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Exploring the Synergy between Structural Stability and Functional Properties of FrXH_3 (X = Sc, Ti, and V) Hydride Perovskites for Hydrogen Storage

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Abstract

With the current energy crisis, environmental challenges, and the urgent demand for sustainable energy solution, has gained significant consideration in perovskite hydrides because of their compositionality flexibility and tunable physicochemical characteristics. In this study, DFT based first-principles calculations are employed to investigate the hydrogen storage performance along with structural, electronic, magnetic, elastic, optical, and thermodynamic properties of FrXH_3 (X = Sc, Ti, V) perovskite hydrides. The optimized structural parameters along with negative formation energies from -2516.15 to -3190.70 confirm phase stability, while the calculated elastic constants (C_{11} , C_{12} , and C_{44}) meet the Born stability criteria, ensuring mechanical stability for all compounds. Derived mechanical parameters, such as bulk modulus (B), shear modulus (G), Voigt shear modulus (G_v), Reuss shear modulus (G_R), and anisotropy factor (A), also show systematic trends in stiffness, ductility and anisotropy: $\text{FrVH}_3 > \text{FrScH}_3 > \text{FrTiH}_3$. The gravimetric hydrogen storage capacities of FrScH_3 , FrTiH_3 , and FrVH_3 are calculated as 1.116 wt % hydrogen, 1.104 wt % hydrogen, and 1.092 wt % hydrogen, respectively. The electronic properties confirm the metallic character of the series, and DOS is dominated by the d-states, with smaller contributions from s- and p-states. The transition from the non-magnetic behavior of FrScH_3 to the spin-polarized states of FrTiH_3 and FrVH_3 , originates from significant exchange-induced splitting of d-states, with minor p-state and negligible s-state contributions. Optically, high absorption, high conductivity and strong interband transitions observed in the low-energy region. Moreover, the thermodynamic parameters suggest that the lattice stiffness and thermal stability are enhanced for the case of FrTiH_3 compared to FrVH_3 , whereas the lattice behavior is intermediate for FrScH_3 and the anharmonicity is almost constant. Among the studied compounds, FrScH_3 is potentially

suitable for hydrogen storage applications because of its structural stability, lattice flexibility, and thermal behavior.

Keyword: Perovskite hydrides, DFT study, Metallic behavior, Stability, Hydrogen storage

1. Introduction

The global energy demand coupled with population growth, has increased the energy crisis and raised serious environmental concerns due to the continued dependence on fossil fuel resources [1]. Conventional energy resources (oil, gas, petroleum) and greenhouse gas emissions have played a major role in climate change [2]. Therefore, there is an urgent need of sustainable and clean sources of energy. Traditional storage methods like cryogenic liquefaction and high pressure compression are not suitable for large-scale storage due to their energy-intensive nature, high investment costs and safety concerns [3]. Hydrogen is one of the most promising renewable energy carriers because of its high gravimetric energy density, environmental benignity, and potential for carbon-neutral energy conversion [4]. Efficient storage and transportation of hydrogen, remain key challenges that limit wider adoption. In this regard, solid-state hydrogen storage materials which propose greater safety, reversibility, and improved storage efficiencies than traditional compressed or liquefied hydrogen storage systems. Perovskite-type hydrides (ABH_3) materials have recently gained significant interest for hydrogen storage because of their compositional flexibility, structural tunability, and low weight [5]. Their ability to accommodate different elements at the A and B sites for the optimization of various properties, make this attractive material for energy storage applications. Specifically, perovskite-type transition metal hydrides have better stability and favorable hydrogen interactions, which are mainly related to strong metal-hydrogen interaction [6].

Furthermore, first-principles calculations based on the density functional theory (DFT) exhibit reliable and predictive framework to explore the fundamental properties prior to experimental realization. This approach permits detailed understanding of the electronic structure, bonding characteristics, elastic, and magnetic behavior, which are crucial to determine the material stability and functionality. Particularly, for hydrogen storage performance, first-principles calculations facilitate the evaluation of hydrogen-metal interactions, adsorption energetics, and diffusion pathways, which are essential for

understanding hydrogen uptake and releasing mechanisms. In this context, several studies have been reported, some of these are; Hudabia et al. reported stable $AClH_3$ ($A = Rb, Cs, K$) hydrides with gravimetric and volumetric capacities of 3.35-3.88 wt% and 31.10-35.48 g H_2/L , and desorption temperatures above 350 K [7]. Kashif Masood et al. investigated structurally stable, metallic, and anisotropic mechanical behavior of $XSnH_3$ ($X = Rb, Cs, Fr$) perovskite hydrides with hydrogen storage capacities of 0.87-1.45 wt% [8]. Naura et al. investigated $NaXH_3$ ($X = Tc, Ru, Rh$) hydrides, confirming their structural, mechanical, and thermodynamic stability with metallic behavior, and reported hydrogen storage capacities of 2.08-2.44 wt% with a desorption temperature of 365 K for $KTcH_3$ [9]. Azdad et al. reported structurally stable $XCrH_3$ ($X = Na, K, Sr$) hydrides with metallic and half-metallic behavior along with gravimetric hydrogen storage capacities of 2.119-3.876 wt% [10]. Othman Hakami et al. reported structurally stable, metallic XBH_3 ($X = Li, Na, K, Rb$) hydrides with high gravimetric (8.21 wt%) and volumetric capacities (82.12 g H_2/L), and desorption temperatures of 259-313 K [11]. With the continuous advancement of modern technology, the demand for novel perovskite hydrides materials for efficient hydrogen is increasing. Despite significant progress, many reported hydride systems remain limited by poor reversibility, instability under ambient conditions, and complex synthesis routes, which limit their practical applicability [12]. These challenges require the exploration of new material compositions with enhanced hydrogen storage performance and improved physicochemical stability. In this regard, the introduction of transition metal ions like Sc, Ti, and V into the perovskite structure seems to be prime because of their multiple oxidation states and favorable metal-hydrogen interactions. Such intrinsic tunability is essential for attaining an optimal electronic structure and bonding properties, signifying enhanced hydrogen storage capabilities without compromising structural integrity and paving the way for future energy storage applications.

Despite extensive advances in perovskite-hydride research, the mechanistic role of transition-metal substitution in tailoring lattice rigidity and its direct correlation with hydrogen-storage functionality remains an open scientific challenge. Specifically, Fr-based perovskite hydrides have not been explored, shows gap in understanding impact of large alkali cations and transition metals on bonding interactions and structural stability. To the best of our knowledge, first-principles investigation of Fr-based perovskite hydrides $FrXH_3$

(X = Sc, Ti, V) remain unexplored. In this work, we systematically explore the structural, electronic, magnetic, elastic, optical, and thermodynamic properties of these compounds and evaluate their potential for hydrogen storage applications. By identifying this trade-off between structural stability and hydrogen mobility, the key aspect of present study provides new insights into the role of transition metal (Sc, Ti, V) substitution in tuning the structural stability, bonding characteristics, electronic behavior, and hydrogen storage performance. The current work is significant, because it bridges the literature gap, and provide a solid foundation for future experimental synthesis, beneficial to the development of hydrogen-related energy technology.

