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Hydrogen Storage In A Novel Destabilized Hydride System, Ca_2SiH_x: Effects of Amorphization

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Crystalline Ca_2Si was synthesized via the 873 K evacuation of a $2CaH_2 + Si$ ball-milled mixture. The resulting Ca_2Si readily absorbs hydrogen below 0.1 MPa within the temperature range 473−523 K, leading to the formation of crystalline Ca−Si-based hydrides as well as the reformation of crystalline CaH_2. In contrast, hydrogen absorption at pressures greater than 0.5−0.7 MPa leads to an unusual amorphous metal-hydride phase, stable in a range up to 523 K as evidenced by neutron powder diffraction, neutron vibrational spectroscopy, and absorption isotherm measurements. The formation of such a phase is discussed in relation to other known amorphous intermetallic hydrides and the role of "chemical frustration." The hydrogenation process from Ca_2Si to Ca_2SiH_x is completely reversible but requires high desorption temperatures.

Introduction

Metal hydrides have the potential for reversible on-board hydrogen storage and release at low temperatures and pressures. The operating storage requirements for fuel-cell vehicular applications are in the range of 1−10 atm and 298−473 K.[1] Many metal-hydride types that incorporate hydrogen into their crystal structures can function in this range. These include AB_5 (e.g., $LaNi_5H_6$), AB_2 (e.g., $ZrMn_2$), AB (TiFe), A_2B (e.g., Mg_2NiH_4), and AB_3.[2] However, their gravimetric capacities are too low (∼1−3 wt %) and their costs too high for vehicular applications. Many efforts have also been made on light-metal hydrides such as LiH and MgH_2 because of their relatively high hydrogen-storage densities (>5 wt %). However, most of them have rather slow absorption kinetics, relatively high thermal stability, and/or problems with the reversibility of hydrogen absorption/desorption cycling. Recently, alloying with Si or Ge has been shown to effectively destabilize these hydrogen-rich but strongly bound light-metal hydrides at significantly lower temperatures.[3] Yet, important challenges still remain in improving their absorption kinetics and cycling capability.

Considerable interest has recently been focused on Ca−Si intermetallic compounds for their potential applications for hydrogen storage. Among them, CaSi was found to reversibly absorb and desorb hydrogen in a moderate temperature range.[4] Our recent investigation[5] showed that CaSi can be successfully prepared via evacuation of a ball-milled $CaH_2 + Si$ mixture at a temperature 350 K lower than the conventional metal-melt method. Using combined high-resolution neutron powder diffraction (NPD)[6] and neutron vibrational spectroscopy (NVS)[7] techniques, we also determined the structural variations and probed the dynamics and bonding states in the $CaSiH_{1+x}$ ternary-hydride system.[5] Despite the interesting Ca−H and Si−H bonding observed in this system, the formation of such a stable ternary hydride precluded the desired absorption/desorption destabilization cycle $CaSi + H_2 \leftrightarrow CaH_2 + Si$, even at 473 K and 10 MPa H_2.

Ca_2Si is more Ca-rich than CaSi. Thus, it has the potential for twice as much hydrogen absorption as CaSi per formula unit, assuming the destabilization cycle $Ca_2Si + 2H_2 \leftrightarrow 2CaH_2 + Si$. To compare its hydriding properties with the related yet hard-to-hydride Mg_2Si alloy,[3,8] we have extended our investigation to this compound, which we formed via the dehydrogenation of ball-milled 2:1 CaH_2:Si mixtures. As for CaSi, using this method, the crystalline metal−silicide phase can be synthesized at temperatures significantly lower than the conventional metal-melt method.[9] Ca_2Si crystallizes

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in an orthorhombic anti-$PbCl_2$ or Co_2Si-type structure.[10] Full hydriding of Ca_2Si to $2CaH_2 + Si$ would translate into a 3.57 wt % maximum hydrogen uptake. In this paper, we present a systematic study of the structural behavior and absorption properties of the $2CaH_2/Si$ system, including the formation of 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 Co_2Si-type structure. We discuss our results with respect to other intermetallic compound systems that are well-known for such behavior.

