Structural variations and hydrogen storage properties of Ca$_5$Si$_3$ with Cr$_5$B$_3$-type structure

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**ABSTRACT**

The structure and phase variation of Ca$_5$Si$_3$ upon hydrogenation were systematically investigated using combined neutron powder diffraction (NPD), neutron vibrational spectroscopy (NVS), and first-principles calculations. The hydrogen absorption equilibrium was first attained with formation of Ca$_5$Si$_3$H(D)$_{0.53}$ (I4/mcm) with H exclusively located in Ca$_4$-tetrahedral sites. More hydrogen absorbed into the system under higher pressure leads to dissociations into CaH$_2$ (an amorphous hydride at higher pressures) and CaSi. The hydrogen-induced formation of an amorphous phase under higher pressures is very unusual in Cr$_5$B$_3$-type compounds and the observed formation of CaH$_2$ upon hydrogen absorption confirmed the proposed composition equilibrium between A$_5$T$_t$$_3$ (A = Ca, Sr; Tt = Si, Ge, Sn) and AH$_2$.

**1. Introduction**

Extensive efforts are being made to develop sustainable and clean energy sources to replace the use of carbon-based fuels. Successful development of hydrogen as a primary fuel will simultaneously reduce dependence on fossil fuel and emissions of greenhouse gases and pollutants. One of the major challenges to realize a future hydrogen economy is the lack of suitable hydrogen storage materials with the operating storage requirements for fuel-cell vehicular applications in the range of 0.1–1 MPa and 298–473 K [1]. Metal hydrides are an important family of materials that can be potentially used for safe, efficient and reversible on-board hydrogen storage. Particularly, intense interest has been focused on light-weight metal hydrides such as LiH and MgH$_2$ due to their relatively high hydrogen-storage densities. However, most of these hydrides have rather slow absorption kinetics, relatively high thermal stability, and/or problems with the reversibility of hydrogen absorption/desorption cycling. Therefore, so far there is no such candidate system that can meet all the requirements simultaneously.

Recently, alloying with Si has been shown to effectively destabilize LiH and MgH$_2$ at significantly lower temperatures by forming Li–Si and Mg–Si intermetallic compounds upon dehydrogenation [2]. These Si-alloying studies have been extended to CaH$_2$ and the hydrogen-storage properties of the resulting Ca–Si intermetallic compounds [3–5]. Among them, CaSi was found to reversibly absorb and desorb hydrogen in a moderate temperature range of 473–573 K [3]. Ca$_2$Si shows even more rapid absorption kinetics with the formation of a reversible amorphous hydride phase in the temperature range of 473–523 K [5]. These prior studies motivated us to investigate hydrogen storage properties and structural variations upon hydrogenation/dehydrogenation of Ca$_5$Si$_3$, another important intermetallic phase in the Ca–Si system.

The crystal structure of Ca$_5$Si$_3$, as well as other alkaline-earth tetralides, A$_5$T$_t$$_3$ (A = Ca, Sr, and Ba; Tt = Si, Ge, Sn and Pb), belongs to the frequently encountered tetragonal Cr$_5$B$_3$-type structure, which features an equal number of monomeric and dimeric anions so that the divalent cations formally meet the structure criterion [6] for Zintl phases, (A$^{2+}$)$_5$[(Tt$^{2-}$)$_5$](Tt$^{4-}$)$_5$), in terms of oxidation states. The presence of a significant A$_4$-tetrahedral cavity in this structure type allows a ready incorporation of small quantities of hydrogen or fluoride into the structure, resulting in oxidation of the substrate. The oxidation of A$_5$T$_t$$_3$ phases to hydride or fluoride derivatives has been shown to have significant impact on their electronic and magnetic properties [7,8]. In the present study, we will focus mainly on the structure variations upon hydrogenation and the resulting hydrogen storage properties.

