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Synthesis of Mg_2FeD_6 under Low Pressure Conditions for Mg_2FeH_6 Hydrogen Storage Studies

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Abstract

Mg_2FeD_6 is successfully synthesised with various degrees of purity using reactive ball milling and annealing under low pressure deuterium conditions to a maximum of 10 bar. The deuteride of the low cost ternary metal hydride Mg_2FeH_6 , is synthesised to enable further characterisation studies such as isotopic exchange behaviour. Both on laboratory and industrial scales, keeping the pressure low reduces the need for expensive compression systems and also minimises the quantity of gas necessary for use; therefore it is important to

assess synthesis under these cost effective conditions. This is especially the case when using a specialised gas such as high purity deuterium. The maximum pressure chosen is 10 bar, to comply with the High Pressure Safety Act in Japan. This Safety Act limits the use of any gas including hydrogen and deuterium to 10 bar eliminating the use of traditional synthesis methods for Mg_2FeH_6 or Mg_2FeD_6 synthesis at high pressure (120 bar). Ball milling parameters such as milling times, ball to powder ratios as well as sintering times were altered to achieve improved Mg_2FeD_6 yields under these low pressure conditions.

Keywords

hydrogen storage; magnesium iron deuteride; magnesium iron hydride; complex hydrides; low pressure

Introduction

Solid state hydrogen storage materials are of increasing interest for the development of complete clean green energy and storage systems. In particular, intermittent renewable energy production from the most common sources such as solar or wind, can produce hydrogen from water during times of excess load, then stored to be used with a fuel cell system at times of low production. This then allows continuous supply of energy independent of renewable source availability. Storing hydrogen as a solid within a metal matrix is a cost effective method of hydrogen storage without the need for compressing or liquefying hydrogen in the traditional storage method sense. One example of this metal matrix is the low cost ternary metal hydride Mg_2FeH_6. This material has octahedral coordination of Fe by hydrogen forming a FeH_6^{4-} anion that is surrounded by eight Mg^{2+} in a cubic K_2PtCl_6 structure type configuration [1, 2]. Mg_2FeH_6 is stable and reversible for more than 500 cycles [3] with a storage capacity of hydrogen up to 5.47 wt. % and several publications have stated that this material has a standard formation enthalpy of 98 ± 3 [1], 86 ± 6 [4] or 77.4 kJ/mol H_2 [3]. This reaction enthalpy is comparable to that of the more commonly known metal hydride, MgH_2 (74.06 kJ/mol H_2) [5], however, the advantage of Mg_2FeH_6 is its significantly high volumetric capacity 150 kg/m^3 [6]. Properties such as excellent cyclability and high thermal stability also allows Mg_2FeH_6 to be a promising candidate for heat storage within concentrated solar plants [3, 7-9] thus broadening its use as a practical material and highlighting the importance of material properties' characterisation.

Similarly, the deuteride, Mg_2FeD_6 is an important material to synthesise and study as it can be used to further investigate hydrogen interaction properties when studying isotopic exchange behavior or neutron diffraction. One such study used neutron diffraction to analyse the absorption and desorption processes of Mg-Fe-H system and Mg_2FeD_6 was used to further understand these reaction mechanisms [10]. Mg_2FeH_6 has also been widely combined with other hydrides to improve hydrogen properties of the overall system especially with regards to thermodynamic stability [11-14]. Examples where Mg_2FeD_6 is used are the recent studies that Mg_2FeH_6 used in reactive hydride composite (RHC) systems together with light weight metal borohydrides namely Li-, Na-, Mg-, Ca- and K-borohydrides [12, 15-17] have shown unique sorption behaviour different from the individual components. Chaudhary *et. al.*[15] and Li *et. al.* [16, 17] both reported the appearance of single step desorption behaviour with these RHC at specific anionic stoichiometries with a suggestion of hydrogen exchange contributing to this phenomenon [18]. In order to observe this hydrogen exchange, Mg_2FeD_6 was synthesised and combined with the borohydride. The results showed evidence of H-D formation, either during ball milling or upon heating up to 400 °C, as H-D was released during the desorption process. In order to achieve such information, keeping the pressure low during raw material synthesis reduces the need for expensive compression systems and also minimises the quantity of gas necessary for use. This is especially the case when using high purity deuterium as it is much more expensive to purchase when compared to hydrogen gas.

