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Prediction of new complex hydride phases with high H-content

(M 24)

Abstract

The crystal, electronic structure, and thermodynamical properties of the $MCaH_3$ ($M = \text{Li, Na, K, Rb, Cs}$) series have been studied by state-of-the-art density-functional calculations. For the experimentally known $RbCaH_3$ and $CsCaH_3$ phases, the ground-state structure has been successfully reproduced within the accuracy of the density-functional approach. The ground-state crystal structures for $MCaH_3$ ($M = \text{Li, Na, K}$) phases have been predicted from structural optimization of a number of structures using force as well as stress minimizations. The predicted crystal structures for $LiCaH_3$ and $NaCaH_3$ are found to have rhombohedral and triclinic structures respectively, with insulating behaviour. $KCaH_3$ stabilizes in orthorhombic structure whereas $RbCaH_3$ and $CsCaH_3$ stabilize in cubic structures. Formation energies for the $MCaH_3$ series are calculated for different possible reaction pathways. For all these phases we propose that synthesis from elemental M and Ca in hydrogen atmosphere should be a more feasible route. The phonon density of states for the lattices are calculated by using a direct force constant method and it shows that all the predicted phases are dynamically stable.

The ground state structure of the CaB_2H_2 phase is predicted to be in tetragonal structure [space group $P-3m1$ (no. 161)]. From our lattice dynamic simulation we found that this phase is dynamically stable and we also simulated Raman spectra for this phase.

I) Structural investigation and thermodynamical properties of alkali calcium trihydrides

i) Structural investigation

Among the $MCaH_3$ phases, in $LiCaH_3$ and $NaCaH_3$ phases one can store H up to 6 and 4.6 wt.%, respectively. The rest of the considered phases have relatively low wt.% of H content. However, these phases may have potential application in electronic industry as we proposed in our earlier studies on this type of hydrides. In addition, these phases may coexist as by-products/mixed-phases of the multi phase light-weight hydrides during synthesis. Hence, the understanding about the structural phase stability of these phases is very important. Thirty potentially applicable structure types (ABX_3 ; A and B represent the first and second elements in the following structures and X is either O, F, or H) have been used as starting inputs in the structural optimization calculations for the $MCaH_3$ compounds. The present types of theoretical investigations are highly successful to predict the ground state structure of hydrides. Among the considered structure models for $LiCaH_3$, an $PbGeS_3$ -derived atomic arrangement occurs at the lowest total energy. Our symmetry analysis shows that during the structural relaxation processes the low symmetry triclinic and monoclinic structural modifications of $PbGeS_3$ transform into the somewhat high symmetry hexagonal (Fig. 1a; R-3C) phase. For the $NaCaH_3$ phase, USPEX-1-derived atomic arrangements have the lowest total energy. After the structure relaxation the high symmetry monoclinic structure ($C2$ transforms into low symmetry triclinic phase; Fig. 1b, P-1). It is often observed that, instead of relaxing to the local minimum, the system may relax to the global minimum, as it is the

case here. The results obtained from structural optimizations for KCaH_3 phase shows that the GdFeO_3 -derived model structures proved to have the lowest total energy. It is interesting to note that during the theoretical simulations many of the initially assumed different trial structures relaxed toward the GdFeO_3 -type structure (viz. strongly emphasizing that this particular atomic arrangement is energetically more favourable for KCaH_3). For the RbCaH_3 and CsCaH_3 phases, CaTiO_3 -type atomic arrangement has the lowest energy than the other considered structure types, consistent with the experimental findings.

