



YMgGa as a hydrogen storage compound

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ABSTRACT

The hydrogen absorption and desorption properties of the recently found ternary phase YMgGa have been studied. This compound absorbs 2.2 wt% hydrogen during the first cycle, but only 1.1 wt% can be stored reversibly for the following cycles under the applied pressure and temperature conditions. Hydrogen absorption and desorption properties were investigated by measuring the thermal desorption spectra and the pressure-composition isotherms while the crystal structure was determined using X-ray diffraction (XRD). The compound absorbs hydrogen at pressures above 0.2 MPa and 250 °C by decomposing into YH₃ and MgGa. This reaction is reversed when heating the hydride in a He atmosphere; hydrogen is released and the YMgGa phase is partially recovered together with YGa₂ and YH₂. The reformation of YMgGa occurs at temperatures below 450 °C on the expenses of hydrogen desorption from YH₂. This is not expected under these temperature conditions as YH₂ normally does not desorb hydrogen below 800 °C.

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1. Introduction

The potential use of hydrogen as an energy carrier has been studied extensively in the last 20 years. Many different storage systems have been suggested, from high-pressure tanks to chemical storage in various compounds [1]. Many studies have focused on metal hydrides as suitable compounds for hydrogen storage [2].

Mg–Y and Mg–Ga based alloys have been studied in our group recently [3–8]. This research has shown that the hydrogen diffusion is improved with the amount of Y in Mg–Y thin films [9].

The hydrogen absorption in Mg₂₄Y₅ leads to decomposition into YH₃ and MgH₂. This reaction is irreversible as YH₂ is very stable and a temperature above 800 °C is needed to release the hydrogen [10]. Mg₅Ga₂ reacts with hydrogen gas and MgH₂ and Mg₂Ga₅ are formed [6].

Hydrogen absorption in the Mg–Y and Mg–Ga systems has been shown to be accompanied by microstructural modifications. In Mg₂₄Y₅, hydrogen absorption leads to the formation of nanosized 1D whiskers of MgH₂, growing from the surface of the host grains [7]. These whiskers are proved to be single crystals. During hydrogen desorption the whiskers are transformed to carved nanotubes of Mg [8]. The microstructural modifications are different for hydrogen absorption in Mg₅Ga₂. MgH₂ whiskers were observed, but with a different growth

mechanism. Here, the 1D growth is mediated by a host grain at the top of the whisker [7].

Recently, the new ternary compound YMgGa was synthesized and the crystal structure was determined to be the hexagonal ZrNiAl type-structure, $a = 7.2689$ (10) Å and $c = 4.4205$ (9) Å [5]. The atomic arrangement can be described by a 3D network of Mg–Ga atoms with Y atoms situated inside the distorted hexagonal channels.

The present paper reports on the hydrogen absorption/desorption properties and phase transformations of YMgGa.

2. Experimental details

2.1. Synthesis

The starting material was synthesized by heating appropriate amounts of the element inside a sealed tantalum tube under argon atmosphere inside an induction furnace up to ca. 1100 °C. The elements were Mg (99.95% claimed purity, Alfa Aesar), Ga (99.95% claimed purity, Johnson Matthey) and Y (99.9% claimed purity, Highways International). No reaction between the sample and the tantalum could be observed. The sample was crushed and physically grounded to powder using an agate mortar.

2.2. Hydrogenation

The sample was hydrogenated by solid–gas reactions at different hydrogen pressures and temperatures for at least 10 h.

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Prior to hydrogenation the reactor was evacuated to ~ 1 Pa and flushed with argon several times. Oxide formation due to the short exposure to air during loading of the reactor is considered to be negligible.

2.3. Absorption/desorption isotherms and thermal desorption spectra (TDS)

The absorption/desorption isotherms and the thermal desorption spectra were recorded by using a volumetric thermal desorption analyzer (Hiden Isochema). The system was used either in Sieverts mode or in thermal desorption mode by applying a constant temperature increase under a flow of inert gas. Prior to any experiment the reactor was evacuated to a base pressure of 10^{-4} Pa.