To date, Mg_2FeH_6 and Mg_2FeD_6 (D_2 content 10.37 wt. %) are not produced commercially and are synthesised in individual laboratories [1, 19-23]. Mg and Fe do not exist as an intermetallic compound but can be chemically bound in the form of Mg_2FeH_6 or Mg_2FeD_6, thus posing some challenges to the synthesis method. The first reported synthesis of the compounds used elemental Mg and Fe sintered at 500 °C under hydrogen or deuterium pressures between 60 and 120 bar for up to 10 days [1] however, there were significant amounts of MgH_2 or MgD_2 together with unreacted Mg and Fe remaining in the finished product. Subsequent studies have shown improved purity of Mg_2FeH_6 when Mg was first hydrogenated to MgH_2 before combining with Fe [3, 19, 21, 24]. Since this was an effective method of increasing the reaction yield, this study has extended this idea with deuterium instead of hydrogen to first synthesis MgD_2 before further reacting with Fe and D_2 to produce Mg_2FeD_6. The literature also showed that reactive ball milling (milling in H_2 atmosphere) provided an improved synthesis route, however, evidence of MgH_2, Fe and MgO was still present. High purity Mg_2FeH_6 synthesis was achieved more recently, by Polanski *et. al.*[21] as the conditions used (500 °C and 120 bar H_2) were able to achieve a reaction yield of 94 – 97 %. The work presented here limits the synthesis pressure of both reactive ball milling and direct annealing to 10 bar, the lowest pressure reported to date for, an order of magnitude lower than the high purity work shown in Polanski *et. al.*[21]. In order to gain a high yield of product, various methods were used and compared including reactive milling in D_2 atmosphere and direct pressure to ascertain which method was best whilst keeping the pressure low to a maximum of 10 bar.

For some research institutes, in particular those in Japan, the use of any gas, including hydrogen and deuterium, is limited to 10 bar due to the High Pressure Gas Safety Act (Act No. 204 June 7, 1951). This poses some synthesis challenges. This work presented here addresses some of these challenges to provide a new high-yield production route for Mg_2FeD_6 under the given pressure limitations focusing on reactive planetary ball milling and the influence of synthesis parameters on the reaction yield.

Experimental Methods

All materials for this work were handled in an argon atmosphere glovebox (Miwa, Japan) with a constant gas purifying system to reduce any risk of contamination from oxygen or water (O_2 < 1 ppm, H_2O < 1 ppm).

In order to synthesise Mg_2FeD_6, MgD_2 was first prepared from desorbed MgH_2 (Alfa Aesar, 98 %), followed by deuterium D_2 (Asahi sunsoshokei, 99.99 %) absorption at 10 bar. Table 1 gives the synthesis parameters used for the four batches of MgD_2 that were later used to prepare Mg_2FeD_6. All batches of MgD_2 were prepared by loading as supplied or ball milled MgH_2 into a tube reactor where the material was heated to release H_2 and later low pressure D_2 was applied. Only batch 4 used ball-milled MgH_2 prior to heat treatment in a planetary mill for 6 hours at 670 rpm with a ball-to-powder ratio of 20:1, by using stainless steel vials and balls.

Table 1: MgD_2 synthesis conditions

Processing Step	Batch 1	Batch 2	Batch 3	Batch 4
1st Step Desorption				
Desorption Temperature (°C)	400	450	450	450

Vacuum Pressure (bar)	4×10^{-5}	4×10^{-5}	4×10^{-5}	4×10^{-5}
Desorption time (h)	1	4	2	4
Absorption Temperature (°C)	360	360	400	400
Deuterium Pressure (bar)	10	10	10	10
Absorption Time (h)	2	12	4	4
2nd Step Desorption				
Desorption Temperature (°C)	400	-	-	-
Vacuum Pressure (bar)	$4 \times e^{-5}$	-	-	-
Desorption time (h)	1	-	-	-
Absorption Conditions				
Absorption Temperature (°C)	360	-	360	360
Deuterium Pressure (bar)	10	-	10	10
Absorption Time (h)	10	-	6	6

Mg_2FeD_6 was synthesised by combining the pre-prepared MgD_2 with Fe (nano-powder, Sigma Aldrich, > 99%) in the stoichiometric ratio of 2:1 and milled under a reactive D_2 atmosphere followed by heat treatment of 10 bar D_2 for some batches (Table 2). Nano-sized Fe was used for the Mg_2FeD_6 synthesis to increase the Mg-Fe interface area during the reactive milling process thus increasing reaction yield [25]. A planetary Fritsch Pulverisette 7 (Germany) mill was used for the reactive ball milling together with a pressurised stainless steel 30 ml vial with 7 mm stainless steel balls. By monitoring the pressure it was seen that there was little residual D_2 remaining after the different milling times shown in Table 2. After milling, batches 3 and 4 underwent further heat treatment in the tube reactor.

