Structural phase stability studies on $M\text{BeH}_3$ ($M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) from density functional calculations

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Density-functional-theory calculations within the generalized-gradient approximation are used to establish the ground-state structure, equilibrium structural parameters, and electronic structure for $M\text{BeH}_3$ phases. From the 24 structural arrangements used as inputs for structural optimization calculations, the ground state crystal structures of $M\text{BeH}_3$ phases have been predicted. At ambient condition $\text{LiBeH}_3$ and $\text{NaBeH}_3$ crystallize with perovskite related orthorhombic and cubic structures, respectively. The remaining phases $\text{KBeH}_3$, $\text{RbBeH}_3$ and $\text{CsBeH}_3$ are crystallize in a monoclinic structure. In the predicted phases one can store up to 15.93 wt.% of hydrogen. The formation energy for the $M\text{BeH}_3$ phases have been investigated along different reaction pathways. The electronic structures reveal that all these phases are insulators with estimated band gap vary between 1.79 to 3.44 eV. Thermodynamical and kinetic aspects of this new series of materials should be investigated to check for their potentiality for hydrogen storage applications.

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I. INTRODUCTION

The crystal structure, shape, size, and surface composition of materials are major factors that control the hydrogen absorption properties for energy storage applications. To act as an efficient energy carrier, hydrogen should be absorbed and desorbed in materials easily and in high quantities. Alkali- and alkaline-earth-based complex hydrides are expected to have a potential as viable modes for storing hydrogen at moderate temperatures and pressures.¹⁻⁷ These hydrides (e.g., $\text{LiAlH}_4$, $\text{NaAlH}_4$, etc.) have higher hydrogen storage capacity at moderate temperatures and lower cost than conventional hydride systems based on intermetallic compounds. The disadvantage for the use of these materials for practical applications is the lack of reversibility and poor kinetics. Recent experimental findings have shown that the decomposition temperature for certain complex hydrides can be modified by introduction of additives³⁻⁴ and/or reduction of particle size.⁵⁻¹¹ This has open up for research activity on identification of appropriate admixtures for known or hitherto unexplored hydrides. As proposed in our earlier communications¹²⁻¹⁴ it should be possible to form several series of hydrides with alkali and alkaline-earth metals in combination with Group III elements of the Periodic Table. In our recent publication we have solved the crystal structure of the entire $M\text{MgH}_3$ ($M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) series¹⁵, where the crystal structure and equilibrium structural parameters for experimentally known phases have been reproduced and the structure of $\text{LiMgH}_3$ has been predicted. In the $M\text{BeH}_3$ phases one can store up to 15.93 wt. % of hydrogen (in $\text{LiBeH}_3$). However, Be is an extremely toxic material and special precautions are employed in its handling. So the structure of most of these phases is not yet established experimentally. In order to fulfill this gap, in this work we are reporting the electronic and crystal structure of all the $M\text{BeH}_3$ phases as derived from Density-functional-theoretical calculations.

A. Computational details

It is well known that the generalized-gradient approximation (GGA)¹⁶ generally gives better equilibrium structural parameters as well as energetics of different phases and hence we have used GGA for all the present calculations. The structures are fully relaxed for all volumes considered using force as well as stress minimization. The projected-augmented-wave (PAW)¹⁷ implementation of the Vienna ab initio simulation package (VASP)¹⁸ was used for the total-energy calculations to establish phase stability and transition pressures. In order to avoid ambiguities regarding the free-energy results same energy cutoff and a similar k-grid density for convergence were always used. In all calculations 500 k points in the whole Brillouin zone were used for $\alpha\text{-BeH}_2$ and a similar density of k points was used for all structural arrangements. A criterion of 0.01 meV atom⁻¹ was placed on the self-consistent convergence of the total energy, and all calculations used a plane-wave cutoff of 500 eV. The formation energies ($\Delta E$) have been calculated according to the reaction equations:

\[
\text{MH} + \text{BeH}_2 \rightarrow M\text{BeH}_3
\]

\[
M + \text{BeH}_2 + \frac{1}{2} \text{H}_2 \rightarrow M\text{BeH}_3
\]

\[
\text{MH} + \text{Be} + \text{H}_2 \rightarrow M\text{BeH}_3
\]

\[
M + \text{Be} + \frac{3}{2} \text{H}_2 \rightarrow M\text{BeH}_3
\]
FIG. 1: (a) Predicted crystal structures of LiBeH$_3$ (NaCoF$_3$; Pnma), (b) NaBeH$_3$ (CaTiO$_3$ type; ideal perovskite; P$m3m$), (c) KBeH$_3$ and RbBeH$_3$ (CaCO$_3$(II); P121/c), and (d) CsMgH$_3$ (KClO$_3$; P121/m1).