Experimental Section

A Ca_2Si powder sample was synthesized by the following procedures. Stoichiometric 2:1 amounts of CaH_2 (Aldrich,[11] 99.9%) and Si (Alfa Aesar, 99.999%) were mixed via ball-milling with a Fritsch Pulverisette 7 planetary mill at 400 rpm for 30 min. The mixture was then heated under a dynamic vacuum for 10 h at 873 K to remove H_2. The product was ground again in an agate mortar in a He-filled glovebox for further measurements. Using this method, we can decrease the formation temperature of the metal−silicide phase, Ca_2Si, by ∼500−550 K compared to the conventional metal-melt method.[9] Hydrided and deuterided samples were prepared using this Ca_2Si 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. During the high-temperature hydrogenation, Ca_2Si powders were wrapped in a Mo envelope and sealed in a stainless steel tube. The isotherm measurements were performed using a Sieverts-type volumetric system to monitor the hydrogenation reaction. Samples were kept at each data point for 3 min to reach a quasi-equilibrium. The hydrogen absorption rate greatly diminished after this period. Although 3 min is not enough time to allow for true equilibrium, we used this measurement to monitor the hydrogenation reaction, given that a longer waiting period was not practical for the current isotherm study. All sample handling was performed in a He-filled glovebox to avoid oxidation reactions.

All neutron scattering measurements were performed at the NIST Center for Neutron Research (NCNR). The neutron powder diffraction (NPD) data were collected using the BT-1 high-resolution powder diffractometer[6] with the Cu(311) 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.[12] The neutron vibrational spectra (NVS) were measured using the BT-4 filter-analyzer neutron spectrometer[7] with the Cu(220) 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 hydride samples were measured using the neutron prompt γ activation analysis (PGAA) facility.[13] During the measurement, a sample is continuously irradiated with a beam of neutrons. The constituent elements of the sample absorb some of these neutrons and emit prompt γ-rays, whose energies and intensities identify the neutron-capturing elements (including hydrogen) and their concentrations. A pure CaH_2 sample was used as the standard material to normalize γ-ray intensities. Deuterium content was determined by gravimetric measurements.

Results and Discussion

Evacuation of the ball milled CaH_2/Si mixture in a ratio of 2:1 at 873 K yielded a single-phase Ca_2Si alloy. The NPD pattern (Figure 1) of this alloy contains only lines of a Co_2Si-type orthorhombic structure (*Pnma*) with refined lattice parameters $a = 7.6910(3)$ Å, $b = 4.8174(1)$ Å, and $c = 9.0477(3)$ Å, which agree well with previous values.[10] The refined structure parameters of the Ca_2Si product are listed in Table 1. Hydrogen absorption isotherms were measured for the Ca_2Si alloy at 473 and 523 K (see Figure 2). It is notable that Ca_2Si reacts readily with H_2 (below 0.1 MPa) and achieves a maximum hydrogen capacity of $\approx$2.1 wt % at moderate pressures ($<$3 MPa). If we plot the isotherms with pressure logarithmically (Figure 2 inset), there is no obvious pressure plateau. This is in contrast to the isotherms measured for other destabilized metal-hydride systems,[3,14] but very similar to those observed in some amorphous alloys,[15] especially for high-pressure treatments (i.e., $>$0.5 MPa at 473 K; $>$0.7 MPa at 523 K). The lack of an isotherm plateau for hydrogenation in amorphous materials reflects the broad range of interstitial sites with slightly different local environments. PGAA measurements indicated a composition of $Ca_2SiH_{2.41}$ at maximum hydrogen uptake (at 6 MPa and 523 K), whereas samples equilibrated at pressures as low as 0.1 MPa yielded a composition of $Ca_2SiH_{1.97}$. The hydrogenated samples start to desorb hydrogen only above 723 K, which implies the formation of very stable hydride phases.

