The search for novel hydrogen storage materials: a theoretical approach

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Abstract: Density Functional Theory (DFT) is a powerful tool to predict the crystal structure of hitherto experimentally unknown phases. In this article, we demonstrate the predicting capability of DFT on the structural properties of hydrogen storage materials from different input structure models. An experimentally known structural framework is successfully reproduced for NaMgH3 and the positional and unit-cell parameters are found to be in good agreement with the experimental findings. The crystal structure of LiMgH3 has been predicted and this compound should have ferroelectric properties. The calculated phonon spectrum indicates that LiMgH3 is an energetically and thermodynamically stable phase. A pressure-induced structural transition has been identified for this phase and it transforms into CaCO3-type modification at 38 GPa.

Keywords: complex hydrides; structural investigation; hydrogen storage; high-pressure study.


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1 Introduction

The high-capacity solid-state storage of hydrogen is becoming increasingly important for fuel cells, automotives and electrical utility applications. Compared to liquid hydrogen, one of the major drawbacks of the known reversible metal hydrides applicable for hydrogen storage is their low gravimetric hydrogen content (expressed in wt.% of H in the material): MgH$_2$ (7.6%) and the hydrides of Mg alloys (e.g., Mg$_2$NiH$_4$, 3.8%) represent in this respect the current optimum. However, for their use as storage materials, a sufficient amount of heating (ca. 300°C) is necessary for the desorption of hydrogen. The disadvantages of the presently known low- and medium-temperature reversible hydrides are the high costs for the intermetallic alloys suitable for this purpose (LaNi$_5$H$_6$, TiFeH$_2$) combined with a storage capacity that is four to five times lower (1.8%) compared to, say, MgH$_2$.

As proposed in our earlier communications (Vajeeston, 2004; Vajeeston et al., 2004; 2006; 2008a–b), it should be possible to form several series of hydrides with alkali and alkaline-earth metals in combination with Group 3 elements of the periodic table, but only few members of this series have so far been experimentally explored. For example, alkali metal-based aluminium/borate/galate hydrides, AMH$_4$ (A = Li, Na, K, Rb, Cs; M = B, Al, Ga) and a mixture of these phases have been found to have a potential as viable modes for storing hydrogen at moderate temperatures and pressures. These hydrides have been demonstrated to have a higher hydrogen storage capacity at moderate temperatures. However, a serious problem with these materials is their poor kinetics and the lack of reversibility with respect to hydrogen absorption/desorption. Bogdanovic and Schwickardi (1997) and Bogdanovic et al. (2000) have recently established that sodium aluminium hydrides, which were earlier considered irreversible in actual practice with respect to hydrogen absorption/desorption, can be made reversible by doping with Ti. Zaluska et al. (2000) and Jensen and Gross (2001) have also exerted effort to improve the hydrogen reversibility of NaAlH$_4$ by ball milling with or without additives. This has opened up research activity on the identification of appropriate admixtures for known or hitherto unexplored complex hydrides. In line with this, we have investigated the structural stability of the series of AMH$_4$, $A_3$MH$_6$, $A'MH_5$, AA'H$_3$, AA'MH$_6$ (A = alkali;
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$A'$ = alkaline-earth metals; $M$ = B, Al) phases (Vajeeston et al., 2004; 2006; 2008a–b; Klaveness et al., 2006). Later, such predictions are confirmed by experimental findings (Hauback et al., 2005). In this article, we will demonstrate how the Density Functional Theory (DFT) is used to predict the crystal structures of the unknown phases.

