

First-principles investigation of structural, hydrogen storage, and physical properties of M_2CaZnH_6 ($M = K, Rb, Cs$) double perovskite hydrides

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Abstract

The urgent need for clean renewable energy has stimulated extensive researches into hydrogen storage materials. Double perovskite hydrides have emerged as promising candidates due to their tunable structures and excellent storage capabilities. This study employs first-principles to systematically investigate the structural, hydrogen storage, mechanical, electronic, and optical properties of M_2CaZnH_6 ($M = K, Rb, Cs$) perovskites. The results reveal that the hydrogen storage capacities of M_2CaZnH_6 ($M = K, Rb, Cs$) are 3.19, 2.14, and 1.60 wt.%, and the desorption temperatures are 835, 589, and 247 K respectively.

Mechanical stability was verified by the elastic constants. K_2CaZnH_6 is ductile, while Rb_2CaZnH_6 and Cs_2CaZnH_6 exhibit brittle behavior. Electronic structure reveals their semiconductor characteristics, and optical properties demonstrate high absorption in the ultra-violet (UV) region, indicating potential applications in UV photodetectors. These findings highlight the potential of M_2CaZnH_6 as versatile materials for hydrogen storage.

Key words: hydrogen storage, double perovskite hydrides, DFT calculations, physical properties

1. Introduction

Global warming and the depletion of fossil fuel reserves have driven an urgent transition toward renewable energy sources. Hydrogen (H_2) has emerged as a frontrunner among clean energy carriers due to its exceptional energy density (142 MJ kg^{-1}) and zero greenhouse gas emissions during combustion [1, 2]. However, the widespread adoption of hydrogen energy is hindered by the lack of safe, efficient, and cost-effective storage technologies. Conventional methods such as high-pressure tanks and cryogenic liquefaction suffer from safety risks, high energy consumption, and significant volumetric inefficiencies. Solid-state hydrogen storage materials, particularly metal hydrides and perovskite hydrides, offer a viable alternative by enabling hydrogen storage under moderate temperature and pressure conditions [3, 4].

Double perovskite hydrides, characterized by the

general formula A_2BCR_6 ($A = \text{alkali/alkaline earth cation}$, $B/C = \text{transition metals}$, $R = \text{hydride anion}$), have garnered increasing attention due to their structural flexibility, high hydrogen content, and tunable physicochemical properties [5–7]. The incorporation of different A-site cations allows for systematic modulation of lattice parameters, bonding interactions, and hydrogen storage performance [8]. Previous studies on double perovskite hydrides such as Na_2CaCdH_6 and Cs_2CaTiH_6 have demonstrated their potential for hydrogen storage, though their gravimetric capacities ($\leq 1.78 \text{ wt.}\%$) remain limited [7, 9, 10]. Magnesium and titanium-based perovskites have shown higher storage capacities, but the exploration of zinc-containing double perovskite hydrides remains scarce.

Zinc-based compounds offer unique advantages such as low toxicity, abundance, and favorable electronic configurations that can stabilize hydride bonds

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(H^-) within the perovskite lattice [11]. The M_2CaZnH_6 ($M = K, Rb, Cs$) system represents an underexplored class of double perovskite hydrides, where the variation of A-site alkali metals (K, Rb, Cs) provides an opportunity to study the effects of ionic radius and electronegativity on material properties. To date, no comprehensive theoretical investigation has been conducted on the structural stability, hydrogen storage capability, and multifunctional properties of these compounds.

This study aims to fill this research gap by performing DFT-based calculations to investigate the structural, hydrogen storage, mechanical, electronic, and optical properties of M_2CaZnH_6 ($M = K, Rb, Cs$) perovskites. The specific objectives include: (1) Establish whether these compounds are thermodynamically and mechanically stable; (2) Calculate the gravimetric hydrogen storage capacity and dehydrogenation temperature, compare the performance with reported hydrides, and analyze the essential reasons for the complementary relationship between capacity and desorption temperature; (3) Calculate elastic constants and derived mechanical parameters, clarify the ductile/brittle nature and elastic anisotropy of the materials, and discuss their adaptability to cyclic hydrogen absorption and desorption; (4) Characterize electronic band structure and density of states, explore orbital hybridization between atoms, and build the link between electronic structure, bonding nature and hydrogen storage behavior; (5) Analyze dielectric function, reflectivity and absorption coefficient, reveal optical transition mechanisms, and evaluate the application potential of the materials in ultraviolet photodetectors. The findings provide valuable insights for the design and development of advanced hydrogen storage materials and expand the application scope of double perovskite hydrides.

2. Computational method

All DFT calculations were performed using the CASTEP software package [12], a plane-wave pseudopotential-based code widely used for ab initio simulations of solid-state materials. The exchange-correlation potential was described by the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [13], which is well-suited for predicting structural, mechanical, and electronic properties of hydride materials [7, 14]. Norm-Conserving Pseudopotentials (NCP) were employed to represent the core-valence electron interactions, ensuring accurate description of bonding between metal cations and hydride anions. A cutoff energy of 700 eV was selected for the plane-wave basis set, based on convergence tests showing that energy differences below 1×10^{-6} eV/atom were achieved. The Brillouin

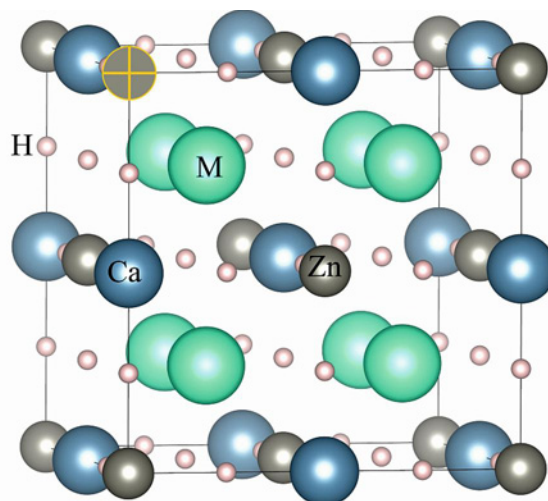


Fig. 1. Crystal structure of M_2CaZnH_6 ($M = K, Rb, Cs$) double perovskite hydride materials.

zone integration was performed using a Monkhorst-Pack k -point mesh of $6 \times 6 \times 6$ [15], which balanced computational efficiency and accuracy for cubic perovskite structures. Geometry optimization was carried out using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm with strict convergence criteria: energy convergence of 5.0×10^{-6} eV/atom, maximum force of 0.01 eV/Å, maximum stress of 0.02 GPa, and maximum displacement of 5.0×10^{-4} Å.

