges and future directions. Theoretical studies have revealed the existence of diverse hydrogen species at high pressure that can lead to high-$T_c$ superconductivity. For example, SrH$_6$ containing H$_3$ units, SnH$_{12}$ containing H$_4$ units, ScH$_9$ containing H$_5$ units, and HfH$_{10}$ containing H$_{10}$ units have predicted $T_c$ values of 156 K (250 GPa), 93 K (250 GPa), 163 K (300 GPa), and 234 K (250 GPa), respectively.$^{96–102}$ However, currently, no general mechanism can accurately predict the $T_c$ of hydrides. For example, H$_{32}$ cage-structured PrH$_{10}$ has a low $T_c$ of 1.4 K,$^{89}$ demonstrating that not all hydrogen cage-structured hydrides possess high superconductivity. Fortunately, there are some indicators of high superconductivity. As summarized in Fig. 4b, high-$T_c$ hydrides will have a high contribution of H-states at the Fermi level; without this, the $T_c$ is low. This represents a convenient way to assess whether a predicted hydride is a high-$T_c$ superconductor, as calculations of the electronic density of states are much less time consuming than those of electron–phonon coupling parameters that are necessary for calculation of $T_c$.

The superconducting $T_c$ of hydrides can be estimated by using the Allen–Dynes modified McMillan equation, which is suitable for those compounds with electron-phonon coupling parameter ($\lambda$) less than 1.5. However, the recent studies have demonstrated that certain superhydrides have very strong electron-phonon coupling parameters $\lambda$ (e.g., 2.19 for H$_4$S, 2.69 for CaH$_6$, and $\sim$4 for Li$_2$MgH$_{16}$), posing a challenge to use Allen–Dynes modified McMillan equation for the calculation of the $T_c$ values for the predicted hydrides. An alternative method is to estimate $T_c$ directly from the spectral function ($\alpha^2\Gamma(\omega)$) by...
numerically solving the Eliashberg equations,\textsuperscript{188} which gives a better description of systems with $\lambda$ larger than 1.5.

A limitation of high-$T_c$ hydrides is that their stability is maintained only under extremely high pressures, which precludes any immediate practical application. A research aim is therefore to search for superhydrides that can be synthesized at moderate pressures and are quenchable to ambient conditions as metastable phases. Currently, ternary hydrides display high potential as high-$T_c$ superconductors, as exemplified by CSH$_x$ (288 K)\textsuperscript{20} and Li$_2$MgH$_{16}$ (473 K).\textsuperscript{88} We expect that the relatively more complex interactions in ternary systems could form hydrides at moderate pressures. Theoretical predictions, especially those employing CSP methods, will undoubtedly play a key role in achieving this goal.

4.2 Polymeric nitrogen

Solid nitrogen at ambient pressure adopts a diatomic molecular form, characterized by strong triple N≡N bonds within each N$_2$ molecule (Fig. 5a). High pressure can efficiently break the triple bonds to form single N–N bonds, allowing the formation of polymeric phases. The large energy difference between the single (~160 kJ mol$^{-1}$) and triple (~954 kJ mol$^{-1}$) bonds means that the transformation from single to triple bonds releases much energy, making polymeric nitrogen or nitrides containing N–N bonds ideal high-energy-density materials. Theoretical studies have guided experimental efforts to synthesize the proposed high-energy-density materials. Here, we provide an overview of recent discoveries initiated by theoretical design of high-energy-density materials at high pressure, specifically polymeric nitrogen crystals and N-rich compounds (Table 2).

4.2.1 Pure nitrogen. This field emerged in 1985, when a new phase of nitrogen solely composed of single-bonded nitrogen atoms was first predicted by computational simulation to be stable at ~50 GPa (ref. 104) (cg-N, Fig. 5b). Experiments have attempted to synthesize cg-N; however, only amorphous products, probably composed of small clusters of nonmolecular phases, were initially obtained during compression at room temperature. In 2004, however, a transparent single-bonded cubic phase was first synthesized at ~110 GPa and 2000 K;\textsuperscript{24,25} it was found to be the theoretically predicted cg-N. This successful synthesis, initiated by theoretical design, greatly promoted the exploration of other types of polynitrogen under high pressure. In addition to the three-dimensional cg-N, another polymeric phase of nitrogen with a layered black phosphorus structure (BP–N, Fig. 5c) was also proposed at high

Fig. 4 (a) Summary of the computed (green) and measured (blue) $T_c$ of several typical superconducting superhydrides. (b) Proportion of H-s electron states at the Fermi level for selected superconducting superhydrides.
(a) alpha-N  
(b) cg-N  
(c) BP-N  
(d) Pba2-N  
(e) I-43m-N  
(f) P42bc-N.

