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Hydrogen sites analysed by X-ray synchrotron diffraction in $Mg_7TiH_{13–16}$ made at gigapascal high-pressures

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Abstract

The structure of a new hydrogen rich Mg-based transition metal hydride, i.e. Mg_7TiH_{16}, was investigated with high-energy X-ray synchrotron radiation data from the facility SPring-8, Japan. The hydride phase was in advance prepared at 8 GPa and 873 K with a cubic anvil press. The high-energy beam also enabled hydrogen to be observed. With the Rietveld method the best result was obtained when two tetrahedral sites are fully occupied by hydrogen atoms with a minimum H—H distance of 1.8 Å. A sample that had been stored for a longer time before analysis appeared to have less hydrogen corresponding to the formula unit of Mg_7TiH_{13} and also a smaller unit cell volume.

Keywords: Hydrogen storage material; Gas–solid reaction; X-ray diffraction; Synchrotron radiation; High pressure

1. Introduction

On the road to find new hydrogen rich compounds with >5 wt.% hydrogen, a series of hydrogen containing Mg-transition metal (Ti, V, Cr or Mn) compounds has been synthesized under high-pressures. The hydride phases were prepared at 6–8 GPa and 873 K with a cubic anvil press, a technique that has only been used to a small extent for investigating the occurrence of new metal hydrides. Details about desorption behavior and metal atom structures can be found in our previous papers [1–5]. The hydrogen atoms positions could not be determined because of their low X-ray scattering factor. In order to get clues to better understand the mechanism behind the diffusion process, we wanted to determine the location of the hydrogen atoms. The metal hydride with the presumably highest hydrogen content of the four above mentioned new compounds was selected, that is, Mg_7TiH_{16} (7 wt.%) and was investigated with high-energy X-ray synchrotron radiation data from the facility SPring-8, Japan. According to our previous investigation [1] it has lower hydrogen desorption temperature than the corresponding binary hydrides of MgH_2 and $TiH_{1.9}$, respectively as revealed by TDS (thermal desorption spectroscopy)-experiments, suggesting that the ternary hydride has a weaker metal to hydrogen bonding than the two binary hydrides. No binary Mg_7Ti existed after releasing hydrogen. Therefore this ternary hydride can only exist by the support of hydrogen atoms. Under gigapascal high-pressures hydrogen seems to stabilize metastable metal–atom structures, leading to increased hydrogen amount, which is useful for finding new promising metal hydrides with good storage capacities and reasonable desorption temperatures.

2. Experimental

2.1. High-pressure synthesis

The binary hydrides of MgH_2 (Aldrich Chemical Company, 90%) and $TiH_{1.9}$ were mixed in a molar ratio of 7:1. Titanium hydride was first prepared by solid–gas reaction of

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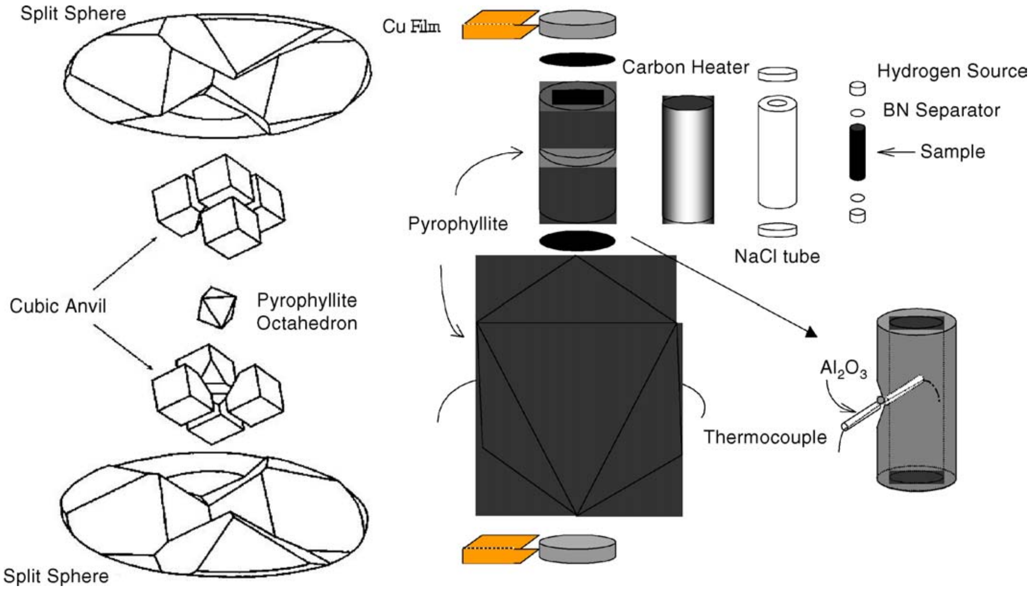

