**Research Report**

# Development of New Hydrogen Storage Material CaSi : Theoretical Prediction and Experiment

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## Abstract

We report a new finding that CaSi reversibly absorbs and desorbs hydrogen. Its hydriding and dehydriding properties were investigated both theoretically and experimentally. Before experiment, first-principles calculation was performed with the ultrasoft pseudopotential method based on the density functional theory, and it was predicted that CaSi hydride is thermodynamically stable. In actual measurement, the pressure-composition isotherms clearly had plateau pressures in a temperature range of 473- 573 K, and the maximum hydrogen content was 1.9 wt% under a hydrogen pressure of 9 MPa at 473 K, which means CaSi forms $CaSiH_{1.3}$. The theoretical and experimental values of the enthalpy of $CaSiH_{1.3}$ were estimated as -42 $kJ/molH_2$ and -62 $kJ/molH_2$, respectively. They are almost in agreement, within a typical error of 20 $kJ/molH_2$. From the X-ray diffraction profiles, it is confirmed that the crystal structure of CaSi changes reversibly with the absorption and desorption of hydrogen.

## 1. Introduction

Hydrogen is considered to be one of the most promising clean energy sources, with the capability of replacing fossil fuels. The use of hydrogen-based energy in practical applications such as fuel cell vehicles, however, requires the development of safe and efficient hydrogen storage technology. Although metal hydrides are considered to be among the promising materials for hydrogen storage, those developed so far do not possess sufficient gravimetric hydrogen storage capacity for practical applications. Accordingly, the development of new hydrides of light metals possessing large hydrogen storage capacities is strongly desired.

It is well known that ZrNi with the CrB-type structure (space group *Cmcm*) absorbs a large number of hydrogen atoms per metal atom and forms $ZrNiH_3$.[1-4] Other alloys with the same structure are also expected to have large hydrogen storage capacities. Therefore, we turned our attention to CaSi[5-6] which has the CrB-type structure, since its average atomic weight is 34 and it consists of Ca and Si which are much lighter elements than Zr and Ni. In addition, Ca and Si have the advantage of being low-cost elements compared with the existing hydrogen storage materials in which rare metals such as Ni and La are used.

Up to now, in exploring new hydrogen storage materials, hydriding experiments have been carried out with no certainty that a new hydride would actually be formed thereby. However, recently some first-principles studies on existing metal hydrides and alkali complex hydrides have been performed, and it has been reported that these calculations predict with sufficient accuracy characteristics, such as formation enthalpy, of hydrides.[7-8] If theoretical calculation can predict whether a new hydride is generated in advance, more efficient development of hydrogen storage materials is attained. As far as we know, there are no reports of a CaSi hydride anywhere. Thus, in the present study we performed first-principles calculations to predict the hydriding properties of CaSi first, and then we conducted an experiment to investigate these properties with some certainty based on the theoretical predictions.

This study is the first report on new hydrogen storage material development based on theoretical predictions, and it is expected that such a development technique using first-principles calculations will greatly aid exploration of other new hydrogen storage materials.

## 2. Method

### 2.1 Computational details

First-principles calculations were performed to investigate the stability of CaSi hydride by the ultrasoft pseudopotential method[9] based on the density functional theory.[10] The generalized gradient approximation formula[11] was applied to the exchange-correlation energy.

The interaction between the ion cores and electrons was described by the norm-conserving pseudopotential[12] for Si and by the ultrasoft pseudopotential[9] for Ca and H. In a pseudopotential generation scheme, the pseudo-wave functions and the pseudo-charge-augmentation functions were optimized by a method similar to that proposed by Rappe *et al*.[13] We chose 3*s*, 3*p*, 3*d*, 4*s*, 4*p* and 4*d* states for Ca pseudopotential as the reference states, 3*s*, 3*p*, and 3*d* states for Si, and 1*s*, 2*s*, and 2*p* states for H, respectively. Moreover, the partial core correction[14] was taken into account for Ca and Si pseudopotentials.