Fig. 5  Crystal structures of (a) alpha-N, (b) cg-N, (c) BP-N, (d) Pba2-N, (e) I-43m-N, and (f) P42bc-N.

4.2.2 Nitrogen-rich compounds. Polymeric nitrogen, stabilized by highly compressing pure nitrogen, has yet to be recovered under ambient conditions, precluding its application as a high-energy-density material. Nitrides are potential alternatives that can form single N–N bonds at lower pressure. Alkali metal azides AN₃ (A = Li, Na, K, Rb, or Cs) containing double N=N bonded linear N₃⁻ anions initially attracted attention, as double N=N bonds with lower bonding energy (418 kJ mol⁻¹) than triple N≡N bonds could transform to single bonds much more easily than pure N₂. Indeed, theoretical studies have shown that azides can polymerize at low pressures of ~50 GPa, with the formation of pseudobenzene N₆ rings containing both double N=N and single N–N bonds (Fig. 6). However, the pressures needed to form three-dimensional polymerized Nitridic N₅₅ nitride, with the formation of pseudobenzene N₆₆ N₆ rings containing both double N=N and single N–N bonds (Fig. 6).
are sometimes much higher than those predicted, different to the cases in most of other compounds. A plausible explanation is that the triple $\text{N}≡\text{N}$ bond is the strongest bond in nature, making a need for an extra pressure or temperature to overcome the energy barrier for the transformation of a triple bond into a single bond. For example, in actual experiments, an extra pressure of $\sim60$ GPa evidences as compared to the theoretical one for the synthesis of cg-N and WN$_6$. However, it is still a challenge to evaluate the exact extra pressure needed to synthesize the predicted nitrides. One might calculate energy barrier by using methods such as climbing image nudged elastic band for a good estimation of the aforementioned extra pressure. Besides the above mentioned theoretical examples that received the subsequent experimental confirmation, many other proposed nitrogen-rich compounds$^{130–135,142–146}$ are to be verified, representing significant challenges to experimentalists. Furthermore, although nitrogen-rich compounds could be synthesized at low pressure and even recovered under ambient conditions, their energy densities are lower than that of pure cg-N due to the introduction of other elements, for example, $3.48\text{ kJ g}^{-1}$ in MgN$_{10}$ (ref. 147) and $5.39\text{ kJ g}^{-1}$ in BeN$_{10}$. Theoretical studies have identified two candidate routes to design new materials with high energy density. One is to search for nitrides with extremely high nitrogen contents, such as HeN$_{22}$ whose energy density reaches 10.44 kJ g$^{-1}$. The other is to design pure polymeric nitrogen by removing the non-N elements from compounds that can be obtained at high pressure; for example, polymeric t-N has been predicted to be achievable by removing He from HeN$_4$ (ref. 149) and to have a high energy density of 11.3 kJ g$^{-1}$. We expect that further study using CSP methods can help design alternative N-containing high-energy-density materials for their future synthesis.

### 4.3 Inorganic electrides

Electrides represent a distinct class of ionic compounds, in which electrons distributed in lattice cavities or channels can occupy non-nuclear orbitals and serve as anions individually rather than being attached to atoms. They are potentially useful as catalysts, electron donors, and reducing agents due to their unique physicochemical properties. At the pressures currently achievable, the hybridized valence electrons could be repulsed by core electrons into lattice interstices when compression is sufficiently strong that atomic cores start to overlap, leading to the formation of electrides. Therefore, pressure application is an efficient approach to the design of electrides. Their formation under high pressure is often accompanied by changes in electronic properties, for example, the metal–insulator transition in alkali metals or the emergence of superconductivity. Little progress was made in the experimental synthesis of electrides until the development of computational approaches for screening electrode materials. Here, we introduce some important progress in the theory-guided discovery of electrides, including elemental Na and Li and the binary systems of Ca$_2$N and Sr$_2$P$_3$ (Table 3).