NPD patterns were collected on deuterium-loaded Ca_2Si samples under several different pressures. Each sample was kept under pressure for a long enough period (e.g., 8−10 h) to obtain equilibrium hydrogen concentrations and a homogeneous phase distribution for the later diffraction analysis. Figure 3 shows the NPD pattern and the agreement between the observed and calculated intensities of a sample equilibrated under 0.1 MPa D_2 pressure (yielding $Ca_2SiD_{1.90}$ from gravimetric measurement). Compared to single-phase Ca_2Si, this powder pattern contains several phases. CaD_2 (*Pnma*),[16,17] $Ca_5Si_3D_x$ (*I*4/*mcm*),[18] and CaSi (*Cmcm*)[10,19] were identified as the major phases in this sample. Besides these phases, there are additional small peaks that appear to be due to a small fraction of an unknown hydride phase. The reflections of this phase were also observed for previous CaSi hydride phases after hydrogenation at high temperatures and

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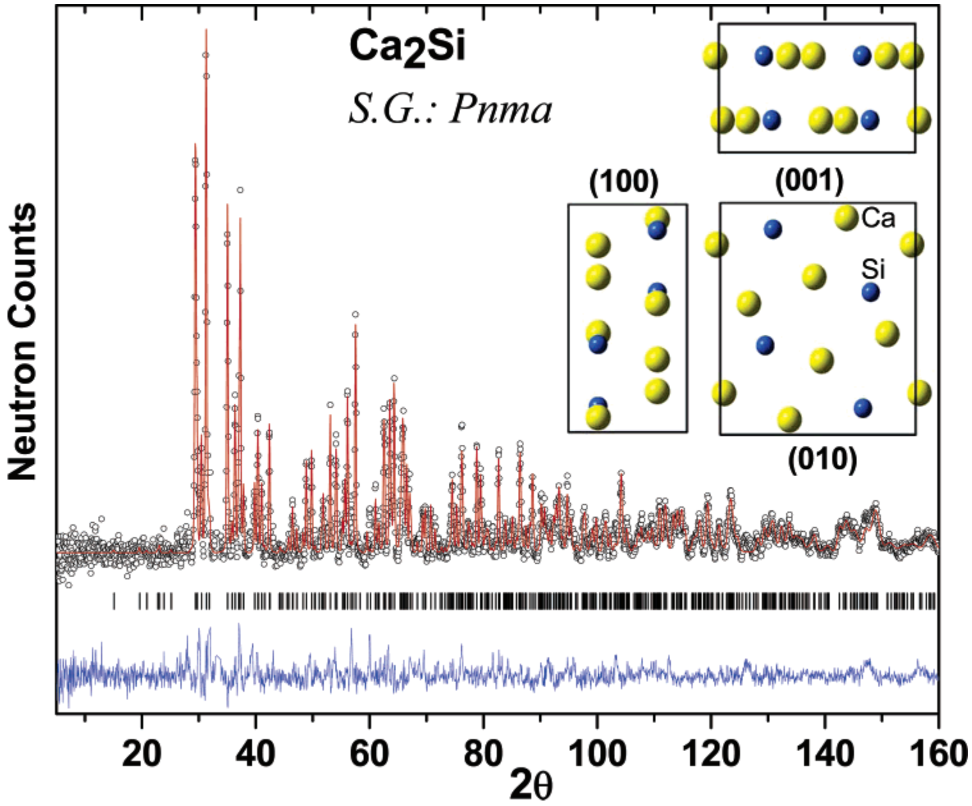

Figure 1. Experimental (circles), calculated (line), and difference (line below observed and calculated patterns) NPD profiles for Ca_2Si. The refined crystal structure in the [100], [010], and [001] projections is presented as insets. Large light and small dark spheres are Ca and Si, respectively.

Table 1. Crystallographic Data Refined from the Neutron Diffraction Pattern for Ca_2Si at 295 K[a]

	site	occupancy	*x*	*y*	*z*	U_{iso} (× 100 Å)
Ca1	*4c*	1.00	0.5207(4)	0.25	0.6759(3)	1.99(6)
Ca2	*4c*	1.00	0.6545(4)	0.25	0.0730(3)	1.49(6)
Si1	*4c*	1.00	0.2552(5)	0.25	0.1072(3)	1.06(6)

[a] Space group *Pnma* No. 65; $a = 7.6910(3)$ Å, $b = 4.8174(1)$ Å, $c = 9.0477(3)$ Å, $V = 335.226(28)$; $R_{wp} = 0.0580$, $R_p = 0.0460$, $\chi^2 = 1.484$.