2. Computational Approach

To perform the entire computation of FrXH_3 (X = Sc, Ti, V) perovskite hydrides, first-principles calculations based on the density functional theory (DFT) and the Cambridge Serial Total Energy Package (CASTEP) were conducted [13]. Electron-ion interaction was described using ultrasoft pseudopotentials to reduce computational cost. The exchange-correlation functional was implemented within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) scheme, to describe the structural and electronic properties [14]. A plane-wave cutoff energy of 326 eV was selected based on convergence test. Structural optimization was carried out using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm, ensuring efficient and reliable convergence to the ground-state configuration [15]. The convergence thresholds were set to 2.0×10^{-5} eV/atom for total energy, 0.05 eV/Å for maximum force, 0.1 GPa for maximum stress, and 2.0×10^{-3} Å for atomic displacement. Brillouin zone integration was performed using a Monkhorst-Pack k-point grid of $6 \times 6 \times 6$.

3. Results and Discussions

3.1 Structural Properties

the structural framework of perovskite-type hydrides FrXH_3 (X = Sc, Ti, V) is systematically investigated. These compounds adopt a highly symmetric cubic perovskite structure with space group Pm-3m (No. 221) [16], as illustrated in Fig. 1. The crystal structure formed by a three-dimensional network of corner-sharing XH_6 octahedra, the

transition-metal (X) ions being situated at the centre of each octahedron, based on structurally coherent and dynamically stable framework [17]. The Fr atoms reside at the A-site, stabilize the lattice through ionic interactions. The calculated structural parameters for FrXH_3 ($X = \text{Sc}, \text{Ti}, \text{V}$) perovskites are presented in Table 1, shows lattice stability and bonding properties of these perovskite-type hydrides. The optimized lattice constant and cell volume follow the trend $\text{FrTiH}_3 > \text{FrScH}_3 > \text{FrVH}_3$, with lattice constants ranging from 4.2981 Å for FrTiH_3 to 4.5247 Å for FrVH_3 . The enhancement highlights the pronounced effect of V incorporation on bonding characteristics and structural relaxation.

Furthermore, the formation energy (F.E) was calculated by using the given relation [18].

$$E_f^{\text{FrXH}_3} = E_t^{\text{FrXH}_3} - (E_t^{\text{Fr}(bulk)} + E_t^{X(bulk)} + 3E_t^{H(bulk)})$$

where $E_t^{\text{FrXH}_3}$ corresponds to the total energy of the hydride, while $E_t^{\text{Fr}(bulk)}$, $E_t^{X(bulk)}$, and $E_t^{H(bulk)}$ denote the reference energies of the constituent atomic and molecular species. These values denotes the most stable phase of FrVH_3 because of stronger metal-hydrogen interactions and better bonding coherence in perovskite framework [19].

Table 1: The structural parameters for FrXH_3 ($X = \text{Sc}, \text{Ti}, \text{V}$) Perovskite Hydrides

Properties	FrScH_3	FrTiH_3	FrVH_3
a_0 (Å)	4.3874	4.2981	4.5247
G_0 (1/ Å)	1.4727	1.4618	1.3712
V_0 (Å ³)	84.4587	79.4017	96.1973
F.E (eV)	-2516.15	-2834.80	-3190.70

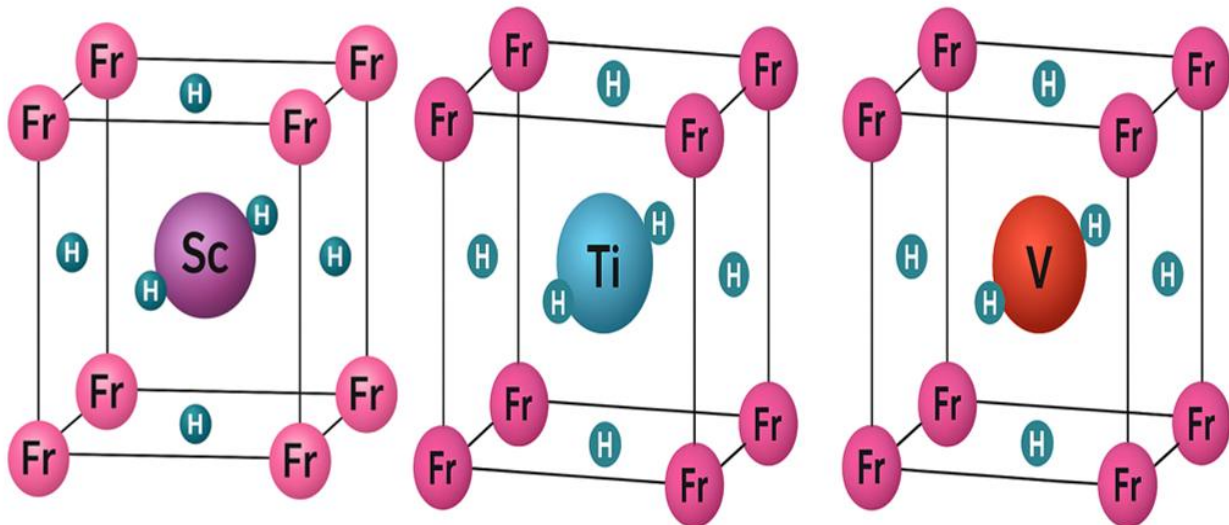


Fig. 1: Unit cell structure for FrXH₃ (X = Sc, Ti, V) Perovskite Hydrides

3.2 Hydrogen storage performance

An efficient hydrogen storage system is one of the most significant challenges for the practical use of hydrogen as a clean energy source. The gravimetric hydrogen storage capacity ($C_{wt}\%$) was calculated according to the equation [20].

$$C_{wt}\% = \frac{pM_H}{M_{com} + pM_H} \times 100\%,$$

where p is the number of hydrogen atoms per formula unit, M_H is the molar mass for hydrogen, and M_{com} is the molar mass of the host lattice. The computed gravimetric hydrogen storage capacities of FrXH₃ (X = Sc, Ti, V) are 1.116 wt % for FrScH₃, 1.104 wt % for FrTiH₃, and 1.092 wt % for FrVH₃. The observed decreasing trend from Sc to V, shown in Fig.2 arises from the progressive increase in the atomic mass of the transition metal cation. The lattice volume per hydrogen atom is almost constant, signifying that the decrease in gravimetric fraction is mainly mass-induced rather than structural contraction [21]. Consequently, the gravimetric hydrogen storage capacity of these stoichiometric hydride perovskites is inversely related to the mass of the cation, which indicates that the compositional effects dominate. Despite the slight reduction in gravimetric capacity, the nearly invariant lattice volume preserves the volumetric hydrogen density, ensuring efficient hydrogen storage within a compact crystal framework [22]. Together with the negative formation energies, these findings suggest that these hydride perovskites are thermodynamically stable with predictable, mass-dependent hydrogen storage capacity.