Table 2: Mg_2FeD_6 synthesis parameters

Processing Step	**Batch 1**	**Batch 2**	**Batch 3**	**Batch 4**
MgD_2 Batch used	1	1	3	4

Milling Conditions				
Milling time (h)	6	6	12	12
Ball to powder ratio	20:1	40:1	20:1	20:1
Milling speed (rpm)	670	670	670	670
Deuterium pressure during milling (bar)	10	10	10	10
Annealing conditions				
Temperature (°C)	-	-	360	360
Time (h)	-	-	48	48
Deuterium pressure (bar)	-	-	10	10

A Rigaku Ultima IV X-Ray Diffractometer (XRD) (Japan) with a Cu anode (λ = 1.54051 Å) for a 2θ range of 10 to 80° and a step size of 0.01° was used to obtain information on the crystalline phases. The data presented here show the range 20 to 70 ° to improve 2θ peak position resolution on the x-axis as there were no significant diffraction peaks beyond this range. The silicon single crystal sample holder was sealed in argon atmosphere using Scotch tape. Bruker *Diffracplus TOPAS* version 4.2 was used to analyse the XRD data obtained from the diffractometer and Crystallographic Information Files (cif) were obtained from the International Centre for Diffraction Data (ICDD) database. The fundamental parameter (FP) approach was employed within the Rietveld refinement process with all XRD data analyses to determine quantitative data and lattice parameters of the crystalline samples present. Quality of fit and uncertainties were taken from *TOPAS* in terms of the difference curve (the difference between the raw data and the calculated refinement values) and the *TOPAS* generated uncertainties reported use the bootstrap method of error determination. A point to note is that these uncertainties are for the mathematical fit of the calculated pattern to the measured pattern.

Simultaneous Differential Thermal Analysis and Thermogravimetric Analysis (DTA-TG, Rigaku Thermo - Evo II TG8120 - Canon, Japan) experiments were used to characterise the thermal properties of MgD_2 and Mg_2FeD_6. The heating programme used for each sample was to heat from room temperature to 400 °C at a heating rate of 5 °C/min.

Results and Discussion

Prior to MgD_2 syntheses, XRD analyses were done on the as supplied MgH_2 and the samples desorbed under the conditions given in Table 1 to confirm the purity of the material (Figure 1). The pattern from Figure 1(A) confirms the presence of MgH_2 with a small amount of Mg (< 5 wt.%), consistent with the analytical data given by this manufacturer. The resultant desorption patterns Figure (B), (C) and (D) indicate that all the hydrogen was released under the conditions shown in Table 1 (desorption) with trace elements of MgO present (taken from Rietveld analysis (Table 3)). These results show that subsequent D_2 absorption will not be affected by any contamination from H_2.