TABLE I: Optimized equilibrium structural parameters, bulk modulus ($B_0$), and pressure derivative of bulk modulus ($B'_0$) for the MBeH$_3$ ($M = \text{Li, Na, K, Rb, Cs}$) series.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit cell (Å)</th>
<th>Positional parameters</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBeH$_3$ (NaCoF$_3$; Pnma)</td>
<td>$a = 4.5361$</td>
<td>Li(4c) : 0.4500, $\frac{1}{4}$, 0.4897</td>
<td>63.1</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>$b = 6.2992$</td>
<td>Be(4b) : 0.0, 0.0, $\frac{1}{4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 4.4104$</td>
<td>H1(4c) : 0.9835, $\frac{1}{4}$, 0.4305</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H2(8d) : 0.7083, 0.9644, 0.2895</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaBeH$_3$ (CaTiO$_3$ type; Pm$ar{3}$m)</td>
<td>$a = 3.3189$</td>
<td>Na(1b) : 1/2, 1/2, 1/2</td>
<td>62.7</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>$b = 3.3189$</td>
<td>Be(1a) : 0, 0, 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 4.4104$</td>
<td>H(3d) : 0, 0, 1/2</td>
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<td></td>
</tr>
<tr>
<td>$\alpha$-KBeH$_3$ (CaCO$_3$(II); P121/c)</td>
<td>$a = 7.0850$</td>
<td>K(4e) : 0.76352, 0.7448, 0.7832</td>
<td>10.9</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>$b = 5.5621$</td>
<td>Be(4e) : 0.7492, 0.2534, 0.0021</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 8.9483$</td>
<td>H1(4e) : 0.6158, 0.3263, 0.8605</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\beta = 107.45$</td>
<td>H2(4e) : 0.8609, 0.4262, 0.1037</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H3(4e) : 0.7832, 0.0100, 0.0362</td>
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<td></td>
</tr>
<tr>
<td>RbBeH$_3$ (CaCO$_3$(II); P121/c)</td>
<td>$a = 7.4390$</td>
<td>Rb(4e) : 0.7576, 0.7458, 0.7705</td>
<td>10.5</td>
<td>4.87</td>
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<tr>
<td></td>
<td>$b = 5.7899$</td>
<td>Be(4e) : 0.73874, 0.2521, 0.0047</td>
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<td></td>
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<tr>
<td></td>
<td>$c = 9.4579$</td>
<td>H1(4e) : 0.6162, 0.3583, 0.8779</td>
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<tr>
<td></td>
<td>$\beta = 108.05$</td>
<td>H2(4e) : 0.8604, 0.3885, 0.1172</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>H3(4e) : 0.7476, 0.0101, 0.0159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsBeH$_3$ (KClO$_3$; P121/m1)</td>
<td>$a = 5.0969$</td>
<td>Cs(2e) : 0.8178, $\frac{3}{4}$, 0.2310</td>
<td>8.6</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>$b = 5.9359$</td>
<td>Be(2e) : 0.2390, $\frac{1}{4}$, 0.2386</td>
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<tr>
<td></td>
<td>$c = 7.8451$</td>
<td>H1(2e) : 0.0930, $\frac{1}{4}$, 0.3608</td>
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</tr>
<tr>
<td></td>
<td>$\beta = 107.97$</td>
<td>H2(4f) : 0.3031, 0.4513, 0.1724</td>
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</tbody>
</table>

The total energies of $M$, MH, and $\alpha$-BeH$_2$ have been computed for the ground-state structures, viz. in space group $Im\bar{3}m$ for $M$, $Fm\bar{3}m$ for MH, and the previously reported$^7$ Ibam for $\alpha$-BeH$_2$, all with full geometry optimization. To gauge the bond strength we have used crystal orbital Hamilton population COHP analyses, as is implemented in the TBLMTO-47 package$^{19}$ and this functionality is not yet implemented in VASP. The COHP which is the Hamiltonian population weighted density of states (DOS), is identical with the crystal orbital overlap population.