In the solid-state calculations, the pseudo-wave functions were expanded by plane waves with a cutoff energy equal to 15 hartrees. The cutoff energy for the charge density and potential was set to be 120 hartrees. The integral over the Brillouin zone was approximated by the summation on an $18 \times 6 \times 8$ Monkhorst-Pack[15] *k*-point mesh. The preconditioned conjugate-gradient technique was employed to minimize the Kohn-Sham energy functional. A procedure based on the iterative diagonalization scheme[16] and the Broyden charge mixing method[17] was adopted in the present study. Optimization of crystal structures was performed so that the atomic forces and the macroscopic stresses were less than $5 \times 10^{-4}$ hartree/bohr and 0.1 GPa, respectively. During the structural optimization process, the partial occupation numbers near the Fermi level were determined by the Fermi-Dirac distribution function with $k_B T = 3 \times 10^{-3}$ hartrees, and

the Helmholtz free-energy functional[18] including the entropy term was minimized instead of the Kohn-Sham energy functional. Then, the improved tetrahedron method[19] was used in order to minimize the Kohn-Sham energy functional in the optimized structure.

### 2. 2 Experiments

A CaSi sample was prepared by melting a mixture of Ca and Si in a high-frequency induction furnace under an argon pressure of 0.2 MPa. The alloy was then heat-treated in an argon atmosphere at 1223 K for 30 h and finally quenched in water. The sample was examined for pressure-composition ($p$-$c$) isotherms and by X-ray diffraction (XRD) analysis (Rigaku RINT-TTR). The volumetric method was used to obtain $p$-$c$ isotherms when CaSi was dehydrided at 473 K, 523 K, and 573 K. Before each measurement, the sample was hydrogenated at 473 K under a hydrogen (purity 99.99999%) pressure of 9 MPa. The XRD measurements were carried out with Cu $K\alpha$ radiation at room temperature.

## 3. Results

### 3. 1 Theoretical calculation on CaSi hydride

The optimized lattice constants of CaSi are shown in **Table 1**. The calculation values are in good agreement with the experimental ones,[5-6] and it is confirmed that our calculation has sufficient accuracy. The cohesive energy of CaSi was 3.8134 eV/atom, which agreed with the reported value of 3.882 eV/atom computed by the linear muffin-tin orbital (LMTO) method[20] very well.

In the present calculations for CaSi hydride, hydrogen was put on the same site as ZrNiH (4c site surrounded by four Ca atoms)[1] and ZrNiH$_3$ (4c site surrounded by three Ca and two Si atoms and 8f site surrounded by three Ca and one Si atoms)[1-2]

**Table 1** Lattice constants of CaSi with the CrB-type structure (space group: *Cmcm*).

| | Lattice constants (Å) | | | Reference |
|---|---|---|---|---|
| | $a$ | $b$ | $c$ | |
| Calculation | 4.517 | 10.725 | 3.886 | This work |
| Experiment | 4.559 | 10.725 | 3.893 | This work |
| Experiment | 4.561 | 10.735 | 3.891 | Ref. 5) |
| Experiment | 4.545 | 10.728 | 3.890 | Ref. 6) |

because CaSi has a CrB-type structure, the same as ZrNi. The structure model of CaSiH is shown in **Fig. 1**. For the optimized structures of CaSiH and CaSiH$_3$, the cohesive energies were calculated as 3.3455 eV/atom and 2.7825 eV/atom, respectively.

The enthalpy of hydride formation was obtained by subtracting the cohesive energies of CaSi and the hydrogen molecule from that of its hydride. The calculation for the hydrogen molecule was performed using a cubic supercell with size of $6{\times}6{\times}6\,\text{Å}^3$. The bond length and the binding energy were predicted to be 0.755 Å and 4.536 eV/H$_2$, respectively, which agree with the experimental values of 0.741 Å[21] and 4.747 eV/H$_2$.[22] The enthalpies of formation for CaSiH and CaSiH$_3$ obtained by this calculation were -27 kJ/molH$_2$ and +33 kJ/molH$_2$, respectively, where the effects of the zero-point energy were not taken into consideration. Although the value of the enthalpy for CaSiH$_3$ is positive, that for CaSiH is negative. These results of theoretical calculation suggest that CaSi absorbs hydrogen and forms CaSi hydride (CaSiH).

