Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

# Supporting Information for: Formation of $CaB_6$ in the thermal decomposition of the hydrogen storage material $Ca(BH_4)_2$

Christoph J. Sahle,*[a] Christian Sternemann,[b] Carlotta Giacobbe,[a] Yigang Yan,[c] Christopher Weis,[b] Manuel Harder,[b,d] Yury Forov,[b] Georg Spiekermann,[d,e] Metin Tolan,[b] Michael Krisch,[a] Arndt Remhof[c,f]

Received Date
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

## 1 Supporting Information

In these supporting information, we will summarize in a tabular form the results of our multi-component fits which are represented in graphical form in Fig. 4 in the main article.

Tables 1 and 2 hold all results from the Rietveld refinement of the powder XRD experiments in numerical form. The refinement included phases and unit cells of $CaH_2$, CaO, $Ca(OH)_2$, $CaB_2H_2$, and $CaB_6$. We also estimated the mean crystal size of $CaB_6$. All refinements and errors estimates reported in the table are based on the least-squares refinement procedures within TOPAS 4.2[1]. Fig.s 1, 2, 3, and 4, again show the measured data, the refined curves, the resuduals, and the peak-positions of the used reference materials.

In table 3 we summarized the results of the multi component fits of the Ca $L_{2,3}$-edges spectra in numerical form. In the least squares minimization routine we used linear combinations of spectra from polycrystalline $Ca(BH_4)_2$, $CaB_6$, $CaH_2$, B, CaO and $Ca(OH)_2$ reference powders. The errors presented in table 3 were estimated using results from different spectral fit ranges.

Table 4 summarizes all results from the fingerprinting analysis of the B K-edge spectra. In the least squares minimization routine we used linear combinations of spectra from polycrystalline $CaB_6$, B, and $Ca(BH_4)_2$. As in table 3, dashes in the table indicate that we excluded the respective compound from the the analysis. As described in the main text, we performed two different analyses for the spectrum of the sample annealed at 400 °C for 0.5 h: in the first, we included all three compounds ($CaB_6$, B, and $Ca(BH_4)_2$) in the fit routine. In a second attempt, we excluded $CaB_6$ from the fit based on the analysis of the XRD and Ca $L_{2,3}$-edges data and observe excellent agreement between data on B inferred from the Ca $L_{2,3}$-edges and the weights of this constrained fit. This table furthermore includes the relative abundancies of B containing phases as based on stoichiometric considerations and the fits of the Ca $L_{2,3}$-edges. The errors presented in table 4 were estimated using results from different spectral fit ranges.

[a] *European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France. E-mail: christoph.sahle@esrf.fr*
[b] *Fakultät Physik/DELTA, Technische Universität Dortmund, Dortmund, Germany. E-mail: christian.sternemann@tu-dortmund.de*
[c] *Materials for Energy Conversion, Empa, Ch-8600 Dübendorf, Switzerland.*
[d] *Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607 Hamburg, Germany.*
[e] *Deutsches GeoForschungsZentrum, Section 3.3, Potsdam, Germany.*
[f] *Crystallography, Institute for Geo- and Environmental Science, Albert-Ludwigs-University Freiburg, D-79098 Freiburg im Breisgau, Germany.*
† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

**Table 1** Results of the Rietveld refinement procedure of the high-resolution powder XRD (content in %). An asterix (*) adjacent to the numbers implies that these values are only based on the nanocrystalline part of the according compound.

| **XRD refinement** | | | | | |
|---|---|---|---|---|---|
| | $CaH_2$ [%] | CaO [%] | $Ca(OH)_2$ [%] | $CaB_2H_2$ [%] | $CaB_6$ [%] |
| 350 °C (50h) | $53.8 \pm 0.8$ | $25.2 \pm 0.4$ | $7.7 \pm 0.2$ | – | $13.2^* \pm 1.2$ |
| 400 °C (0.5h) | $19.9 \pm 0.9$ | $5.1 \pm 0.2$ | $16.0 \pm 3.6$ | $59.0 \pm 2.5$ | – |
| 400 °C (2h) | $71.1 \pm 0.9$ | $6.9 \pm 0.4$ | – | – | $22.0^* \pm 0.5$ |
| 400 °C (15h) | $76.3 \pm 1.0$ | $7.4 \pm 0.3$ | – | – | $16.3^* \pm 0.6$ |

**Table 2** Crystal sizes for (nano-)crystalline $CaB_6$ content and $R_{wp}$ values for the refinement of the high-resolution powder XRD patterns.

