# Experimental Report

06/01/2014

**Proposal:** **5-22-721** **Council:** 10/2012

**Title:** Crystal structures and bonding of hydrides and deuterides of Zintl phases MSi (M = Ca, Sr, Ba, Eu)

**This proposal is a new proposal**

**Researh Area:** Chemistry

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**Samples:** CaSi
CaSiHx
CaSiDx
SrSiHx
EuSiDx
BaSiDx
SrSiDx
BaSiHx
EuSiHx

| Instrument | Req. Days | All. Days | From | To |
|---|---|---|---|---|
| D20 | 2 | 2 | 29/07/2013 | 31/07/2013 |

**Abstract:**

The Zintl phase CaSi is a potential light-weight hydrogen storage material. Its hydrides CaSiHx (0.9 < x < 1.3) show fascinating bonding properties. Hydrogen oxidizes the Zintl-anion and is located as a hydride-ion (H-) in interstitial sites of the crystal structure. Therefore the bonds in the Zintl-anion change from two-bonded Si atoms in one-dimensional chains [Si]&#8734;1 to interconnected chains with two- and three-bonded Si atoms– the hydride is described as a Zintl-phase hydride. In order to better understand the chemical bonding in such Zintl phase hydrides we would like to investigate the presumably isotypic hydrides and deuterides of the Zintl phases MSi (M = Ca, Sr, Ba, Eu). Special care will be taken for the neutron absorption of Eu. In view of the use of CaSi as hydrogen storage material we would also like to investigate the reaction pathway of its hydrogenation (deuteration). In a previous experiment we got hints for an intermediate hydride (deuteride) phase, which might be of importance in view of the reversibility of the hydrogenation process. In situ neutron diffraction studies will be carried out in our sapphire single crystal gas pressure cell developed within LTP

# Experimental report for experiment No. 5-22-721 („Crystal structures and bonding of hydrides and deuterides of Zintl phases MSi (M = Ca, Sr, Ba, Eu)“)

The topic of the experiment was the investigation of silicides of the alkaline earth metals calcium, strontium and barium as well as the rare-earth metal europium. All of these monosilicides MSi are Zintl phases that form hydrides of the so-called „Zintl phase hydride“-type [1,2]

There were two aims that have been pursued during the experiment:
1) The hydrides of SrSi, BaSi and EuSi were first observed by Armbruster et al. [2] but the structures of the compounds could not been fully described. At least for $SrSiH_x$, a structure was published but without the positions of hydrogen atoms.[2] Therefore, one goal was to solve the structures of both the hydrides and deuterides of the silicides.
2) The hydride and deuteride of CaSi is well known but the formation process is not examined yet. In a previous experiment we got preliminary results (see experimental report 5-22-714), which were to be completed in this proposal.

We got the results as listed in the following:

1) Structures of the hydrides and deuterides of SrSi, BaSi and EuSi:
By XRD-data, all hydrides and deuterides could be indexed to have the same structure-type as $CaSiH_x$ ($x = 1.0 – 1.3$) as also assumed by Armbruster et al.[2] The structures of the strontium and barium compounds were confirmed by the neutron data as taken on D20 in vanadium containers sealed by indium wire (Tab. 1).

Table 1: Lattice parameters of the hydrides and deuterides of SrSi and BaSi as refined from the neutron data. All compounds are indexed in space group *Pnma* (No. 62).

| compound | a [Å] | b [Å] | c [Å] | V [Å³] |
|---|---|---|---|---|
| $SrSiH_x$ | 15.126(3) | 3.9528(7) | 12.341(3) | 737.8(3) |
| $SrSiD_x$ | 15.094(3) | 3.9524(8) | 12.329(2) | 737.5(3) |
| $BaSiH_x$ | 15.709(3) | 4.1196(8) | 13.500(4) | 873.6(3) |
| $BaSiD_x$ | 15.651(4) | 4.1172(8) | 13.437(3) | 865.8(3) |

Besides the confirmed indexing a preliminary structure model for these four compounds could be obtained. Based on the model of $CaSiH_x$ we could refine positions of the metal and silicon atoms and furthermore integrate the hydrogen positions via difference Fourier analysis. Figure 1 shows the refinement of the BaSi-hydride as an example. As one can see, there are little differences between the calculation and the measurement. We find similar situations in all four cases and assume them to be due to very small amounts of secondary phases. Moreover we find in all cases some interatomic distances that are too short to be plausible. Nevertheless we consider the models to be good starting points for a final investigation in the future. Because of the high absorbance of $^{nat}Eu$ for thermal neutrons and the non-availability of a double-walled sample container a dilution with aluminium powder was tested (λ = 0.82 Å). Unfortunately, the data quality did not allow for a detailed structure refinement. By considering the promising XRD data of the EuSi compounds, however, a structural model for its hydride and deuterides very similar to those of the strontium and barium compounds may be assumed.