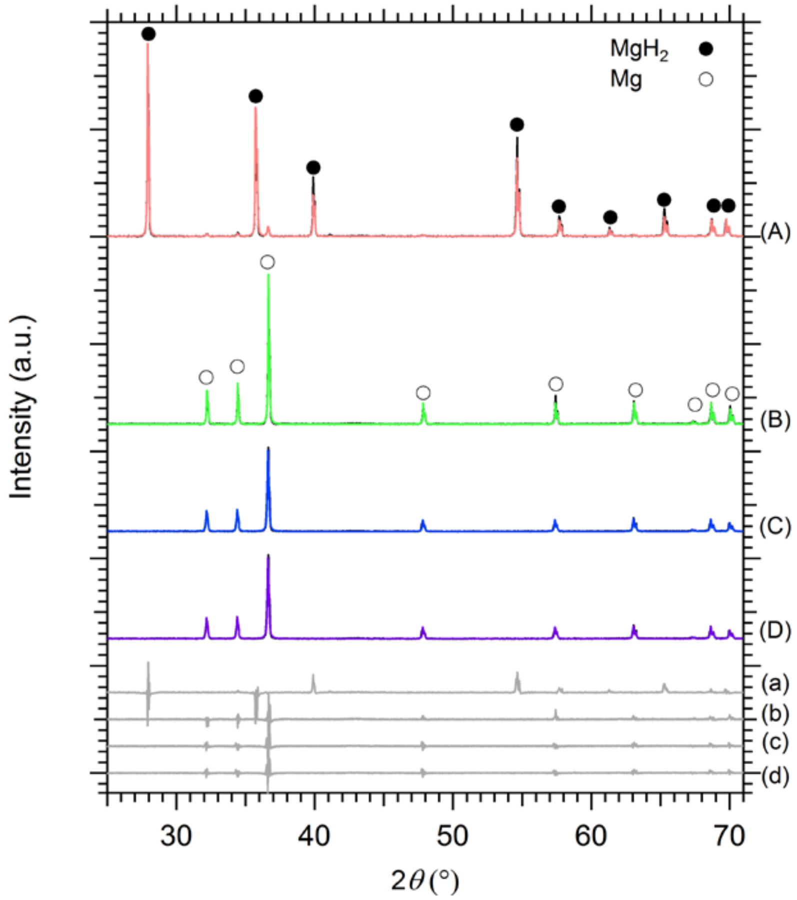

Figure 1: XRD patterns of as supplied MgH_2 before and after desorption. (A) as supplied from Sigma Aldrich (B) after H_2 desorption of batch 1 (C) after H_2 desorption of batch 3 (D) after H_2 desorption of batch 4. The grey curves, (a), (b), (c), (d), show the difference in raw data (black) and the calculated Rietveld (coloured) patterns for (A), (B), (C) and (D) respectively.

Table 3: Weight fraction and lattice parameter results from Rietveld Refinement of as supplied MgH_2 as well as MgD_2 after syntheses at 10 bar D_2 pressure. As a reference, the lattice parameters provided in the Inorganic Crystal Structure Database (ICSD) are given.

Batch/Phase	**Weight fraction observed phases (%)**	**Lattice Parameters (Rietveld) (Å)**	**Lattice Parameters (ICSD) (Å)**	**ICSD Number**
MgH_2 (as supplied)				
MgH_2	95	a = 4.5156, c = 3.0205	a = 4.5168, c = 3.0205	#76145
Mg	5		a = 3.2094, c = 5.2103	#26624

		a = 3.2097, c = 5.2100		
MgH_2 desorbed				
Mg	99	a = 3.2099, c = 5.2119		
MgO	1	a = 4.2161	a = 4.217	#9863
MgD_2 Batch 1				
MgD_2	83	a = 4.5023, c = 3.0122	a = 4.5025, c = 3.0123	#18210
Mg	17			
MgD_2 Batch 2				
MgD_2	77	a = 4.5034, c = 3.0125		
Mg	23			
MgD_2 Batch 3				
MgD_2	60	a = 4.5023, c = 3.0120		
Mg	40			
MgD_2 Batch 4				
MgD_2	98	a = 4.5032, c = 3.0124		
Mg	2			

The diffraction patterns of the D_2 reacted samples (conditions outline in Table 1) are given in Figure 2 and show varying degrees of reaction conversion due to the different synthesis conditions. MgD_2 batches 3 and 4 underwent a second absorption cycle (conditions given in Table 1) to consume any unreacted Mg after the first absorption and maximise the product yield. MgD_2 is structurally identical to MgH_2 (as indicated in Figure 1 (A) and Figure 2), however, a previous study has shown that hydrogen replaced with deuterium for some materials may result in different thermodynamic equilibrium conditions [26] and this may have an effect on synthesis conditions when compared to either MgD_2 or Mg_2FeD_6 synthesis. Rietveld analysis was used to calculate the weight fraction of each phase present together with the lattice parameters for those phases (Table 3) to compare the yield of MgD_2 between each batch. The highest yield of MgD_2 was produced from the ball milled sample; batch 4 (ca. 98%) where higher temperatures were used compared to batches 1 and 2 (400 *vs* 360 °C) and batch 4 was ball milled compared to batch 3. Ball milling the sample prior to absorption has been widely studied as it produces defects and imperfections that add in the transport of H, or in this case D, throughout the metal lattice [27, 28]. It appears that the longer absorption reaction times (batches 1 and 2) or increased number of desorptions (batch 1) had less of an impact on reaction conversion than higher absorption temperatures (batches 3 and 4). The Rietveld analysis showed that larger crystallite sizes were produced for MgD_2 as a result of higher temperatures when compared to the changes in the aforementioned synthesis conditions.