| **XRD refinement** | | |
|---|---|---|
| | $CaB_6$ cryst. size [nm] | $R_{wp}$ [%] |
| 350 °C (50h) | 0.8 | 7.02 |
| 400 °C (0.5h) | – | 7.86 |
| 400 °C (2h) | 3.1 | 5.76 |
| 400 °C (15h) | 3.3 | 8.55 |

**Table 3** Results of the linear combination fitting at the Ca $L_{2,3}$-edges using the reference compounds mentioned in the table. A dash in the table means that we excluded the respective compound from the fit due to information from the Rietveld analysis presented in table 1.

| **Ca $L_{2,3}$-edges** | | | | | |
|---|---|---|---|---|---|
| | $CaH_2$ [%] | CaO [%] | $Ca(OH)_2$ [%] | $Ca(BH_4)_2$ [%] | $CaB_6$ [%] |
| 350 °C (50h) | $49.8 \pm 1.5$ | $23.3 \pm 0.7$ | $7.1 \pm 0.2$ | – | $19.8 \pm 2.5$ |
| 400 °C (0.5h) | $23.9 \pm 2.7$ | $6.1 \pm 0.7$ | $19.1 \pm 2.1$ | $50.9 \pm 5.5$ | – |
| 400 °C (2h) | $67.1 \pm 1.2$ | $6.5 \pm 0.1$ | – | – | $26.4 \pm 1.3$ |
| 400 °C (15h) | $63.8 \pm 1.5$ | $6.2 \pm 0.2$ | – | – | $30.0 \pm 1.7$ |

## References

1 A. A. Coelho, *General Profile and Structure Analysis Software for Powder Diffraction Data, version*, 2007, **4**, year.

**Table 4** Results of the linear combination fitting at the B K-edge using the reference compounds mentioned in the table. An asterisk indicates three component fit, see text for details.

| **B K-edge** | | | |
|---|---|---|---|
| | $CaB_6$ [%] | B [%] | $Ca(BH_4)_2$ [%] |
| 350 °C (50h) | 90.4 ± 4.6 | 9.5 ± 4.6 | – |
| 400 °C (0.5h) | – | 40.0 ± 16.7 | 59.9 ± 16.7 |
| 400 °C (0.5h)* | (41.9 ± 10.9)* | (12.7 ± 7.6 )* | (43.2 ± 16.3 )* |
| 400 °C (2h) | 89.5 ± 6.8 | 10.4 ± 6.8 | – |
| 400 °C (15h) | 93.5 ± 7.9 | 4.8 ± 4.8 | – |

**Table 5** Estimated content of B containing constituents inferred from the Ca $L_{2,3}$-edges and reaction pathways (1) and (3) based on stoichiometric considerations. An asterisk indicates three component fit, see text for details and Fig. 4 d).

| **B K-edge** | **B from Ca $L_{2,3}$-edges** | | |
|---|---|---|---|
| | $CaB_6$ [%] | B [%] | $Ca(BH_4)_2$ [%] |
| 350 °C (50h) | 86.0 | 14.0 | – |
| 400 °C (0.5h) | – | 49.1 | 50.9 |
| 400 °C (2h) | 85.0 | 15.0 | – |
| 400 °C (15h) | 96.0 | 4.0 | – |

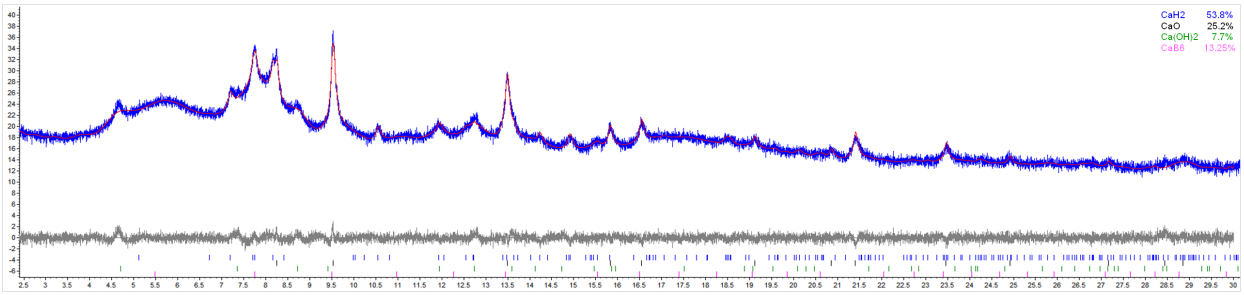


**Fig. 1** Measured data and Rietveld refinement of the sample annealed at 350 °C for 50 h. The data are shown on a 2Θ scale in degrees. The used x-ray wavelength was $\lambda$ = 0.4 Å.