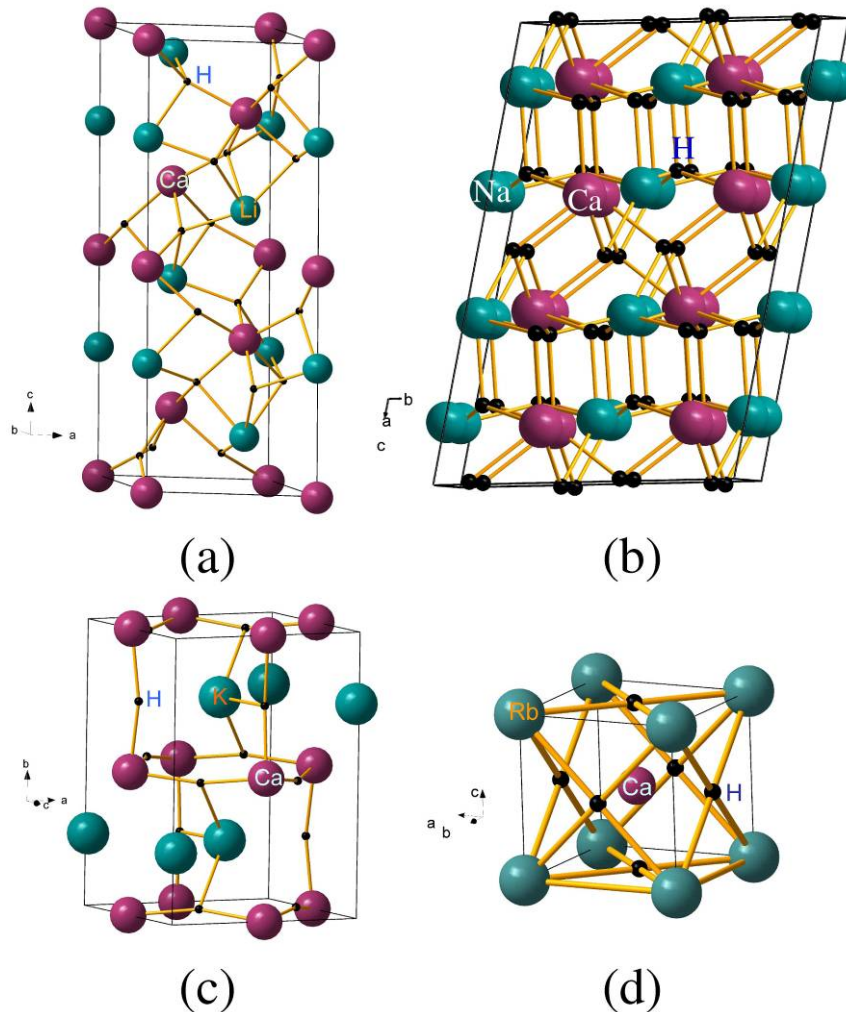


Fig.1: Theoretically predicted crystal structures for LiCaH_3 , (b) NaCaH_3 (c) KCaH_3 , (d) RbCaH_3 , and CsCaH_3 .

ii) Formation-energy considerations and lattice dynamic study

Formation enthalpy is the best aid to establish whether theoretically predicted phases are likely to be stable and also such data may serve as guidelines for possible synthesis routes. In this study we have considered four possible reaction pathways (Eq.1 to 4). The associated formation enthalpy listed in Table 1, are estimated from the calculated total energies without temperature effect. In general, synthesis of MCAH_3 compounds from an equiatomic MCA matrix is not possible as the alkali metals and calcium are immiscible in the solid and liquid state.

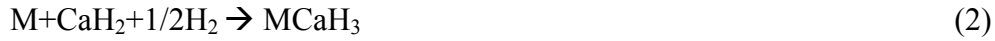


Table I: Calculated hydride formation energy (ΔH ; in kJ/mol.) according to Eqs. 1-4 for the $MCaH_3$ series.

Compound	$\Delta H1$	$\Delta H2$	$\Delta H3$	$\Delta H4$
LiCaH ₃	17.74	-70.01	-273.25	-149.51
NaCaH ₃	34.45	-10.55	-177.79	-132.79
KCaH ₃	17.03	-25.62	-192.86	-150.21
RbCaH ₃	10.32	-24.67	-191.91	-156.93
CsCaH ₃	12.84	-24.26	-191.50	-154.4

The results show that reaction pathways 2-4 give rise to an endothermic reaction for the $MCaH_3$ compounds. Hence, preparation of $MCaH_3$ from MH and CaH_2 (pathway 1) is not likely to be successful. It should be noted that $CsCaH_3$ has been synthesized from its binary hydrides under 200 bar H_2 pressure [Ref.1]. All $MCaH_3$ compounds are seen to exhibit high formation energies according to pathway 3. Hence, for all the studied phases, pathway 3 is energetically more favourable than other paths and we suggest that it should be possible to synthesize/stabilize these compounds using CaH_2 and M by passing H_2 .