Thermal analysis was done on batch 3 to determine the temperature at which the deuterium was released (Figure 3, fine dotted line). The onset desorption temperature above 400 °C is consistent with previously published results showing the data of unmilled MgH_2 [29]. This result also indicates that thermodynamic stability of MgD_2 is comparable to that of MgH_2 and that the isotopic exchange does not affect desorption temperatures in the unmilled state. The TG result shows a released D_2 mass that is less than the theoretical capacity of pure MgD_2. This finding is in accordance with the weight fraction calculated from the Rietveld analysis (Table 3) showing the low yield of MgD_2 .

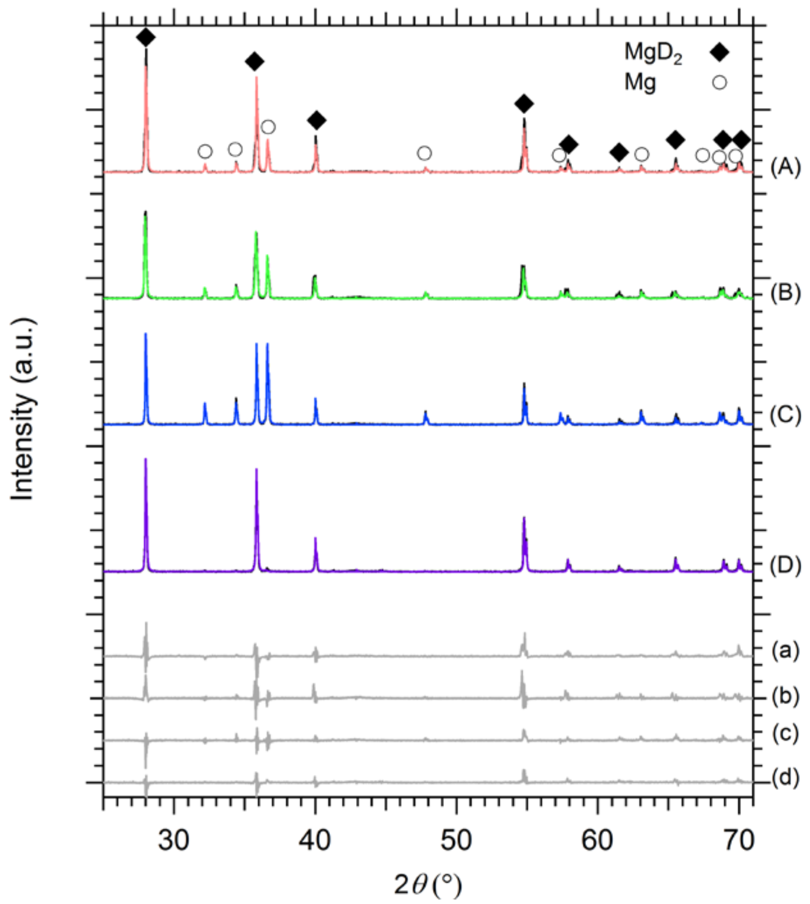

Figure 2: XRD patterns of MgD_2 as a result of varying synthesis conditions (Table 1). (A) MgD_2 batch 1 (B) MgD_2 batch 2 (C) MgD_2 batch 3 (D) MgD_2 batch 4. The grey curves, (a), (b), (c), (d), show the difference in raw data (black) and the calculated Rietveld (coloured) patterns for (A), (B), (C) and (D) respectively.