### 3. 2 Hydriding and dehydriding properties of CaSi

**Figure 2** shows the $p$-$c$ isotherms of CaSi during dehydriding at 473 K, 523 K, and 573 K. The maximum hydrogen content at 473 K under 9 MPa of hydrogen pressure was 1.9 wt%, which means that CaSi forms CaSiH$_{1.3}$ in a greater amount than CaSiH, as suggested by theoretical calculations. Each of the $p$-$c$ isotherms in the temperature range selected for this work clearly showed a plateau pressure and the enthalpy of hydride formation estimated using a van't Hoff plot was -62 kJ/molH$_2$.[23] This value is higher in magnitude than the theoretically obtained value for CaSiH (-27 kJ/molH$_2$). These discrepancies between the experiment and
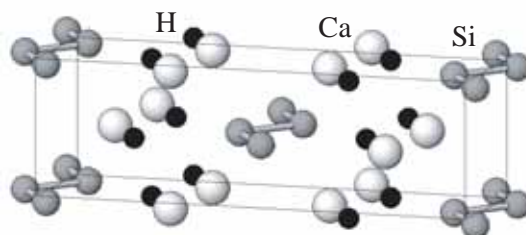


**Fig. 1** The structure model of CaSiH. White, grey and black spheres denote Ca, Si and H, respectively.

calculation are discussed in the following section.

**Figure 3** shows the XRD profiles of the sample (a) as prepared, (b) after hydrogenation and (c) after dehydrogenation at 473 K in all cases. The sample as prepared was composed of the CaSi phase and a small quantity of CaO phase. The lattice parameters of the CaSi phase determined by a Rietveld analysis of the XRD profile are shown in Table 1, which are in good agreement with the values calculated in this work and the previous reports.[5-6] After the sample was hydrogenated at 9 MPa, the diffraction peaks of the $CaSiH_{1.3}$ phase appeared, while those of the CaSi phase disappeared. The details of the crystal structure of the $CaSiH_{1.3}$ phase are described in the following section. After evacuation below $1 \times 10^{-3}$ Pa at 473 K to dehydrogenate the sample, the diffraction peaks of the $CaSiH_{1.3}$ phase disappeared, and those of the CaSi phase appeared again. These results of XRD analysis indicate that CaSi reversibly absorbs and desorbs hydrogen.

## 4. Discussion

We performed the first-principles calculations on the hydriding properties of CaSi first, and predicted that the new hydride CaSiH would be formed. In actual experiment, it was confirmed that CaSi absorbs hydrogen, but there are some discrepancies between the calculated and experimental values of the maximum hydrogen content and the enthalpy of hydride formation. We think that the crystal

structure of CaSi hydride causes these differences.

The crystal structure of $CaSiH_{1.3}$ phase is different from those of ZrNiH and $ZrNiH_3$,[1-4] because the XRD spectra of $CaSiH_{1.3}$ shown in Fig. 3(b) indicate neither the triclinic lattice found in the ZrNiH phase nor the orthorhombic *Cmcm* symmetry as in $ZrNiH_3$. On the other hand, hydrogen was put on the same site as ZrNiH and $ZrNiH_3$ in our calculations for CaSiH and $CaSiH_3$, respectively. Further, the detailed structure of CaSi hydride has been investigated by precise X-ray diffraction measurement using synchrotron radiation which is a high intensity X-ray source. Then, the re-calculation of CaSi hydride was performed based on the crystal structure parameters of $CaSiH_{1.3}$ determined by Rietveld refinements of synchrotron XRD data.