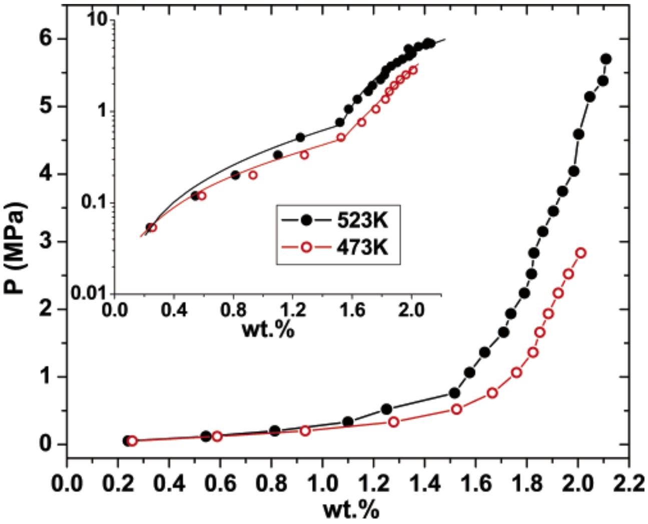

Figure 2. Hydrogen absorption isotherms for Ca_2Si at 473 and 523 K, under conditions that lead to an amorphous phase. Inset shows the same isotherms plotted logarithmically.

do not match the diffraction pattern of any known Ca silicide compound. Further evidence for this unknown component is provided by NVS (see below). Upon hydrogenation at a higher pressure, e.g., >0.5 MPa at 473 K, the NPD pattern revealed an unexpected formation of an amorphous phase with an almost featureless diffraction pattern (Figure 4), which is consistent with the amorphous-type isotherm plots (Figure 2).

Neutron vibrational spectra for the samples under different hydrogenation conditions are shown in Figure 5. For the hydrogenated samples under 0.1 MPa H_2, the most prominent groups of phonon modes represent the hydrogen vibrations in calcium hydride (CaH_2),[17] the major component in the resulting mixed-phase hydride. (N.B., the NVS of pure CaH_2 is also presented as a reference spectrum.) Peaks at ~102 meV between the two CaH_2 phonon groups are assigned to the hydrogen vibrations in a $Ca_5Si_3H_x$ solid-solution phase in which all H atoms are located in Ca_4-type tetrahedral sites.[20] Finally, there is an additional peak observed in the lower-energy portion (50−60 meV) and a peak at ~108 meV that could be due to the small unknown hydride-phase component observed in the NPD pattern. Further work on this phase is in progress to determine its composition and structure as well as to better understand the overall destabilization processes.

Consistent with the diffraction pattern (Figure 4) and the isotherm measurements, the neutron vibrational spectrum collected on the same batch of hydrogenated samples dramatically illustrates that the entire sample has been transformed into an amorphous phase under high pressure. Thus, the highly pressurized Ca_2SiH_x sample shows a very broad band over the 40−160 meV energy range that is due to the broad distribution of hydrogen sites in the disordered

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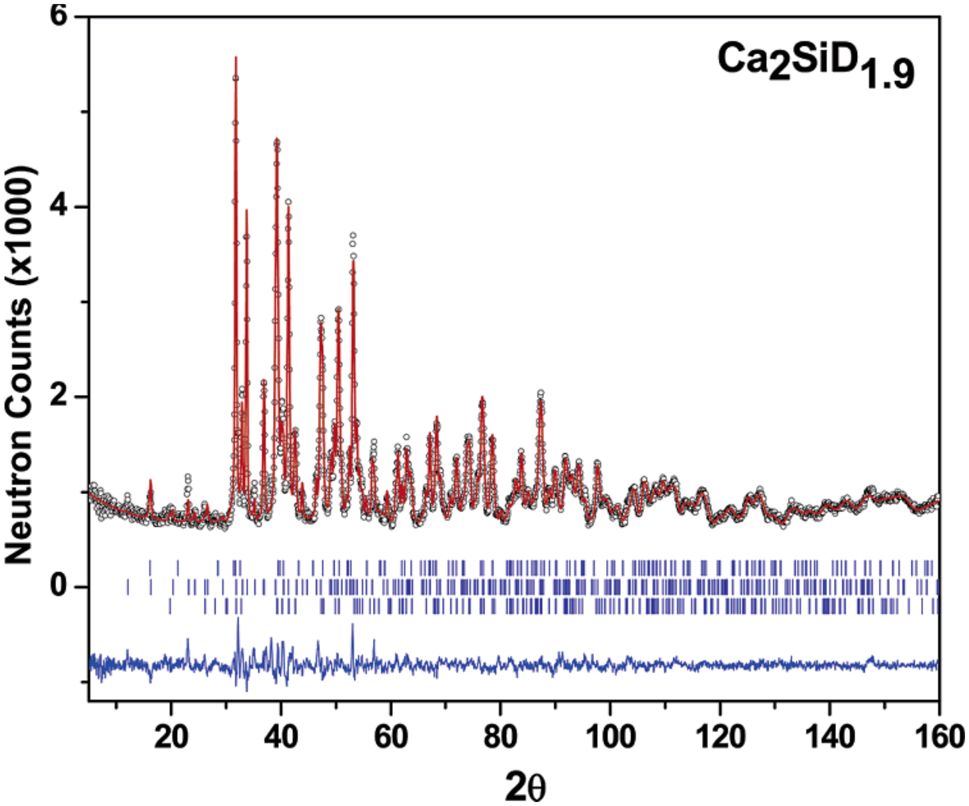