In our earlier studies in CaSi and Ca$_2$Si [4,5], we have developed a method of preparing crystalline metal-silicide phases upon the dehydrogenation of ball milled CaH$_2$ and Si mixtures. Using this method, the intermetallic phases can be synthesized at temperatures significantly lower than the conventional metal-melt method [9,10]. Our hydrogenation studies were undertaken on samples prepared by this method. In this Letter, we address the structural behavior and absorption properties of the Ca$_5$Si$_3$ system using combined neutron powder diffraction (NPD), neutron vibrational...
spectroscopy (NVS) and first-principles calculations. From the refinement of NPD data on a deuterided sample, we discuss the crystal structure of Ca$_5$Si$_3$H$_2$ and correlate its detailed structural features with other hydrogenated Cr$_5$B$_3$-type alkaline-earth tetrahalides. Upon hydrogenation at higher pressure or higher temperature, complete hydrogenation of Ca$_5$Si$_3$ yielded a maximum hydrogen uptake of 1.4 wt% rather than 0.35 wt% assuming the formation of fully hydrogenated Ca$_5$Si$_3$H. Extra hydrogen absorbed into the system leads to the formation of CaH$_2$ and an unexpected amorphous phase. To the best of our knowledge, this is the first reported observation of hydrogen-induced amorphization in an intermetallic compound with a Cr$_5$B$_3$-type structure.

2. Experimental section

A Ca$_5$Si$_3$ powder sample was synthesized by the following procedures. Stoichiometric 5:3 amounts of CaH$_2$ (Aldrich [11], 99.9%) and Si (Alfa Aesar 99.999%) powders were mixed under one atmosphere He gas via ball milling with a Fritsch Pulverisette 7 planetary mill at 400 rpm for 30 min. The mixture was then heated under dynamic vacuum for 10 h at 873 K to remove H$_2$. The product was ground again in an agate mortar with a pestle in a He-filled glovebox for further measurements. Using this method, the formation temperature of the metal-silicide phase, Ca$_5$Si$_3$, can be decreased by ∼500–550 K compared to the conventional metal-melt method [9]. Hydrided and deuterided samples were prepared using this Ca$_5$Si$_3$ by direct reaction with gas-phase H$_2$ and D$_2$ (99.999%), respectively, at various pressures and temperatures as detailed in the next section. All dehydrogenation and hydrogenation reactions were carried out in Mo envelopes that were sealed in a stainless steel tube and heated either under dynamic vacuum or under gas pressure in a conventional tube furnace, depending on the target. All reagents and products were handled in an ultra-pure He-filled glovebox.

All neutron scattering measurements were performed at NIST Center for Neutron Research (NCNR). The NPD data were collected using the BT1 high-resolution powder diffractometer [12] with the Cu(3 1 1) monochromator at a wavelength of 1.5403(2) Å and an in-pile collimation of 15 min of arc. Data were collected over the 2θ range of 3–168°. Rietveld structural refinements were done using the GSAS package [13]. The neutron vibrational spectra were measured using the BT-4 Filter-Analyzer Neutron Spectrometer [14] with the Cu(2 2 0) monochromator under conditions that provided full-width-at-half-maximum energy resolutions of 2–4.5% of the incident energy over the range probed. Hydrogen contents of samples were measured using the neutron prompt-activation analysis (PGAA) facility [15]. A pure CaH$_2$ sample was used as the standard material to normalize γ-ray intensities. Deuterium content was determined by gravimetric measurements.

First-principles calculations were performed within the plane-wave implementation of the generalized gradient approximation to density functional theory (DFT) using the PWSCF package [16]. We used a Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 400 eV and a 4 × 4 × 4 k-point mesh were found to be enough for the total energy to converge within 0.5 meV/atom and 0.005 eV/Å. Structure optimizations were performed with respect to lattice parameters and atomic positions. The phonon calculations were conducted with the optimized structure using the supercell method with finite difference [17,18].

3. Results

A single-phase Ca$_5$Si$_3$ alloy is formed upon dehydrogenation of the ball milled CaH$_2$/Si mixture in a ratio of 5:3 at 873 K. The NPD pattern (Fig. 1) of this alloy contains only reflections of a Cr$_5$B$_3$-type tetragonal structure (space group I$4/mcm$) with refined lattice parameters $a = 7.64988(9)$ Å, and $c = 14.8268(3)$ Å, which agrees well with previous reported values [8,10]. Annealing this sample at 573 K under 0.1 MPa H$_2$ resulted in an equilibrium composition Ca$_5$Si$_3$H$_{0.5}$ as determined by the PGAA technique. Refinement of the NPD data (Fig. 1) from the deuterided composition at the same conditions yielded a similar $I4/mcm$ tetragonal structure with the reduced lattice parameters, $a = 7.6394(2)$ Å and $c = 14.7935(1)$ Å, and a deuterium occupancy of 0.530(1). The refined lattice parameters, fractional coordinates, site occupancies, thermal parameters,
and reliability factors for Ca$_{5}$Si$_3$ and Ca$_{5}$Si$_3$D$_{0.53}$ measured at 295 K are summarized in Tables 1 and 2. Table 3 lists important interatomic distances.

