



	Experiment title: Phase transitions in magnesium borohydride.	Experiment number: 01-02-805
Beamline: BM01A	Date of experiment: from: 5-July-08 to: 8-July-08	Date of report: 26-Feb-09
Shifts: 6	Local contact(s): Yaroslav FILINCHUK	<i>Received:</i>

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Magnesium borohydride $Mg(BH_4)_2$, was prepared in Geneva according to a modified synthesis procedure outlined in ref [1].

In-situ powder diffraction:

Diffraction data for the polycrystalline sample were collected on a 0.5 mm glass capillary filled in a high purity Ar-atmosphere with a fine powder of $Mg(BH_4)_2$. A MAR345 Imaging Plate detector at the sample-to-detector distance of 250 mm and synchrotron radiation at $\lambda = 0.770294 \text{ \AA}$ were used. The capillary was heated from 100 K to 500 K and then cooled down to 100 K at a 120 K per hour rate, while synchrotron powder diffraction data were collected *in-situ*. Temperature was controlled with an Oxford Cryostream 700+. Each pattern was collected during 60 sec exposure time, while the capillary was rotated by 60 degrees, followed by a readout during 83 sec.

Pure α -phase starts to transform into the β -phase at about 490 K and the conversion completes at 500 K within a few minutes. It is indeed remarkable that the high-temperature β -phase does not transform back to the α -phase when cooled down to 100 K. Within the 100-500 K temperature range the unit cell parameters for the α -phase can be approximated by a polynomial equations, where the variation of the a parameter is highly non-linear, with a minimum at ~ 170 K. Thermal expansion for the β -phase is highly anisotropic and very non-uniform: only the cell parameter c and the cell volume V can be approximated by polynomials, while the fits for a and b are bad for low-order polynomials and give unreasonable values for the high-order ones. Indeed, the cell parameter b reveals very complex temperature behaviour: it shows a maximum at about 275 K and a minimum at 345-350 K. The other two cell parameters also show an unusual behaviour: a and c display minima at ~ 200 and ~ 450 K, respectively, increasing towards lower temperatures. Stability of the two phases in the wide temperature range can be considered as a broad hysteresis, which indicates an existence of two similar energy minima separated by a barrier.

Single crystal diffraction:

A crystal of ~50 μm size has been selected from the powder sample which was annealed for one week under 1 bar of argon at 453 K. The crystal was selected under protective layer of oil and rapidly transferred to a 100 K nitrogen stream. Diffraction data were taken at 100 K using the MAR345 Image Plate detector, at the wavelength 0.770294 \AA and the crystal-to-detector distance of 150 mm. 219 frames with 1° rotation and 10 sec exposure time have been collected.

The structure of the low-temperature α -phase, originally reported by two independent groups in the space group $P6_1$ [2, 3], is revised in the space group $P6_122$, using 100 K single-crystal diffraction data. The revision supports the suggestion made in the DFT study [4] of the $P6_1$ structure. Analysis of the published $P6_1$ models shows that location of the H-atoms from powder data posed the main problem for the identification of the correct symmetry: wrongly determined orientations of some BH_4 groups hampered a successful detection of the true $P6_122$ symmetry by automatic algorithms. On the other hand, the restrained refinement in $P6_122$, using our new high-resolution powder data, allows to approach the accuracy of the single-crystal study.

Experimentally determined B-H distances are statistically identical, displaying the 1.142 \AA mean over 20 independent bond lengths. The BH_4 groups are coordinated by Mg atoms via the two opposite edges, but the Mg- H_2BH_2 -Mg fragments are not strictly linear – the Mg-B-Mg angles range from 148 to 170° . H-B-H angles in the Mg- H_2B fragments are in average by 2° more open than for the non-coordinated ones. A detectable distortion of the tetrahedral BH_4 groups can be attributed to the strong polarizing effect of the Mg^{2+} cation or to a partially covalent Mg- BH_4 interaction.

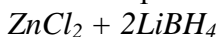
The dodecahedral MgH_8 coordination of the three independent Mg atoms in $\alpha\text{-Mg}(\text{BH}_4)_2$ can be described as a slightly distorted snub disphenoid. Four BH_4 groups around each Mg can be grouped in two pairs, each forming a nearly planar $\text{BH}_2\text{-Mg-H}_2\text{B}$ fragment, with the two fragments forming $\sim 90^\circ$ dihedral angle. The shortest H...H distances between the BH_4 groups (2.18-2.28 \AA) appear within these $\text{BH}_2\text{-Mg-H}_2\text{B}$ fragments. All other intermolecular H...H contacts in $\alpha\text{-Mg}(\text{BH}_4)_2$ are longer than 2.47 \AA , but typically range from 2.7 to 2.9 \AA . The single-crystal study gives a narrow, 1.92-2.16 \AA , range of Mg-H distances, which is only slightly broader than the theoretical 2.00-2.13 \AA range.

We found that $\alpha\text{-Mg}(\text{BH}_4)_2$ contains an unoccupied void, overlooked in the previously reported $P6_1$ models, accounting for 6.4% of space in the structure. It is large enough (37 \AA^3) to accommodate a small molecule, like H_2O . The void forms an infinite channel along 00z direction, which may provide a path for hydrogen diffusion during initial stages of hydrogen desorption. It is remarkable that by $\sim 3\%$ less dense high-temperature β -phase contains no unoccupied voids.

A smooth variation of the cell parameters for the α -phase indicates that there is no hypothetical transition from the $P6_122$ structure to $P6_1$ or vice versa, and therefore the structure revision for the hexagonal phase is valid at all temperatures.

The results have been published in ref. [5].

Other samples were also studied by in-situ powder diffraction :



Sample from Geneva, prepared by ball milling, temperature ramp 100-500 K.

The measurement was then completed by the data measured in Dec 2008 within the project no. 01-02-834.

The results are being prepared for publication.

[1] Chłopek, K.; Frommen, Ch.; Léon, A.; Zabara, O.; Fichtner, M. *J. Mater. Chem.* **2007**, *17*, 3496-3503.

[2] Cerny, R.; Filinchuk, Y.; Hagemann, H.; Yvon, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 5765-5767.

[3] Her, J.-H.; Stephens, P. W.; Gao, Y.; Soloveichik, G. L.; Rijssenbeek, J.; Andrus, M.; Zhao, J.-C. *Acta Crystallogr. B* **2007**, *63*, 561-568.

[4] Dai, B.; Sholl, D. S.; Johnson, J. K. *J. Phys. Chem. C* **2008**, *112*, 4391-4395.

[5] Filinchuk, Y.; Černý, R.; Hagemann H.; *Chem. Mat.* 2009, in press. DOI: 10.1021/cm803019e