Fig. 1. Left: the set-up of the cubic anvil press. Right: the set-up of sample holders.

Ti powder (Rare Metallic Co. Ltd., 99.9%) with hydrogen in a Sieverts apparatus and had a XRD pattern consistent with the data of cubic $TiH_{1.9}$ (JCPDS 25-0982). The mixture of the binary hydrides was pressed into a pellet in an argon-filled glove box and enclosed together with two pellets of a hydrogen source of $NaBH_4$ (Aldrich Chemical Company, 98%) and $Ca(OH)_2$ (Wako Pure Chemical Industries Ltd., 99.9%). In order to prevent contamination and only allow hydrogen to diffuse to the sample, the pellets were separated by BN discs and sealed in a NaCl capsule further surrounded by a carbon heater placed in a pyrophyllite octahedron. In Fig. 1 the cubic anvil set-up and sample holder set-up are shown. Further details can be found in our previous publications [1,6]. The cell was compressed almost isotropically up to 8 GPa by using a high-pressure generating machine with 6–8 multi-anvils. The sample was heated to 873 K for 1 h.

2.2. Synchrotron X-ray diffraction

XRD data was collected at the synchrotron radiation facility SPring-8, Japan, at beam line BL19B2 which is a medium-length hard X-ray bending magnet beam line. A large Debye-Scherrer camera is installed in order to perform accurate structure analysis of powder diffraction patterns. A standard double-crystal monochromator enables photon energies from 5 to 117 keV. The camera with radius of 286.5 mm has an Imaging Plate (IP) on the 2θ arm as a detector. In the present experiment the diffraction pattern was recorded in the 2θ range 3°–75° and the pixel size of the IP was selected to 50 μm. The wavelength was calibrated to $\lambda = 0.05$ nm by using CeO_2 as a standard. Two different samples from two different syntheses were prepared. The exposure time of X-rays was 5 min for both samples and an extra exposure was made for one of the samples during 120 min. The sample powders were contained in glass capillaries ($D = 0.2$ mm) and sealed with glue in an Argon filled glove box to prevent contamination.

3. Discussion and results

3.1. Rietveld refinement

The atomic scattering factor for H atoms is very low and therefore it is generally impossible to determine their location from powder diffraction data. However, with high-energy synchrotron data it was here possible to extract information about the atomic parameters for hydrogen with the Rietveld method using the program FullProf [7]. In the Rietveld method, which is a structure refinement method, the least-squares refinements are carried out until the best fit is obtained between the entire observed powder diffraction pattern and the entire calculated pattern based on the simultaneously refined models for the crystal structures. In order to evaluate the proceeding of the refinements, a set of numerical criteria of fit, or R-values, are reported after every least-squares refinement. The R_{wp} best reflects the progress of the fitting of the calculated pattern to the observed pattern. The Bragg agreement index, R_B, reflects the fit of the calculated crystal-structural model to the observations. For single-phase, crystalline powder diffraction patterns, R-values below 10% reflect a satisfying structural model.