To understand the spectra and correlate the observed phonon density of states with the refined crystal structures, we performed first-principles phonon calculations on Ca$_{5}$Si$_3$H. The phonon calculations were performed with the optimized structure using the supercell method with finite difference [18]. A cell of $1a \times 1b \times 1c$ was used and the full dynamical matrix was obtained from a total of 14 symmetry-independent atomic displacements (0.02 Å). The NV spectra of Ca$_{5}$Si$_3$H were computed for a 10$^4$-point grid within the incoherent approximation with the instrumental resolution taken into account [19]. The primitive cell of Ca$_{5}$Si$_3$H contains two formula units (i.e., 18 atoms), giving rise to a total of 54 phonon branches with $I^g (q = 0 ) = 3[3A1g(R) + 2A1u + 3A2g + 6A2u(IR) + 2B1g(R) + 3B1u + 4B2g(R) + 1B2u + 9Eu(IR) + 68g(R)]$, where $R$ and IR correspond to Raman- and infrared-active modes.
were not measured. Fig. 3 also compares the calculated phonon modes with the observed NV spectra. Calculations considering 1-phonon and (1 + 2) phonon contributions to the NV spectra yield similar spectra in the measured energy range. The observed phonon modes in the range of 85–110 meV in the NV spectra of CaSi3H0.5 include six phonon modes (1A 2u + 1 B2g + E u + E g), all originated from H (4b) atoms in the Ca4-tetrahedral sites. The higher-energy phonon band (including 1A 2u + 1 B2g modes) corresponds to the in-phase and out-of-phase vibrations of H along the c direction, and the lower band (including E u + E g modes) is assigned to the in-phase and out-of-phase vibrations of H along the (110) direction. In Fig. 3 the measured spectra showed phonon bands with lower energies compared to the calculations, likely due to the partial filling of H sites in the actual structure with consequent weakening H-metal bonding. Nonetheless, the calculated phonon modes agree reasonably well with the observed NVs, and thus are consistent with the refined structure determined from the NPD data.

Upon hydrogenation of Ca5Si3 at higher pressure, the system showed some interesting and unexpected structural variations. Fig. 4 shows NV spectra for the samples upon hydrogenation under different pressures and annealing temperatures. Annealing at 573 K with a relatively high H2 pressure, i.e. 3 MPa, produces an equilibrium composition of Ca5Si3H4.41. The most prominent groups of phonon modes for this composition represent the hydrogen vibrations in calcium hydride (CaH2) [20]. The spectrum of pure CaH2 is shown for comparison. There is an additional strong peak observed in the lower-energy portion (50–60 meV), which is due to the dissociation of the alloy phase upon hydrogenation and was also present in the previous H2-pressurized CaSi3 system [5]. The third noticeable feature in the NV spectrum is the partial filling of H sites in the actual structure with consequent weakening H-metal bonding. Nonetheless, the calculated phonon modes agree reasonably well with the observed NVs, and thus are consistent with the refined structure determined from the NPD data.

Annealing at higher temperature while keeping the small pressure unchanged, i.e. 0.1 MPa at 873 K, also generates an equilibrium composition, Ca5Si3H4.08. The vibrational spectrum of this phase is in progress to determine its composition and structure, as well as to better understand the overall destabilization processes.

Fig. 4. Neutron vibrational spectra for Ca5Si3H4 equilibrated at (a) 573 K and 0.1 MPa, (b) 573 K and 3 MPa and (c) 873 K and 0.1 MPa. Arrows point to the phonon modes from the unknown hydride phase(s). The spectra of CaH2 (Ref. [20] and amorphous hydride phases (Ref. [5]) are also plotted for comparison.
[33.6%], CaSi [66.4%] and small amounts of unknown phases as observed previously, consistently with the NVS results. The products of Ca5Si3 under various treatment conditions are summarized in Table 4.

All the products after hydrogenation can be recycled. After dehydrogenating at 873 K, a single-phase intermetallic compound Ca5Si3 was recovered (see Supplementary material), which confirms the reversible hydrogenation of this system.

4. Discussion

In order to have a better understanding of the Ca5Si3 phase and its hydrogenation process, in this section, we will compare the structure of Ca5Si3H4 with its fluoride analogue and other A5Tt3 hydrides/fluorides, and discuss the degradation process of Ca5Si3 alloy upon hydrogenation.