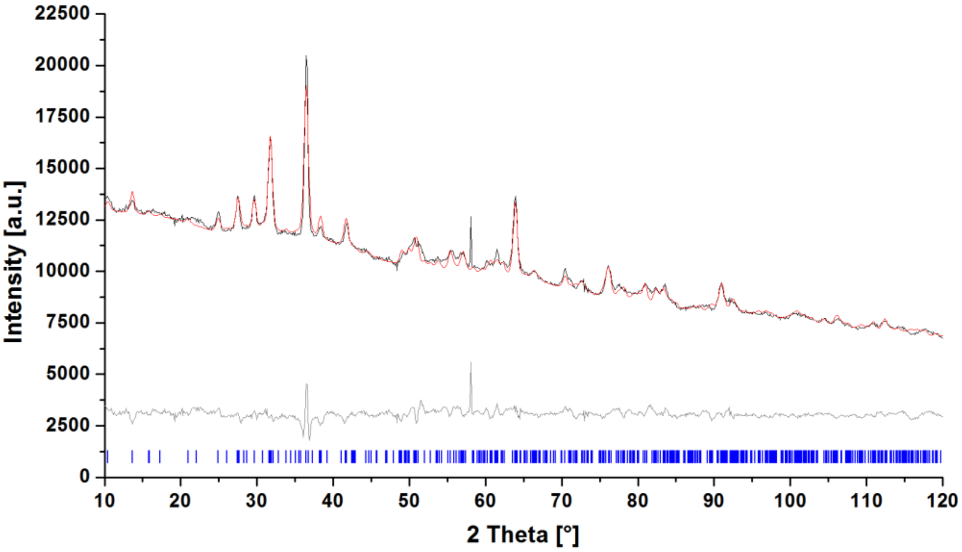

Figure 1: Rietveld-analysis of the neutron powder diffraction data of $BaSiH_x$ (λ = 1.8647(2) Å).

2) Reaction pathway of the deuteration of CaSi:
*In situ* diffraction studies were performed using a sapphire single crystal based gas pressure cell with an automatic gas pressure control and a 2x40W laser heating developed within LTP-5A-1 [3]. Diffraction data with a time resolution of 2 minutes were taken on D20 at a wavelength λ = 1.8647(2) Å. During the experiment, we observed a pressure-dependent reversible quick step in the range of 280 and 330°C. As the pressure was reduced from about 54 bar to 1 bar and risen again we observed a change of the pattern during one scan (about 2 minutes). As the procedure was repeated we got the same response of the system as can be seen in the overview in figure 2. After about 12 hours reaction time, the formation of the already known deuteride was observed.

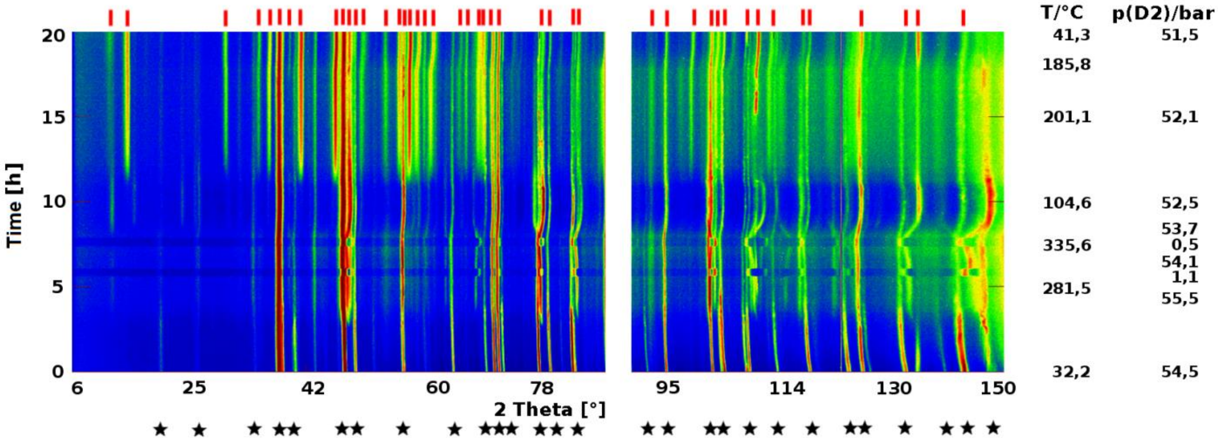

Figure 2: Overview of the deuteration of CaSi. Black stars mark the positions of CaSi-reflections, red bars are those of $CaSiD_x$. Temperature and pressure are given on the right-hand side. At about 90° 2θ one sapphire single crystal peak has been cut out (λ = 1.8647(2) Å).