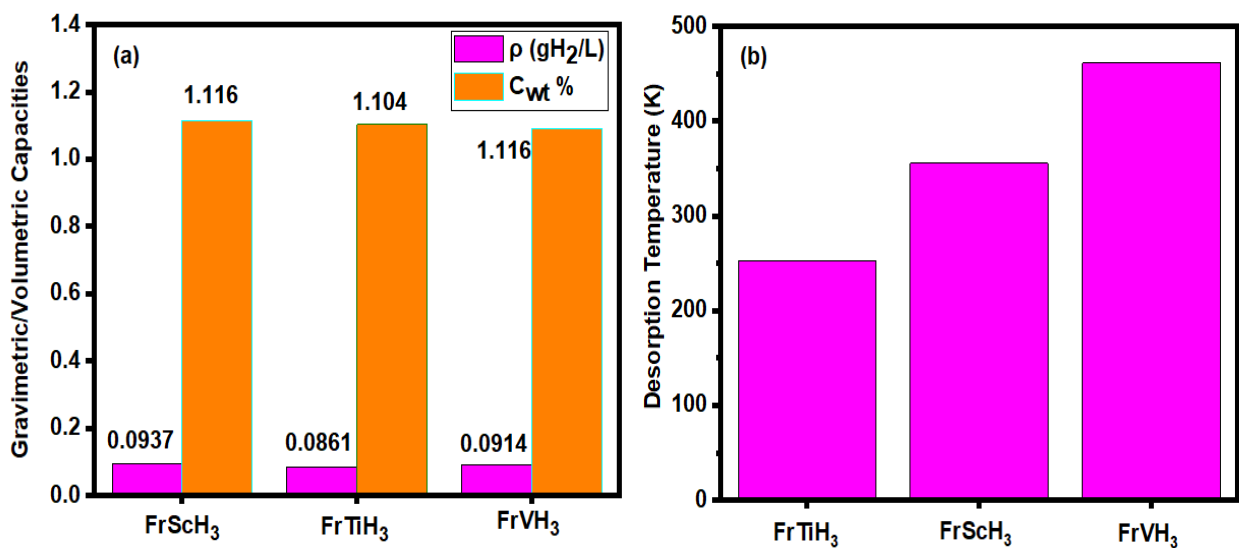


Fig. 2: Gravimetric and volumetric capacities, (b) Desorption temperature for FrXH₃ (X = Sc, Ti, V) Perovskite Hydrides

3.3 Electronic properties

The electronic band structure of FrXH₃ (X = Sc, Ti, V) along the high-symmetry k-point path (X–R–M– Γ –R) shows that all compounds exhibit metallic character, as shown in Fig. 3(a-c) [23]. The band dispersion near the Fermi level propose moderate charge carrier mobility, while the presence of relatively flat bands in certain regions specifies the localized electronic states [24]. Furthermore, the deeper energy levels near -10 eV are relatively flat, suggesting strongly localized energy levels which are expected to be hydrogen derived orbitals that have hybridized with transition metal d-states. The change in the d-orbital occupancy and the hybridization strength from Sc to V causes subtle variation in the curvature of bands.

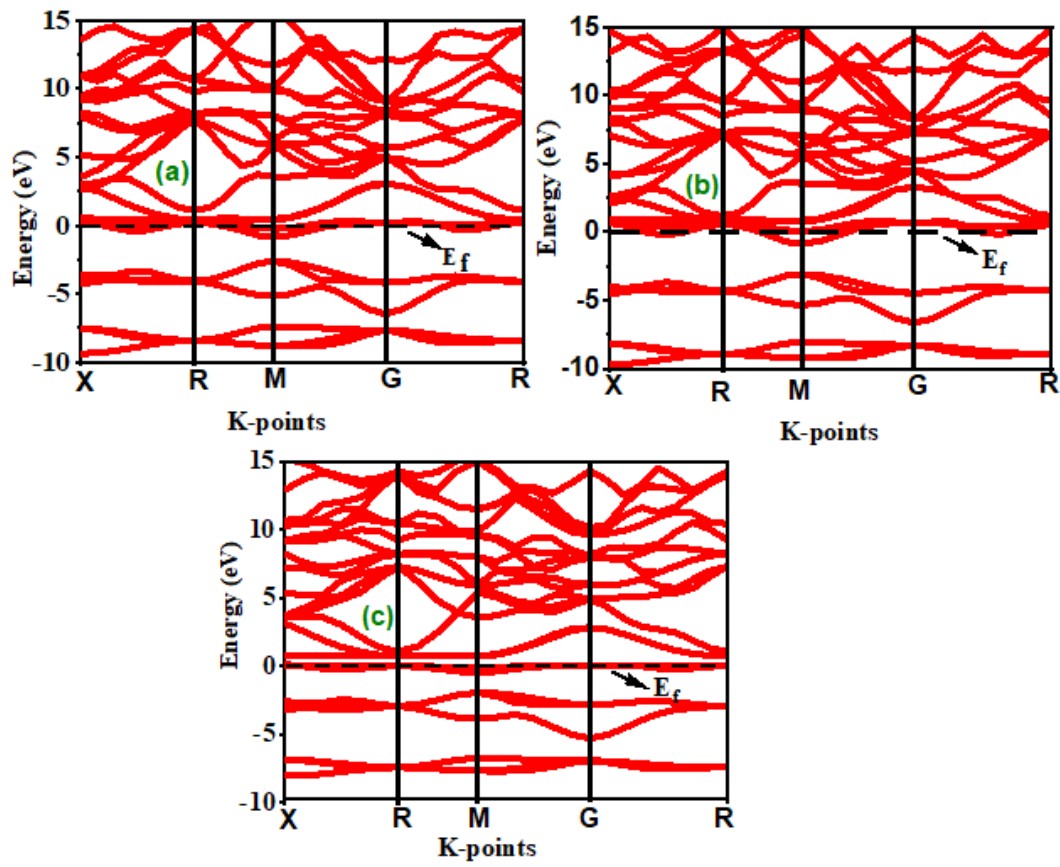


Fig. 3: Band structure (a) FrScH₃, (b) FrTiH₃, and (c) FrScH₃ perovskite hydrides

The total density of states (TDOS) presented in Fig. 4(a-c), further confirms that the compounds are metallic materials. The absence of available electronic states is fully consistent with the band structure results. The conduction band region exhibit some broader and dispersed peak above the fermi level, signifying more delocalized electronic states [25]. This indicates that the charge carriers in the conduction band can have comparatively higher mobility than those in deeper valence states [26]. There is a marked difference in peak intensity and distribution among FrScH₃, FrTiH₃, and FrVH₃. This trend is due to the energy shift of the transition metal d-orbitals, Sc to V, causing the modification of the degree of hybridization and the overall electronic structure.