3. Results and discussion

3.1. Structure properties

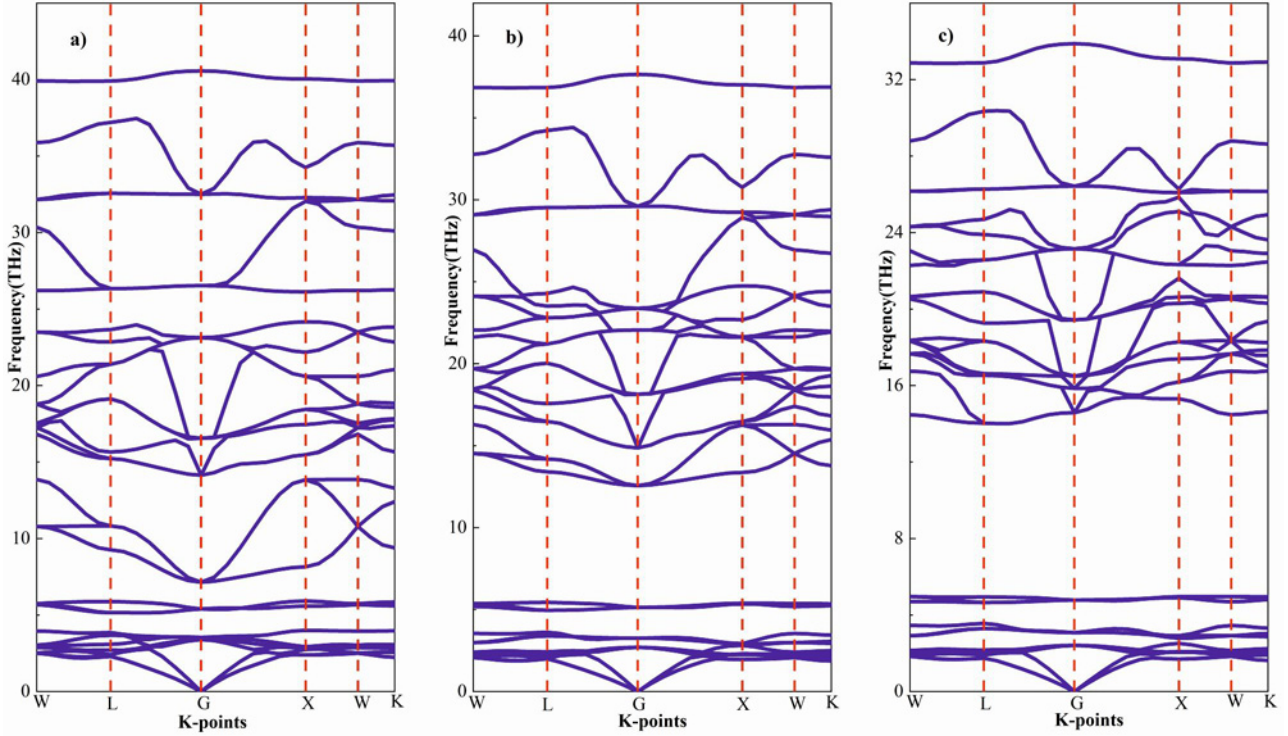
The optimized crystal structures of M_2CaZnH_6 ($M = K, Rb, Cs$) is presented in Fig. 1. All compounds adopt a cubic double perovskite structure belonging to the $Fm-3m$ (space group 225) symmetry, consistent with the general A_2BCR_6 configuration [7, 16]. In this structure, A-site cations (K, Rb, Cs) occupy the (0.25, 0.25, 0.25) positions, Ca ions are located at the center (0.5, 0.5, 0.5), Zn ions occupy the (0.0, 0.0, 0.0) sites, and hydride anions (H^-) are positioned at (0.25, 0.0, 0.0), forming $[ZnH_6]^{6-}$ octahedra that corner-share to form the cubic lattice.

Table 1 presents the key structural parameters of M_2CaZnH_6 perovskites. The lattice constant ($a = b = c$) increases linearly with the ionic radius of the A-site cation (K: 1.38 Å, Rb: 1.52 Å, Cs: 1.67 Å), resulting in unit cell volumes of 511.62, 532.23, and 560.29 Å³ for K_2CaZnH_6 , Rb_2CaZnH_6 , and Cs_2CaZnH_6 , respectively. This trend is attributed to the larger ionic radii of heavier alkali metals, which expand the lattice to accommodate the cations [8]. The density (ρ) also increases with the atomic weight of X, rang-

Table 1. Structural parameters, hydrogen storage and hydrogen desorption properties of $M_2\text{CaZnH}_6$ ($M = \text{K}, \text{Rb}, \text{Cs}$)

Compounds	$a = b = c$ (Å)	V (Å ³)	ρ (g cm ⁻³)	E_f (eV)	$C_{\text{wt.}\%}$ (wt.%)	T_{des} (K)
K_2CaZnH_6	7.998	511.62	2.46	-1.131	3.19	835
$\text{Rb}_2\text{CaZnH}_6$	8.104	532.23	3.53	-0.798	2.14	589
$\text{Cs}_2\text{CaZnH}_6$	8.244	560.29	4.47	-0.334	1.60	247

Notes: $a = b = c$ are Lattice constants, V is unit cell volume, ρ is density, E_f is formation energy, $C_{\text{wt.}\%}$ is gravimetric hydrogen storage capacity, and T_{des} is hydrogen desorption temperature.

Fig. 2. Phonon dispersion of $M_2\text{CaZnH}_6$ ($M = \text{K}, \text{Rb}, \text{Cs}$): (a) K_2CaZnH_6 , (b) $\text{Rb}_2\text{CaZnH}_6$, and (c) $\text{Cs}_2\text{CaZnH}_6$.

ing from 2.46 g cm⁻³ of K_2CaZnH_6 to 4.47 g cm⁻³ of $\text{Cs}_2\text{CaZnH}_6$, which is consistent with the increasing unit cell mass.

The formation energy (ΔE_f) is a critical indicator of thermodynamic stability, with negative values indicating spontaneous formation of the compound, which can be calculated as follow equation:

$$\Delta E_f = E_{\text{t}(\text{M}_2\text{CaZnH}_6)} - (2E_{\text{M}} + E_{\text{Ca}} + E_{\text{Zn}} + 3E_{\text{H}_2}), \quad (1)$$

where $E_{\text{t}(\text{M}_2\text{CaZnH}_6)}$ is the total energy of the perovskite, and E_{M} , E_{Ca} , E_{Zn} , and $3E_{\text{H}_2}$ are the ground-state energies of the respective elemental species and H_2 molecule.

