# Synthesis, structure and thermal stability of Yb$_4$Mg$_4$Fe$_3$H$_{22}$

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## Abstract

Yb$_4$Mg$_4$Fe$_3$H$_{22}$ and its deuteride were prepared by sintering mixtures of YbMg, Fe and LiH (LiD) powders in the ratio YbMg:Fe:LiH (LiD) = 4:3:1 at 510–520 °C and 120–155 bar hydrogen (deuterium) pressure, and were characterized by X-ray and neutron powder diffraction. They crystallize with cubic symmetry (space group, $P4/mmm$; hydride, $a = 6.6936(4)$ Å; deuteride, $a = 6.6839(5)$ Å, and are isostructural with the calcium analogue Ca$_4$Mg$_4$Fe$_3$H$_{22}$. The deuteride contains octahedral [FeD$_6$]$^{4-}$ complex anions with bond distances [Fe–4D1] = 1.586(5) Å and [Fe–2D2] = 1.554(7) Å, and tetrahedrally coordinated D$^-$ anions with bond distances [D3–Mg] = 1.915(9) Å and [D3–3Yb] = 2.411(7) Å. At a hydrogen pressure of 6 bar, the Yb compound decomposes at about 480 °C into YbH$_2$, Mg and Fe, whereas the Ca analogue decomposes at about 450 °C into Ca$_2$FeH$_6$, Mg and Fe. The enthalpies of desorption, as measured from pressure–composition isotherms, are 137(3) kJ (mol H$_2$)$^{-1}$ for Yb$_4$Mg$_4$Fe$_3$H$_{22}$ and 122(4) kJ (mol H$_2$)$^{-1}$ for Ca$_4$Mg$_4$Fe$_3$H$_{22}$.

## 1. Introduction

Recently, we have reported a new Fe-based quaternary metal hydride of composition Ca$_4$Mg$_4$Fe$_3$H$_{22}$, which contains a mixture of octahedral [FeH$_6$]$^{4-}$ complex anions, conforming to the 18-electron rule, and quasi-isolated H$^-$ anions [1]. In this paper, we report the synthesis and structure of its Yb analogue Yb$_4$Mg$_4$Fe$_3$H$_{22}$. Thermal stabilities were measured on both compounds from pressure–composition isotherms during desorption and reaction mechanisms during decomposition were investigated.

## 2. Experimental details

### 2.1. Synthesis

Binary alloys of nominal composition YbMg were prepared from the elements (Yb (Alfa Products, chips, 99.9%); Mg (CERAC, 1/8 in, 99.99%)) by arc melting. The ingots were powdered, mixed with Fe powder (JMC, London, 99.99%) or Fe wires (Goodfellow, England, 99.5%) and LiH (deuteride) powder (Alfa products, 98%) in the atomic ratios YbMg:Fe:LiH (LiD) = 4:3:1, wrapped in Mo foil and placed in a high temperature, high pressure autoclave. LiH (LiD) was added to the samples, because it was found to favour the synthesis with a high yield. After evacuating to about 10$^{-2}$ mbar and flushing several times with Ar, the autoclave was charged with H$_2$ (D$_2$) gas (H$_2$, Polygaz, 99.9999%; D$_2$, AGA, 99.8%) to an initial pressure of about 75 bar at room temperature. The temperature was increased to 510–520 °C, yielding an H$_2$ (D$_2$) pressure of 155 bar, this temperature was maintained for 2 weeks, during which the pressure decreased to about 120 bar, and then the temperature was lowered to the ambient temperature. After releasing the H$_2$ (D$_2$) pressure, the autoclave was opened and the samples transferred to an Ar-filled glove box. The final products were black in colour and were stable in air for several weeks.