So we found a new intermediate of the deuteration reaction which seems to be only stable at higher gas pressure. This intermediate finally reacts to the $CaSiH_x$ compound. The pattern of the intermediate could be indexed to an orthorhombic cell and a preliminary structure model found in space group *Pnma* (No. 62; a = 10.990(2) Å; b = 3.8895(5) Å; c= 13.529(2) Å; V = 578.3(2) Å³). The structure is both similar to the CaSi and $CaSiH_x$ structures and obtained via a triplication of the initial a-axis. Deuterium positions were again received by difference Fourier analysis. The refined occupancy gives a formula of $CaSiD_{0.49}$ meaning about half of the deuterium content compared to the known $CaSiD_x$ (x = 1.0 – 1,3). Because of some short interatomic distances and a prevalent misfit in the Rietveld refinement (Fig. 3), we consider this structure model as preliminary.

The new deuteride $CaSiD_{\approx 0.49}$ marks the discovery of the first intermediate of a reaction of a Zintl phase with hydrogen (deuterium). This is of importance, because in a recent study on the deuteration of $SrGa_2$ to $SrGa_2D_2$ neither intermediates nor non-stoichiometry in any of the compounds was found. [4] This seems to reflect the different bonding properties in the deuterides. $SrGa_2D_2$ belongs to the so-called polyanionic hydrides (deuterides), which apparently favor stoichiometric compositions, thus diminishing the possibilities of intermediates. $CaSiH(D)_x$ on the other hand is a Zintl phase hydride with interstitial hydrogen (deuterium) atoms of varying occupation, thus making intermediates more likely. These differences in the formation mechanism might be relevant to reversibility and reaction kinetics, which is of great importance to potential applications as hydrogen stores. In this respect the high reaction rate of the formation and decomposition of $CaSiD_{\approx 0.49}$ with less than two minutes to completion is worthwhile mentioning.

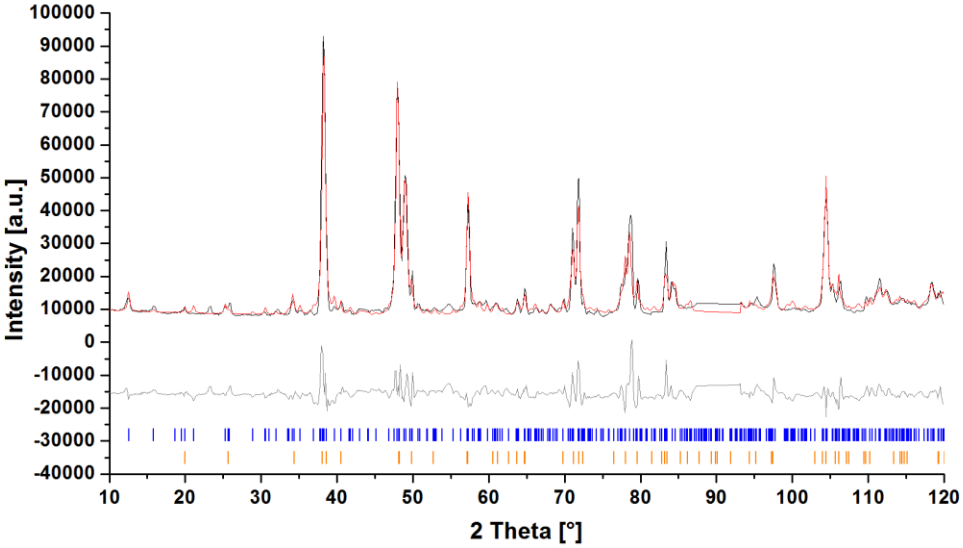

Figure 3: Rietveld-analysis of the CaSi-intermediate in space group type *Pnma* (λ = 1.8647(2) Å). Bragg markers are blue for the new structure and orange for CaSi.

Literature

[1] U. Häußermann, *Z. Kristallogr.* **2008**, *223*, 628-635.

[2] M. Armbruster, M. Wörle, F. Krumeich, R. Nesper, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1758–1766.

[3] H. Kohlmann, N. Kurtzemann, T. C. Hansen, *Powder Diffr.* **2013**, *28*, 242-255.

[4] P. Wenderoth, H. Kohlmann, *Inorg. Chem.*, **2013**, *52*, 10525–10531.