As shown in Table 1, all $M_2\text{CaZnH}_6$ perovskites exhibit negative ΔE_f values, demonstrating that these compounds can form spontaneously from constituent elements under 0 K. Among them, K_2CaZnH_6 has the most negative formation energy of -1.131 eV, indi-

cating the highest single-phase formation tendency; as the A-site cation changes from K to Rb and Cs, the absolute value of formation energy gradually decreases to -0.798 and -0.334 eV, respectively. This trend originates from the increasing ionic radius of alkali metal cations: larger Rb^+ and Cs^+ expand the crystal lattice, enlarge the distance between A-site cations and $[\text{ZnH}_6]^{6-}$ octahedral groups, weaken the electrostatic interaction between cations and anionic clusters, and consequently reduce the overall lattice bonding strength. Combined with the reported results of similar double perovskite hydrides such as $\text{Cs}_2\text{CaCdH}_6$ and $\text{Na}_2\text{CaCdH}_6$ [7, 16], the formation energy of K_2CaZnH_6 in this work is more negative, which also proves that Zn-based double perovskite hydrides have better thermodynamic synthesis potential than Cd-based systems.

It should be noted that formation energy alone cannot fully determine the practical synthesizability and

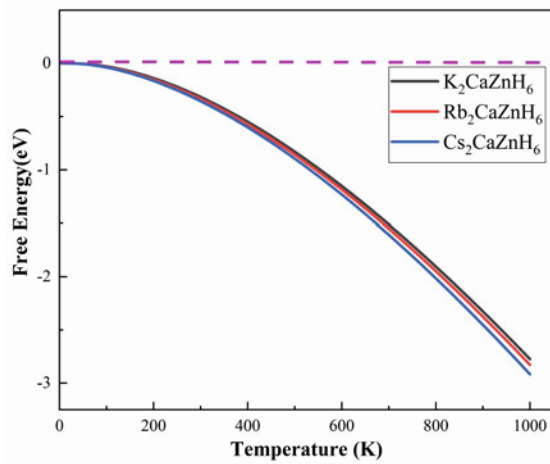


Fig. 3. Temperature of free energy of $M_2\text{CaZnH}_6$ ($M = \text{K}, \text{Rb}, \text{Cs}$).

relative phase stability of a material under real conditions. As pointed out by the convex hull approach for thermodynamic stability analysis [17], accurate evaluation of phase stability requires comprehensive comparison of the total energies of all competing phases in the multicomponent composition space. A negative formation energy only confirms the thermodynamic possibility of forming a single $M_2\text{CaZnH}_6$ phase, but cannot exclude the existence of more stable competing phases. Constructing a complete convex hull phase diagram for this quaternary M-Ca-Zn-H system involves massive calculations of numerous competing hydrides, elemental phases and intermediate phases, which is beyond the scope of the current work.

In addition to thermodynamic feasibility evaluated by formation energy, we further calculated phonon dispersion curves to assess the dynamic stability of the three hydrides (Fig. 2). It can be seen that $M_2\text{CaZnH}_6$ ($M = \text{K}, \text{Rb}, \text{Cs}$) show no imaginary frequencies across the entire Brillouin zone, confirming their dynamic stability at 0 K. The positive phonon frequencies in the full Brillouin zone indicate that the lattice atoms of the three hydrides will not undergo spontaneous displacement or lattice distortion under low temperature conditions, which is a basic prerequisite for their long-term stable hydrogen storage service. The gradual shift of phonon frequency peak position with A-site cation substitution also reflects the change of lattice vibration mode caused by mass difference of alkali metal cations.

To further quantitatively evaluate the thermal stability of the three hydrides under varying temperatures, we calculated the temperature-dependent Helmholtz free energy (F) via phonon dispersion calculations within the quasi-harmonic approximation (QHA) [24], as presented in Fig. 3. The Helmholtz free energy follows the formula $F = E_{\text{total}} + F_{\text{vib}}$, where

E_{total} represents the static ground-state total energy derived from DFT calculations and F_{vib} stands for the vibrational free energy contribution acquired from the phonon density of states.

As illustrated in Fig. 3, the free energy of all three $M_2\text{CaZnH}_6$ phases declines monotonically with rising temperature, a characteristic thermodynamic feature driven by the entropic term ($-TS$). Throughout the entire 0–1000 K temperature window, the free energy of each compound maintains negative values without upward inflection or crossing, demonstrating that all three hydrides retain favorable thermodynamic stability as temperature increases. Moreover, obvious free energy gaps persist between the three curves up to 1000 K, revealing that structural destabilization triggered by temperature is improbable under conventional hydrogen storage working conditions. These thermal free energy results collectively verify that such Zn-containing double perovskite hydrides are promising materials for reversible hydrogen storage applications.

3.2. Hydrogen storage capacity

The gravimetric hydrogen storage capacity ($C_{\text{wt.}\%}$) is a key metric for evaluating hydrogen storage materials. The gravimetric hydrogen storage capacity ($C_{\text{wt.}\%}$) was calculated using the formula [18]:

$$C_{\text{wt.}\%} = \left(\frac{\left(\frac{H}{M} \right) m_{\text{H}}}{m_{\text{Host}} + \left(\frac{H}{M} \right) m_{\text{H}}} \right) \times 100\%, \quad (2)$$

where m_{H} is the molar mass of hydrogen, m_{Host} is the molar mass of the host perovskite, and H/M is the ratio of hydrogen atoms to total atoms in the compound.

As calculated from the formula in Section 2, the $C_{\text{wt.}\%}$ values for K_2CaZnH_6 , $\text{Rb}_2\text{CaZnH}_6$, and $\text{Cs}_2\text{CaZnH}_6$ are 3.19, 2.14, and 1.60 wt.%, respectively (see in Table 1). The decreasing $C_{\text{wt.}\%}$ with increasing atomic weight of X is due to the higher molar mass of heavier alkali metals, which reduces the relative contribution of hydrogen to the total mass of the compound.

While these values are lower than those of high-capacity hydrides such as $\text{Li}_2\text{MgTiH}_6$ [1] and Mg_2FeH_6 [5], they still outperform conventional double perovskite hydrides like $\text{Cs}_2\text{CaCdH}_6$ (1.39 wt.%) [7] and $\text{Cs}_2\text{CaTiH}_6$ (1.78 wt.%) [19]. Moreover, K_2CaZnH_6 delivers 3.19 wt.%, edging out even NaAlH_4 whose usable capacity is effectively limited by poor reversibility rather than by its theoretical 3.7 wt.%[20].

Essentially, the gravimetric hydrogen storage capacity of the double perovskite hydride is determined by the ratio of total hydrogen mass to the molecular

weight of the whole crystal. With the sequential substitution of K, Rb, and Cs, the atomic weight of A-site alkali metal increases significantly. Although the number of hydrogen atoms in a single unit cell remains unchanged, the total molecular mass of the hydride increases sharply, which directly leads to the continuous decline of relative hydrogen mass fraction. Compared with Cd and Tl elements with larger atomic weight used in previous double perovskite hydrides [7, 19], Zn has lower atomic mass, which is the fundamental reason why the M_2CaZnH_6 system in this work achieves higher gravimetric hydrogen capacity. From the perspective of practical application, 3.19 wt.% hydrogen capacity of K_2CaZnH_6 has reached the medium level of metal hydride hydrogen storage materials, which has basic application value.