In order to understand the stability of the predicted phases we have calculated phonon density of states for the equilibrium structures for these phases which are shown in Fig.2. For all these compounds no imaginary frequency was observed indicating that, all the predicted structures are ground-state structures for these systems, or at least they are dynamically stable. As the predicted phases are expected to be stable, we need experimental verification. Since the mass of H atom is much smaller than that of M or Ca atom, Fig. 2 shows that the high frequency modes above 10THz are dominated by H atom, and the low frequency modes below 10THz are mainly dominated by M (except Li) and Ca atoms. The centre of the Ca mode frequency in all these cases is always present around 5 THz. If one moves from Li to Cs, due to the mass difference between the M atoms, the vibrational mode frequencies from M are systematically shifted towards low frequency region.

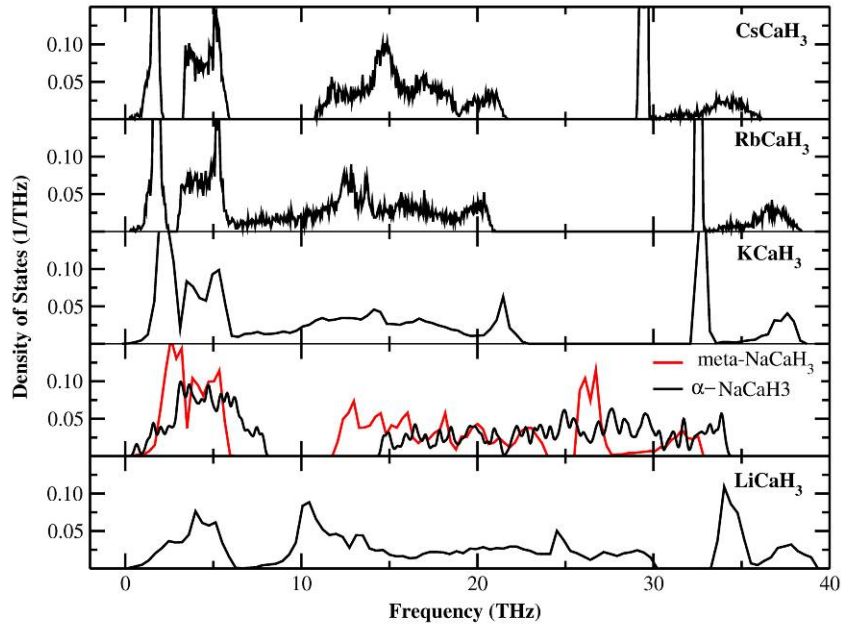


Fig. 2: Calculated total phonon DOS for $MCaH_3$ compounds. For the $NaCaH_3$ phase $R3c$ space group structure (meta $NaCaH_3$) is also dynamically stable (the phonon DOS is plotted in red colour) and the involved energy difference between these two structures is only $0.06eV$ only.

From our theoretical simulation we found that all the studied $MCaH_3$ phases are wide-band-gap insulators and the insulating behaviour is associated with well localized, paired s -electron configuration at the H site. The chemical bonding character of these compounds is predominantly ionic according to analyses of DOS, charge density, ELF, Bader charges, and BOP. [Ref.2]

II) Finding crystal structure of CaB_2H_2

$Mg(BH_4)_2$ and $Ca(BH_4)_2$ are suggested to have more favourable thermodynamics than $LiBH_4$ while maintaining attractive hydrogen capacities (14.9 and 11.5 mass% respectively). Based on density functional theory (DFT) calculations, the decomposition enthalpy for $Ca(BH_4)_2$ has been estimated to be 32 kJ/mol. This enthalpy corresponds to an equilibrium pressure of 1 bar at temperatures below $100^\circ C$ meaning that $Ca(BH_4)_2$ could be considered as a low/medium-temperature hydride. Experimental investigations of the phase transformations and the decomposition route of $Ca(BH_4)_2$ show, however, a more complex behaviour than the proposed reaction by DFT. A new intermediate decomposition product, CaB_2H_x , has been identified experimentally and the hydrogen content is not known precisely. [Ref.3] We assume the hydrogen content to be 2 and solved the structure using ICSD approach. At ambient condition the CaB_2H_2 crystallizes in the tetragonal structure (see Fig.3).