Absorption/desorption isotherms were recorded volumetrically (Sieverts method) by a step-wise increase/decrease of the pressure. The volumes of dosing and reactor chambers are approximately 5 cm^3 . The maximum pressure and temperature were 8 MPa and 375°C , respectively, and the thermal stability during the isothermal measurements was $\pm 0.3^\circ\text{C}$. The instrument was leak-tested prior to all measurements at high pressure and room temperature over a period of several hours. The isothermal measurements were repeated and found to be in good agreement when performed using a similar volumetric instrument which gave comparable results. Long equilibrium times were used for the isothermal measurements allowing more than 5 h per aliquot.

For the TDS measurements, the reactor was connected to a high sensitivity dynamic sampling mass spectrometer by a heated flexible quartz capillary. The absorbed hydrogen was thermally desorbed in a constant helium flow by heating the sample with a linear temperature increase ($5^\circ\text{C}/\text{min}$). The amount of desorbed hydrogen was determined by measuring the hydrogen partial pressure of the mass spectrometer as a function of time.

2.4. Phase analysis with X-ray powder diffraction

Diffraction data were recorded on a X-ray powder diffractometer, Bruker D8, equipped with a Vântec PSD (4° opening) using $\text{CuK}\alpha_1$ radiation. The reaction pathways were investigated by *in situ* measurements in a hydrogen flow at different temperatures. Pressures up to 600 kPa and temperatures up to 350°C were used, with a temperature step of 50°C . Each pattern was recorded for 30 min at a constant temperature. LaB_6 was used as an internal calibration standard. Phase analysis were performed using the Rietveld method [11] implemented in the program FULLPROF [12].

The previously determined crystal structure parameters of the observed phases were used as input parameters in the phase analysis. The peak shape was described by the pseudo-Voigt function and the background was modelled by interpolation between fixed points. The varied profile parameters were: 2θ zero point (1); scale factor (1); profile shape parameter (1); half-width parameters (3); asymmetry parameters (2). Refinements of the structural parameters showed no significant deviation from the previously reported crystal structure determinations.

3. Results

3.1. YMgGa

The YMgGa sample contained small impurities of YGa and Y_2MgGa_2 (see Fig. 1); the total amount of these phases is estimated to be less than 10 wt%, as calculated by the FULLPROF

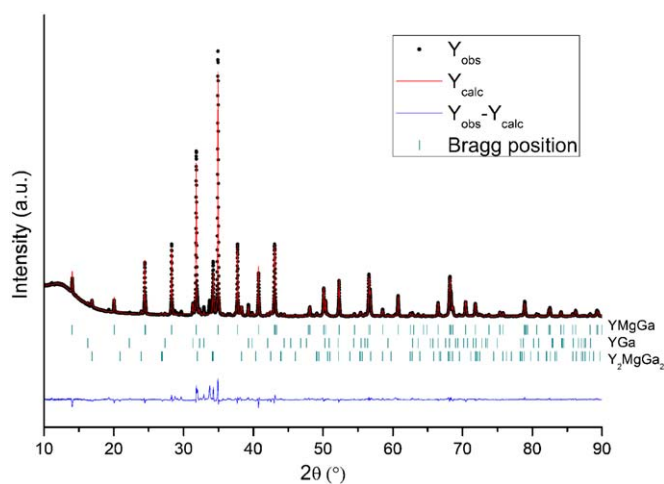


Fig. 1. XRD pattern of the YMgGa compound, recorded at 23°C . The total amount of YGa and Y_2MgGa_2 phases was estimated to be less than 10 wt%.