Figure 1 The crystal structures of $\alpha$-LiMgH$_3$ (a), $\beta$-LiMgH$_3$ (b) and NaMgH$_3$ (c) (see online version for colours)

2 Calculation details

Total energies have been calculated by the Projected Augmented Wave (PAW) (Blöchl, 1994; Kresse and Joubert, 1999) implementation of the Vienna Ab Initio Simulation Package (VASP) (Kresse and Hafner, 1993; Kresse and Furthmüller, 1996). The Generalised Gradient Approximation (GGA) (Perdew, 1991; Perdew et al., 1996a–b) was used to obtain accurate exchange and correlation energies for particular configurations of atoms. Ground-state geometries were determined by minimising stresses and Hellman-Feynman forces with the conjugate gradient algorithm until the forces on all atomic sites were less than $10^{-3}$ eV Å$^{-1}$. Brillouin zone integration is performed with a Gaussian broadening of 0.1 eV during all relaxations. In order to span a wide range of energetically accessible crystal structures, the cell volume, cell shape and atomic positions were relaxed simultaneously in a series of calculations made with progressively increasing precision. A final high-accuracy calculation of the total energy was performed after the completion of the relaxations with respect to $k$-point convergence and plane-wave cutoff. From the various sets of calculations, it was found that for the KMgH$_3$ structure, 512 $k$-points in the whole Brillouin zone with a 500 eV plane-wave cutoff are sufficient to ensure optimum accuracy in the computed results. A similar density of $k$-points was used for the other structures considered. In order to avoid ambiguities regarding the free-energy results, we have always used the same energy cutoff and a similar $k$-grid density for convergence in all the structural variants tested. The present type of theoretical approach has recently been applied successfully (Vajeeston et al., 2003a–b; 2002) to reproduce ambient and high-pressure phases of many series of hydrogen storage materials.
The Phonon program developed by Parlinski et al. (1997) was used for lattice dynamic calculations. The required supercell and force calculations were computed using the VASP code and the resulting data were imported into the Phonon program. The $2 \times 2 \times 2$ supercells were constructed from the optimised structure that contains 80 and 160 atoms for the LiMgH$_3$ and NaMgH$_3$ phases, respectively. The Hessian (harmonic approximation) was determined through numerical derivation using steps of 0.03 Å in both positive and negative directions of each coordinate to estimate the harmonic potentials. The sampling of the phonon band structure for the phonon DOS calculations were set to ‘large’ in the Phonon program (Parlinski et al., 1997) with a point spacing of 0.05 THz. When polarisation effects were included, these were approximated by a non-analytical semi-empirical term (Pick et al., 1970), as implemented in the Phonon program.

3 Structural investigation: a challenging task

The crystal structures of the pure elements and most of the binary compounds have been frequently studied and are well characterised. On turning to ternary compounds, however, the amount of knowledge is considerably less extensive (with an estimated 10% coverage of structural information) and for quaternary and multicomponent phases, the structural knowledge is extremely poor. For hydrides, owing to the complexity in structural arrangements and the difficulties involved in establishing hydrogen positions by X-ray diffraction methods, structural information is very limited (Yvon, 1994). As we mentioned in the previous section, from the high hydrogen content (in wt.%) point of view, only a limited number of elements with their combinations should be used for this purpose. From this aspect, alkali and alkaline-earth metals in combination with elements of Groups 3, 4 and 5 of the periodic table get considerable interest. However, within this limitation itself, one can have numerous well-defined series of phases, but only few members of these series have so far been experimentally explored. From the theoretical point of view, there is no unique way to find the crystal structure of the unknown phases. Several approaches like the guess-structure/Inorganic Crystal Structure Database (ICSD) approach, simulated annealing, genetic algorithm, force-field approach, molecular dynamic study, etc., are being used to reach the global minima for a chosen chemical composition. Based on our experience, the ICSD approach is the best where existing structural information (within a similar chemical formula; e.g., AB$_2$; A and B are elements in the periodic table) is used as a starting point. In this approach, the validity of such a prediction depends upon the number of guess structures (the more phases there are, the better the reliability). Moreover, most of the binary, ternary and quaternary (not for all combinations) phases’ more structural information are available and this approach is more suitable. When we move to quaternary and multicomponent systems, only few/no structural inputs are available. Hence, one requires a different approach for such cases. The main drawback of the other methods is that the optimisation mostly reaches the local minima instead of the global minima. These methods are more suitable for energetic studies where the structure does not need to be completely correct (the error will be within 10 KJ/mole).
Figure 2  The cell volume versus the total energy curves for LiMgH\textsubscript{3} in different possible structural arrangements (a) and the calculated pressure-volume curve for LiMgH\textsubscript{3}.