#### 4.3.1 Alkali metal electrides

Alkali and alkaline-earth metals such as Li, Na, K, Rb, Cs, Mg, and Ca
tend to form electrides at high pressure due to the strong overlap of core electrons from two neighboring atoms. Na is a typical electride whose discovery was guided by theory. In 2019, Ma et al. predicted an unusual phenomenon of anti-Wilson transition: a good metal of sodium becomes a transparent insulator at megabar pressures, violating the wisdom of traditional Wilson transition, an accepted trend of high pressures favoring metallicity. Electronic calculations revealed strong localization of valence electrons in the lattice interstices induced by the overlap of core–core electrons, making hP4-Na an electrode analogous to the NiIn-type structure, where the ionic cores form the Ni sublattice and the interstitial density maxima form the quasiatom In sublattice. Interestingly, photographs taken under combined transmitted and reflected illumination revealed that Na becomes optically transparent at pressures of 200 GPa, signaling a metal-to-insulator transformation. X-ray diffraction (XRD) observation of transparent Na confirmed the hP4 structure of insulating Na, proving the formation of electrode Na at high pressure. Li was observed two-dimensional (2D) electride with excess electrons, making them potential electrides; therefore, high pressure provides many opportunities to search for new electrides. Theoretically, identifying an electride by simulating, for example, the electron localization function, electronic density, or charge-density difference, is easy. However, experimental investigations face significant challenges, as localized electrons are hardly detected. Verification of the theoretically predicted electrides generally involves indirect probes such as XRD, transport, X-ray photoemission spectroscopy, magnetic susceptibility, and angle-resolved photoemission spectroscopy (ARPES) measurements, with comparison of observed and calculated results. An ARPES measurement of Y2C indicated that electron–hole electrode bands exist near the Fermi energy, as predicted by ab initio calculations, suggesting that Y2C is indeed a 2D electrode. Noteworthy, ARPES only detects ambient-pressure electrides owing to its incompatibility with high-pressure set-ups. Therefore, theoretical simulations play a key role to discover high-pressure electrides.

### Table 3: Examples of theory-initiated discovery of inorganic electrides under high-pressures

| Materials | Brief description | Year | References |
|-----------|------------------|------|------------|
| Na        | Na is predicted and observed to form an insulating electrode at 200 GPa | 2019 | 16         |
| Li        | Li is predicted to form a semiconducting electrode at 60–80 GPa | 2011 | 38         |
| Ca₂N      | Ca₂N is predicted to transform into a zero-dimensional insulating electrode at 9.7 GPa | 2017 | 28         |
|           | Experimental observation of Li electrode above 60 GPa | 2011 | 158 and 159|
|           | Experimental confirmation of the insulating electrode Ca₂N at 11 GPa | 2018 | 161        |

Fig. 7 Three-dimensional electron localization function maps of (a) hP4-Na at 200 GPa, (b) anti-CdCl₂-type Ca₂N at ambient pressure, and (c) I₄2d Ca₂N at 20 GPa to show electron localization in the lattice interstices.
4.4 Chemistry of noble elements

Noble elements are characterized by their full electron shells and chemical inertness. The long-held belief that an element cannot react further if it has full valence orbitals was questioned with the first theoretical proposal of the chemical reaction of Xe by Pauling in 1933 (ref. 168) and disproved with the first synthesis of XePtF6 in 1962 by Neil Bartlett. Noble gases are common in the universe and are generally considered to exist only in planetary atmospheres rather than in their interiors due to their chemical inertness. Recent studies using CSP methods have predicted a large number of noble gas compounds that are stable at high pressures and temperatures corresponding to the conditions inside the earth or large icy planets. These compounds are therefore essential to the understanding of the interior structure of planets.\textsuperscript{4,170–177} Here, we summarize the theory-guided synthesis of noble gas compounds, paying particular attention to Xe and He compounds (Table 4).

4.4.1 Xe-bearing compounds. Studies of Earth’s atmosphere have shown that more than 90% of the expected amount of Xe is depleted, a finding often referred to as the missing Xe paradox. It represents one of the most challenging enigmas of planetary science. Theoretical studies have provided feasible explanations to help resolve the paradox. Theoretical calculations suggest that Xe could be trapped as solid compounds inside the Earth’s inner core, as indicated by the predicted reactions of Xe with Fe and Ni (the main constituents of the core) to form XeFe3 and XeNi3 (ref. 4) (Fig. 8a and b). Subsequently, XeFe3 and XeNi3 have been successfully synthesized at high pressures of 210 and 150 GPa, respectively.\textsuperscript{18,19} The XRD patterns of these compounds are well indexed to the predicted structures, highlighting the key role of CSP methods in aiding the discovery of unknown materials.