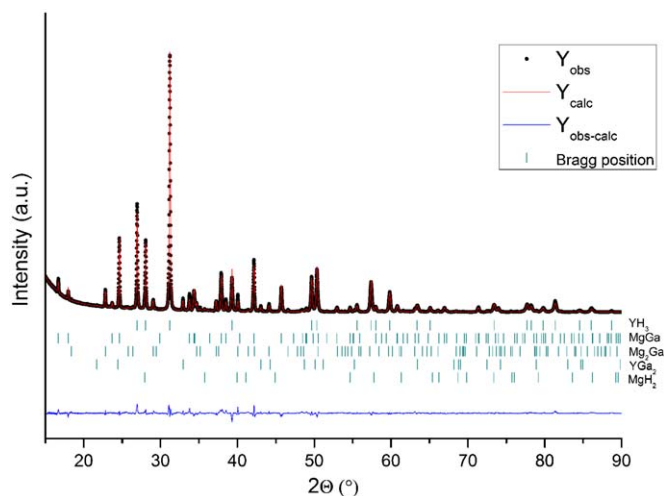


Fig. 2. XRD pattern from YMgGa hydrogenated at 6 MPa and 375°C . YH_3 and MgGa were the majority phases with small amounts of MgH_2 , Mg_2Ga and YGa.

program. The obtained structural parameters agreed with the previously reported crystal structure determinations [3,5,13]. Several different samples and thermal treatments were performed but it was not possible to gain a completely monophased sample.

3.2. Hydrogen absorption

At 6 MPa hydrogen pressure and 375°C , YMgGa reacted with hydrogen and formed YH_3 and MgGa and small amounts of MgH_2 , Mg_2Ga and YGa₂ (estimated to be less than 6 wt%), see Fig. 2.

In situ powder X-ray diffraction (XRD) measurements, at 600 kPa hydrogen pressure, showed that YMgGa absorbs hydrogen through decomposition into YH_3 and YGa₂ and some small amounts of other phases, as shown in Fig. 3. The compound started to absorb hydrogen at temperatures above 200°C , and YGa₂, YH_3 and Mg_2Ga were formed.

Phase analysis after hydrogenation at different hydrogen pressures and temperatures are presented in Table 1; no significant deviation from previously reported crystal structure determinations were observed [13–18]. At low hydrogen pressures the yttrium containing compounds were mainly YGa₂ and yttrium

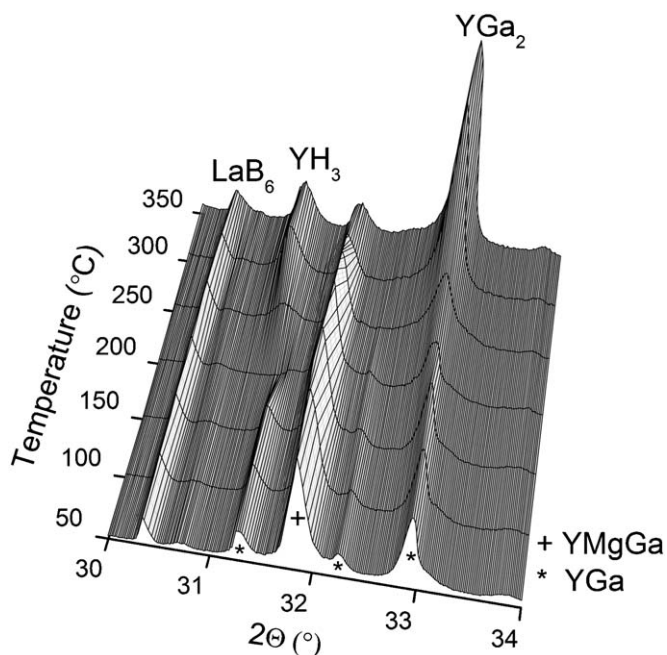


Fig. 3. *In situ* powder X-ray diffraction, measured at 600 kPa hydrogen pressure and a stepwise increase of temperature from 50 to 350 °C. LaB₆ has been used as internal calibration standard.

Table 1
Phase analysis after hydrogenation.