Notes: Structure-type inputs are specified in (a).
For clarity, only the nine variants with the lowest total energy are documented.
The pressure-induced phase transition point is marked by an arrow.

4 Structural study on LiMgH\textsubscript{3} and NaMgH\textsubscript{3}

Approximately 24 potentially applicable structure types have been used as inputs in the structural optimisation calculations for the LiMgH\textsubscript{3} and NaMgH\textsubscript{3} compounds (the known structure type and Pearson structure classification notation in parenthesis):

- KMnF\textsubscript{3} ($tP20$)
- GdFeO\textsubscript{3} [NaCoF\textsubscript{3} ($oP20$)]
- KCuF\textsubscript{3} ($tI20$)
- BaTiO\textsubscript{3} [RbNiF\textsubscript{3} ($hP30$)]
- CsCoF\textsubscript{3} ($hR45$)
- CaTiO\textsubscript{3} [CsHgF\textsubscript{3} ($cP5$)]
- PCF\textsubscript{3} ($tP40$)
- KCuF\textsubscript{3} ($tP5$)
- KCaF\textsubscript{3} ($mP40$)
- NaCuF\textsubscript{3} ($aP20$)
- SnTlF\textsubscript{3} ($mC80$)
• KCaF$_3$ ($mB40$)
• 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$_3$ ($hR45$)
• $\alpha$-CsMgH$_3$ ($Pnmn$) (ICSD, 2007; Renaudin et al., 2003).

From the structural starting points above, full geometry optimisation has been carried out without any constraints on the atomic positions and unit-cell parameters. As we saw in the previous section, the reliability of the calculation depends upon the number of structural inputs involved in the calculation. The $ABX_3$ composition has 2545 entries in the ICSD database. It is a tedious process to include all these structures into consideration, which requires tremendous computations. However, several compounds/phases have the same structure type and, in some cases, have only a small variation in the positional parameters (only for certain atoms). These possibilities are omitted because after complete geometry optimisation, we mostly obtained similar types of structural arrangements in spite of using different positional parameters. For this particular composition, 24 structure types have almost unique structural arrangements and, hence, we have used only 24 applicable structures as input in the structural optimisation.

The crystal structure of LiMgH$_3$ is hitherto not experimentally determined. Among the considered structures, an LiTaO$_3$-type ($\alpha$-LiMgH$_3$) atomic arrangement (Table 1 and Figure 1a) occurs at the lowest total energy (Figure 2). However, an FeTiO$_3$-type variant appears energetically very close to the ground-state phase. The involved energy difference between these two phases is only 0.01 eV/f.u. The LiMgH$_3$ structure consists of corner-sharing MgH$_6$ octahedra (see Figure 1a). From the interatomic Mg-H distances and H-Mg-H angles (ranging between 76.8° and 104.9°), it is evident that the MgH$_6$ octahedra are highly distorted. Li is surrounded by 6 H atoms within the distance from 1.934 to 2.794 Å, but here, the Li-H distances are a little longer than the normal Li-H distances in other Li-based hydrides. The shortest H-H separation in the LiMgH$_3$ structure exceeds 2.58 Å and is comparable with the H-H separation found in other compounds of $ABH_3$ (A = alkali; B = alkali-earth) series. It is interesting to note that in the $\alpha$-LiMgH$_3$ phase, there is no inversion symmetry found; hence, it should have ferroelectric properties.
Table 1  The optimised equilibrium structural parameters, bulk modulus ($B_0$) and pressure derivative of bulk modulus ($B'_0$) for the $MMgH_3$ ($M = Li, Na$) series