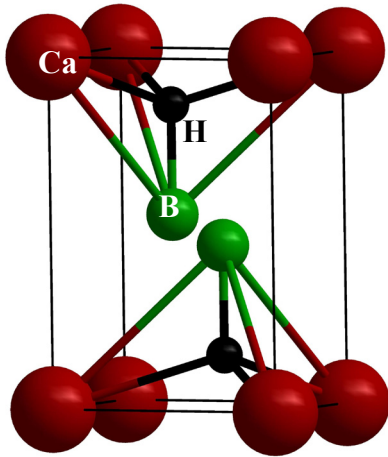


Fig. 3: The predicted crystal structure of CaB_2H_2 [space group $P-3 m1$ (no. 161); $a = 3.4739\text{\AA}$, $c = 3.9784\text{\AA}$; $\text{Ca} = 0, 0, 0$; $\text{B} = 2/3, 1/3, 0.46218$; $\text{H} = 2/3, 1/3, 0.1511$].

In a stable crystal all the phonon frequencies must be positive. An optimization of the crystal structure under constraints of the space group symmetry elements may lead to an atomic configuration, which does not yet correspond to a global energy minimum. In this case some phonon frequencies may appear as negative values (soft modes). In the CaB_2H_2 phase we have not found any soft modes (see Fig. 4a). Hence, the predicted structure is dynamically stable. We also calculated the Raman spectra for the CaB_2H_2 phase and it might be also very useful for the experimentalists to verify their result if one has mixed phases. [Ref. 4]

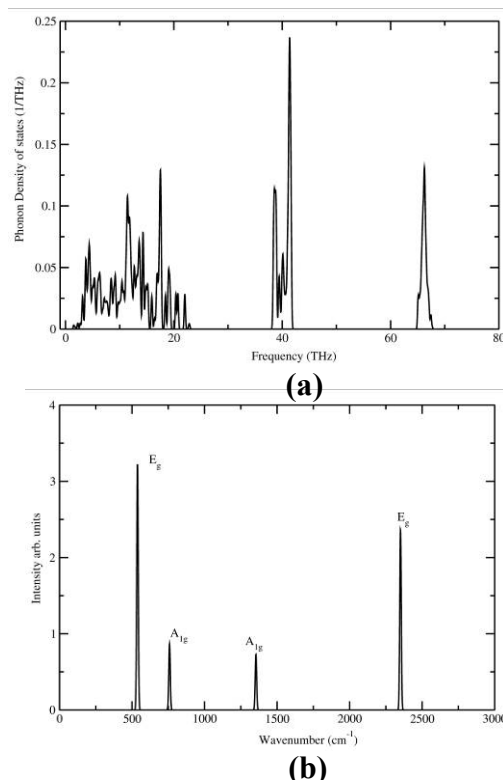


Fig. 4: Theoretically-simulated phonon (a) and Raman spectra (b) for the CaB_2H_2 phase.

III) Predicting new materials for hydrogen storage application

Knowledge about the ground-state crystal structure is a prerequisite for rational understanding of solid-state properties of new materials. To act as an efficient energy carrier, hydrogen should be absorbed and desorbed in materials easily and in high quantities. Owing to the complexity in structural arrangements and difficulties involved in establishing hydrogen positions by x-ray diffraction methods, structural information of hydrides are very limited compared to other classes of materials (like oxides, intermetallics, etc). This can be overcome by conducting computational simulations combined with selected experimental study which can save environment, money, and man power. The predicting capability of first-principles density functional theory (DFT) is already well recognized and in many cases structural and thermodynamic properties of single/multi component system are predicted. This review will focus on possible new classes of materials those have high hydrogen content, demonstrate the ability of DFT to predict crystal structure, and search for potential meta-stable phases. Stabilization of such meta-stable phases is also discussed. [Ref. 5]

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