II. RESULTS AND DISCUSSION

Twenty four potentially applicable structure types have been used as inputs in the structural optimization calculations for the MBeH$_3$ compounds (Pearson structure classification notation in parenthesis): KMnF$_3$ (tP20), GdFeO$_3$ [NaCoF$_3$ (oP20)], KCuF$_3$ (tI20), BaTiO$_3$ [RbNiF$_3$ (hP30)], CsCoF$_3$ (hR45), CaTiO$_3$ [CaHgF$_3$ (cP5)], PFC$_3$ (tP40), KCuF$_3$ (tP5), KCaF$_3$ (mP40), NaCuF$_3$ (aP20), SnTiF$_3$ (mC80), KFeF$_3$ (mB40), LiTaO$_3$ (hR30), KCuF$_3$ (oP40), PbGeS$_3$ (mP20), CaKF$_3$ (mP20), KNbO$_3$ (tP5), KNbO$_3$ (oA10), KNbO$_3$ (hR5), LaNiO$_3$ (hR30), CaTiO$_3$ (oC10), FeTiO$_3$ (hR30), SrZrO$_3$ (oC40), BaRuO$_3$ (hR45), and $\alpha$-
should be noted that most of the alkali or alkaline-earth based hydrides are well defined stoichiometric compounds and the hydrogen site occupancy in the matrix is always one. But in LiBeH₃ phases the reported H occupancy is almost 0.188 which is similar to the metal hydride systems. From this point of view Selvam and Yvon have proposed that the experimentally established structure for LiBeH₃ may not be correct.

Among the considered structures, an NaCoF₃- and NaCuF₃-type atomic arrangements occurs at the lowest total energy and both phases are having exactly the same total energy. This type of situation some times arises when we do the full geometry optimization. Hence, we performed the symmetry analysis for the optimized data for both phases. Our symmetry analysis show that during the structural relaxation processes the low symmetry (triclinic) NaCuF₃ phase of LiBeH₃ transform into the somewhat high symmetry (NaCoF₃-type orthorhombic) phase. It is well known that the system some time instead of relaxing to the local minimum they relax to the global minima as it is the case here. The LiBeH₃ structure consist of corner sharing BeH₆ octahedra [see Fig. 1(a)]. From the interatomic Be−H distances (vary from 1.604 to 1.632 Å) and H−Be−H angles (ranging between 89.3 and 90.7°) it is evident that the BeH₆ octahedra are slightly distorted. Li is surrounded by 8 H atoms and the Li−H distances are vary from 1.967 to 2.168 Å. The shortest H−H separation in the LiBeH₃ structure exceeds 2.301 Å, and is consistent with the H−H separation found in other complex/metal hydrides.

2. Structural features of NaBeH₃

According to the structural optimization calculations with the considered 24 structural inputs, the CaTiO₃ type variant [Table I, Fig. 1(a)] is found to have the lowest total energy. The NaBeH₃ structure consists of corner sharing ideal BeH₆ octahedra [see Fig. 1(a)]. In NaBeH₃, Na is surrounded by twelve H in cuboctahedral coordination at a distance of 2.31 Å and Be is octahedrally coordinated to six H at a distance of 1.63 Å, H is surrounded by two Be and four Na, and the shortest H−H separation is 2.31 Å. The crystal structure of both NaBeH₃ and NaMgH₃ belongs to perovskite family. Generally, the A-site cations in an ideal perovskite structure (ABX₃) are larger than the B-site cations and similar in size to the X-site anions. In relation to NaBeH₃ we note that the tabulated ionic radius for Na is larger than that for Be²⁺ and H³⁻, but the Be²⁺ radius is only around half of the H³⁻ radius. The present finding for stabilization of inverse perovskite structure in NaBeH₃ phase appears to emphasize the significance of size factors associated with both Na and Be cations. It should be noted that, in general, perovskites containing the Li⁺ ion plus alkali earth elements or Eu²⁺, commonly adopt the inverse perovskite structure (eg. BaLiF₃, BaLiH₃ EuLiH₃, SrLiH₃).
3. Structural features of KBeH₃, RbBeH₃, and CsBeH₃

The results obtained from structural optimizations for KBeH₃ and RbBeH₃ phases show that the PbGeS₃-type input structure proved to have the lowest total energy. But the symmetry analyzes for the optimized data gives the CaCO₃(II)-type structural arrangement which was not included in the starting structures. Both CaCO₃(II) and PbGeS₃ phases have monoclinic structure with P121/c symmetric. However the only main difference between these structures is that the formal one consists of almost planar CO₃ molecules in the Ca matrix and the later has ideal GeS₄ tetrahedral arrangement in the Pb matrix.