3.3 Desorption temperature

The desorption temperature (T_{des}) determines the practicality of hydrogen storage materials, with the U.S. Department of Energy (DOE) targeting a range of 233–333 K (–40 to 60 °C) for automotive applications [21, 22]. The hydrogen desorption Temperature (T_{des}) is likewise a pivotal factor for hydrogen storage materials, and the formula for calculating their hydrogen desorption temperature is as follows:

$$T_{des} = \frac{\Delta H}{\Delta S}. \quad (3)$$

In the formula (Eq. (3)), ΔH denotes enthalpy change of hydrogen desorption and ΔS represents the entropy change of desorption. Following the well-established convention in first-principles studies of hydrogen storage materials [7, 22], the entropy change of hydrogen desorption (ΔS) is approximated by the standard entropy of gaseous H_2 molecule at room temperature ($130.7 \text{ J mol}^{-1} \text{ K}^{-1}$).

As shown in Table 1, the T_{des} values of M_2CaZnH_6 perovskites decrease with increasing cation size: $T_{K_2CaZnH_6} > T_{Rb_2CaZnH_6} > T_{Cs_2CaZnH_6}$. The hydrogen desorption temperature is positively correlated with the bond dissociation energy of H^- in the lattice. Larger Cs^+ ions expand the unit cell, increase the distance between $[ZnH_6]^{6-}$ octahedra and peripheral cations, weaken the overall lattice constraint on hydride anions, and lower the energy barrier for H_2 desorption. In contrast, smaller K^+ has strong electrostatic restraint on H^- , resulting in a high desorption temperature that requires high temperature to drive hydrogen release. This trend is attributed to the weaker bonding between larger A-site cations and H^- anions, which reduces the energy required for hydrogen release.

The hydrogen desorption Temperature (T_{des}) of Cs_2CaZnH_6 is 247 K, which falls within the DOE tar-

Table 2. Mechanical property parameters of M_2CaZnH_6 (M = K, Rb, Cs) hydrides

	K_2CaZnH_6	Rb_2CaZnH_6	Cs_2CaZnH_6
C_{11}	45.009	44.348	45.066
C_{12}	24.163	22.375	21.170
C_{44}	23.239	26.680	29.050
B (MPa)	31.112	29.700	29.135
E (MPa)	45.507	46.349	49.502
ν	0.256	0.240	0.217
G (MPa)	16.845	18.691	20.341
B/G	1.847	1.589	1.432
C_p	0.924	–4.305	–7.880
A	2.723	3.030	3.457

Notes: B is bulk modulus, E is Young modulus, ν is Poisson ratio, G is shear modulus, C_p is Cauchy pressure, and A is anisotropy factor.

get range, making it a promising candidate for near-ambient hydrogen storage. Such a low desorption temperature means that Cs_2CaZnH_6 can realize hydrogen desorption under refrigeration or normal temperature conditions, avoiding the high energy consumption caused by high-temperature heating in traditional hydride systems. In view of the excessively high desorption temperature of K_2CaZnH_6 and Rb_2CaZnH_6 , combining with the existing modification strategies of hydrides, transition metal doping or nanostructure refinement can further optimize the local bonding environment of H^- , reduce the hydrogen desorption barrier, and improve their practicability [23].

3.4 Mechanical properties

Mechanical stability and performance are essential for hydrogen storage materials, as they must withstand volume changes during hydrogenation/dehydrogenation cycles. The elastic constants (C_{11} , C_{12} , C_{44}) of M_2CaZnH_6 perovskites are presented in Table 2. For cubic crystals, mechanical stability is verified by the Born criteria [24]:

$$C_{11} - C_{12} > 0, C_{11} - 2C_{12} > 0, C_{11} > 0, C_{44} > 0. \quad (4)$$

All compounds satisfy these criteria, confirming their mechanical stability.

The bulk modulus (B) represents resistance to uniform compression. The decreasing B with increasing cation size indicates that larger lattices are more compressible, consistent with the expanded unit cell volumes [25]. Young's modulus (E) increases from 45.507 GPa of K_2CaZnH_6 to 49.502 GPa of Cs_2CaZnH_6 , suggesting that Cs_2CaZnH_6 is the stiffest among the three compounds. The shear modulus (G) also increases with cation size, indicating enhanced resistance to shear deformation.