As mentioned in the introduction, the crystal structure of Ca5Si3, as well as other Cr5B3-type alkaline-earth tetralides A5Tt3, features an equal number of monomeric and dimeric anions and the presence of an A(2)8-tetrahedral cavity. A small quantity of hydrogen or fluorine can be readily incorporated into the structure without a change in the symmetry, forming a hydride or fluoride phase via heating the alloy under 0.1 MPa or less pressure at moderate temperatures. In some extreme cases, the binary alloy does not even exist and can only be stabilized through interstitial binding, i.e. Ca5Sn3Hx and Sr5Pb3Fx. Apparently, the amount of hydrogen or fluorine incorporated depends on the size of such cavities and the binding strength between H(F), alkaline-earth cations (A2-site), and the tetralide dimers. In Fig. 5, the known A5Tt3Fx compounds with the refined deuteride and fluoride occupancies are mapped as a function of tetrahedral anion radii. Variations in the size of tetrahedral site (e.g. A2-Z) with Tt radius changes are also plotted for Ca5Tt3 and Ca5Tt3Fx. In general, the content of F or H in the structure increases with the size of Tt given the same radius of A (e.g. Ca). This is a fairly straightforward size effect, as the tetrahedral cavity increases with increasing Tt at fixed A (green open triangle line in Fig. 5).1 The effect of binding H+ or F− relative to the empty binary version reduces the sizes of the tetrahedral cavity (Fig. 5, black open square and red open circle lines), the decrements of which are reasonably proportional to the H or F content (Fig. 5, solid square and red solid circle lines). Substitution of F in the tetrahedral cavity results in smaller occupancy and hole size decrements than those for H at fixed A and Tt, which is consistent with their comparative radii. From the present comparison between the empty and filled A4-tetrahedral sizes with Tt radii and H or F content, the questionable trend of the reduced empty Sr4-tetrahedral hole size with larger Tt in Sr5Tt3Fx [Fig. 5, blue open diamond line] suggests probable hydrogen contamination for the reported Sr5Ge3Fx [21] and Sr5Sn3Fx [22].

Without contamination of H or F, the decrease in the top and bottom edges of A(2)8-antiprisms about Tt1. Such effects also extend to the section of the structure that contains the Tt2 dimer, which will split the degeneracies of the p levels on the dimers. Therefore, with increasing concentration of H or F, the interstitials would withdraw more p orbitals from the heavier and weaker dimers and the Tt2–Tt2 bond lengths in the dimers would generally shorten as p electrons are removed. For binary A5Tt3 with empty tetrahedra for larger Tt (Tt = Sn and Pb), the absence of interstitial binding will yield too short distances between the A2 sites around the larger Tt2, which would consequently destabilize the structure. As a result, the

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Table 4

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<td>Ca5Si3H4</td>
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<td>-</td>
<td>NVS, PGAA</td>
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<td>unknown hydrides</td>
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<td>6.815(1)</td>
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Fig. 5. Schematic illustration of the effect of Tt and A radii and the size of A5Tt3 tetrahedral cavities on Z occupancies in A5Tt3Pz (Z = H, F). Solid symbols indicate the determined occupancies of Z (left axis); open symbols represent the calculated radius of tetrahedral cavities (right axis). The data for these compounds except Ca5Si3 and Ca5Si3D0.53 are from Refs. [7,8,21,22].

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1 For interpretation of color in Fig. 5, the reader is referred to the web version of this article.
binary version of Ca₅Sn₃ and Sr₅Pb₃ has never been reported, and only examples of Ca₃SmZ₂ and Sr₅PbF₄ ternaries occur.

On the other hand, Fig. 5 also indicates that the occupancy of F decreases with increasing size of A at fixed Tt. This is in contrast to their tetrahedral hole sizes. Considering our studies in Ca₅Si₃ and its hydrogenation products at various pressures, we propose as a possible explanation that the H content in the A₅Tt₃H₄ structure is related to its equilibrium with AH₂ (see the discussion below). The equilibrium would move toward the formation of AH₂ with higher H₂ pressure (more H), greater electronegativity of A (stronger A–H bond), and increasing temperatures.