Similarly for CsBeH₃ phase also the PbGeS₃-type structural input was found to have lowest total energy and the symmetry analyzes gave KClO₃-type structure as a final structure. Both CaCO₃(II) and KClO₃ structure types are monoclinic structures and the atomic arrangements are also having close similarity (see Fig.1d). These structures consist of almost separated BeH₂ planar molecules and are linked by alkali atoms. This structural feature is entirely different from sofar known compounds in ABH₃ family.35–39 All these three phases are having almost similar Be-H distance (around 1.4 Å), which is much smaller than that in LiBeH₃ and NaBeH₃. Similarly the H-H separation in these compounds is ~2.4 Å. Some of these phases having interesting high-pressure behavior and the results will be published in a forth coming article along with that for the AMgH₃ series.

Although these compounds have ionic electronic configurations for all involved components they stabilize rather different crystal structures. The broad features of the structural arrangement vary from Li to K along the series is from orthorhombic-cubic-monoclinic. Generally the variation in the crystal structures of ABX₃ compounds can be rationalized in terms of the Goldschmidt tolerance factor (t). The value of t may be used as an indicator of the tendency for structural transitions and for specification of the deformation in the octahedral coordination at the B site in a given perovskite-family member.40 For cubic arrangement t should be in the range 0.89–1.00, the range 0.8–0.89 should be indicative of tetragonal or orthorhombic distortion of the cubic symmetry, and t above 1 should single out hexagonal (trigonal) stacking variants of the perovskite family. The t values for the compounds under investigation [0.89 (LiBeH₃), 1.08 (NaBeH₃), 1.31 (KBeH₃), 1.36 (KBeH₃), and 2.02 (CsBeH₃)] varies from 0.89 to 2.02. Consistent with the Goldschmidt empirical rule, t takes a value close to one for cubic NaBeH₃ and this undistorted perovskite arrangements contains perfect octahedra. For the cases with t below one (viz. M = Li) there occur distorted octahedra. In the case of KBeH₃, RbBeH₃, and CsBeH₃ the ground-state structures are deviates from a perovskite-like frame-work.

By fitting the total energy as a function of cell volume using the so-called universal equation of state41 the bulk modulus (B₀) and its pressure derivative (B₀') are obtained (Table I), but no experimental data for comparison are yet available. The bulk modulus decreases monotonically when we move from Li to Cs and its pressure derivative increases correspondingly. The variations in B₀ and B₀' are accordingly correlated with variations in the size of M and consequently also with the cell volume. Compared to intermetallic-based hydrides these compounds have low B₀ values implying that they are soft and easily compressible. The soft character of the MBeH₃ materials arises from a high degree of ionic character in the chemical bonding. Hence, one can expect that de-stabilization of some of the hydrogen atoms from the matrix may be feasible. However, the Be-H bonds are likely to be strong. Accordingly the integrated crystal orbital Hamilton population (ICOHP) study on these phases shows that the Be-H interaction is much stronger than the other interactions. The calculated ICOHP values for Be-H along this series vary from 0.68 to 1.14 eV (following the sequence Li<Na<K<Rb-Cs). On the other hand when we move from Li to Cs the calculated ICOHP values for the M-H interactions are reducing from 0.34 to 0.06 eV (following the sequence Cs<Rb<K<Na<Li). This may be the possible reason (due to the strong Be-H and Li-H/Na-H bonding interaction) why LiBeH₃ and NaBeH₃ have higher bulk modulus than the rest of the phases on this series. This finding suggest that one need more energy to break the Be-H bond in order to remove the hydrogen from these phases. In fact, the experience from other complex aluminum-containing hydrides shows that one needs high temperature to break Al-H bonds. From this point of view, one can expect this MBeH₃ phase also release hydrogen at elevated temperature only. Hence, this materials may not suitable for onboard transportation applications. However, additive substitution/(particle size control) may be reduce the decomposition temperature considerably as it was observed in alanates. Further research is needed on this direction.

