Experimental report

22/12/2016

Proposal:	**5-21-1096**	**Council:**	4/2015
Title:	Formation and decomposition of deuterides of the Zintl phases KSi andCsGe		
Research area:	Chemistry		

This proposal is a new proposal

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Samples:	KSi CsGe

Instrument	Requested days	Allocated days	From	To
D20	3	3	07/12/2015	10/12/2015

Abstract:

The hydrogenation (deuteration) of the Zintl phases KSi and CsGe will be followed under in situ conditions by neutron powder diffraction in a user provides sapphire single crystal cell. In situ X-ray powder diffraction at 80 bar H2 pressure showed the formation of KSiH3 at 110°C and K8Si46 at 200 °C. The neutron diffraction experiment addresses a possible homogeneity range of KSiH3-x during the formation. In advance the clathrate phase K8Si46 will be investigated in regard of trapped H2 (D2) molecules as indicated in the literature. Since the system KSi/KSiH3 is reversible, the dehydrogenation step under vacuum will be followed as well. CsGe as a homologue compound shows a similar behavior with the formation of a clathrate phase. The hydrogenation (deuteration) products will be fully structurally characterized. This will gain insight into the bonding behavior of the Zintl anions, especially in their interaction with hydrogen atoms.

Formation and decomposition of deuterides of the Zintl phases KSi and CsGe

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The reaction of KSi and CsSi were investigated *in situ* under 5 MPa D_2 pressure. Due to technical issues the proposed system CsGe could not be investigated since the laser heating showed a malfunction and could not reach the desired temperatures. Instead CsSi as an analogue system was investigated.

The *in situ* experiment shows that the reaction KSi to $KSiD_3$ is a one step process. No intermediate phases where found. The reaction was done isobaric at 5 MPa D_2 pressure. In a first isothermic step, the reaction was kept for 2 h at 375 K but no change of the diffraction pattern could be obtained. Further heating lead to the formation of $KSiD_3$. At the final temperature of 515 K a turnover of 75% was reached. The decomposition to K_8Si_{46} was not observed at this temperature.

Serial Rietveld refinement was done on *in situ* collected data which were acquired with 2 min time resolution per pattern (numor). For refinements a summation over 5 data sets was used giving a time resolution of 10 min per frame. Fig. 1 shows the evaluation of the phase fraction, lattice parameters as well as deuterium content x of $KSiD_x$. $KSiD_3$ crystallizes in space group type $Fm\bar{3}m$ and the heavy metal partial structure resembles the NaCl-structure type. Therefore there are no free atomic parameters for potassium and silicon. The deuterium atoms are rotationally disordered on a pseudo sphere around the silicon atoms and are described by a partially filled 96*k*-site. The fractional coordinates were evaluated carefully and do not change within 2 e.s.u. Therefore these values were refined once and kept fixed during the serial Rietveld refinement. Debye-Waller factors were used from the literature [1] and an overall *B* factor was refined. Using this approach the site occupancy factor of the D site could be obtained with high precision. The occupation does not show a significant change during the *in situ* experiment and gives a chemical formula $KSiD_{3.04(4)}$. Lattice parameters show a thermal expansion as suspected. KSi does not show any solubility of D_2. $KSiD_3$ shows a fixed KSi:D ratio of 1:3, thus both are line phases with negligible phase width.

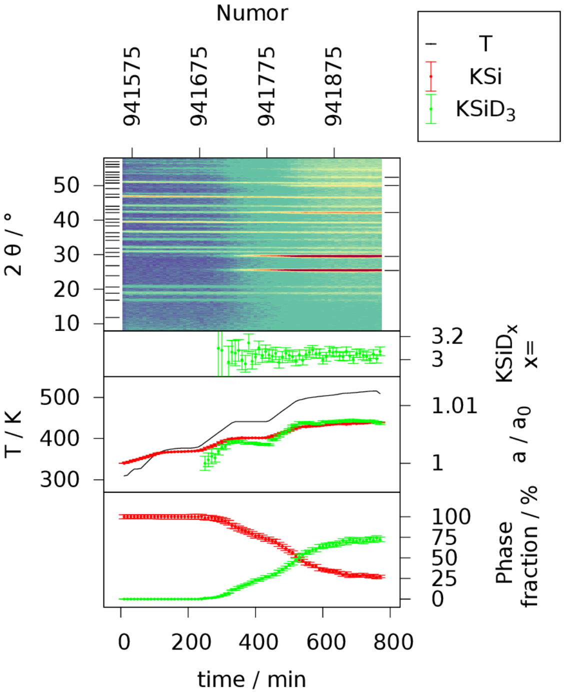

Fig 1: *In situ* neutron powder diffraction data taken at D20 (λ = 187 pm) of KSi under 5 MPa deuterium gas pressure. Bragg markers of the 2D-plot belong to KSi (left) and KSiD$_3$ (right).