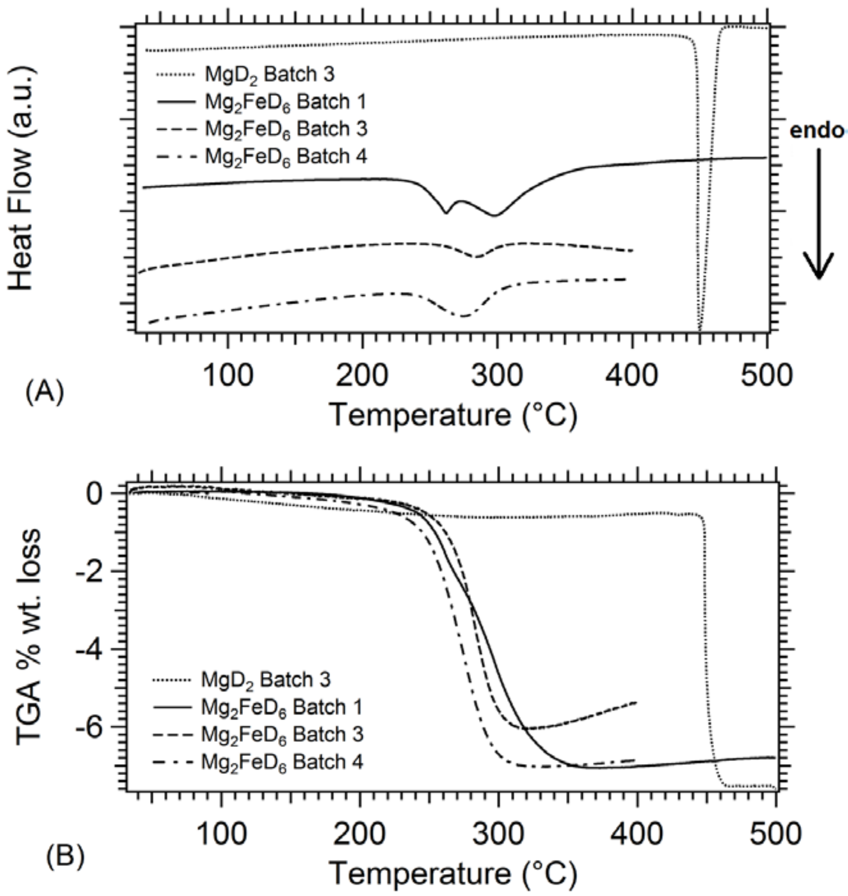

Figure 3: (A) Differential Thermal Analysis and (B) Thermogravimetric analysis of MgD_2 batch 3 and Mg_2FeD_6 batches 1, 3 and 4.

Mg_2FeD_6 synthesis was undertaken using MgD_2 batches 1, 3 and 4 milled with Fe in the molar ratio of 2:1 under a D_2 pressure of 10 bar (Table 2). MgD_2 batch 1 was used to compare the effect of different ball to powder ratios and consequent energy transfer from the milling process to the powder to produce Mg_2FeD_6 batches 1 and 2. The energy transfer was calculated using the mathematical model developed by Burgio *et. al.* [30] and further adapted by Busch *et. al.* [31]. MgD_2 batches 3 and 4 were used to show the effect of deuterium concentration in the respective MgD_2 samples to produce Mg_2FeD_6 batches 3 and 4 respectively. Again, XRD diffractograms were obtained (Figure 4) and Rietveld analysis was used to identify and quantify the crystalline phases present in each batch and calculate the lattice parameters (Table 4). From these analyses it can be seen that different synthesis methods resulted in vastly different yields of Mg_2FeD_6.