Theoretical calculations also uncovered the reason for the emergence of chemical activity in Xe at high pressure. The full 5p shell of Xe opens at high pressure, making Xe a 5p-like element with the ability to transfer electrons to Fe or Ni. This form of Xe has been predicted to react with many other elements or molecules at high pressure to produce, for example, XeFe3,\textsuperscript{10} XeN6,\textsuperscript{178} LiXe,\textsuperscript{179} MgXe,\textsuperscript{165} XeF3,\textsuperscript{180} Xe2O12H12,\textsuperscript{181} Xe2FeO2,\textsuperscript{170} CsXe,\textsuperscript{182} and Xe–H2.\textsuperscript{183–185} Among these, Xe2O2 and XeN6 were subsequently synthesized. The reactivity of Xe with O was previously confirmed to occur at pressures as low as 3 GPa, with the formation of the van der Waals compound Xe(O2)2.\textsuperscript{186} Later, CSP methods predicted the formation of a new XeO2 (Fig. 8c) compound above 75 GPa.\textsuperscript{30} Recent experiments successfully synthesized this compound (at 97 GPa) as well as the unpredicted compound Xe2O3 (88 GPa).\textsuperscript{17} A prediction of Xe–N was made at pressures of 100–300 GPa, with the finding of stable XeN6 above 146 GPa, indicating the reactivity of Xe with N2.\textsuperscript{176} These elements were later experimentally reacted at much lower pressure (5 GPa) to form the van der Waals compound Xe(N2)2.\textsuperscript{187} Much higher pressures are needed to synthesize the predicted stoichiometric XeN8.

4.4.2 He-bearing compounds. As the most chemically inert element, helium is generally considered to be uncatchable inside ice giants such as Uranus and Neptune, and it may exist only in their gaseous atmospheres. Surprisingly, recent theoretical and experimental efforts have demonstrated the chemical reactivity of helium at high pressure and temperature, \textit{via} a theory-initiated discovery of the He-bearing Na3He compound (Fig. 8d), which was predicted to be stable above 160 GPa, with later experimental confirmation.\textsuperscript{19} The high-pressure chemical activity suggests the possibility of helium being trapped with compounds inside the ice giants. Recent theoretical works have explored possible stable compounds formed by helium and the interior components of ice giants (e.g., CH4, NH3, and H2O). CSP methods have predicted many such compounds at high pressure and temperature conditions corresponding to those in planet interiors, such as He(NH3)3,\textsuperscript{172} He(H2O)2,\textsuperscript{173,174} He2H2O,\textsuperscript{174} He2H2O,\textsuperscript{174} He2CH4,\textsuperscript{176} and HeCH4.\textsuperscript{179} Some of these compounds were predicted to have

| Materials       | Brief description                                      | Year  | References |
|-----------------|-------------------------------------------------------|-------|------------|
| XeFe3 (XeNi3)  | Theoretical predictions of stable XeFe3 and XeNi3 above 200 and 150 GPa, respectively | 2014  | 4          |
|                | Experimental synthesis of XeNi3 at ~150 GPa           | 2017  | 18         |
|                | Experimental synthesis of XeFe3 and XeNi3 at 210 and 155 GPa, respectively | 2018  | 19         |
| Xe2O2          | Theoretical prediction of stable Xe2O2 above 75 GPa   | 2014  | 30         |
|                | Experimental synthesis of Xe2O2 at 97 GPa             | 2016  | 17         |
| Na2He          | Theoretical prediction and experimental confirmation of Na2He at high pressure | 2017  | 5          |

Fig. 8 Predicted and confirmed crystal structures of (a) XeFe3, (b) XeNi3, (c) Xe2O2, and (d) Na2He.
a superionic characteristic. Although these predicted compounds have yet to be confirmed, these theoretical results might be helpful for the understanding of the planet interior models and planets’ evolution.

A recent theoretical study demonstrated that helium could also be trapped in Earth’s lower mantle by the prediction of stable FeO2He. Helium was even predicted to react with a broad range of ionic A2B- and AB2-type compounds, such as Li2O, CaF2, and MgF2, and react with nitrogen to form stable HeN4, HeN6, HeN10, and HeN22 (ref. 148) at high pressures. A common feature of these compounds is the formation of host-guest structures with guest helium atoms intercalated into the lattice interstices, with almost no charge transfer between helium and the other elements. These predicted He compounds have yet to be experimentally confirmed.