Both samples contained the ternary Mg–Ti–H phase, $TiH_{1.9}$, γ-MgH_2, β-MgH_2, MgO and also NaCl from the sample holder. Sample No. 1 that was exposed during 5 and 120 min contained the ternary Mg–Ti–H phase (54%), a substantial amount of $TiH_{1.9}$ (36%) and smaller amounts of γ-MgH_2 (1%), β-MgH_2 (2%), MgO (4%) and NaCl (3%). All

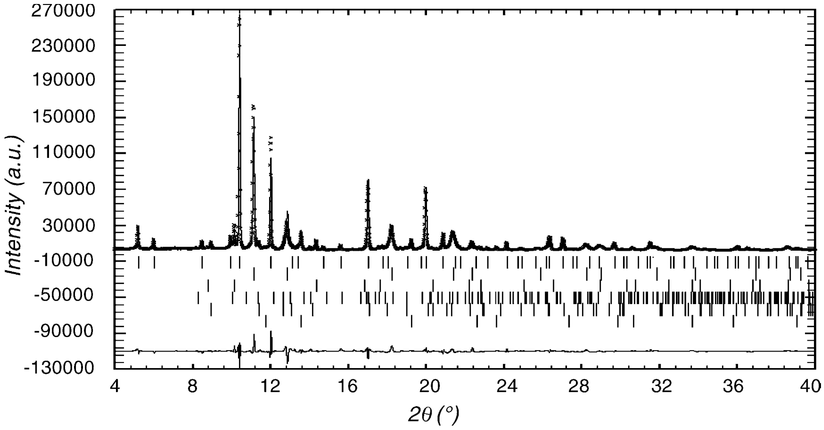

Fig. 2. Difference plot from the Rietveld refinements of Sample No. 1. The phases are from top to bottom: $Mg_7TiH_{16.0}$, $TiH_{1.9}$, NaCl, γ-MgH_2, β-MgH_2 and MgO.

these phases were included in the Rietveld refinements. The same result was obtained for the two data sets (except for 1% higher R-values for the shorter exposure time), so hereafter the details will be presented for the 120 min exposure only. The metal atom structure of the ternary Mg–Ti–H phase was previously suggested to be similar to Ca_7Ge [8] with Mg in 4*b* and 24*d* and Ti in 4*a*, space group $Fm\bar{3}m$ (no. 225) [1]. This was confirmed with the present synchrotron data reaching R-values of $R_B = 9.53$ and $R_{wp} = 9.09\%$. Both tetrahedral and octahedral sites for hydrogen were tested, but the best profile fit was obtained with hydrogen fully occupying two tetrahedral sites, 32*f*, leading to a unit formula of $Mg_7TiH_{16.0}$, i.e. about 7 wt.% hydrogen. When hydrogen was added in the refinements the calculated pattern of the first peaks fitted better to the observed pattern and also the R-values were lowered to $R_B = 6.58$ and $R_{wp} = 8.81\%$. The unit cell parameter was refined to $a = 9.564(2)$ Å. The difference plot from the Rietveld refinement is shown in Fig. 2. The crystallographic information can be found in Table 1. Of the other sites that was added to the two 32*f* sites, only the octahedral site 8*c* that has hydrogen atoms in between the Mg-atoms in 24*d* gave a low R-value ($R_B = 6.52\%$) and reasonable bonding distances. However, the profile fit became slightly less satisfying and therefore a definite conclusion could not be made as whether this site is occupied or not. Other sites, i.e. 24*e*, 48*g*, 48*h*, gave higher R-values ($R_B = 8$–11%) and the refined coordinates resulted in bonding distances of H–H and Mg–H that were too short in highly distorted arrangements.