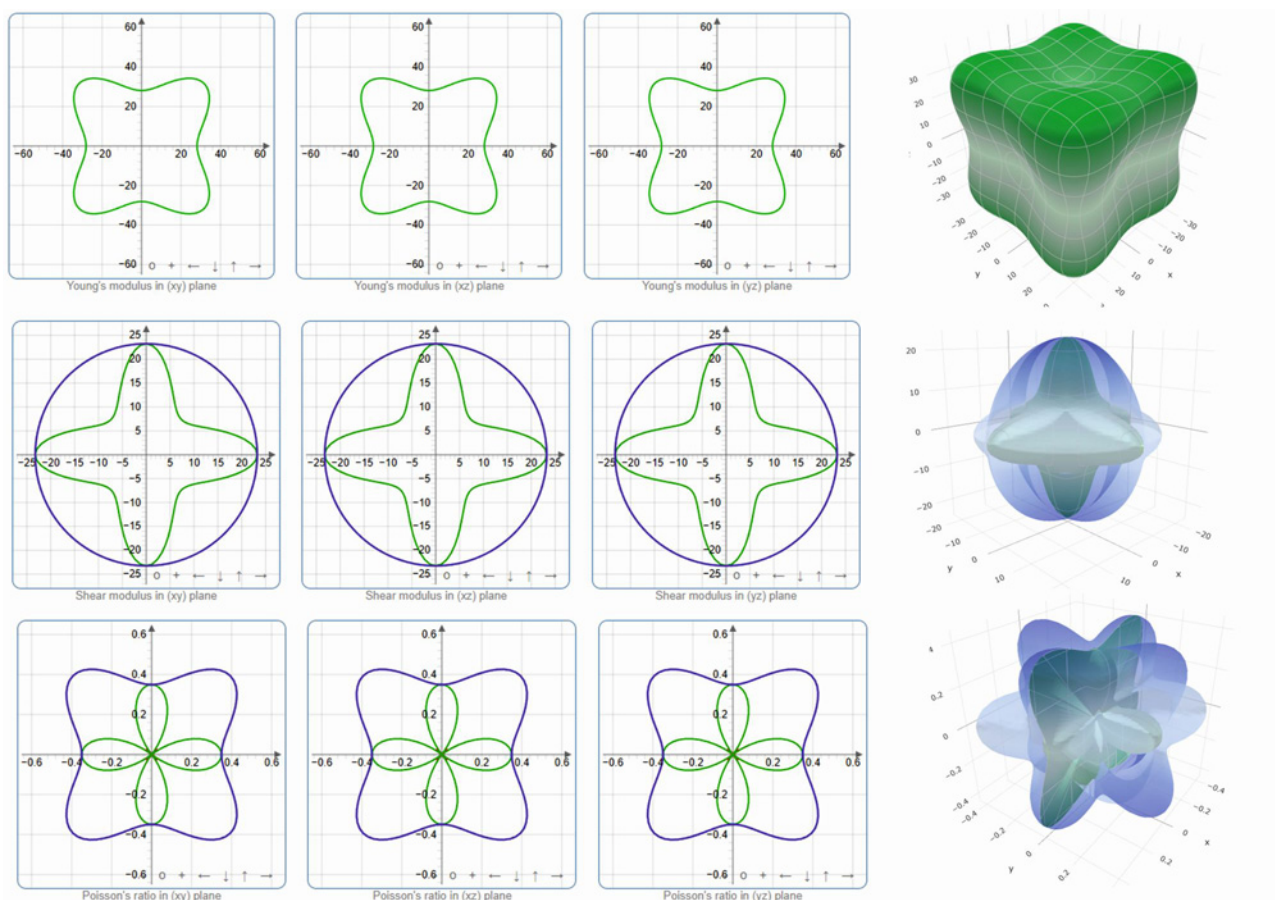


Fig. 4. K_2CaZnH_6 , 2D and 3D, visualization of Elastic Moduli.

The B/G ratio is used to distinguish ductile ($B/G > 1.75$) and brittle ($B/G < 1.75$) materials [26]. Our calculated B/G ratios indicated that K_2CaZnH_6 is ductile, while Rb_2CaZnH_6 and Cs_2CaZnH_6 exhibit brittle behavior. In the process of hydrogen absorption and desorption, hydride materials will produce periodic volume expansion and contraction. The ductile characteristic of K_2CaZnH_6 enables it to adapt to cyclic volume deformation and avoid lattice cracking, which is conducive to improving cycle stability; while brittle Rb_2CaZnH_6 and Cs_2CaZnH_6 are prone to structural damage under repeated volume changes, which is an unfavorable factor for long-cycle hydrogen storage application. Poisson's ratio (ν) values of these three hydrides, close to 0.25, suggesting predominantly ionic bonding [12]. Cauchy pressure ($C_p = C_{12} - C_{44}$) is negative confirmed brittle characteristics for Rb_2CaZnH_6 and Cs_2CaZnH_6 [27].

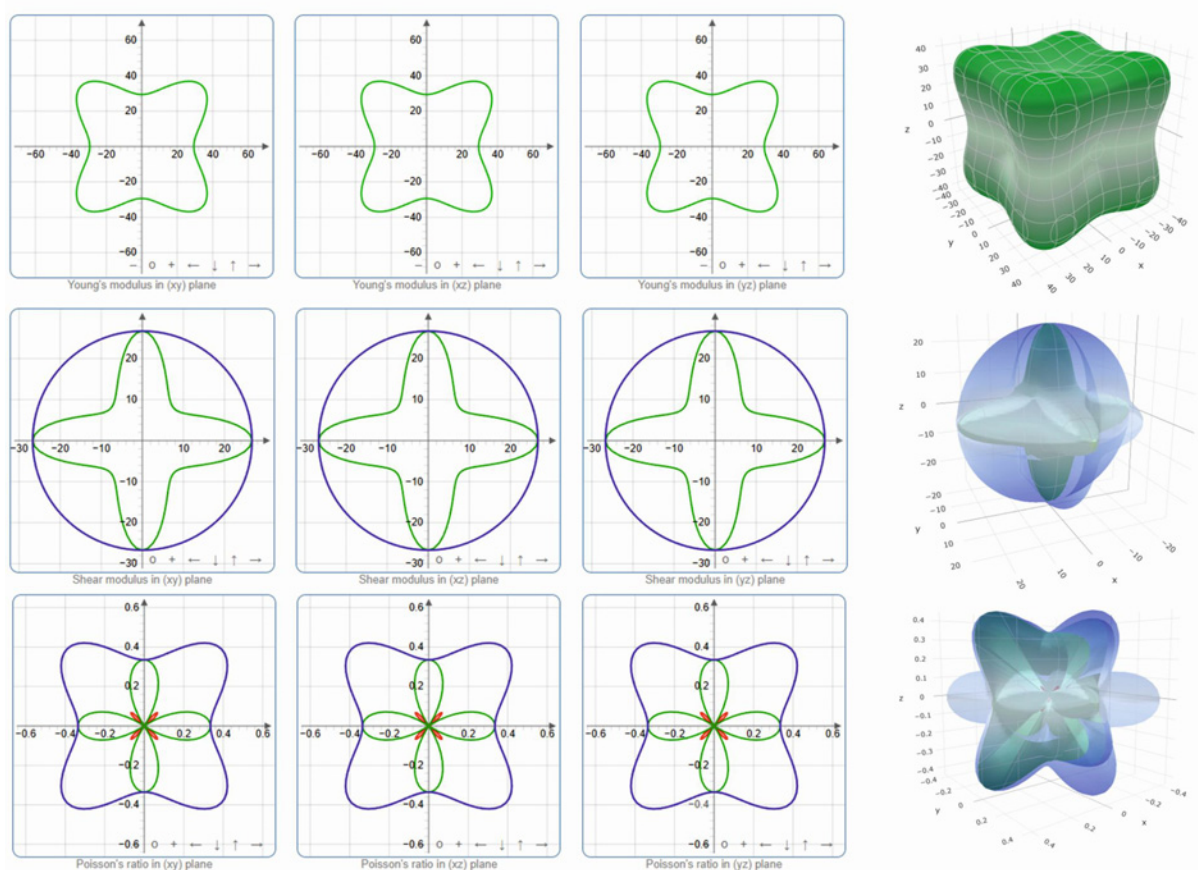
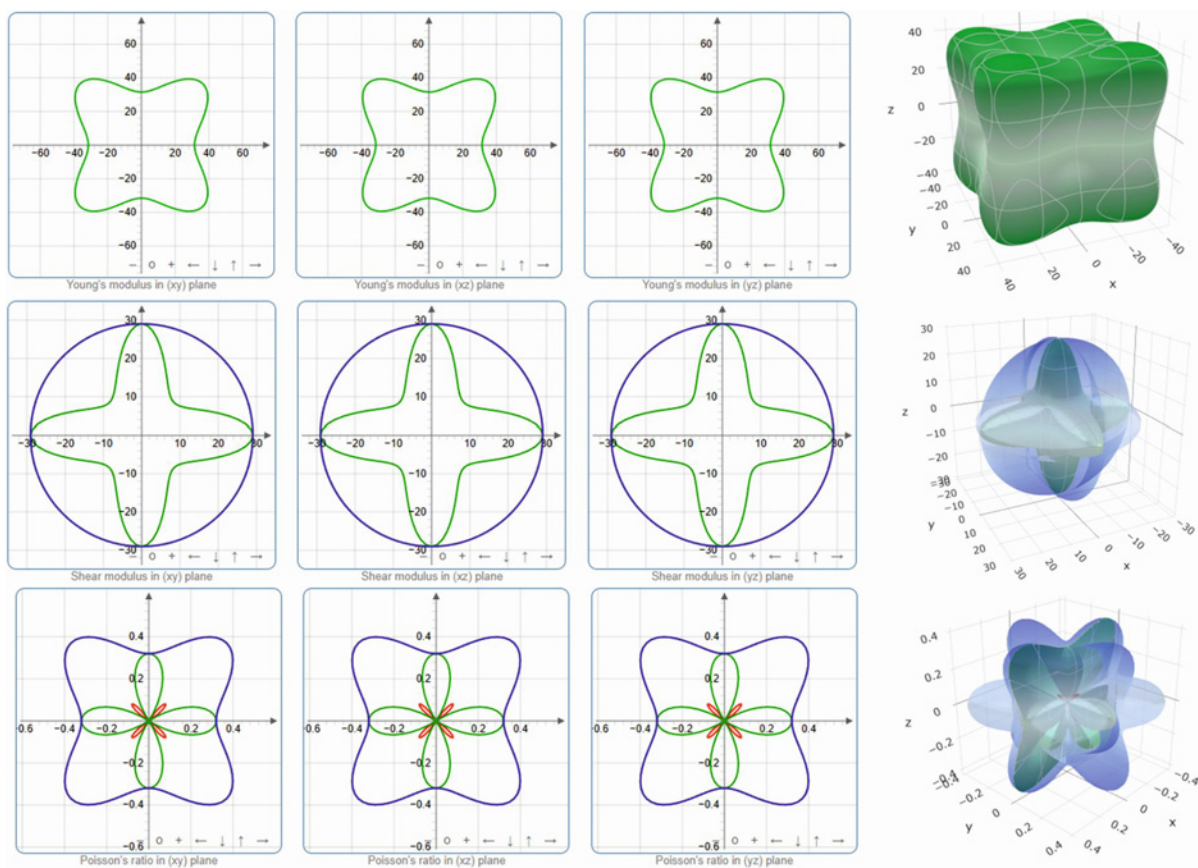
The anisotropy factor (A) is calculated as $A = 2C_{44}/(C_{11} - C_{12})$, with $A = 1$ indicating isotropic behavior. The values of three compounds indicate significant anisotropy, which is visualized in the 2D and 3D elastic modulus plots (Figs. 4–6). The deviation from spherical symmetry in the 3D plots confirms anisotropic mechanical responses, with Cs_2CaZnH_6