Hydrogen-pressure (MPa)	Temperature (°C)	Phase content
Unreacted	23	YMgGa+(YGa+Y ₂ MgGa ₂)
0.2	400	YMgGa+YH ₂ +YGa ₂ +(Y ₂ MgGa ₂)
0.5	375	YH ₂ +YH ₃ +YGa ₂ +(Mg ₂ Ga+unknown)
2	375	YH ₃ +YGa ₂ +Mg ₂ Ga
6	375	YH ₃ +MgGa+(YGa ₂ +Mg ₂ Ga+MgH ₂)

The minority phases are in brackets (estimated to be less than 10 wt%).

hydrides (YH₂ and YH₃). The amount of the formed yttrium hydride increases with increasing hydrogen pressures and at 6 MPa the amount of YGa₂ is negligible. At these high hydrogen pressures MgH₂ and MgGa were also formed. Any influence on the hydrogen absorbing properties due to the small amounts of impurity phases is considered to be negligible.

3.2.1. Pressure-composition-isothermal measurements

All pressure-composition isotherms (PCI) were recorded at 375 °C at pressures up to 8 MPa. The first (circle) and second (triangle) isotherms are shown in Fig. 4. At 8 MPa the first hydrogen absorption cycle showed a maximum uptake of 2.2 wt%, which is not completely desorbed during dehydrogenation (see Fig. 4). The second cycle stores hydrogen reversibly with a capacity of 1.1 wt%. This behaviour is stable, as discussed later, for further hydrogenation/dehydrogenation up to 13 cycles. A plateau pressure was noticed below 10 kPa. This plateau was followed by an increase of the hydrogen content with pressure. The total storage capacity of 2.2 wt% is explained by 1.6 wt% hydrogen in YH₃ and 0.6 wt% originated from the formation of small amounts of MgH₂. The second absorption of hydrogen showed that the first hydrogen uptake is not completely reversible at 375 °C. During desorption ~1.1 wt% hydrogen was recovered. The shape of the second isotherm was similar to the part of the first isotherm after the plateau. Very long equilibrium times were

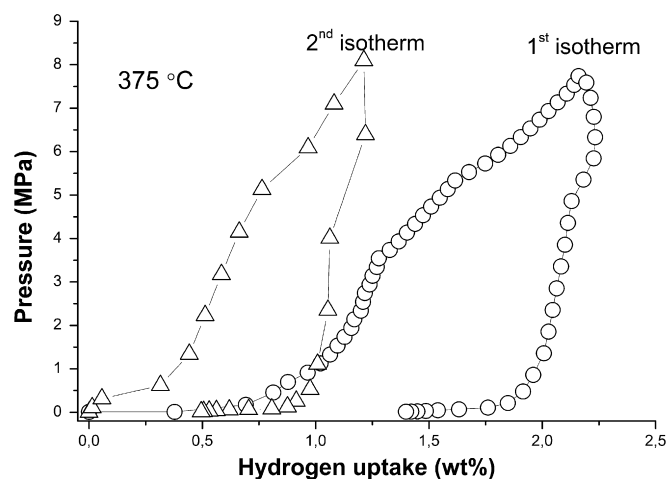


Fig. 4. The PCI curves at 375 °C for the first and second cycle. The second isotherm starts with a hydrogen content of ~1.0 wt%.