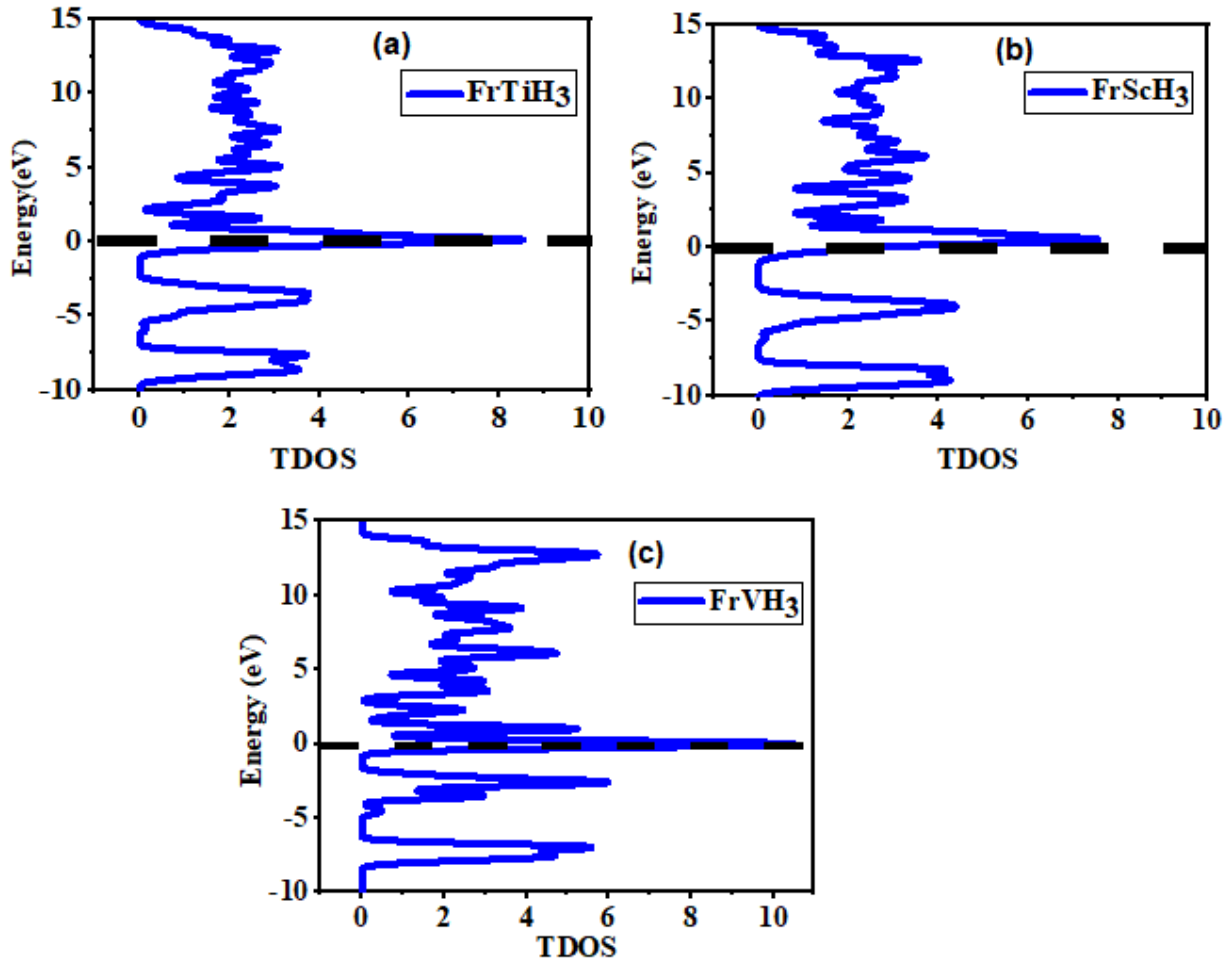


Fig. 4: (a-c) TDOS for FrXH_3 ($X = \text{Sc, Ti, V}$) perovskite hydrides

The partial density of states (PDOS) shown in Fig. 5(a-c) clearly show that the H-s and X-p states are the major contributors to the valence band region, with some contribution from X-d states, which is indicative of strong p-d hybridization. While on the other hand, conduction band is largely governed by the transition metal d-orbitals, implying that electronic excitation across the band gap predominantly involves transitions from hybridized p-d states in the valence band to d-states in the conduction band [27]. Moving from Sc -Ti- V, the d-state contribution near the band edges is observed, significantly enhances the density and localization of d-states near the band edges, which in turn slightly alters the band gap and electronic distribution [28]. Therefore, the observed trend is confirmed the interplay between H-s, X-p, and X-d orbitals.