<table>
<thead>
<tr>
<th>Compound (structure type; space group)</th>
<th>Unit cell (Å)</th>
<th>Positional parameters</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-LiMgH$_3$ (LiTaO$_3$ type; R3c)</td>
<td>$a = 4.958$, $c = 13.337$</td>
<td>Li(6a) : 0.0, 0.0, 0.2887; Mg(6a) : 0, 0, 0, H(18b) : 0.0376, 0.3626, 0.5637</td>
<td>40</td>
<td>3.1</td>
</tr>
<tr>
<td>β-LiMgH$_3$ (CaCO$_3$ type; P121/c1)</td>
<td>$a = 3.9083$, $b = 4.1876$, $c = 5.5286$, $β = 93.92$</td>
<td>Mg(4e) : 0.25, 0.25, 0.5, H(4e) : 0.0406, 0.041, 0.2898, H(4e) : 0.0.25, 0.6451, 0.5</td>
<td>34</td>
<td>3.6</td>
</tr>
<tr>
<td>NaMgH$_3$ (GdFeO$_3$ type; Pnma)</td>
<td>$a = 5.4525$ (5.4634)$^a$, $b = 7.6952$ (7.7030)$^a$, $c = 5.3683$ (5.4108)</td>
<td>Na(4c) : 0.0209, 1/4, 0.006; Mg(4b) : 0, 0, 1/2, H1(4c) : 0.503, 1/4, 0.093, H2(8d) : 0.304, 0.065, 0.761</td>
<td>38.4</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Note:  $^a$ Experimental values from Bouamrane et al. (2000).

It should be noted that when we apply pressure, the stable $\alpha$ modification transforms into another CaCO$_3$-type modification ($\beta$-LiMgH$_3$; $P121/c$ symmetry) at 38 GPa and the estimated volume discontinuity at the transition point is ca 4.2 Å$^3$/f.u. (see Figure 2a). In this structural arrangement, similar to the $\alpha$ modification, Li is surrounded by six H atoms (see Figure 1b) and the calculated distances vary between 1.45 to 1.48 Å. On the other hand, Mg is surrounded by nine H atoms and the distances vary from 1.66 to 2.01 Å. This increment in the coordination number is expected upon the application of pressure. The calculated minimum Li-Mg distance is 2.32 Å and H-H separation is around 2 Å.

NaMgH$_3$ takes a distorted perovskite structure analogous to the GdFeO$_3$ type (Figure 1c) (Geller, 1956; Rönnebro et al., 2000). Consistent with the experimental findings, this atomic arrangement has a lower energy than the considered alternatives (see above) and the calculated unit-cell dimensions and positional parameters at 0 K and ambient pressure are in good agreement with the room temperature experimental findings (see Table 1). The deviations from the experimental unit-cell parameters $a$ and $b$ are almost negligible and the underestimation of 1.2% in the $c$ direction is typical for the state-of-the-art approximation of DFT. The findings show that one can reliably reproduce/predict structural parameters for even quite complex atomic arrangements using this type of approach. As seen from Figure 1(b), the MgH$_6$ octahedra in NaMgH$_3$ are somewhat distorted (H-Mg-H angles in the range of 88.2° to 91.8°). A similar structure with the same type of distortions is incidently also found for NaMgF$_3$ (Rönnebro et al., 2000). In general, most of the hydride and fluoride families show pronounced analogies in the structural aspect. High-pressure study shows that no pressure-induced structural transitions were observed in NaMgH$_3$, indicating that this phase is very stable at elevated pressures.
By fitting the total energy as a function of cell volume using the so-called universal equation of state (Vinet et al., 1989), the bulk modulus ($B_0$) and its pressure derivative ($B'_0$) are obtained (Table 1), but no experimental data are yet available for comparison.