Figure 3. Experimental (circles), calculated (line), and difference (line below observed and calculated patterns) NPD profiles for $Ca_2SiD_{1.9}$. The refinement shows that $Ca_2SiD_{1.9}$ is composed of CaD_2, $Ca_5Si_3D_{0.84(1)}$, and CaSi, with the calculated positions of Bragg peaks for each phase indicated by the vertical bars from bottom to top, respectively. Refinement on these three phases yields $R_{wp} = 0.0466$, $R_p = 0.0364$, and $\chi^2 = 2.114$. The unknown calcium−silicide−hydride phase was not included in the refinement, which can be clearly seen from the difference profile.

structure. The apparent spectral smearing is similar to that commonly observed in other amorphous hydride compounds such as $TiCuH_x$[21] and $Pd_{85}Si_{15}H_x$.[22] The amorphous phase remains stable to at least 500 K, but typical of such systems, crystallization did occur after an extended annealing at higher temperature (e.g., 650 K) under 0.1 MPa H_2 for 3 days. A small hydrogen atmosphere was maintained in order to prevent any loss of H content from the amorphous Ca_2SiH_x during the extended heat treatment. Crystallization is evidenced by the appearance of sharper phonon peaks in the vibrational spectrum (Figure 5) and well-defined diffraction peaks in the NPD pattern (Figure 4). In Figure 5, the vibrational spectrum of the annealed amorphous Ca_2SiH_x is dominated by CaH_2. Small peaks featured from the unknown hydride phase mentioned earlier are also observed. The spectrum still contains an amorphous component, as evidenced by the slightly higher background compared to the rather flat baseline observed for pure crystalline CaH_2. Careful analysis of the crystalline NPD reflections revealed a mixture of CaH_2, Ca_2Si, and CaSi. The diffraction pattern also includes the unknown calcium−silicide phase observed in Figure 3, as evidenced by the difference profile, but no $Ca_5Si_3H_x$ phase. This suggests that the $Ca_5Si_3H_x$ phase, which is a product of low-pressure-hydrided (at 0.1 MPa) Ca_2Si, might further decay into CaH_2 and other silicide or hydride phases. The products of Ca_2Si under various H_2 pressures are summarized in Table 2.

The interesting hydrogen-induced transformation into an amorphous phase with different storage behavior is at first glance unexpected. Because the starting Ca_2Si prepared from the ball-milling forms a crystalline phase, as evidenced by the NPD result (Figure 1), the observed amorphous phases after hydrogenation are not likely caused by the ball-milling process. Such a hydrogen-induced amorphization (HIA) phenomenon is frequently observed in families of intermetallic compounds with certain crystal structures such as C14 (AB_2 Laves phases, e.g., $NdMn_2$), C15 (AB_2 Laves phases, e.g., A = Y, rare earth, etc., B = Fe, Co, Ni), C23 (A_2B phases, e.g., A = rare earth, B = Al), $B8_2$ (A_2B phases, e.g., A = Ni, rare earth, etc., B = In), $D0_{19}$ (A_3B phases, e.g., A = Ti, rare earth, etc., B = Al, Ga, In, Sn), and $L1_2$ (A_3B phases; e.g., A = Zr; B = Al, In, Rh, etc.).[23−26] However, the formation of (possibly nanoparticulate) amorphous phases upon hydrogenation have not been observed in any alloys with a Co_2Si-type structure.