showing the highest anisotropy due to the asymmetric distribution of large Cs cations in the lattice. This anisotropy may influence hydrogen diffusion pathways, as mechanical properties vary with crystallographic direction [28]. The higher elastic anisotropy of Cs_2CaZnH_6 means that the lattice stiffness differs greatly in different crystal directions, which will form preferential channels for the migration of H^- anions in the lattice. This directional diffusion characteristic is beneficial to accelerate the hydrogen absorption and desorption kinetics, which also explains why Cs_2CaZnH_6 has a lower hydrogen desorption temperature from the perspective of mechanical lattice.

3.5. Electronic properties

The electronic structure of hydrogen storage materials is closely related to their structural stability, bonding characteristics, and hydrogen adsorption-desorption behavior, as it determines the distribution of electron states and the interaction mechanism between constituent atoms. The electronic band structures and density of states (DOS) of M_2CaZnH_6 ($M = K, Rb, Cs$) are presented in Figs. 6 and 7, respectively.

As shown in Fig. 7, all three compounds ex-

Fig. 5. $\text{Rb}_2\text{CaZnH}_6$, 2D and 3D, visualization of Elastic Moduli.Fig. 6. $\text{Cs}_2\text{CaZnH}_6$, 2D and 3D, visualization of Elastic Moduli.

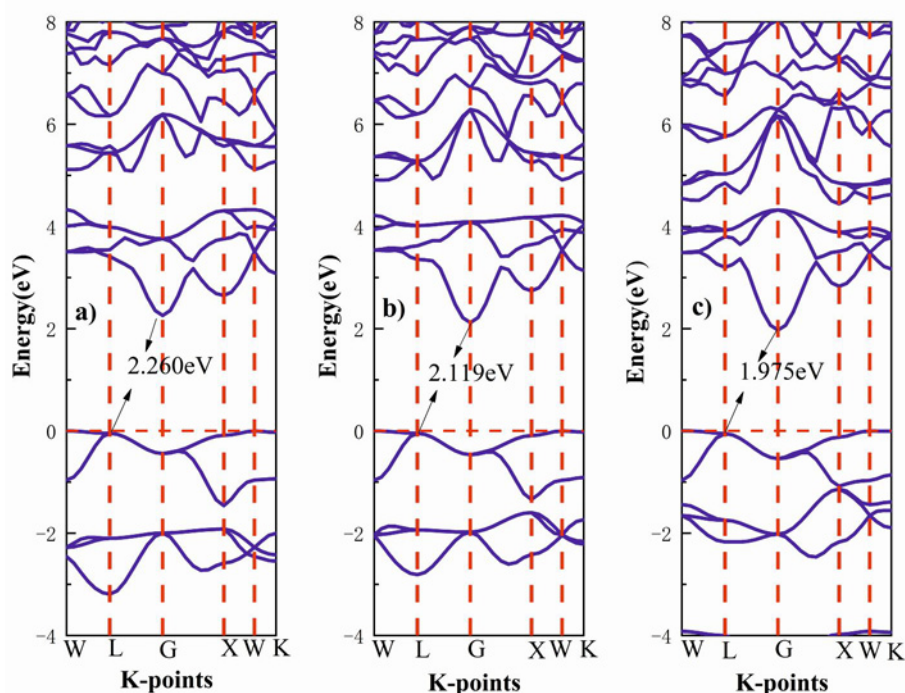


Fig. 7. Band structure of M_2CaZnH_6 ($M = K, Rb, Cs$).