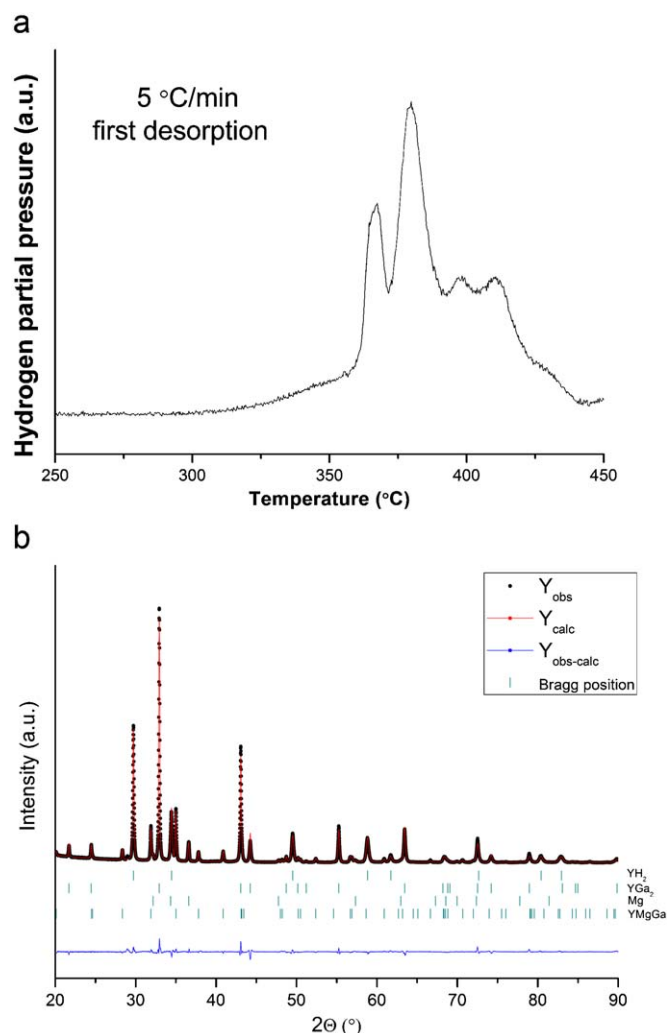


Fig. 5. (a) Thermal desorption spectrum from YMgGa after hydrogenation at 6 MPa and 375 °C. (b) XRD pattern of the desorbed sample.

needed for the isothermal measurements. The small apparent increase in uptake during desorption between 8 and 6 MPa indicated a small additional absorption with long thermodynamic equilibration.

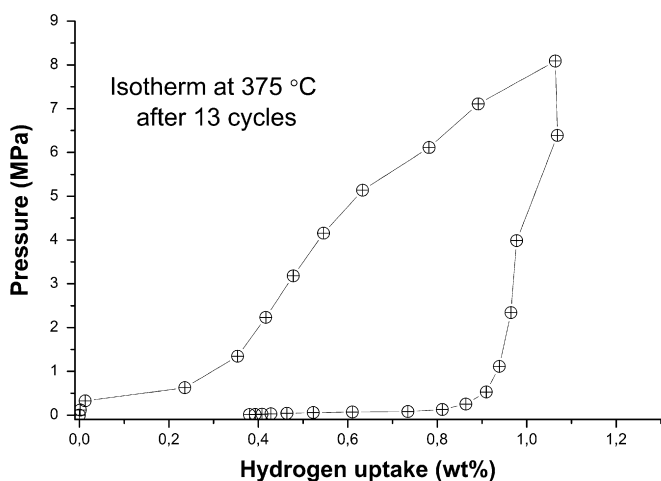


Fig. 6. PCI curve at 375 °C after 13 absorption/desorption cycles.

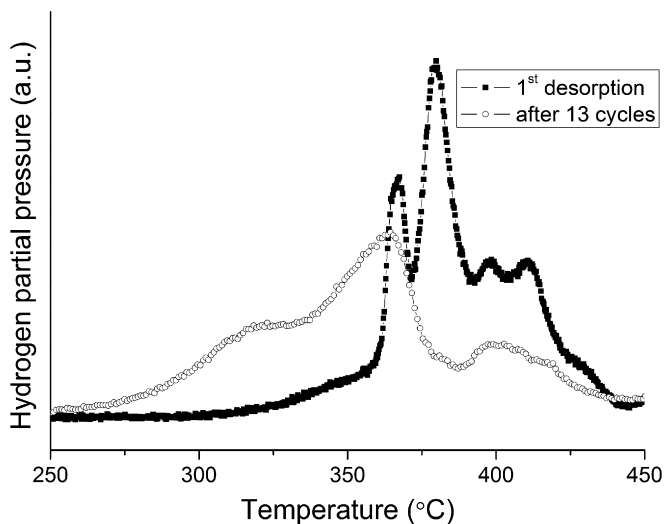


Fig. 7. Thermal desorption spectrum after cycling. For a comparison, the first thermal desorption spectrum is also displayed.