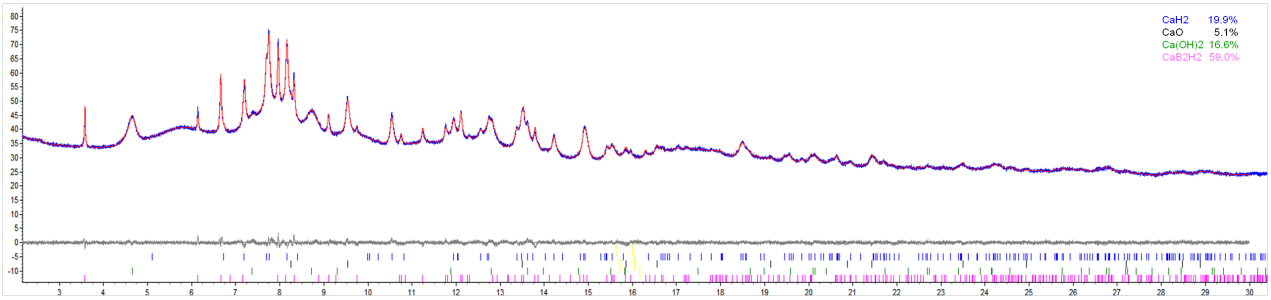


**Fig. 2** Measured data and Rietveld refinement of the sample annealed at 400 °C for 0.5 h. The data are shown on a 2Θ scale in degrees. The used x-ray wavelength was $\lambda$ = 0.4 Å.

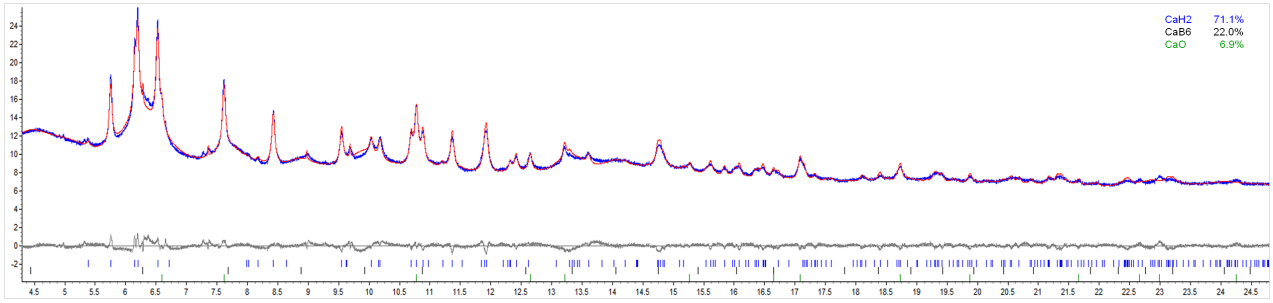


**Fig. 3** Measured data and Rietveld refinement of the sample annealed at 400 °C for 2 h. The data are shown on a 2Θ scale in degrees. The used x-ray wavelength was $\lambda$ = 0.32 Å.

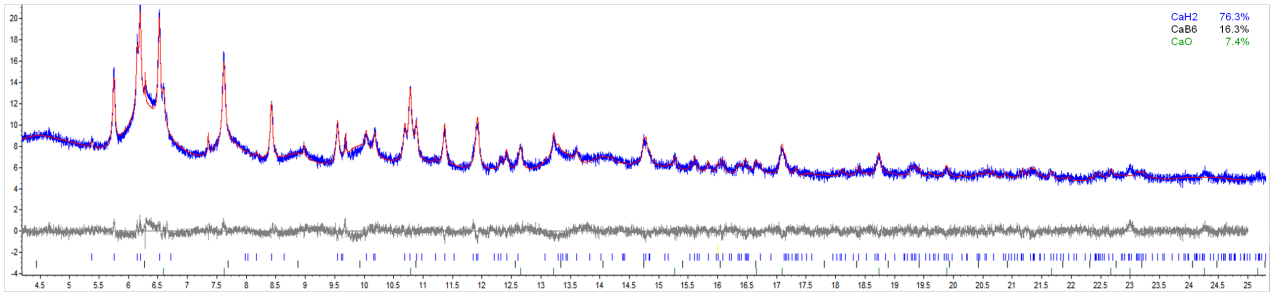


**Fig. 4** Measured data and Rietveld refinement of the sample annealed at 400 °C for 15 h. The data are shown on a 2Θ scale in degrees. The used x-ray wavelength was $\lambda$ = 0.32 Å.