When we move from LiMgH$_3$ to NaMgH$_3$, the $B_0$ is reduced considerably. The variations in $B_0$ and $B'_0$ are accordingly correlated with the variations in the size of $M$ and, consequently, also with the cell volume. Compared to intermetallic-based hydrides, these compounds have low $B_0$ values, implying that they are soft and easily compressible.

Even though both $\alpha$ and $\beta$ modifications of LiMgH$_3$ have almost similar equilibrium volumes, the $B_0$ value for $\alpha$ modification is larger than the $\beta$ modification. As compensation, the $\alpha$ modification has a smaller $B'_0$ value than the $\beta$ modification.

The calculated phonon DOS for the equilibrium structures for both phases are shown in Figure 3. In both cases, no imaginary frequency was observed, indicating that both structures are thermodynamically stable phases. The ground-state structure for NaMgH$_3$ is already known experimentally, but that for LiMgH$_3$ is not yet known. As there are no negative phonon frequencies observed for LiMgH$_3$, the predicted structure is expected to be stable and it needs experimental verification. Both LiMgH$_3$ and NaMgH$_3$ have almost similar phonon DOS. Hence, we have displayed in Figure 4 the partial phonon DOS for LiMgH$_3$ only. The partial phonon DOS is plotted along three directions viz. $x$, $y$ and $z$. For Li and Mg atoms, the vibrational modes along the $x$ and $y$ directions are identical and the modes along the $z$ direction are slightly different from those of the $x$ and $y$ directions. Since the mass of the H atom is much smaller than that of the Li or Mg atom, Figure 4 shows that the high-frequency modes above 15 THz (in NaMgH$_3$, it is 10 THz) are dominated by H atoms and the low-frequency modes below 15 THz are dominated by Li and Mg atoms. Due to the mass difference between the Li and Mg atoms, a considerable difference between 3 to 13 THz is observed.
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Figure 4  The calculated total and partial phonon DOS in LiMgH$_3$ (see online version for colours)

Notes: The bottom panel is the total phonon DOS and the upper panels are the partial phonon DOS for Li, Mg and H atoms, respectively. The partial DOS is plotted along three directions: $x$ (shaded), $y$ (red colour) and $z$ (green colour).

In order to establish the existence of the studied compounds, we have calculated the formation enthalpy ($\Delta H_F$) using the following reaction pathway: $A\text{H}_2 + \text{MgH}_2 \rightarrow A\text{MgH}_3$ ($A = \text{Li, Na}$) and zero-point energy correction is also included in the estimation of the standard enthalpy of formation. The estimated $\Delta H_F$ for NaMgH$_3$ is $-143$ kJ/mol, which is in very good agreement with the experimental finding of $-144$ kJ/mol by Ikeda et al. (2005). The corresponding value for the LiMgH$_3$ phase is $-162$ kJ/mol and no experimental data are available for comparison. This finding suggests that the two considered compounds are stable phases and experimental verification is needed for the LiMgH$_3$ phase.
5 Conclusion

The present study showed that from state-of-the-art density functional calculation, one can reproduce/predict the crystal structure of the known/unknown phases from the guess-structure/ICSD approach. The ground-state crystal structures have been identified from the structural optimisation of a number of structures using force as well as stress minimisations. For the experimentally known compounds, the ground-state structures are successfully reproduced within the accuracy of the density-functional approach. The crystal structure of LiMgH$_3$ has been predicted. The calculated phonon DOS shows that the predicted phase is either thermodynamically stable or metastable but not an unstable phase. The crystal structure of LiMgH$_3$ has been predicted to be of the LiTaO$_3$ type (note: lacking inversion symmetry) at 0 K and atmospheric pressure. LiMgH$_3$ should be an ionic insulator and we predict that it will exhibit ferroelectric properties. By the application of pressure, this phase transforms to CaCO$_3$-type modification at 38 GPa and no pressure-induced structural transitions were observed in NaMgH$_3$.

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References