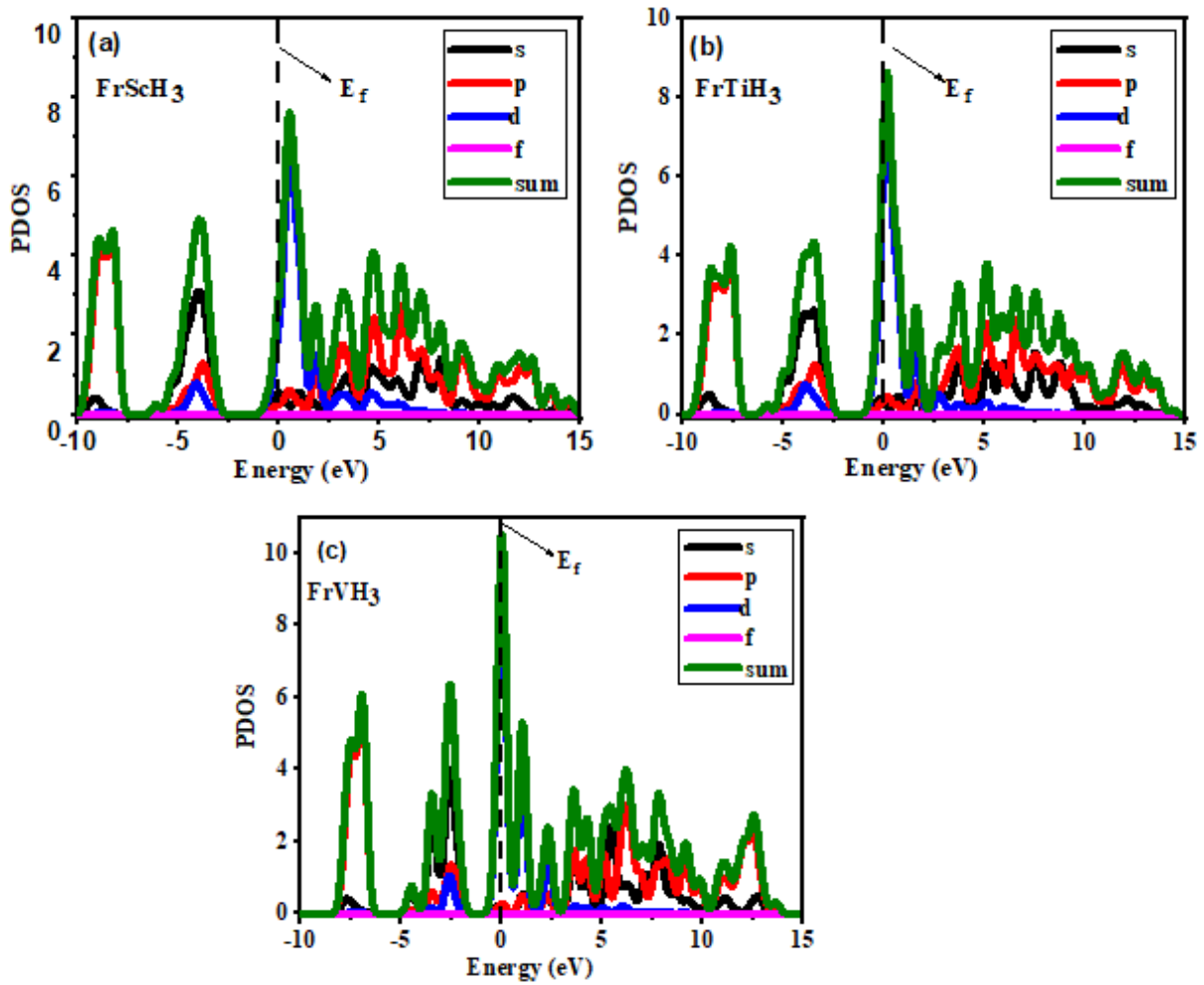


Fig. 5: (a-c) TDOS for FrXH_3 ($X = \text{Sc, Ti, V}$) perovskite hydrides

3.4 Magnetic Properties

The magnetic behavior of FrXH_3 ($X = \text{Sc, Ti, V}$) shown in Fig. 6(a-c), are fundamentally understood from the electronic configuration and the occupation of transition metal d-orbitals. In the case of FrScH_3 , Sc^{3+} possesses an empty 3d shell, resulting to complete absence of unpaired electrons and, consequently, non-magnetic ground state with negligible spin asymmetry [29]. For FrTiH_3 , Ti^{3+} has $3d^1$ configuration, introduces the presence of single unpaired electron, which gives rise to finite magnetic moment and weak magnetism. In FrVH_3 , V^{3+} adopts a $3d^2$ configuration, contributes two unpaired electrons and hence enhanced spin polarization, comparatively stronger magnetic response than Ti-based compound. This systematic evolution from non-magnetic to magnetic behavior is directly linked with the increasing number of unpaired d-electrons. Furthermore, the degree of magnetic interaction is influenced by the hybridization between H-1s and X-d orbitals,

which induces partial delocalization of spin density. However, the dominant factor remains the d-electron occupancy, primarily dictated the spin polarization [30].

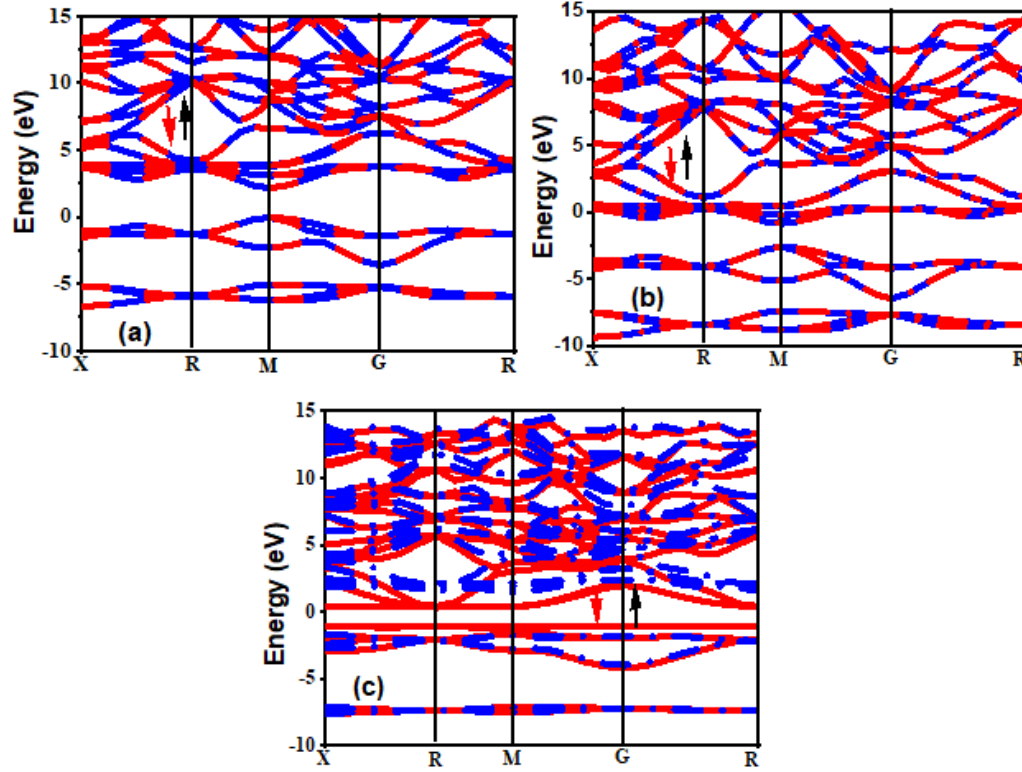


Fig. 6: Spin up and spin down behavior for (a) FrScH₃, (b) FrTiH₃, and (c) FrScH₃ perovskite hydrides