Besides the crystal structure, other factors such as atomic size ratio, electron concentration, thermal stability of original compounds, and the size of hydrogen interstitial sites are also involved in the occurrence of the HIA process.[25] For example, it has been shown that HIA occurs only in compounds with an atomic size ratio larger than 1.37 among C15 Laves AB_2 phases. Besides, some C15 and C14 Laves

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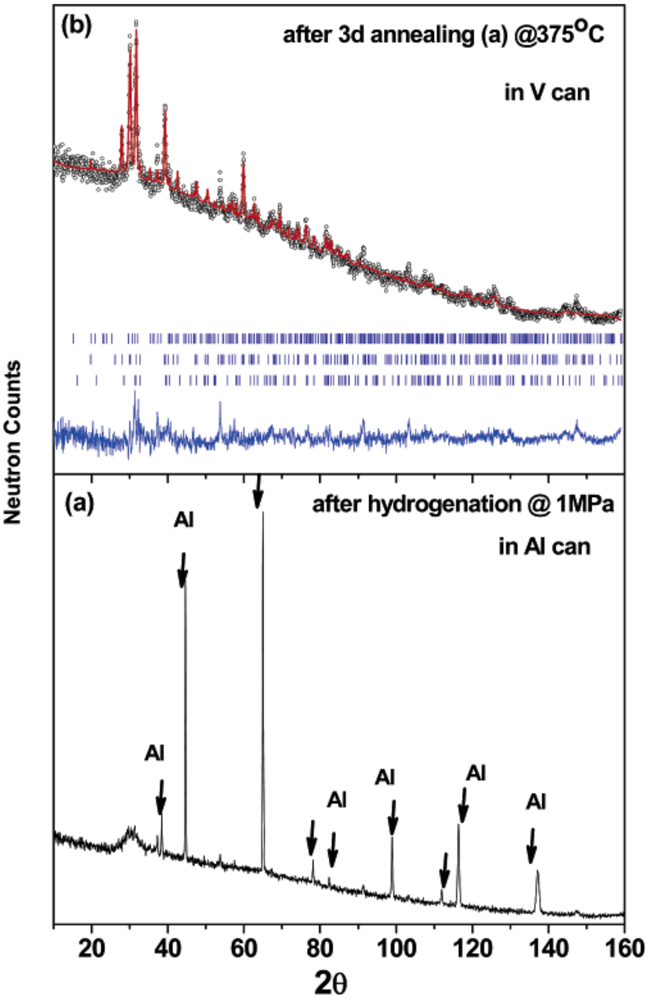

Figure 4. Neutron powder diffraction patterns for $Ca_2SiH_{2.41}$: (a) amorphous phase after high-pressure hydriding (1 MPa), with arrows pointing to reflections from the Al sample can, and (b) crystallization after prolonged annealing of (a) at 650 K for 3 days (annealing was conducted under 1 atm H_2 to prevent any loss of H). The refinement on (b) shows that $Ca_2SiH_{2.41}$ is composed of Ca_2Si, CaH_2, and CaSi, with the calculated positions of Bragg peaks for each phase indicated by the vertical bars from top to bottom, respectively. Refinement on these three phases yields $R_{wp} = 0.0313$, $R_p = 0.0250$, and $\chi^2 = 1.567$. The unknown calcium−silicide−hydride phase was not included in the refinement, which can be seen from the difference profile.

phases amorphize only above a critical hydrogen pressure.[26,27] The Ca_2Si phase does not belong to any of the above structure families. Yet, its structure (C37 compound, Co_2-Si-type, space group *Pnma*) is similar to that of the C23 compounds ($PbCl_2$-type, space group *Pnma*) with the same A_2B stoichiometries (A = hydride-forming element; B = non-hydride-forming element). Also, it satisfies the general requirements[24] described for amorphous or metal-glass formation in a solid-state reaction: (i) at least a 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 mechanism by which crystalline Ca_2Si is transformed to the amorphous state during hydriding might be similar to those proposed in previous studies.[24] We did not detect a Ca_2SiH_x single-phase crystalline hydride; thus, the free energy of such