### 2.2. X-ray and neutron diffraction

The samples were characterized by X-ray powder diffraction at room temperature (Guinier camera, Co K$\alpha$ radiation; internal standard was silicon powder with $a = 5.4308$ Å). The film data, as measured on a computer-controlled microdensitometer [2], showed the presence of a new quaternary hydride phase which was indexed on a cubic lattice with refined cell parameters $a = 6.6936(4)$ Å (hydride) and $a = 6.6839(5)$ Å (deuteride). Intensity calculations confirmed that the metal atom arrangement was isostructural to Ca$_4$Mg$_4$Fe$_3$H$_{22}$ [1].

The atomic parameters of hydrogen were refined from neutron powder diffraction data on the deuteride collected on the DMC diffractometer [3] at the SAPHIR reactor at PSI, Villigen (Ge(311); $\lambda = 1.7040$ Å, angular $2\theta$ range, $3.0°$–$135.0°$, $2\theta$ step, $0.1°$; $T = 295$ K). The sample (about 6 g) was enclosed in a cylindrical V container of inner diameter 8 mm and measured in the high intensity mode. The profile refinements were performed using DBWS-9006 [4]. The structure model based on the atomic parameters of $Ca_4Mg_4Fe_3D_{22}$ (space group $P\bar{4}3m$) was refined by taking into account the contribution of two impurity phases, *i.e.* LiD and $Yb_2O_3$ [5]. The nuclear scattering lengths ($\times 10^{-12}$ cm) 0.6671 (D), $-0.190$ (Li), 0.5803 (O), 0.5375 (Mg), 0.945 (Fe) and 1.243 (Yb) were taken from ref. 6. Preliminary refinements showed that the occupying factors of the three deuterium sites did not differ significantly from 100%. Thus, they were fixed at unity in the final refinement. The results are summarized in Table 1. The interatomic distances and D–D contact distances are given in Table 2. The observed, calculated and difference neutron patterns are shown in Fig. 1.

## 2.3. Thermal stability

Pressure–composition ($P$–$c$) isotherms during desorption were measured on both Yb- and Ca-based hydride samples using a high pressure, high temperature microbalance, as described before [7]. The system was augmented by a computer-controlled IGA pressure regulation and data acquisition system (HIDEN Analytical Ltd., England) [8]. The $P$–$c$ isotherms were measured during desorption at pressure intervals of 0.6 bar. The step time was typically 40 min, except in the plateau region, where it varied between 12 and 24 h, depending on the time necessary to reach equilibrium. The plateau pressure $P_{eq}$ was defined as the beginning of any significant weight loss.

Representative $P$–$c$ isotherms at various temperatures are given in Fig. 2. Those of the Yb-based compound

TABLE 1. Refinement results on neutron powder diffraction data for Yb₄Mg₄Fe₃D₂₂ ($T = 295$ K)

| Atom | Position | $x$ | $y$ | $z$ | $U_{iso}$(Å²×100) |
|------|----------|-----|-----|-----|-------------------|
| Yb | 4(e) | 0.7136(4) | $x$ | $x$ | 1.56(8) |
| Mg | 4(e) | 0.2103(10) | $x$ | $x$ | 1.6(2) |
| Fe | 3(d) | 1/2 | 0 | 0 | 0.05(7) |
| D1 | 12(h) | 0.2373(7) | 1/2 | 0 | 1.98(8) |
| D2 | 6(f) | 0.2675(11) | 0 | 0 | 2.1(1) |
| D3 | 4(e) | 0.3757(9) | $x$ | $x$ | 3.8(2) |

Space group: $P\bar{4}3m$ (No. 215).
Cell parameters: $a = 6.6839(5)$ Å.
Agreement indexes: $R_B = 6.8\%$; $R_F = 4.7\%$; $R_p = 5.4\%$; $R_{wp} = 7.2\%$.
Form of temperature factor: $T = \exp[-8\pi^2 U_{iso}(\sin \theta)^2/\lambda^2]$.
Estimated standard deviations in parentheses.