We next discuss the hydrogen-induced degradation behavior in Ca₅Si₃. The parent Cr₅B₃-type lattice is essentially maintained with hydrogen atoms exclusively occupying Ca₄ tetrahedral sites under 0.1 MPa at 573 K. Such a Cr₅B₃-type structure will collapse and dissociate under higher pressures or at higher temperatures. Considering the NPD spectrum of Ca₅Si₃Hₓ (Fig. 3) and refined NPD data for the hydrogenation products (Table 4 and Supplementary material), where the crystalline CaH₂ phase can be clearly detected, Ca₅Si₃ presumably decomposed through following route:

\[ \text{Ca}_5\text{Si}_3 \rightarrow (\text{Ca}_5\text{Si}_3\text{H}_2)_0.53 + 2\text{H}_2 \rightarrow 2\text{CaH}_2 + 3\text{CaSi} \]

(+ amorphous hydride phase at P = 3 MPa)

The hydrogen-induced amorphization (HIA) phenomenon is frequently observed in families of intermetallic compounds with certain crystal structures such as laves phases. The Ca₅Si₃ phase does not belong to any of these structure families, however, the current system satisfies the general requirements [23] described for amorphous or metal-glass formation in a solid state reaction: (i) at least one ternary system, (ii) a large disparity in the atomic diffusion rates of two of the species, and (iii) the absence of a polymorphic crystalline alternative as a final state. Therefore, the formation of an amorphous hydride phase upon relatively higher pressure hydrogenation (P = 3 MPa in the present study) can be explained by the previously proposed ‘chemical frustration effect’, where the glassy hydride would appear to be a metastable alternative of the crystalline phase because it does not require the interdiffusion of metal species (i.e., Ca and Si), which is much slower than the highly mobile hydrogen atoms with increasing H₂ pressure [23,5]. In addition, in Ca₅Si₃, the amorphization under high pressure did not change below ~573 K with hydrogenation time. In other words, the amorphous phase could still be observed even after hydrogenating a Ca₅Si₃ sample for a long period, e.g., 8–10 h, at this temperature. Thus, we believe this chemical frustration effect, rather than kinetic effects, is primarily responsible for the transition to the amorphous state.

The composition of final product (2CaH₂ + 3CaSi) is in good agreement with the stoichiometries of the high pressure (Ca₅Si₃Hₓ, x ≈ 0.53) products determined by PGAA. The hydrogen content more than four may be contributed by the unknown hydride phase as observed in the NPD data. Nonetheless, the observed formation of CaH₂ confirms our proposed absorption equilibrium between A₅Tt₃ and AH₂.

The facile absorption behavior and the complete reversibility make Ca₅Si₃ an intriguing system for hydrogen storage, particularly if the absorption/desorption temperatures could be further reduced by the use of dopants and/or catalysts. In that sense, the current system can aid us in designing new hydride materials with lighter metal substituents and thus higher storage capacities.

5. Conclusions

The structure and phase variation of Ca₅Si₃ alloy upon hydrogenation process were systematically investigated using combined NPD, NVS and first-principles calculations. Upon hydriding under 0.1 MPa at 573 K the absorption equilibrium was attained with the formation of a Cr₅B₃-type structure Ca₅Si₃H(D)ₐₓₐₘ (J/mcm, No. 140) with H exclusively located in Ca₄-tetrahedral sites. From the refined NPD data, Ca₅Si₃Hₐₓₐₘ shows a contraction in cell dimension and Ca₄-tetrahedral cavity size compared to Ca₅Si₃. Our refined structures also indicate the changes in positional parameters and the resulting complicated relationships among them with the interstitial binding, which is primarily responsible for the oxidation state, electronic structure, bonding strength, and stability of the structures. Upon hydrogenation under higher pressures (i.e., 3 MPa, 573 K) or higher temperature (i.e., 873 K, 0.1 MPa) Ca₅Si₃ absorbs hydrogen and dissociates into CaH₂ (amorphous hydride at high pressure) and CaSi. Such structure behavior upon hydrogenation has not been previously reported in any A₅Tt₃-type intermetallic compounds (A = Ca, Sr; Tt = Si, Ge, Sn). The observed formation of CaH₂ upon hydrogen absorption confirms the proposed composition equilibrium between A₅Tt₃ and AH₂. The hydrogen-induced formation of an amorphous phase at higher pressures is very unusual in intermetallic compounds with the Cr₅B₃-type structure, but could be rationalized as previously described in Ca₅Si₃.

Acknowledgments

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Appendix A. Supplementary material

NPD patterns of hydrogenation products of Ca₅Si₃ under 30 MPa at 573 K and under 1 MPa at 873 K. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcpLet.2008.06.018.

References

[11] Certain commercial suppliers are identified in this Letter to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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