The spin-polarized density of states (DOS) provides direct insight into the origin of magnetism through the asymmetry between spin-up and spin-down channels [31]. Fig.7(a-c) reveals that the magnetic behavior originates from exchange splitting of partially filled transition metal d-orbitals, as clearly evidenced by the asymmetry between spin-up and spin-down states. In FrScH₃, the d-states are nearly symmetric around the Fermi level, indicating negligible exchange splitting and thus a non-magnetic ground state, which is consistent with the empty d-shell (3d⁰) of Sc³⁺. Whereas, the spin asymmetry of FrTiH₃ and FrVH₃ is strong, especially of the d-states near the Fermi level, which is characteristic of magnetism. This asymmetry is due to the exchange interaction of partially filled d-orbitals that energetically favors unequal spin channel occupation, giving rise to a net polarization of spins [32]. The induced spin polarization of the p-states is caused by hybridization with the d-orbitals, while the s-states are mostly symmetric and localized and

therefore do not contribute to the magnetic moment. Furthermore, the spin splitting degree increases with increasing number of d-electrons (from Ti to V) and exchange interaction [33]. Therefore, the observed magnetic properties correlate with the hybridization effects that transfer the spin polarization to other orbitals, and with the trends observed in the band structure and total DOS, is fully consistent with the band structure and total DOS analysis.

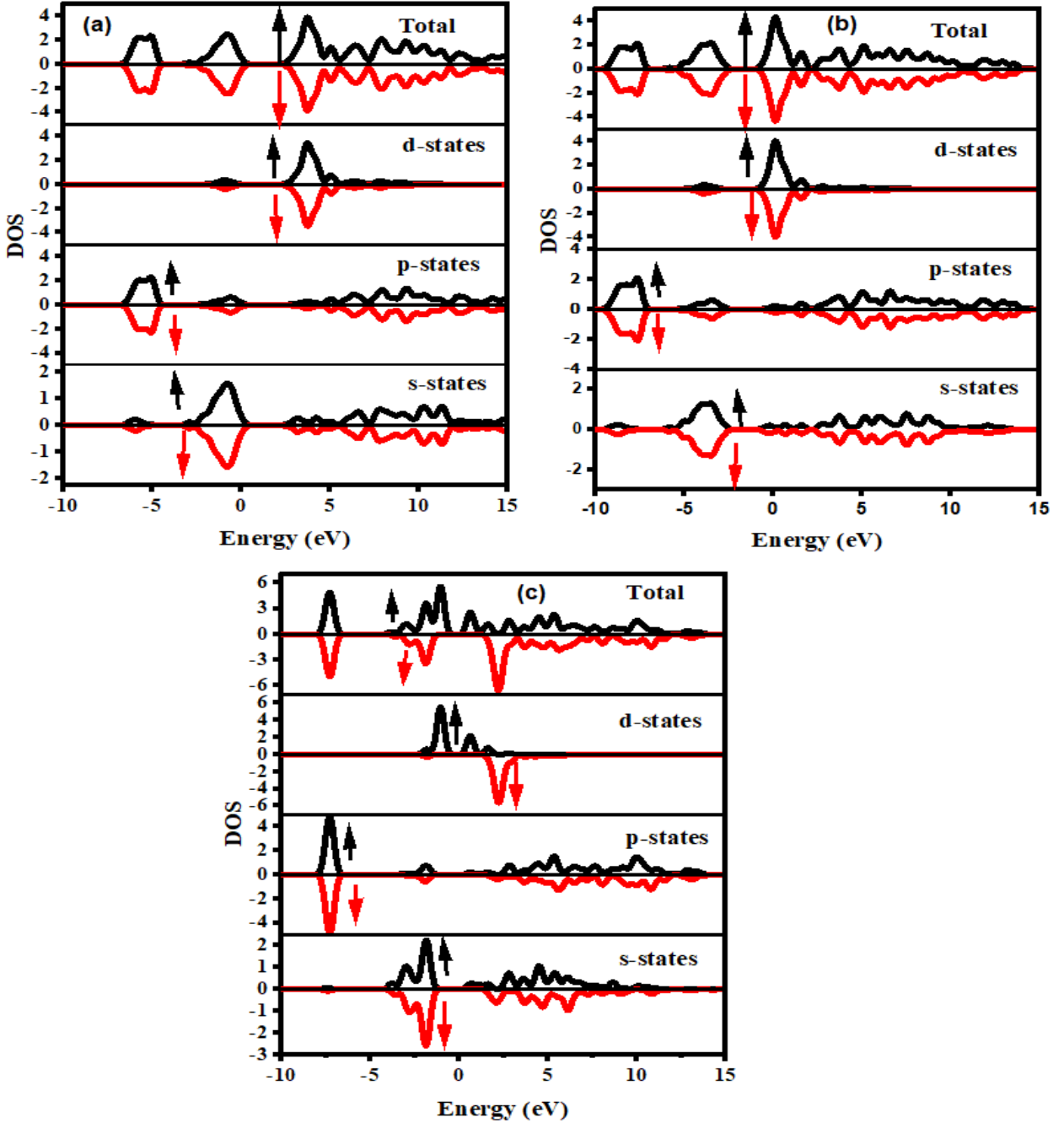


Fig. 7: Spin-polarized density of states (DOS) (a) FrScH₃, (b) FrTiH₃, and (c) FrScH₃ perovskite hydrides

3.5 Optical properties

The optical properties such as reflectivity, absorption coefficient, complex dielectric function, optical conductivity, and refractive index have been thoroughly investigated [34]. These parameters were calculated using the following equations [35].

$$R(\omega) = \frac{(n + k + 1)^2 + k^2}{(n + k - 1)^2 + k^2}$$

$$\alpha(\omega) = \sqrt{2}\omega \left[\sqrt{\varepsilon_2^1(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)} \right]^{\frac{1}{2}}$$

$$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$$

The absorption coefficient shown in Fig. 8(a) represents strong absorption in the low-energy region (~5-20 eV), then decreases in the range of ~20-30 eV, and finally sharper peaks in the higher energy region shift from FrScH₃ to FrVH₃, indicating changes in the electronic structure. The reflectivity graph illustrated in Fig. 8(b) shows moderate reflection at low energies that decreases with increasing frequency, with small features at higher energies corresponding to those same transition peaks [36]. Additionally, Furthermore, the moderate reflectivity and absence of a dominant free-electron response imply these are not purely metallic hydrides, which is beneficial because overly metallic systems often bind hydrogen too weakly, whereas partially covalent/ionic bonding (as suggested here) supports reversible hydrogen uptake and release [37]. The real and imaginary part of the dielectric function shown in Fig. 8(c-d) starts high and decreases with energy, approaching or crossing zero in the region, which indicates a plasma-like response and reduced polarization, while the imaginary part has strong peaks in the low-energy region, indicate active interband transitions involving hybridized metal-hydrogen states [38], which directly linked to the strength and nature of metal-hydrogen bonding, support the DOS results.