### Table II: Calculated hydride formation energy (ΔH; in kJ mol⁻¹) according to Eqs. 1–4 for the MBeH₃ series.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH₁</th>
<th>ΔH₂</th>
<th>ΔH₃</th>
<th>ΔH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBeH₃</td>
<td>-28.85</td>
<td>-58.89</td>
<td>8.74</td>
<td>-79.01</td>
</tr>
<tr>
<td>NaBeH₃</td>
<td>-0.200</td>
<td>-20.21</td>
<td>-20.37</td>
<td>-65.37</td>
</tr>
<tr>
<td>KBeH₃</td>
<td>-2.94</td>
<td>-45.59</td>
<td>-23.05</td>
<td>-65.70</td>
</tr>
<tr>
<td>RbBeH₃</td>
<td>-10.37</td>
<td>-45.36</td>
<td>-30.49</td>
<td>-65.48</td>
</tr>
<tr>
<td>CsBeH₃</td>
<td>-16.75</td>
<td>-53.85</td>
<td>-36.87</td>
<td>-73.96</td>
</tr>
</tbody>
</table>

xxxx have you removed the error in the table?

A. Formation-energy considerations

Formation enthalpy is the best aid to establish whether theoretically predicted phases are likely to be stable and also such data may serve as guides for possible synthesis.
routes. In this study we have considered four possible reaction pathways (Eq.1 to 4) and estimated the associated formation enthalpy as listed in Table II. In general, synthesis of $M$BeH$_3$ compounds from an equiatomic MBe matrix is not possible as the alkali metals and beryllium are immiscible in the solid and liquid state (except Be$_2$K phase in K-Be phase diagram). Schumacher and Weiss have suggested that the ternary $MMgH_3$ hydrides can be synthesized directly by a reaction between $M$ and Mg in hydrogen atmosphere at elevated temperatures. A similar approach may also valid for the $MB$H$_3$ series. However, most of the $MMgH_3$ compounds have also been synthesized from the appropriate combination of binary hydrides. This shows that, among the considered reaction pathways, paths 1 and 4 are experimentally verified whereas paths 2 and 3 are open for verification or rejections.

The results show that reaction pathways 1—4 give rise to an exothermic reaction for the $M$BeH$_3$ compounds (except for LiBeH$_3$). Hence, preparation of LiBeH$_3$ from LiH and BeH$_2$ (pathway 1) and LiH + Be + H$_2$ (pathway 3) are not likely to be successful. All $M$BeH$_3$ compounds are seen to exhibit high formation energies according to pathway 4. Hence, for all the studied phases, pathway 4 is clearly the energetically most favorable than other paths and we suggest that it should be possible to synthesis/stabilize these compounds using this preparatory route.

FIG. 3: Calculated total density of states for $M$BeH$_3$. The Fermi level is set at zero energy and marked by the vertical dotted line.

B. Chemical bonding

In previous studies on hydrides we have demonstrated that several theoretical tools are needed in order to draw more assured conclusions regarding the nature of the chemical bonding. In $MMgH_3$ series we found that all the phases are basically saline hydrides similar to the parent alkali-/alkaline-earth mono-/di-hydrides. Generally one may expect that these $MBeH_3$ series may also have almost similar bonding behavior.

The total density of states (DOS) at the equilibrium volumes for the ground-state structures of the $M$BeH$_3$ compounds are displayed in Fig. 3 and site projected DOSs for LiBeH$_3$ and CsBeH$_3$ are shown in Fig. 4. All $MMgH_3$ compounds have finite energy gap ($E_g$ vary between 1.8 and 3.3 eV) between the valence band (VB) and the conduction band (CB) and hence these phases can be considered as insulators. It is commonly recognized that theoretically calculated energy gaps for semiconductors and insulators are strongly dependent on the approximations used and in particular on the exchange and correlation terms of the potential. In general, the band gaps obtained from the density-functional calculations are always underestimate the experimental band gap. According to textbook chemistry the insulating behavior of these materials can be explained as follows: each formula unit, one electron from $M$ fill one of the three originally half-filled H-s orbitals and the other two are filled by electrons from Be, resulting in a complete filling of the VB and accordingly an insulating behavior. The complex hydrides $MA$H$_5$ ($M$ = Mg, Ba), $M_5$AlH$_6$ ($M$ = Li, Na, K), and $MA$H$_4$ ($A$ = B, Al, Ga) also exhibit similar insulating behavior. This suggests that, one can generally expect wide band gap in complex hydrides with octahedral/tetrahedral coordinated structural units. On moving from LiBeH$_3$ to CsBeH$_3$, owing to the enlargement of the interatomic distances, the calculated width of VB degreases from 9.6 to 6.8 eV. In both LiBeH$_3$ and NaBeH$_3$ the VB region becomes single, when one move to KBeH$_3$, RbBeH$_3$ and CsBeH$_3$ it becomes split into three regions (in KBeH$_3$ the third region is present at $-12$ eV which was not shown in Fig.3). This may be due to the variation in the coordination number for Be. The lowest energy region is mainly originated from $M$ ($M$ = K, Rb, Cs) -p states, whereas the middle region is mainly originated from Be-s with considerable contribution from H-s states. The similarity in shape and degenerate nature of the DOS distribution from Be-s and H-s states indicate the presence of hybridization interaction between these atoms. The third region near the $E_F$ is originated from H-s, Cs-s, and Be-p states.