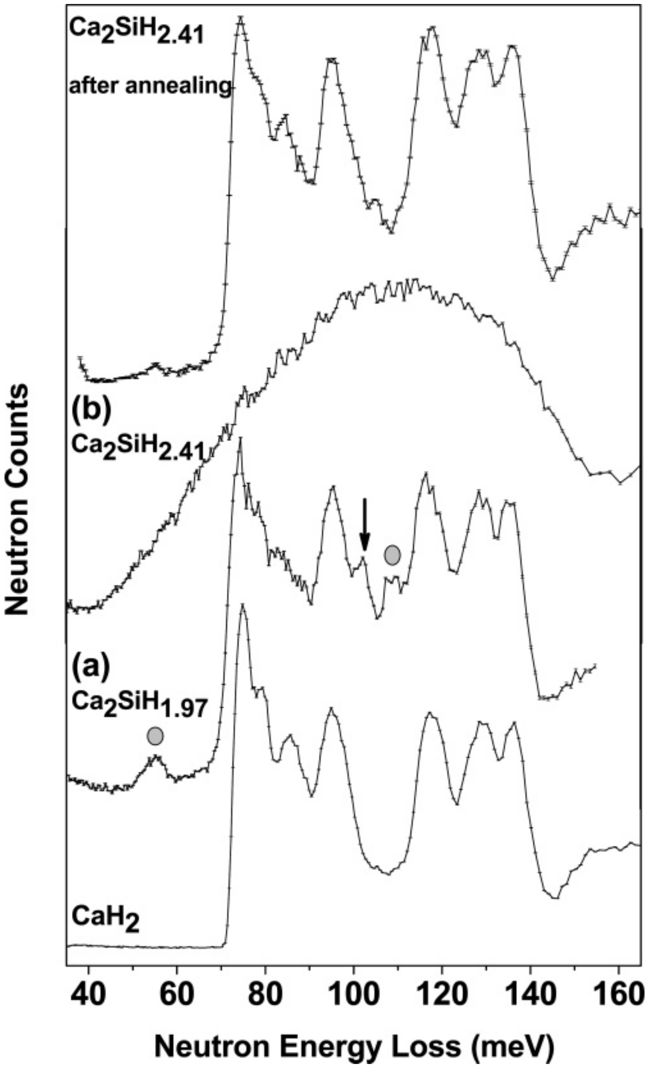

Figure 5. Neutron vibrational spectra for Ca_2SiH_x equilibrated at 473 K and either (a) 0.1 MPa or (b) 1 MPa. Arrows point to the featured peaks from H in $Ca_5Si_3H_x$, and the dot indicates the phonon modes from the unknown hydride phase(s). The spectrum of CaH_2 is also plotted at the bottom for comparison. The spectrum at the top was collected after a 3 day, 650 K annealing of the amorphous phase in (b).

a hydride is assumed to be relatively high. On the other hand, CaH_2 is a comparatively stable crystalline hydride with a relatively low free energy. The formation of the CaH_2 phase involves the interdiffusion of Ca and Si. Yet, apparently with increasing H_2 pressure, the metal atoms cannot "catch up" with the highly mobile hydrogen atoms. Thus the glassy hydride would appear to be a metastable alternative that does not require such interdiffusion of metal species. Our results suggest that the transformation to the amorphous hydride is polymorphic, whereas the crystalline alternative requires "chemical segregation." Moreover, in the current system, the amorphization under high pressure did not change below ∼523 K with pressurizing time. That is, the amorphous phase could still be observed even after hydrogenation of a Ca_2Si sample for a long period, e.g., 8−10 h, at this temperature. Thus we believe that this chemical frustration effect, rather than kinetic effects, is primarily responsible for the transition to the amorphous state.