The optical conductivity illustrated in Fig. 8(e-f), confirming that charge carrier excitation is strongest in the same low-energy interband region, while its imaginary part reflects the phase response of carriers [39]. Finally, in Fig. 8(g-h) exhibit that refractive index (n) decreases with energy, demonstrating normal dispersion, and follows the same trend as absorption, reinforcing the internal consistency. Overall, these optical properties indicate that the materials possess strong metal-hydrogen interaction, electronic stability, and tunable bonding characteristics, beneficial for efficient hydrogen storage systems. From the hydrogen-storage point of view, the same trend is commonly interpreted as moving from relatively easier hydrogen release (Sc) to more balanced behavior (Ti) to stronger hydrogen retention and higher stability (V).

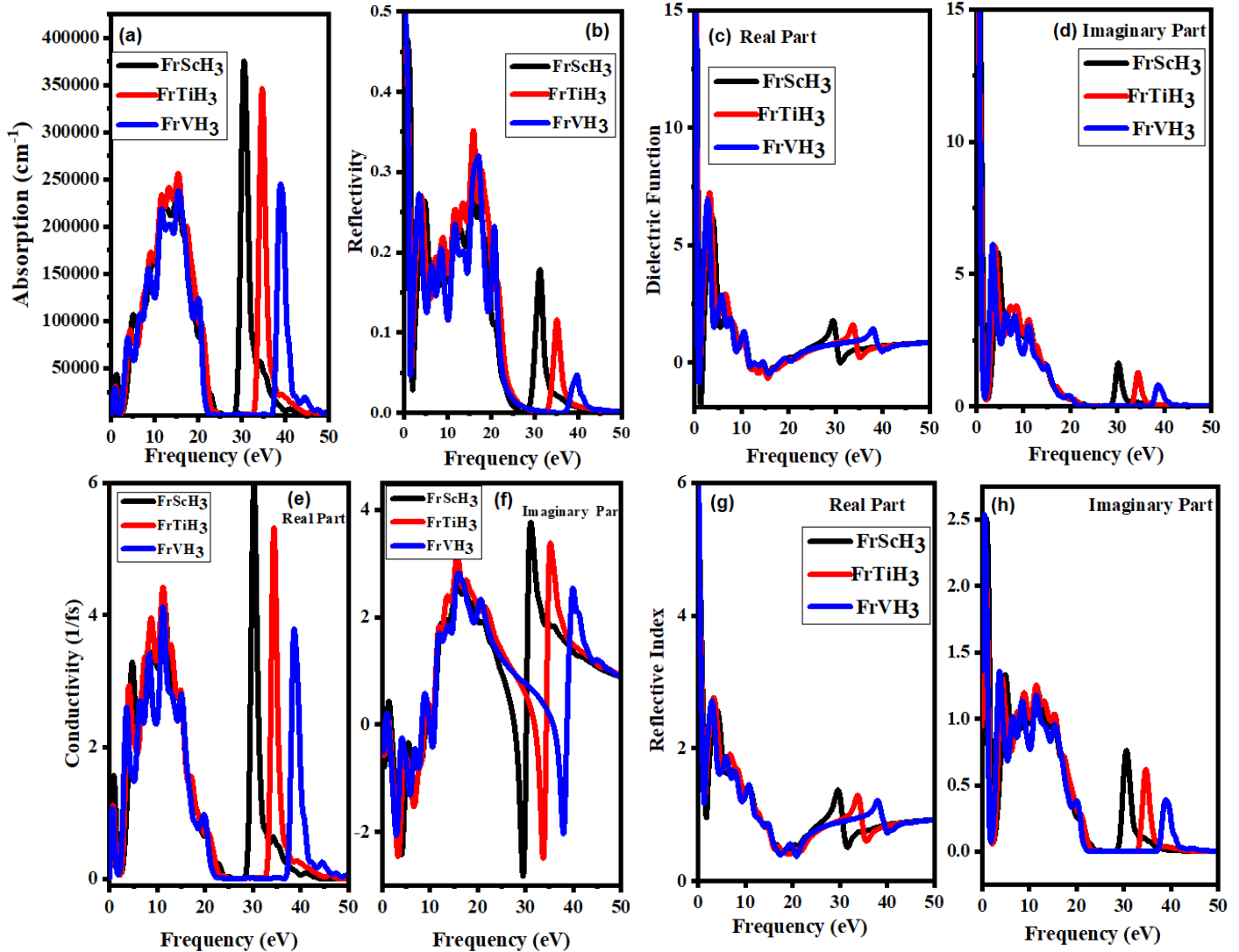


Fig. 8: (a-h) Optical properties for FrXH₃ (X = Sc, Ti, V) perovskite hydrides

3.6 Elastic constants and derived parameters

Elastic constants (C_{11} , C_{12} , and C_{44}) provides important information about the material's stiffness, strength, and resistance to deformation, are directly related to the nature of interatomic bonding [40]. For the investigated FrXH₃ (X = Sc, Ti, V) perovskite hydrides computed values are listed in Table 2. All elastic constants satisfy the Born stability criteria i.e; $C_{11}+2C_{12}>0$, $C_{11}-C_{12}>0$, $C_{44}>0$, confirmed their mechanical stability [41]. In FrScH₃, the values indicate moderate stiffness, where the relatively higher C_{11} compared to C_{12} and C_{44} shows that the crystal exhibit stronger resistance to uniaxial compression [42]. For FrTiH₃, the elastic constants are all smaller than those of FrScH₃, suggesting that this compound is softer and less rigid, with weaker resistance to both axial and shear distortions. Whereas FrVH₃ exhibits an extremely high value of C_{11} , while C_{12} and C_{44} are remain much smaller, indicating a highly unusual mechanical response [43]: the crystal is extraordinarily resistant to longitudinal deformation, but comparatively much less resistant to shear [44].