TABLE 2. Interatomic distances (Å) up to 3.5 Å and D–D contact distances (Å) for Yb₄Mg₄Fe₃D₂₂ ($T = 295$ K)

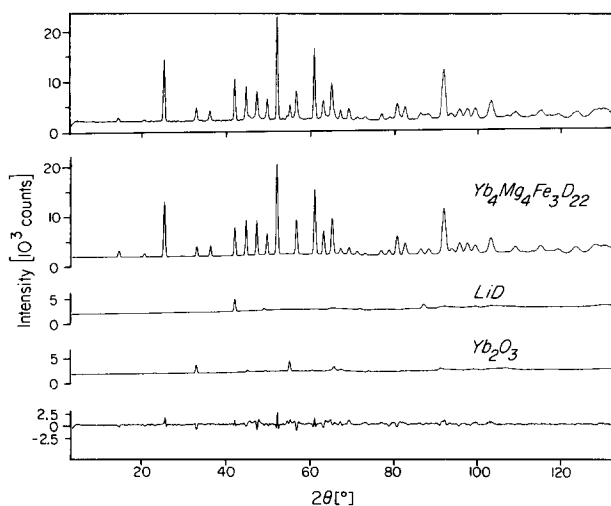| | | | |
|------|----------|------|----------|
| Fe–2D2 | 1.554(7) | D1–Fe | 1.586(5) |
| –4D1 | 1.586(5) | –2Mg | 2.400(7) |
| –4Mg | 2.775(7) | –2Yb | 2.411(3) |
| –4Yb | 3.061(3) | –2D2 | 2.221(6) |
| Yb–6D1 | 2.411(3) | –2D1 | 2.243(5) |
| –3D3 | 2.411(7) | D2–Fe | 1.554(7) |
| –3D2 | 2.710(3) | –2Mg | 2.024(7) |
| –3Fe | 3.061(3) | –2Yb | 2.710(3) |
| –3Mg | 3.397(7) | –4D1 | 2.221(6) |
| –3Mg | 3.440(7) | –4D2 | 2.529(7) |
| Mg–D3 | 1.915(9) | D3–Mg | 1.915(9) |
| –3D2 | 2.024(7) | –3Yb | 2.411(7) |
| –6D1 | 2.400(7) | –3D3 | 2.350(9) |
| –3Fe | 2.775(7) | | |
| –3Yb | 3.397(7) | | |
| –3Yb | 3.440(7) | | |

Estimated standard deviations in parentheses.



Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron diffraction patterns of a sample containing predominantly Yb₄Mg₄Fe₃D₂₂ and the impurity phases LiD and Yb₂O₃ ($\lambda = 1.7040$ Å).

showed only one plateau, which was assigned to the decomposition of quaternary $Yb_4Mg_4Fe_3H_{22}$ into binary $YbH_2$ and elemental Mg, Fe and $H_2$ according to the reaction

$$Yb_4Mg_4Fe_3H_{22} \longrightarrow 4YbH_2 + 4Mg + 3Fe + 7H_2 \qquad (1)$$
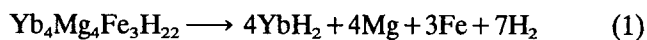
Traces of a ternary phase with f.c.c. symmetry ($a = 7.024(2)$ Å) and likely composition $Yb_2FeH_6$ were detected by X-ray diffraction.