K_8Si_{46} was in investigated *ex situ* in order to probe trapped H_2/D_2 molecules [2]. KSi was oxidized using D_2 as well as H_2 in an autoclave. The formed KD (KH) was removed washing the sample in cold *^{i}Pr*-OH. The washing procedure was similar to [2]. From neutron diffraction there is no evidence for any H/D content of these samples (Fig. 2). Differences of lattice parameters result from a non-stoichiometry of potassium ($K_{7.63}Si_{46}$ prepared by D_2/ $K_{7.30}Si_{46}$ prepared by H_2).

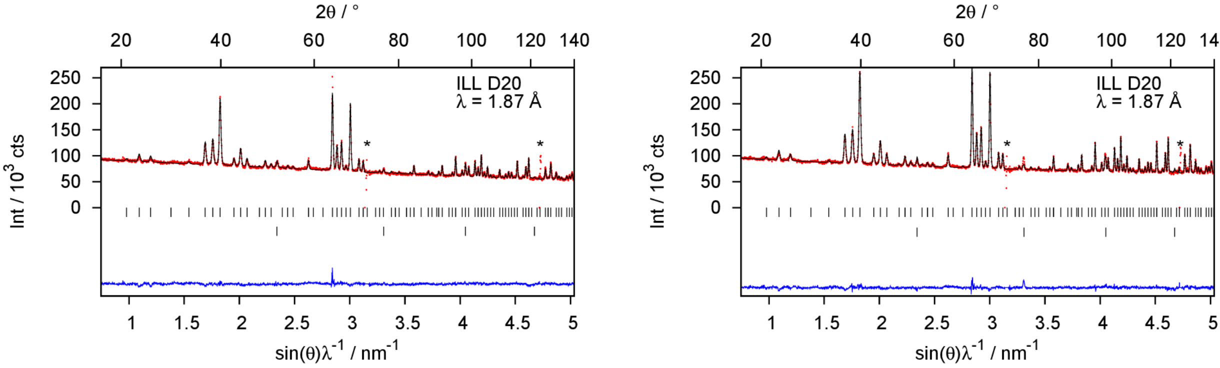

Fig. 2: *Ex situ* neutron powder diffraction data taken at D20 (λ = 187 pm) of K_8Si_{46} prepared by oxidation of KSi with H_2 (**left**) or D_2 (**right)** and Rietveld refinement based on the structural model of the clathrate K_8Si_{46}. There is no evidence for any hydrogen / deuterium trapping in the clathrate. Bragg-marker top: K_8Si_{46}; bottom: V; (*) detector failure.

The reaction of CsSi under 5 MPa isobaric D_2 pressure was evaluated using a serial Rietveld refinement. Data sets were collected with 5 min time resolution per numor. For serial refinement a summation over two numors was done giving a time resolution of 10 min per frame. Fig. 3 shows the same trends as for the KSi-D_2 reaction. The averaged chemical formula is $CsSiD_{3.08(4)}$ In contrast to $KSiD_3$, which decomposes to K_8Si_{46} and KD under 5 MPa D_2 pressure and temperatures above 500 K, $CsSiD_3$ does not show clathrate formation. At 500 K the exothermic decomposition and reformation of CsSi can be seen. Since there is no active cooling of the *in situ* cell a strong temperature leap can be seen leading to the destruction of the cell.

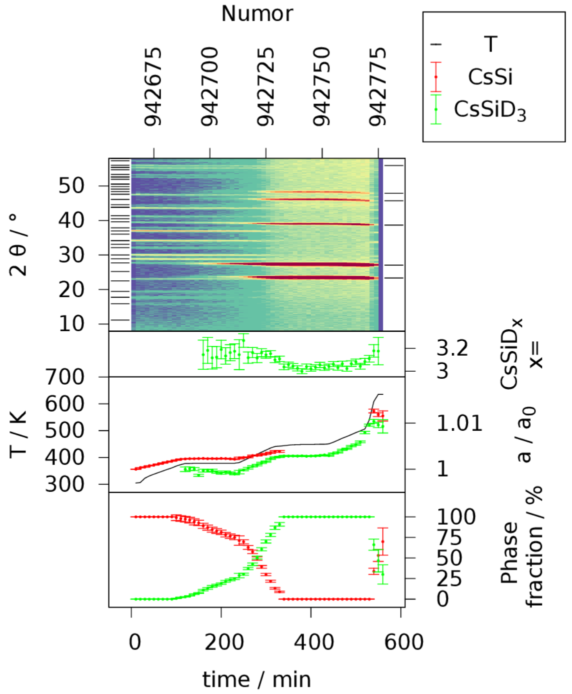

Fig 3: *In situ* neutron powder diffraction data taken at D20 (λ = 187 pm) of CsSi under 5 MPa deuterium gas pressure. Bragg-Marker of the 2D-plot mark the educt (CsSi, right) as well as the product ($CsSiD_3$, left).

Literature

[1] W. S. Tang, J.-N. Chotard, P. Raybaud, R. Janot , *J. Phys. Chem. C* **2014**, *118*, 3409–3419.

[2] D. Neiner, N. L. Okamoto, C. Leonard, C. L. Condron, M. F. Toney, Q. M. Ramasse, P. Yu, N. D. Browning, S. M. Kauzlarich, *Inorg. Chem.* **2010**, *49*, 815-822.