The derived parameters such as bulk modulus (B), shear modulus (G), Young modulus (Y) and Poisson's ratio (ν) were calculated using the given relations [45].

$$B = \frac{C_{11}+2C_{12}}{3}, G_v = \frac{C_{11}-C_{12}+3C_{44}}{5}, G_R = \frac{5C_{44}(C_{11}-C_{12})}{4C_{44}+3(C_{11}-C_{12})}$$
$$G = \frac{G_v+G_R}{2}, \nu = \frac{3B-2G}{2(2B+G)}, A = \frac{2C_{44}}{C_{11}-C_{12}}$$

The bulk modulus (B) defines the resistance to volume compression and the shear modulus (G) defines the resistance to shape deformations. Among these studied compounds, FrScH₃ shows comparative values of B and G, representing balanced resistance to both compressive and shear strains. Whereas, FrTiH₃ exhibits relatively weak values exhibit more mechanically softer structure. Specifically, FrVH₃ has a significantly higher value of B and G, meaning that it has very strong resistance to volume and shear deformation. Furthermore, the Voigt (G_v) and Reuss (G_R) shear moduli are quite different for FrVH₃, indicating high degree of elastic anisotropy, whereas FrScH₃ and FrTiH₃ indicate more

isotropic behavior. The overall results show systematic strengthening of the mechanical rigidity from FrTiH₃ to FrScH₃ and then to FrVH₃. Based on the calculated mechanical properties, FrScH₃, with moderate bulk and shear moduli, is suitable for hydrogen storage while maintaining structural stability during cycling. FrTiH₃, is more compressible and flexible, which may facilitate hydrogen insertion but can reduce the structural integrity [46]. For FrVH₃, bulk and shear moduli are very high, indicating very rigid lattice, which endorse high stability but may limited the hydrogen diffusion and release.

Table 2: Calculated elastic constants and mechanical moduli of FrXH₃ (X = Sc, Ti, V) perovskite hydrides.

Compound	C ₁₁ (GPa)	C ₁₂ (GPa)	C ₄₄ (GPa)	B (GPa)	A	ν	G _v (GPa)	G _R (GPa)	G (GPa)
FrScH ₃	55.99	14.85	28.41	28.57	0.12620	0.15840	25.27	24.65	24.96
FrTiH ₃	31.82	16.94	22.04	21.90	1.564	0.21526	16.20	12.35	14.28
FrVH ₃	938.34	56.26	18.37	350.29	26.46	0.27295	187.44	29.79	108.61

3.7 Thermodynamic properties

The computed thermodynamic parameters, including density (ρ), longitudinal (v_l) and transverse sound velocities (v_t), average sound velocity (v_m), Debye temperature (θ_D), melting temperature (T_m) Grüneisen parameter (γ), and minimum thermal conductivity (K_{min}), are listed in Table 3. These parameters were calculated using the relevant given relations [47].

$$\theta_D = \frac{h}{k_B} \left(\frac{3n}{4\pi V} \right)^{1/3} v_m, \quad v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3}$$

$$v_t = \sqrt{\frac{G}{\rho}}, \quad v_l = \sqrt{\frac{3B+4G}{3\rho}}$$

The sound velocities are directly related to elastic stiffness, therefore, higher velocities indicate stiffer lattice and stronger interatomic interactions [48]. Based on this, the lattice

of FrVH₃ is the most rigid, while that of FrTiH₃ is the most flexible, and the lattice of FrScH₃ is of intermediate rigidity. It is known that a reversible hydrogen cycling system requires an optimum lattice rigidity-flexibility balance among lattice components. This trend is well consistent with the Debye temperature (θ_D), the higher θ_D generally indicates the bonding strength within the crystal [49]. Therefore, the higher value for FrVH₃ indicates stiffer lattice structure, whereas the lower values for FrTiH₃ indicates softer lattice structure. Similarly, the melting temperature (T_m), also shows the expected trend; stronger the bonding, greater the thermal stability. The Grüneisen parameter (γ) is almost the same for all three compounds, suggesting that the lattice anharmonicity is almost the same in the series. This signify that the observed differences in thermodynamic behaviour are mainly due to the changes in the stiffness of the lattice, not to anharmonicity [50]. Furthermore, correlation is found between minimum thermal conductivity (K_{min}) and phonon transport, with higher K_{min} corresponding to better heat conduction in structurally rigid systems. These parameters clearly show that the lattice rigidity and thermal stability of the compounds are in the order FrTiH₃ < FrScH₃ < FrVH₃, indicating that FrVH₃ is the most thermally stable compound and FrTiH₃ is the least thermally stable compound. From hydrogen storage perspective, FrScH₃ exhibit more favorable structural stability and lattice flexibility, which is highly desirable property for efficient hydrogen storage.

Table 3: Computed thermodynamic parameters relevant to lattice dynamics and thermal stability of FrXH₃ (X = Sc, Ti, V) perovskite hydrides

material	ρ (g/cm ³)	v_l (m/s)	v_t (m/s)	v_m (m/s)	(θ_D) (K)	T_m (K)	γ	K_{min} (W/mK)
FrScH ₃	7.5	4.1×10^3	2.9×10^3	3.7×10^3	480	670	1.2	0.7
FrTiH ₃	7.8	3.4×10^3	2.3×10^3	2.9×10^3	350	610	1.2	0.6
FrVH ₃	8.0	6.7×10^3	4.5×10^3	5.6×10^3	700	880	1.2	0.9

Conclusion

In conclusion, the present DFT-based study demonstrates that investigated FrXH_3 ($X = \text{Sc}, \text{Ti}, \text{V}$) perovskite hydrides are structurally and mechanically stable, as confirmed from the negative formation energies and elastic constants (C_{11} , C_{12} , and C_{44}). The mechanical and thermodynamic results consistently indicate a systematic increase in lattice rigidity and bonding strength from FrTiH_3 to FrVH_3 , further supported by higher sound velocities (v_l , v_m , v_t), and Debye temperature (θ_D). The electronic and magnetic properties confirmed metallic behavior dominated by transition metal d-states, directly linked to increasing d-electron occupancy and exchange splitting. Optical analysis further confirmed dominant interband transitions with high absorption and conductivity. The calculated gravimetric hydrogen storage capacities are 1.116 wt% for FrScH_3 , 1.104 wt% for FrTiH_3 , and 1.092 wt% for FrVH_3 , shows slight compositional dependence. Despite the relatively low capacities, FrScH_3 exhibits lattice flexibility and structural stability, essential for hydrogen storage. These results provide valuable insight into the design of perovskite hydrides for efficient, reliable, and friendly hydrogen storage applications.

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Author Contributions:

Conceptualisation: Aziz A. Aziz, S. Aldawood, and Syed Mansoor Ali; Methodology: Aziz A. Aziz and Syed Mansoor Ali; Analysis, Aziz A. Aziz; Investigation, Syed Mansoor Ali and Aziz A. Aziz; Writing-original draft preparation, Aziz A. Aziz; Editing, Syed Mansoor Ali, and S.Aldawood.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Not Applicable

Reference:

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