The $P$–$c$ isotherms of the Ca-based compound showed up to three plateaux. Those at high pressure ($20 \geqslant P_{eq} \geqslant 13$ bar) were attributed to the decomposition of the binary impurity phase $MgH_2$, those at medium pressure ($14 \geqslant P_{eq} \geqslant 2$ bar) to the decomposition of quaternary $Ca_4Mg_4Fe_3H_{22}$ into ternary $Ca_2FeH_6$ and
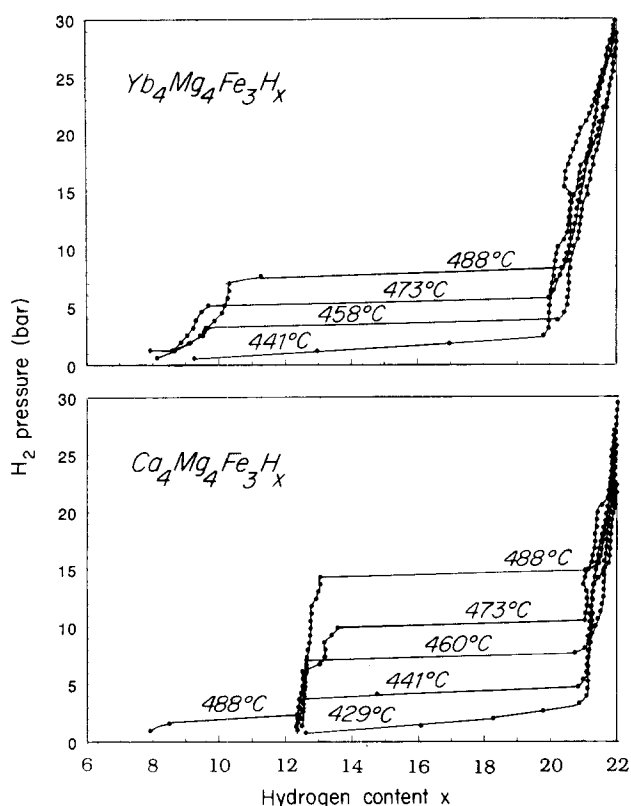
Fig. 2. Pressure–composition isotherms during desorption of $Yb_4Mg_4Fe_3H_{22}$ and $Ca_4Mg_4Fe_3H_{22}$.



Fig. 3. Logarithmic variation of plateau pressure during desorption for $Yb_4Mg_4Fe_3H_{22}$ and $Ca_4Mg_4Fe_3H_{22}$ as a function of inverse temperature.

elemental Mg, Fe and $H_2$, and that at low pressure ($P_{eq} \leqslant 2$ bar) to the decomposition of ternary $Ca_2FeH_6$ into binary $CaH_2$ and elemental Fe and $H_2$, according to the respective reactions

$$MgH_2 \longrightarrow Mg + H_2 \qquad (2)$$

$$Ca_4Mg_4Fe_3H_{22} \longrightarrow 2Ca_2FeH_6 + 4Mg + Fe + 5H_2 \qquad (3)$$

$$Ca_2FeH_6 \longrightarrow 2CaH_2 + Fe + H_2 \qquad (4)$$
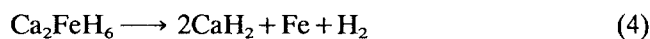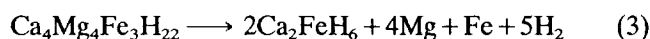
All the assignments were confirmed by the X-ray patterns of the materials which were quenched under the corresponding conditions. At 488 °C, reactions (1)–(4) occurred at $H_2$ pressures of about 8, 20, 14 and 2 bar respectively.

The enthalpies of desorption, as determined from van't Hoff plots (Fig. 3) of the plateau pressures, were found to be $\Delta H_{des} = 137(3)$ kJ (mol $H_2$)$^{-1}$ for $Yb_4Mg_4Fe_3H_{22}$ and $\Delta H_{des} = 122(4)$ kJ (mol $H_2$)$^{-1}$ for $Ca_4Mg_4Fe_3H_{22}$. A reliable value for the decomposition of $Ca_2FeH_6$ could not be derived from these measurements.