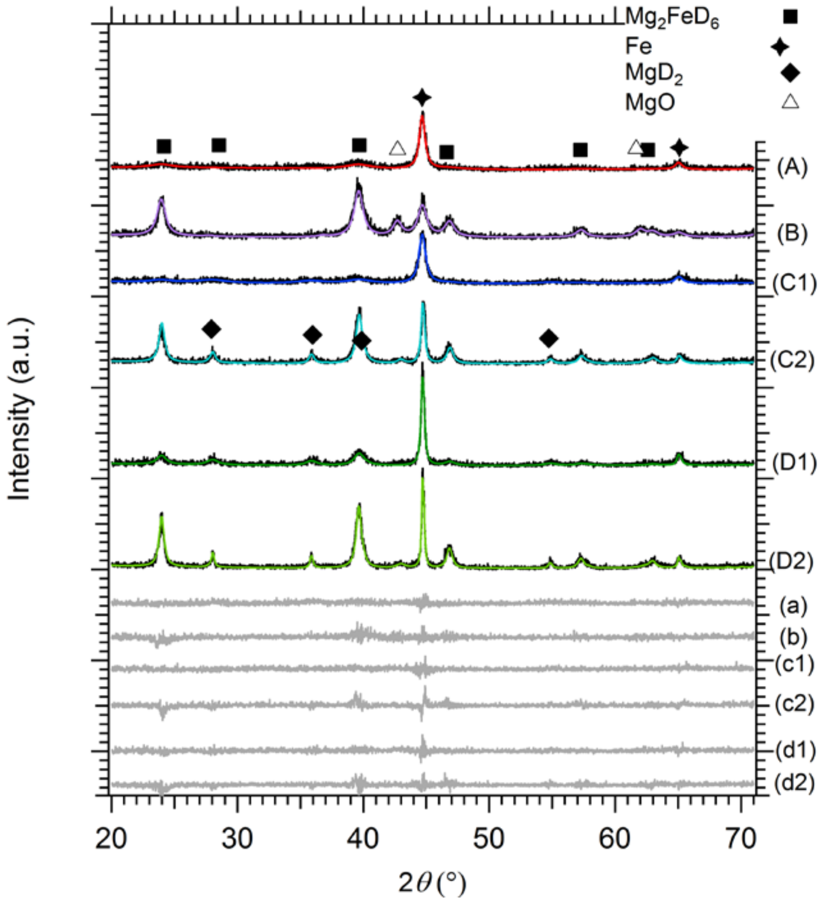

Figure 4: XRD patterns of Mg_2FeD_2 as a result of varying synthesis methods (Table 2). (A) Mg_2FeD_2 batch 1 (B) Mg_2FeD_2 batch 2 (C1) Mg_2FeD_2 batch 3 (C2) Mg_2FeD_2 batch 3 further heat treated at 10 bar D_2 (D1) Mg_2FeD_2 batch 4 (D2) Mg_2FeD_2 batch 4 further heat treated at 10 bar D_2. The grey curves, (a), (b), (c1), (c2), (d1), (d2) show the difference in raw data

(black) and the calculated Rietveld (coloured) patterns for (A), (B), (C1), (C2), (D1) and (D2) respectively.

The transferred energies for Mg_2FeD_6 batches 1 and 2 were calculated to be 68.4 and 137.8 kJ/g respectively and the resultant diffractograms are given in Figure 4(A) and (B). The presence of 37 wt.% Mg_2FeD_6 (Table 4) in Mg_2FeD_6-batch 1 indicates that the lower ball to powder ratio and consequent energy transfer was not enough to produce a high yield of product. Mg_2FeD_6-batch 2, on the other hand, showed a significantly increased amount of Mg_2FeD_6, however, an unexpected quantity of approximately 27 wt.% MgO (Table 2) was also present. A leak of O_2 from the atmosphere during the milling process could also be a source of contamination for this batch, as a rapid pressure drop of D_2 was observed and the vial reached atmospheric pressure within a couple of hours. Due to the presence of MgO, only Mg_2FeD_6-batch 1, and not batch 2, was analysed in the DTA-TG (Figure 3) and shows a much lower onset temperature (< 250 °C) compared to MgD_2 in agreement with Bogdanović *et. al.* [3]. The double peak can possibly be attributed to a wide range of particle sizes produced from the low energy ball milling therefore producing heterogeneous particle and grain sizes resulting in different rates of diffusion of D out of the materials and hence the presence of two thermal events [32-34]. This double transition could also be due to the fast neucleation of Mg_2FeD_6 Batch 1 as indicated by the first peak followed by slower particle growth resulting in more than one thermal transition. Another explanation could be the release of deuterium from Mg_2FeD_6 closely followed by β-MgD_2 (since there is little evidence of the γ- phase in the XRD data). This batch did not undergo annealing to improve the purity of the Mg_2FeD_6 therefore has the lowest conversion of MgD_2 to the desired product.

Table 4: Weight fraction and lattice parameter results from Rietveld Refinement of Mg_2FeD_6 syntheses at 10 bar D_2 pressure. As a reference, the lattice parameters provided in the Inorganic Crystal Structure Database (ICSD) are given.