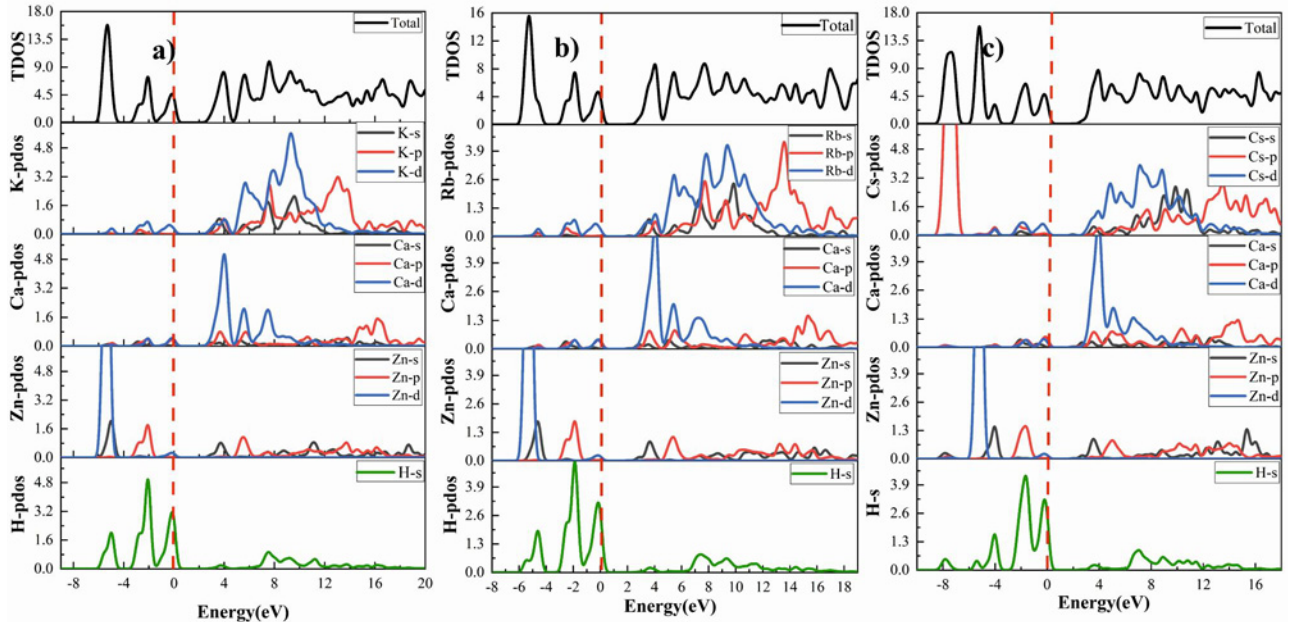
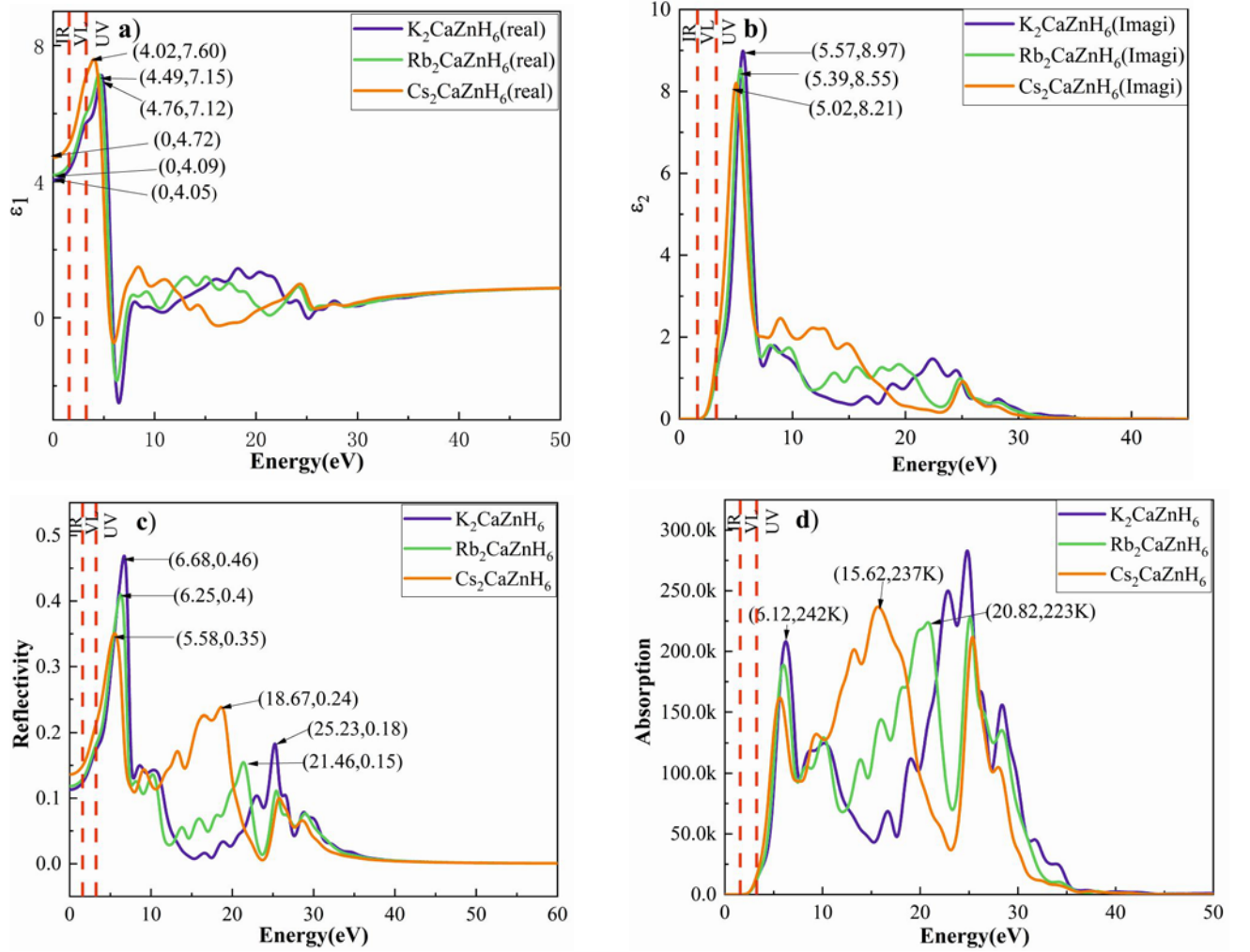
hibit typical semiconductor characteristics with distinct band gaps, and the band gap type is identified as indirect band gap. For three compounds of M_2CaZnH_6 , an indirect band gap is observed. The valence band maximum (VBM) is located along the Γ -X direction, while the conduction band minimum (CBM) is at the G point. The calculated fundamental band gap is approximately 2.26, 2.119, and 1.975 eV for K_2CaZnH_6 , Rb_2CaZnH_6 , and Cs_2CaZnH_6 , respectively. It is necessary to clarify here that the Generalized Gradient Approximation (GGA-PBE) functional adopted in this work is a widely used method for structural and mechanical calculation of solid materials, but it is a common consensus in DFT field that GGA-PBE will seriously underestimate the actual band gap of semiconductor materials. Therefore, the band gap values obtained in this calculation are only used for the relative comparison among the three hydrides in this system, and cannot be regarded as the absolute intrinsic band gap of the materials. If accurate experimental band gap or theoretical band gap close to experimental value is required, hybrid functionals such as HSE need to be adopted for further calculation.