## 3. Results and discussion

The structure of $Yb_4Mg_4Fe_3D_{22}$ contains octahedral $[FeD_6]^{4-}$ complex ions, which conform to the 18-electron
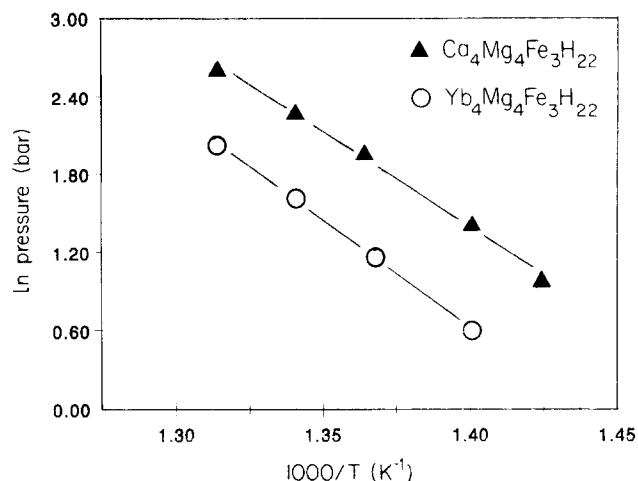
rule, and quasi-isolated $D^-$ anions. The bond distances of the Fe complex $[Fe-D] = 1.586(5)$ Å $(4\times)$ and $1.554(7)$ Å $(2\times)$ do not differ much from those in the Ca analogue $Ca_4Mg_4Fe_3D_{22}$ [1]: $[Fe-D] = 1.583(3)$ Å $(4\times)$ and $1.563(5)$ Å $(2\times)$. In both compounds, these distances are, on average, significantly longer than those in $Mg_2FeD_6$ [9] $([Fe-D] = 1.556(5)$ Å $(6\times))$ and significantly shorter than those in $SrMg_2FeD_8$ [10] $([Fe-D] = 1.578(4)$ Å $(6\times))$ and $Ca_2FeD_6$ [11] $([Fe-D] = 1.618(5)$ Å $(6\times))$, which is in agreement with ionic size considerations. The deuteride anions (D3) in $Yb_4Mg_4Fe_3D_{22}$ (and $Ca_4Mg_4Fe_3D_{22}$) are tetrahedrally coordinated by one Mg and three Yb (Ca) cations.

A detailed comparison of the metal–hydrogen bond lengths in both compounds is not possible, because the observed differences hardly exceed 3 standard deviations. However, in view of the smaller cell volume of the Yb compound compared with that of the Ca analogue, and in view of recent work on other Yb–Ca hydride structure pairs [12], divalent $Yb^{2+}$ appears to have a smaller atomic size in hydrides (or deuterides) than $Ca^{2+}$, in contrast to the cases of halides, oxides and chalcogenides, in which the ionic size of $Yb^{2+}$ is larger than that of $Ca^{2+}$ [13]. This difference is presumably due to the different 'covalent shortening' of the metal–hydrogen bonds [13].

The enthalpy of desorption of $Yb_4Mg_4Fe_3H_{22}$ $(\Delta H_{des} = 137(3)$ kJ (mol $H_2$)$^{-1})$ is slightly bigger than that of $Ca_4Mg_4Fe_3H_{22}$ $(\Delta H_{des} = 122(4)$ kJ (mol $H_2$)$^{-1})$. Both quaternary hydrides are about 50% more stable than the structurally related ternary hydride $Mg_2FeH_6$ $(\Delta H_{des} = 98(3)$ kJ (mol $H_2$)$^{-1})$ [9]. These differences correlate with the thermal stabilities of the corresponding binary alkaline earth (or rare earth) hydrides, which increase in the order $MgH_2$ $(\Delta H = -74$ kJ (mol $H_2$)$^{-1})$, $YbH_2$ $(\Delta H = -182$ kJ (mol $H_2$)$^{-1})$ and $CaH_2$

($\Delta H = -184$ kJ (mol H$_2$)$^{-1}$) [14]. The reasons why Yb$_4$Mg$_4$Fe$_3$H$_{22}$ decomposes mainly into binary YbH$_2$ and elemental Mg and Fe, whereas Ca$_4$Mg$_4$Fe$_3$H$_{22}$ decomposes into ternary Ca$_2$FeH$_6$ and elemental Mg and Fe, are not yet clear to us.

## Acknowledgments

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