The synchrotron XRD profiles suggested that the space group of CaSi hydride was *Pnma* (No.62).[24] This has an orthorhombic symmetry, and the unit cell is three times as long as that of the CrB-type CaSi along the *a*-axis. The structural parameters of $CaSiH_{1.3}$ obtained from the experiment and the most
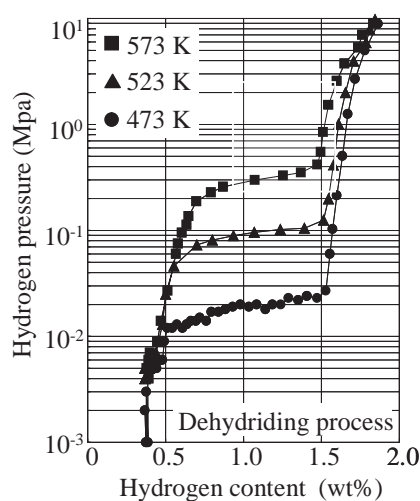


**Fig. 2** The *p-c* isotherms of CaSi in dehydriding processes at 473 K, 523 K and 573 K.
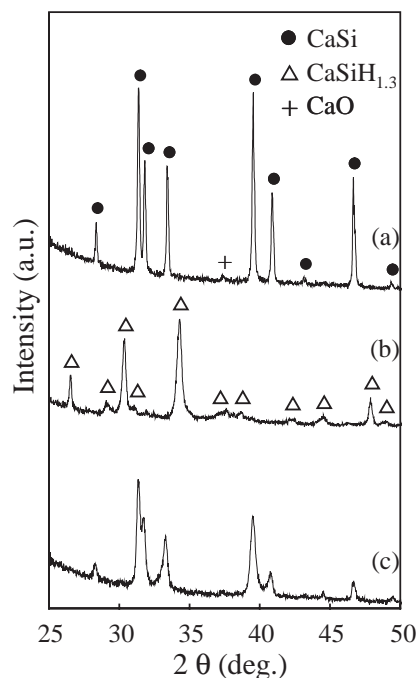


**Fig. 3** X-ray diffraction profiles of CaSi (a) as prepared, (b) after hydrogenation under 9 MPa of hydrogen pressure and (c) after dehydrogenation as evacuation below $1 \times 10^{-3}$ Pa.
Both hydrogenation and dehydrogenation were performed at 473 K.

stable calculated structure are compared in **Table 2**. They are very similar to one another except for the atomic positions of H1 and H2 atoms. We also calculated based on the experimental values for the configurations of atoms, fixing the lattice constants, but the energy was 0.034 eV/atom, higher than the most stable calculated structure. The discrepancy between the experiment and calculation is considered to originate in the occupancy probabilities of H atoms. That is, the experimental occupancy of H4 atom is less than 1.0 , while that of all hydrogen is set to 1.0 in the present calculation. Therefore, if the calculation taking to the fractional occupancy of H atoms into consideration is performed, this discrepancy will be lessened. In this connection we will systematically investigate the detailed structure of CaSi deutride by neutron diffraction measurement as well.

The cohesive energy of the most stable computed structure for $CaSiH_{1.3}$ was 3.2828 eV/atom. Based on this, the enthalpy of hydride formation was estimated as -42 kJ/molH$_2$, this value not including the zero-point energy. The formation enthalpy for $CaSiH_{1.3}$ is more negative than that for CaSiH reported in **Sec. 3** (-27kJ/molH$_2$) and closer to the experimental value (-62kJ/molH$_2$). It also was

**Table 2** Structural parameters of $CaSiH_{1.3}$ obtained from experiment and calculation. The space group is *Pnma* (No.62).

| Experiment [24] | | | | | |
|---|---|---|---|---|---|
| $a = 14.545(3)$ Å, $b = 3.8198(7)$ Å, $c = 11.226(2)$ Å | | | | | |
| Ca 1 | 4c | 0.3625(1) | 1/4 | - 0.0185(2) | 1.0 |
| Ca 2 | 4c | 0.1918(1) | 3/4 | 0.1597(2) | 1.0 |
| Ca 3 | 4c | 0.3369(1) | 1/4 | 0.3492(2) | 1.0 |
| Si1 | 4c | 0.0453(1) | 1/4 | 0.0325(3) | 1.0 |
| Si2 | 4c | 0.4569(2) | 3/4 | 0.1877(2) | 1.0 |
| Si3 | 4c | 0.5423(2) | 1/4 | 0.2462(2) | 1.0 |
| H1 | 4c | 0.248(2) | 3/4 | - 0.023(6) | 1.0 |
| H2 | 4c | 0.242(3) | 1/4 | 0.163(7) | 1.0 |
| H3 | 4c | 0.250(3) | 3/4 | 0.346(7) | 1.0 |
| H4 | 4c | 0.027(3) | 1/4 | 0.524(5) | 0.8(1) |