### 4.4.3 Challenges and future directions

The formation of stable noble gas compounds at high pressure goes against the traditional notion of nonreactivity in elements with full electron shells. As few of these predicted compounds have been experimentally confirmed, there remain notable challenges for experiments. The confirmed Xe or He compounds reveal two future research directions. One is the continuing exploration of stable compounds formed at high pressures and high temperatures by noble elements with components inside planets (e.g., MgO, FeO2, SiO2, Al2O3, CaO, CaSiO3, and MgSiO3), with the aim of improving models of planetary interiors. The other is the design of functional materials by stabilizing these compounds at high pressure, as illustrated by the case of high-energy-density t-N obtained from pressure-stabilized HeN4. The incorporation of helium could effectively modulate the structures and properties of known compounds, thus providing a new pathway to design functional materials. Furthermore, other noble elements also show chemical activity at high pressure, with (N3)2Ne7 being experimentally observed at above 8 GPa. Therefore, future attention might be paid to pressure-stabilized Ne, Ar, and Ke compounds.

### 5 Outlook

In addition to the abovementioned examples, other types of functional materials have been frequently discovered at high pressure, such as superhard, ferromagnetic, ferroelectric, optoelectronic, catalytic, negative compressibility, and thermoelectric materials where theory can also play a vital role in aiding the discovery. Though CSP-based theory is quite successful for the design of materials, challenges remain, in particular for large simulation systems, which contain usually a large number of atoms in the simulation cells, reaching several hundreds and thousands of atoms. The number of the candidate structures increases exponentially with the increasing number of atoms in the simulation system, leading to an extremely complex potential energy landscape with a tremendous number of energy minima for a large system.

Generally, one has to optimize all candidate structures to find the global energy minima, however, a practical problem is that the much time-consuming geometry optimizations makes it is apparently unaffordable for the available first-principles methods. Also, for ternary or quaternary systems, the existence of huge candidate compositions results in unbearable complicated composition landscape, posing a big challenge for the current first-principle methods to calculate the countless possible structures. One strategy might be considered on the development of alternative algorithms that guarantee fast and reliable calculations on total energy and geometry optimization. Force field methods, machine learning potentials, and linear scaling methods (e.g., orbital free density functional theory) might be relied on, but particular caution must be taken for the transferability of the method in dealing with entirely different structures. Besides the use of machine learning potentials, machine learning technique (e.g., deep learning, etc.) can offer an alternative opportunity to aid the material discovery. As a data-driven method, machine learning uses large amounts of data to continuously optimize models and to make reasonable predictions under the guidance of algorithms. Generally, high-quality data can be selected as training and testing sets from the available material databases, such as Open Quantum Material Database, Material Project, Computational Materials Repository, Inorganic Crystal Structure Database, AFDLOWLIB, and CALYPSO structure database, as well as those obtained by local structure optimizations of plenty of structures generated by CSP methods.

The products via high-pressure experiments are largely influenced by many factors, such as the precursors, the grain size of sample, the rate of pressure rise, as well as the temperature used. The current theoretical methods are ready to predict the static crystal structures at a given pressure and zero temperature, however, the lack of the study on the dynamic process of material formation provides no information about the synthetic pathway. A reaction pathway describes the successive steps at the molecular level that takes place in a chemical reaction, while a deep understanding of all reaction pathways is essential to explore the evolution of a system over time given a set of initial conditions such as precursors, pressure and temperature. This provides insight into the choices of reaction conditions that can affect the overall reaction outcome, purity, and reaction rates. The use of CSP simulations in combination with the method for calculations of kinetic energy barriers (KEB) for the chemical reaction or phase transition may help to screen out the possible synthetic routes, thus narrowing down the scope of the experiment trials. To obtain the KEB, one has to find out the minimum energy path and transition state from the astronomically large number of possible solutions. The calculation of KEB can be achieved by a recent reported evolution strategy combining a matrix particle swarm optimization algorithm and an improved nudged elastic band method with the knowledge of the initial state and the final state. However, there is lack of a generally applicable technique on how to account for the dynamic environment of a reacting system with quantum accuracy, posing a challenge for the investigation of the KEB. It is believed that the development of useful strategy to probe the mechanism of chemical reaction is one of the essential issues to accelerate the material discovery initialized by theoretical design.
**Data availability**

Figures, tables and detailed crystallographic information are available from the corresponding author by request.

**Author contributions**

All authors contributed to the preparation of the manuscript. M. X. and Y. L. participated in original draft writing and graphic visualization. Y. M. contributed to the substantial revision of the original draft.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (Grant No. 12074154, 11904142, and 11722433), the Major Program of the National Natural Science Foundation of China (Grant No. 52090024), and the National Key R&D Program of China (Grant No. 2018YFA0305900).

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