In order to elucidate the bonding situation more properly we have calculated the partial density of states (PDOS) for $M$BeH$_3$. Owing to close similarity between the PDOSs for LiBeH$_3$ and NaBeH$_3$ we have only shown the PDOS for LiBeH$_3$ in Fig. 4. As seen from this illustration, the PDOSs for Li show very small contributions at the VB. At the Be site also the amount of valence
FIG. 4: Calculated partial DOS for LiBeH₃ and CsBeH₃ phases. The Fermi level is set at zero energy and marked by the vertical dotted line; s states are shaded.

FIG. 5: (Color online) Calculated plots of (a) valence-electron-charge density and (b) ELF for NaBeH₃. The illustrations refer to the (110) plane.

electron present is much smaller than that in neutral atom and this demonstrates that valence electrons are transferred from the Li and Be sites to the H sites. The Be- \(s\) and \(-p\) states are energetically degenerated almost in the whole valence band region and the considerably broad and energetically degenerate nature of Be- \(s\) with H- \(s\) state indicate noticeable hybridization interaction between these states. We have observed drastic changes in the valence band feature when go from LiBeH₃ and NaBeH₃ to KBeH₃, RbBeH₃ and CsBeH₃ cases and they are having close similarity we displayed only PDOS of CsBeH₃ only. From Fig.1 one can see that Li and Na based system the Be atoms are coordinated by hydrogen octahedrally, whereas in K, Rb, and Cs based hydrides Be is tetrahedrally coordinated by hydrogen. This could be the reason for the drastic change in the valence band feature. In all phases Be- \(p\) and H- \(s\) states are present in the vicinity of the Fermi level. Unlike LiBeH₃ and NaBeH₃
in KBeH$_3$, RbBeH$_3$ and CsBeH$_3$ the Be-$s$ and -$p$ states are well separated. **Wrong stuffs are modified.**

In order to gain further understanding about the bonding situation in $M$BeH$_3$ compounds we turn our attention to charge-density, and electron-localization-function (ELF) plots. Again the different members of the series exhibit similar features and in view of that we have only documented such plots for NaBeH$_3$ in Fig. 5. According to the charge-density distribution at the Na, Be, and H sites, it is evident that the highest charge density resides in the immediate vicinity of the nuclei. As also evidenced from the almost spherical charge distribution, the bonding between Na and H is virtually pure ionic and that between Be and H is predominantly ionic with small directional character. The nature of charge distribution seen in Fig. 5 appears to be typical for ionic compounds. The main distinction between the bonding in $M$BeH$_3$ series and the situation in $MAI$H$_4$ and $M$AlH$_6$ series is that the interaction between Be and H has more ionic character than that between Al and H. The electron population between Na and the BeH$_6$ units is almost zero (viz. charges are depleted from this region), which reconfirms that the interaction between Na and BeH$_6$ units is virtually pure ionic.

The calculated ELF plot (Fig. 5(b); for more information about ELF see Refs. 50–52)) shows a predominant maximum of ca. 1 at the H site and these electrons have a paired character. The ELF values at the Na and Be sites are very low. The inference from this observation is that charges are transferred from the inhabitants of these sites to the H sites and there are certainly very few paired valence electrons left at the Na and Be sites. A certain polarized character is found in the ELF distribution at the H sites in all the complex hydrides we have investigated earlier. The ELF distribution is on the contrary quite isotropic in $M$BeH$_3$ and $M$MgH$_3$. This provides another indication for a higher degree of ionic character in $M$BeH$_3$ series than in $MAI$H$_4$ and $M$AlH$_6$ series.