| Calculation | | | | | |
|---|---|---|---|---|---|
| $a = 14.5603$ Å, $b = 3.8272$ Å, $c = 11.0495$ Å | | | | | |
| Ca 1 | 4c | 0.3608 | 1/4 | - 0.0217 | |
| Ca 2 | 4c | 0.1962 | 3/4 | 0.1571 | |
| Ca 3 | 4c | 0.3392 | 1/4 | 0.3476 | |
| Si1 | 4c | 0.0451 | 1/4 | 0.0324 | |
| Si2 | 4c | 0.4531 | 3/4 | 0.1960 | |
| Si3 | 4c | 0.5467 | 1/4 | 0.2417 | |
| H1 | 4c | 0.2771 | 3/4 | - 0.0114 | |
| H2 | 4c | 0.2785 | 1/4 | 0.1571 | |
| H3 | 4c | 0.2517 | 3/4 | 0.3403 | |
| H4 | 4c | 0.0371 | 1/4 | 0.5533 | |

confirmed from calculation that not CaSiH but $CaSiH_{1.3}$ is formed as the CaSi hydride. Regarding the enthalpy of hydride formation, it is reported that the typical deviation of computed values from experimental is about 20 kJ/molH$_2$.[7] The theoretical value of $CaSiH_{1.3}$ is almost in agreement with experiment, within this error region.

Using the crystal structural parameters determined by the synchrotron XRD data in the calculation, the experimental and computed values of the maximum hydrogen content and the enthalpy of hydride formation are well in agreement. Thus, it was confirmed that this development technique combining theoretical predictions and experiments was very effective in investigating new hydrogen storage materials.

## 5. Summary

It is a new finding that CaSi reversibly absorbs and desorbs hydrogen. The method which combined theoretical predictions and experiments was applied for development of this new material. First-principles calculation was performed first, and it suggested that the CaSi hydride was thermo-dynamically stable. In actual experiment, the pressure-composition (*p-c*) isotherms experiment clearly demonstrated plateau pressures in a temperature range of 473-573 K, and the maximum hydrogen content and the enthalpy of hydride formation of CaSi was 1.9 wt% ($CaSiH_{1.3}$) and -62 kJ/molH$_2$, respectively. The X-ray diffraction profiles indicated that the crystal structure of CaSi changed reversibly with absorption and desorption of hydrogen. The Rietveld refinements of synchrotron XRD data suggested that the space group of $CaSiH_{1.3}$ is *Pnma* (No.62). This has an orthorhombic symmetry, and the unit cell is three times as long as that of the CrB-type CaSi along the *a* axis. The enthalpy of hydride formation obtained by subtracting the energies of CaSi and the hydrogen molecule from that of the hydride thereof which is calculated to be the most stable structure was estimated as -42 kJ/molH$_2$ without the zero-point energy. The theoretical value of $CaSiH_{1.3}$ is almost in agreement with the experimental one, within the typical error value of 20 kJ/molH$_2$.

The hydrogen content of 1.9 wt % for CaSi is

inadequate for practical use as a hydrogen storage material. Therefore, we are investigating the detailed electronic structure of CaSi hydride both theoretically and experimentally in order to improve its performance. Finally, it is noted that the reversible hydriding and dehydriding properties of CaSi suggest a great potential of metal silicides for hydrogen storage. Since silicon is the second most abundant element in the Earth's crust, the hydrogen storage materials of silicides such as CaSi have the great advantage of being low-cost. We are also studying the hydriding and dehydriding properties of other metal silicides by a development technique which combines theoretical predictions and experiments.

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