The systematic reduction in the band gap with increasing ionic radius of the A-site cation ($K \rightarrow Rb \rightarrow Cs$) can be attributed to the expansion of the lattice, which reduces the orbital overlap and decreases the dispersion of the valence bands, thereby narrowing the gap. From the perspective of hydrogen storage, the semiconductor band gap reflects the electron transition difficulty inside the material. A narrower band

gap means that electrons are easier to excite, which can weaken the electron localization of H^- anions in the lattice and reduce the H-H bond formation barrier during hydrogen desorption. This rule is consistent with the changing trend of hydrogen desorption temperature in Section 3.3, Cs_2CaZnH_6 with the smallest band gap has the lowest desorption temperature.

The total density of states (TDOS) and partial density of states (PDOS) are shown in Fig. 8. The TDOS curves clearly reveal that the electronic states near the Fermi level ($E = 0$ eV) are predominantly contributed by the valence band, while the conduction band states appear at energies above approximately 2 eV, giving rise to a distinct band gap that quantitatively matches the indirect-gap values obtained from the band structure calculations.

The PDOS shows significant orbital hybridization between Zn-d orbitals and H-s orbitals in the high-energy sub-region from -4 to 0 eV. The strong orbital coupling proves that there is stable covalent interaction between Zn and H atoms, which is the core bonding mode to maintain the $[ZnH_6]^{6-}$ octahedral structure. Combined with the ionic bonding feature judged by Poisson's ratio in Section 3.4, it can be concluded that M_2CaZnH_6 hydrides belong to the mixed ionic-covalent bonding system, which is a typical structural characteristic of perovskite hydrides. This hybridization effect enhances the covalent characteristic of Zn-H bonds, which not only improves the structural stability of the hydride but also regulates the hydrogen adsorption and desorption behavior by adjust-

Fig. 8. Density states of M_2CaZnH_6 ($M = K, Rb, Cs$).Fig. 9. Optical properties M_2CaZnH_6 ($M = K, Rb, Cs$): (a): real part of dielectric function, (b) imaginary part of the dielectric function, (c) reflectivity, and (d) absorption.

ing the electron density distribution around H atoms [29]. For the conduction band, it is mainly composed of Ca-3d orbitals and Zn-4s/4p orbitals, with negligible contribution from H atoms. This indicates that the excitation of electrons from valence band to conduction band mainly involves the transition of electrons in metal cation orbitals, and the H atoms remain relatively stable in the form of hydride anions (H^-) during this process, which is favorable for the reversible storage of hydrogen. During cyclic hydrogen absorption and desorption, H atoms always exist in the form of H^- anions without valence state mutation, which effectively avoids the irreversible structural damage caused by electron transfer of hydrogen atoms, and guarantees the reversible hydrogen storage performance of the materials.

3.6. Optical properties

The optical properties of M_2CaZnH_6 perovskites were derived from the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where real part (ε_1) describes polarization and imaginary part (ε_2) accounts for light absorption [30]. Figure 9 presents the dielectric function, reflectivity (R), and absorption coefficient (α) of the compounds. The static dielectric constant $\varepsilon_1(0)$ values are 4.05 for K_2CaZnH_6 , 4.09 for $\text{Rb}_2\text{CaZnH}_6$, and 4.72 for $\text{Cs}_2\text{CaZnH}_6$, indicating enhanced charge screening ability in $\text{Cs}_2\text{CaZnH}_6$, which stabilizes H^- anions in the lattice [11]. $\varepsilon_1(\omega)$ reaches maximum values of 7.60 at 4.02 eV, 7.15 at 4.49 eV, and 7.12 at 4.76 eV for K_2CaZnH_6 , $\text{Rb}_2\text{CaZnH}_6$, and $\text{Cs}_2\text{CaZnH}_6$, respectively, with a red shift in the peak position due to larger cation size [31]. The $\varepsilon_2(\omega)$ spectra show strong absorption peaks in the UV region (5–25 eV), corresponding to interband transitions from Zn-d orbitals to Ca-p orbitals [32].

The reflectivity (R) is low in the visible region (VR) for all compounds, indicating high transparency, which is useful for applications such as transparent photodetectors [33]. In the UV region, R reaches maximum values of 0.35 at 5.58 eV, 0.46 at 6.68 eV, and 0.40 at 6.25 eV, suggesting potential use as UV reflectors. The absorption coefficient (α) exhibits strong peaks in the UV region: 237 k cm^{-1} at 15.62 eV for K_2CaZnH_6 , 223 k cm^{-1} at 20.82 eV for $\text{Rb}_2\text{CaZnH}_6$, and 242 k cm^{-1} at 12.1 eV for $\text{Cs}_2\text{CaZnH}_6$, which are comparable to those of commercial UV detectors [34]. This high UV absorption makes X_2CaZnH_6 perovskites promising for multifunctional applications. The strong ultraviolet absorption originates from the interband electron transition between Zn-d and Ca-p orbitals, which is consistent with the electronic structure characteristics in Section 3.5. Compared with traditional wide-bandgap ultraviolet detection materials, the studied hydrides combine hydrogen storage function and ultraviolet optical response, realizing the in-

tegration of energy storage and optoelectronic functions. Among the three materials, $\text{Cs}_2\text{CaZnH}_6$ has both excellent low-temperature hydrogen desorption performance and strong ultraviolet absorption capacity, so it has the most comprehensive application potential in multifunctional devices.

4. Conclusions

This study presents a comprehensive DFT investigation of the structural, hydrogen storage, mechanical, electronic, and optical properties of M_2CaZnH_6 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$) double perovskite hydrides. All compounds crystallize in the cubic Fm-3m space group, with lattice parameters, unit cell volumes, and densities increasing with the ionic radius of A-site cations. Negative formation energies and phonon dispersion results confirm thermodynamic and dynamic stability. K_2CaZnH_6 exhibits the highest gravimetric capacity (3.19 wt.%), while $\text{Cs}_2\text{CaZnH}_6$ shows the lowest desorption temperature (247 K), falling within the DOE target range for practical applications. All compounds are mechanically stable, with K_2CaZnH_6 showing ductile behavior and $\text{Rb}_2\text{CaZnH}_6$ and $\text{Cs}_2\text{CaZnH}_6$ exhibiting brittle characteristics. $\text{Cs}_2\text{CaZnH}_6$ stands out as the most promising candidate for near-ambient hydrogen storage due to its favorable desorption temperature and optical properties. Future research should focus on experimental synthesis and validation of these compounds, as well as optimization of desorption temperatures for K_2CaZnH_6 and $\text{Rb}_2\text{CaZnH}_6$ via doping or nanostructuring. In addition, combined with the mechanical anisotropy and electronic transition characteristics revealed in this work, the hydrogen diffusion kinetics and photoelectric response performance of the materials can be further studied in depth. This work systematically clarifies the regulation mechanism of A-site alkali metal cations on the structure and physical properties of zinc-based double perovskite hydrides, expands the library of double perovskite hydrides for hydrogen storage and provides a theoretical framework for the design of multifunctional energy materials.

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