Sample No. 2 contained 58% of the ternary Mg–Ti–H phase, $TiH_{1.9}$ (13.5%), γ-MgH_2 (6%), β-MgH_2 (17%), MgO (3.5%) and NaCl (2%). Refinement of the metal atom structure gave R-values of $R_B = 10.9$ and $R_{wp} = 9.1\%$. Refining the tetrahedral sites of 32*f* did not lead to as good profile fit as for Sample No. 1. The R-values were $R_B = 9.6$ and $R_{wp} = 8.7\%$. Refining the occupancy of the 32*f* sites led to a decrease in the site for H2 to 59% occupancy, giving the formula unit of $Mg_7TiH_{12.7}$, that is 5.5 wt.% hydrogen which interestingly is the same value obtained in the TDS-measurement (see [1]). This improved the profile fit and lowered the R-values to $R_B = 7.97$ and $R_{wp} = 7.78\%$. The cell parameter was refined to $a = 9.525(2)$ Å which is similar to the value obtained in our previous report [1]. The difference plot from the Rietveld refinement is shown in Fig. 3. The crystallographic information can be found in Table 2. This sample that was also used for the TDS-experiment had been kept longer time in the glove box before the analysis were performed. The difference in unit cell volume between the two samples, i.e. 874.82–864.16 $Å^3$ = 10.66 $Å^3$ corresponds to 3.5 H-atoms if the volume of one H-atom is 3 $Å^3$ as according to Westlake [9]. The difference between the number of H-atoms between the two samples (16.0–12.7) is 3.3 H-atoms. This indicates that the difference in unit cell size correlates to a different H-content.

Table 1
Crystallographic parameters from the Rietveld refinements for $Mg_7TiH_{16.0}$, $a = 9.564(2)$ Å in space group $Fm\bar{3}m$ (no. 225)

Atom	Site	*xyz*	B($Å^2$)	*N*
Ti	4*a*	0 0 0	0.44(3)	1
Mg1	4*b*	$\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$	1.69(3)	1
Mg2	24*d*	$0\,\frac{1}{4}\,\frac{1}{4}$	1.7(3)	1
H1	32*f*	$x = 0.094(2)$	1(1)	1
H2	32*f*	$x = 0.365(2)$	1(1)	1

Note: B is the isotropic thermal displacement factor and N is occupancy where 1 is equal to 100% occupancy.

Table 2
Crystallographic parameters from the Rietveld refinements for $Mg_7TiH_{12.7}$, $a = 9.525(2)$ Å in space group $Fm\bar{3}m$ (no. 225)

Atom	Site	*xyz*	B($Å^2$)	N
Ti	4*a*	0 0 0	0.02(3)	1
Mg1	4*b*	$\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$	1.5(3)	1
Mg2	24*d*	$0\,\frac{1}{4}\,\frac{1}{4}$	1.5(3)	1
H1	32*f*	$x = 0.105(3)$	4(1)	1
H2	32*f*	$x = 0.363(4)$	4(1)	0.59(3)

Note: B is the isotropic thermal displacement factor and N is occupancy where 1 is equal to 100% occupancy.

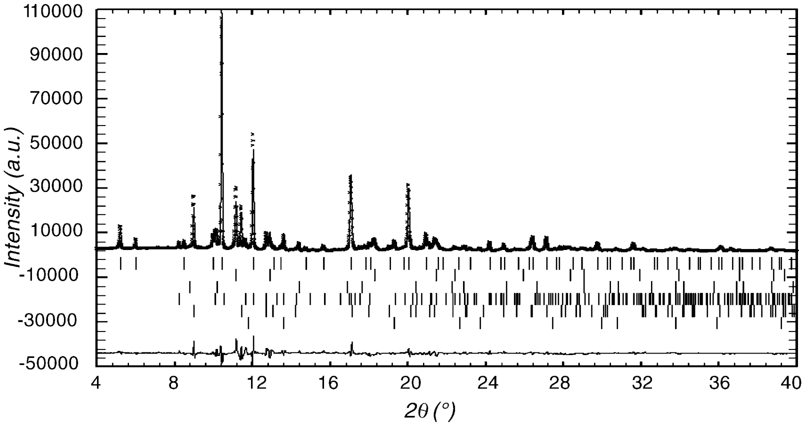

Fig. 3. Difference plot from the Rietveld refinements of Sample No. 2. The phases are from top to bottom: $Mg_7TiH_{12.7}$, $TiH_{1.9}$, NaCl, γ-MgH_2, β-MgH_2 and MgO.