In a effort to quantify the bonding and estimate the amount of electrons on and between the participating atoms, we have made Bader topological analysis. Although there is no unique definition to identify how many electrons are associated with an atom in a molecule or an atomic grouping in a solid, it has nevertheless proved useful in many cases to perform Bader analyses. In the Bader charge (BC) analysis each atom of a compound is surrounded by a surface (called Bader regions) that run through minima of the charge density and total charge of an atom is determined by integration within the Bader region. The calculated BC for the $M$BeH$_3$ series are given in Table III. The BC for M and H in the $M$BeH$_3$ compounds indicates that the interaction between M and BeH$_6$/BeH$_3$ is ionic (in all cases around one electron transferred from M to BeH$_6$/BeH$_3$). This finding is consistent with the DOS and charge density analyzes. Within the BeH$_6$ and BeH$_3$ units, Be consistently donates nearly 1.5 (in LiBeH$_3$, and NaBeH$_3$) and 1.3 (in KBeH$_3$, RbBeH$_3$, and CsBeH$_3$) electrons to the H sites respectively, which is much smaller than the pure ionic picture. This is partly associated with the small covalency present between Be and H and also may be due to the artifact of Bader’s atoms in molecule approach to make the boundaries to integrate charges in each atomic basin. However, consistent with the charge and DOS analysis, the BC analysis always qualitatively shows that M and Be atoms donates electrons to the H site.

## III. CONCLUSION

The crystal and electronic structures of the $M$BeH$_3$ ($M = \text{Li, Na, K, Rb, Cs}$) series have been studied by state-of-the-art density-functional calculations. The ground-state crystal structures have been predicted from structural optimization of a number of structures using force as well as stress minimizations. The predicted crystal structure of LiBeH$_3$ to be NaCoF$_3$-type, NaBeH$_3$ to be CaSiO$_3$-type, KBeH$_3$ and RbBeH$_3$ to be CaCO$_3$(II)-type, and CsBeH$_3$ to be KClO$_3$-type. Formation energies for the $M$BeH$_3$ series are calculated for different possible reaction pathways. For all these phases we propose that synthesis from elemental $M$ and Be in hydrogen atmosphere should be more feasible route. The $M$BeH$_3$ compounds are wide-band-gap insulators and the insulating behavior is associated with well localized, paired $s$-electron configuration at the H site. The chemical bonding character of these compounds is highly ionic according to analyzes of DOS, charge density, ELF, and Bader charges. Our calculations suggest that all these compounds are energetically feasible to form and the thermodynamical as well as kinetic aspects of these materials for hydrogen storage applications need further investigations.

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### TABLE III: Calculated Bader charges (BC) are given in terms of $e$ and energy band gap ($E_g$ in eV) for the $M$BeH$_3$ series.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Atom</th>
<th>BC</th>
<th>$E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBeH$_3$</td>
<td>Li</td>
<td>+0.87</td>
<td>2.29</td>
</tr>
<tr>
<td></td>
<td>Be</td>
<td>+1.46</td>
<td></td>
</tr>
<tr>
<td>NaBeH$_3$</td>
<td>Na</td>
<td>+0.84</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>Be</td>
<td>+1.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>−0.74</td>
<td></td>
</tr>
<tr>
<td>KBeH$_3$</td>
<td>K</td>
<td>+0.84</td>
<td>3.44</td>
</tr>
<tr>
<td></td>
<td>Be</td>
<td>+1.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>−0.71</td>
<td></td>
</tr>
<tr>
<td>RbBeH$_3$</td>
<td>Rb</td>
<td>+0.84</td>
<td>3.27</td>
</tr>
<tr>
<td></td>
<td>Be</td>
<td>+1.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>−0.71</td>
<td></td>
</tr>
<tr>
<td>CsBeH$_3$</td>
<td>Cs</td>
<td>+0.84</td>
<td>3.22</td>
</tr>
<tr>
<td></td>
<td>Be</td>
<td>+1.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>−0.71</td>
<td></td>
</tr>
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</table>
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