3.3. Thermal desorption of hydrogen

The desorption spectrum for the fully hydrogenated sample (6 MPa) was recorded up to 450 °C, as shown in Fig. 5. The TDS spectrum shows four desorption peaks and one small shoulder and the temperature of the maximum desorption rate was 379 °C. The corresponding XRD pattern of the desorbed sample (Fig. 5b) showed formation of YGa_2 , YH_2 , Mg and YMgGa .

3.4. Cycling effect

Thirteen hydrogen absorption/desorption cycles were performed by keeping the temperature constant at 375 °C and varying the pressure from vacuum to 8 MPa of hydrogen. One isotherm was recorded after the cycling (Fig. 6).

The shape of the absorption and desorption isotherm recorded after cycling was very similar to the second isotherm (Fig. 4). The maximum hydrogen uptake was close to 1.1 wt% at 8 MPa, in agreement with the value from the second isotherm.

The hydrogen thermal desorption spectrum of the cycled material is shown in Fig. 7. For comparison, the first spectrum of desorption is also displayed. The onset temperature of desorption

was lowered from 320 to 260 °C and the temperature of the maximum desorption rate (maximum peak) was decreased from 379 to 363 °C after cycling.

4. Discussion

According to *in situ* and *ex situ* XRD phase analysis, YMgGa decomposed during hydrogen absorption, see Fig. 3 and Table 1. The first hydrogen absorption cycle showed a maximum uptake of 2.2 wt% and a plateau pressure was noticed below 10 kPa, which indicated the formation of YH_2 , in agreement with the XRD phase analysis and previous results by Vajda and Daou [19]. By increasing the hydrogen pressure YH_3 and MgH_2 are formed together with a few percent of magnesium and yttrium gallides.

After desorption, YH_3 or MgH_2 were not observed in the sample. The amount of YGa_2 was increasing significantly and the initial YMgGa phase was also reformed to some extent. The amount of YH_2 was considerably less than the corresponding amount of YH_3 in the fully hydrogenated sample. This suggests that hydrogen desorption from yttrium hydride occurred below 450 °C which is unexpected since pure YH_2 desorbed hydrogen at temperatures above 800 °C [10]. The destabilization of YH_2 is believed to be due to the presence of gallium in the sample. YH_2 was destabilized due to the favourable formation of YGa_2 , resulting in hydrogen desorption. There were no signs of metallic yttrium in any of the samples, hydrogenated or desorbed.

PCI measurements after cycling proved that the material was stable after the first hydrogenation and had a maximum reversible hydrogen storage capacity of 1.1 wt% under the applied temperature and pressure conditions. The cycling was not affecting the thermodynamic properties; however, it changed the kinetics of hydrogen desorption. The temperature stability of hydrogen desorption was lowered after cycling.

5. Conclusions

Combining the results from hydrogen absorption/desorption measurements with *in situ* and *ex situ* X-ray diffraction gave us a better understanding of the different reactions and intermediate phases taking place in the YMgGa system.

The hydrogen absorption and desorption properties of the new ternary compound YMgGa have been investigated; the compound can store ~2 wt% hydrogen but only 1.1 wt% reversibly. Improved thermodynamic and kinetic properties of desorption are found as compared to pure YH_3 . The temperature of hydrogen desorption from YH_2 has been lowered by almost 400 °C by alloying with Mg and Ga. This opens up the road of tailoring the desorption temperature of alloy materials for hydrogen storage applications.

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