Batch/Phase	Weight fraction of observed phases (%)	Lattice Parameters (Rietveld) (Å)	Lattice Parameters (ICSD) (Å)	ICSD Number
Mg_2FeD_6 Batch 1				
Mg_2FeD_6	37	a = 6.4769	a = 6.430	#29386
MgD_2	28	a = 4.4855, c = 3.0266	a = 4.5025, c = 3.0123	#18210
Fe	35	a = 2.8664	a = 2.8665	#53451
Mg_2FeD_6 Batch 2				
Mg_2FeD_6	56	a = 6.4341		
Fe	17	a = 2.8679		
MgO	27	a = 4.2349	a = 4.217	#9863
Mg_2FeD_6 Batch 3 after annealing				
Mg_2FeD_6	54	a = 6.4327		
MgD_2	21	a = 4.971, c = 3.0092		
Fe	18	a = 2.8625		
MgO	7	a = 4.2092		
Mg_2FeD_6 Batch 4 after annealing				
Mg_2FeD_6	58	a = 6.4304		
MgD_2	15	a = 4.4983, c = 3.0109		
Fe	17	a = 2.8640		
MgO	10	a = 4.2154		

Mg_2FeD_6 batches 3 and 4 produced from different purity MgD_2 batches 3 and 4 were additionally annealed in low pressure D_2 after reactive milling with Fe (Table 2). The same ball to powder ratio of 20:1 was used for these samples, however, using an increased milling time from 6 to 12 h. The XRD shown in Figure 4 (C1) and (D1) were measured immediately after reactive milling, prior to the annealing step. Once annealed XRD was again performed and is shown in Figure 4 (C2) and (D2). The low intensity broad peaks shown in Figure 4 (C1) and (D1) can be attributed to nano-crystallite formation of MgD_2 and Mg_2FeD_6 during the ball milling process. In contrast, sharper diffraction peaks after heat treatment (Figure 4

(C2) and (D2)) indicate that the crystallite sizes increased again upon annealing. The Rietveld analysis (Table 4) shows that the residual Mg in case of the lower purity starting reagents (Mg_2FeD_6 batch 3) absorbed D_2 and reacted to MgD_2 and Mg_2FeD_2, respectively. The results show that the yield of conversion to Mg_2FeD_6 does not significantly depend on the ratio Mg/MgD2 within the starting material. This is a similar result to Didisheim *et. al.* that synthesised Mg_2FeD_6 from the starting reagents of elemental Mg and Fe [1] even though higher temperatures and longer reaction times were used. Mg_2FeD_6 batch 4 produced a significant yield of Mg_2FeD_6 (58 wt.%) higher than reported in the literature with a significantly reduced annealing time, 12 h instead of 60 h [35]. It is evident from the XRD that batch 2 underwent full conversion of MgD_2 to Mg_2FeD_6 , however, O_2 contamination still remained an issue since MgO is thermodynamically more stable than Mg_2FeD_6.
DTA-TG results from Mg_2FeD_6 batches 3 and 4 are also given in Figure 3. Here the increased milling time from 6 to 12 h resulted in a more homogenous particle size compared to that of Mg_2FeD_6 batch 1 resulting in a single thermal event in the DTA. The onset temperatures of D_2 release remained the same around 250 °C, in agreement with the onset temperature of H_2 release from Mg_2FeH_6 [36]. The TG showed released amounts of deuterium of 5.8 wt.% and 6.8 wt.% for Mg_2FeD_6 batches 3 and 4, respectively. These masses are in good agreement with the calculated quantities of D_2 desorbed from Mg_2FeD_6 according to the purities obtained by Rietveld analysis. However, this is significantly lower than the theoretical D_2 capacity of 10.37 wt.% and this is most likely due to the high content of impurities including MgD_2, Fe and MgO. The difficulties in purity is not uncommon for either Mg_2FeH_6 or Mg_2FeD_6 with a range of synthesis methods [37-39], however, this is the first time for such high purity to be formed under 10 bar pressure.

Conclusions

The results from this study show that Mg_2FeD_6 was successfully synthesised using low pressure resulting in various yields depending on the synthesis conditions. The analysis showed that it is definitely possible to synthesise Mg_2FeD_6 after both reactive ball and sintering using only a pressure of as low as 10 bar D_2. Mg_2FeD_6 low pressure synthesis could be further improved by using improved seals of the milling vials and therefore preventing O_2 contamination as well as increasing rounds of ball milling or reaction times in the annealing vessel whilst still keep the pressure as low as 10 bar.

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