3.2. Structure of Mg_7TiH_{16}

The basic structural building block is an F-centered cubic unit cell; $a = 4.7658(5)$ Å, which is close to the $TiH_{1.9}$ structure ($a = 4.448$ Å), thus the substructure of the hydride has a CaF_2-type structure similar to $TiH_{1.9}$. With a doubling of the unit cell and a partial substitution by titanium in the magnesium atom framework, the observed diffraction pattern can be described by a Mg_7Ti metal atom framework with titanium atoms in 4*a* and magnesium atoms in 4*b* and 24*d*. This atomic arrangement corresponds to the structure of Ca_7Ge space group $Fm\bar{3}m$ (no. 225) [8]. The hydrogen atoms are located in between the close packed layers of magnesium and titanium in tetrahedral sites. The ideal positions of the hydrogen atoms would be $x = 1/8$ and $x = 1/3$ (both in 32*f*) but the refined coordinates are distorted from these positions as can be seen in Tables 1 and 2. The structure is shown in Fig. 4. The tetrahedral environment of H1 consists of 1 Ti-atom on a bonding distance of 1.557 Å and three Mg2-atoms each on a bonding distance of 2.293 Å. The tetrahedral environment of H2 consists of 1 Mg1-atom on a bonding distance of 2.236 Å and 3 Mg2-atoms each on a bonding distance of 2.021 Å. The weaker bonding in the tetrahedron surrounding H2 explains why this site, rather than the tetrahedron surrounding H1, would loose hydrogen as was the case for Mg_7TiH_{13}. Both the Ti–H and Mg–H distances in Mg_7TiH_{16} are in agreement with the corresponding binary hydrides. The minimum H–H bonding distance in Mg_7TiH_{16} is 1.798 Å which is shorter than the average H–H distance in intermetallic compound type hydrides (ca 2.1 Å). Complex type hydrides often have shorter Metal–H and H–H distances due to a more covalent bonding. It though appears that this structure is more similar to a binary hydride doped with a second element. It would be of interest to prepare larger batches of this ternary hydride at more moderate conditions and perform a neutron diffraction experiment in order to reveal the maximum amount of hydrogen.

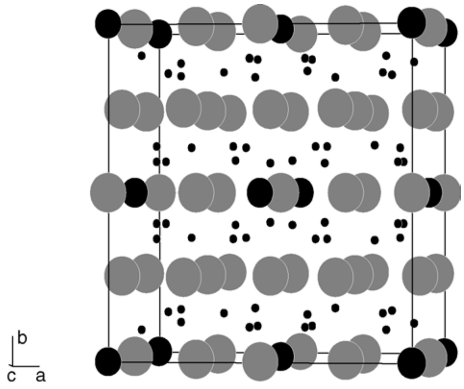

Fig. 4. The structure of Mg_7TiH_{16} with full occupancy of the two tetrahedral (32*f*) sites. Magnesium is grey, titanium is black and hydrogen is small and black.

4. Conclusion

A new hydrogen rich ternary hydride, Mg_7TiH_{16} with 7 wt.% hydrogen was synthesized at a high-pressure of 8 GPa and heated to 873 K and structurally characterized with high-energy synchrotron X-ray powder data. The hydrogen atoms are located in between the close-packed layers of Mg and Ti in two fully occupied tetrahedral sites with a minimum H–H distance of 1.8 Å. This phase appears to be metastable and a sample that had been stored for a longer time before analysis had lower amount of hydrogen, i.e the formula unit of Mg_7TiH_{13}, corresponding to 5.5 wt.% hydrogen. For practical application as a hydrogen storage material another synthesis route has to be realized and the desorption temperature has to be further lowered by substitution of the metal atoms.

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