The hydrogenation behavior of Ca_2Si is unique and completely different from CaSi and Mg_2Si. CaSi starts to react with hydrogen (473 K) only at pressures above 6 MPa

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Table 2. Summary of Ca_2SiH_x Samples Prepared under Different H_2 (D_2) Pressures.

compositions	treatment	major phases	*a* (Å)	*b* (Å)	*c*(Å)	phase fraction	other phase	detection methods
$Ca_2SiH_{1.973}$	473 K, 0.1 MPa H_2	CaH_2, $Ca_5Si_3H_x$					unknown hydrides	NVS, PGAA
$Ca_2SiD_{1.91}$	473 K, 0.1 MPa D_2	CaD_2 (*Pnma*)	5.9503(4)	3.6069(2)	6.8089(5)	$F_{CaD2} = 59.13(2)\%$	unknown hydrides	NPD
		$Ca_5Si_3D_{0.84(1)}$ (*I*4/*mcm*)				$F_{Ca5Si3D0.84(1)} = 26.17(2)\%$		
			7.6466(3)		14.649(1)			
		CaSi (*Cmcm*)	4.550(4)	10.79(1)	3.855(4)	$F_{CaSi} = 16.70(6)\%$		
$Ca_2SiH_{2.41}$	473 K, 5.0 MPa H_2	amorphous						NVS, NPD, PGAA
	650 K, 3 days	CaH_2 (*Pnma*)	5.969(1)	3.6146(6)	6.815(1)	$F_{CaH2} = 68.44(4)\%$	unknown hydrides	
		Ca_2Si (*Pnma*)	7.695(1)	4.836(3)	8.978(8)	$F_{Ca2Si} = 22.98(2)\%$		
		CaSi (*Cmcm*)	4.543(1)	10.962(4)	3.824(1)	$F_{CaSi} = 8.58(1)\%$		

and needs at least 9 MPa to reach a maximum hydrogen content of 1.88 wt %.[4,5] Much effort has been focused on the $2MgH_2/Si$, system which has a potential hydrogen capacity of 5.0 wt %. However, the Mg_2Si product after dehydrogenation has been shown to hardly absorb H_2, even under 10 MPa hydrogen.[3] Contrary to the slower hydrogen absorption kinetics for CaSi and the almost nonexistent hydrogen absorption kinetics for Mg_2Si, current isotherm measurements on Ca_2Si show facile absorption under relatively low H_2 pressure (<0.1 MPa) with quite rapid kinetics (the majority of hydrogen absorption completes in several minutes). This H_2 absorption behavior makes it an intriguing system for hydrogen storage yet still impractical because of the high desorption temperatures required. The unusual amorphous hydride phase, which can be reformed through recycling, is even more interesting, particularly if the absorption/desorption kinetics could be improved by the use of appropriate dopants and/or catalysts. In this sense, Ca_2Si may be a prototype system for understanding the role of amorphization in designing new hydride materials with higher storage capacities. Partially Mg-substituted $Ca_{2-x}Mg_xSi$ systems would be potentially even more promising for hydrogen-storage applications because of the lighter Mg cation. Investigations of these solid solutions are currently being pursued.

Summary

Complete dehydrogenation of a 2:1 CaH_2:Si ball-milled mixture has been shown to occur at 873 K. The formation temperature of the resulting metal−silicide phase, Ca_2Si, is significantly decreased (∼500−550 K lower) compared to the conventional metal-melt method. Structure variations and hydrogen-absorption properties of the Ca_2Si were studied using isotherm measurements and combined NPD and NVS techniques. In contrast to Mg_2Si and CaSi, Ca_2Si was found to absorb hydrogen readily under low pressure (<0.1 MPa) over a temperature range of 473−523 K. The hydriding process for Ca_2Si at 473−523 K shows pressure-dependent reactions and structural changes. Below 0.5−0.7 MPa H_2, the sample disproportionates into a mixture of crystalline CaH_2 and other silicide phases. Yet, above this H_2 pressure, amorphization of the entire alloy−hydride system occurs. Both hydrided phases can be reformed after high-temperature hydrogen desorption. Such hydrogen-induced formation of amorphous phases is very unusual in intermetallic compounds with the Co_2Si-type structure and could be rationalized in terms of similarities in crystal structures, chemistries, and phase stabilities. The creation of such a recyclable amorphous phase (at moderate temperature with higher hydrogen content than its crystalline analogue), which is stable at temperatures up to 523 K, is a new development that could guide the search for even lighter amorphous systems with appropriate properties.

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