

Novel hydrides in Mg–TM systems synthesized by high pressure (TM = Zr, Nb, Hf and Ta)

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Abstract

High-pressure synthesis has been widely used for exploration of novel materials. In this study, new Mg-based ternary hydrides in Mg–TM–H systems (TM = Zr, Nb, Hf and Ta) have been prepared under a pressure of 5 GPa by using a cubic-anvil-type apparatus. In TM = Zr, Nb and Hf, MgTM₂H_y with a monoclinic-type structure were synthesized at 923 K under 5 GPa. Lattice parameters of MgTM₂H_y were $a = 5.816 \text{ \AA}$, $b = 3.3569 \text{ \AA}$, $c = 8.519 \text{ \AA}$, $\beta = 103.06^\circ$ (for TM = Zr); $a = 5.70 \text{ \AA}$, $b = 3.2888 \text{ \AA}$, $c = 7.927 \text{ \AA}$, $\beta = 103.06^\circ$ (for TM = Nb); $a = 5.782 \text{ \AA}$, $b = 3.317 \text{ \AA}$, $c = 8.507 \text{ \AA}$, $\beta = 103.06^\circ$ (for TM = Hf). Results from fusion extraction analysis for MgTM₂H_y (TM = Zr, Nb and Hf) showed their hydrogen contents, giving chemical formula of MgTM₂H_{5.9}. In TM = Nb and Ta, ternary hydrides with an FCC-type structure were synthesized under 5 GPa. These FCC hydrides had lattice parameters of $a = 9.5526 \text{ \AA}$ (TM = Nb) and 9.5376 \AA (TM = Ta). For TM = Nb, hydrogen content was determined from the fusion extraction analysis to be 5.8 mass%, corresponding to Mg_{6.2}NbH₁₄. Among the newly found hydrides, Mg_{6.2}NbH₁₄ showed the lowest dehydrogenation temperature of 595 K with endothermic reaction. Crystal structures and thermal stabilities of these hydrides were also investigated. © 2007 Published by Elsevier B.V.

Keywords: High-pressure synthesis; New hydride; Magnesium; Mg–Nb–H; Mg–Ta–H; Mg–Zr–H; Mg–Hf–H; X-ray diffraction

1. Introduction

It is important to explore new compounds and investigate their hydrogen properties for development of hydrogen storage materials. High-pressure synthesis is an effective technique in exploring new compounds. In metal–hydrogen systems, one can obtain further freedom for exploring new hydrides by using high pressure as a processing parameter as well as compositions and temperatures. Several new hydrides Mg₂Ni₃H_{3.4} [1,2], (Ca_{1-x}Mg_x)₂NiH_y ($x \leq 0.4$) [3–6], MgCaH_y [5,6], MgY₂H₈ [7–10], Mg₃MnH_y [9] and Mg₃REH₉ (RE = La, Ce, Pr) [10,11] were synthesized by using a cubic-anvil-type apparatus in our previous works. A few new intermetallic compounds were also synthesized under high pressure and their hydrogen storage abilities were investigated [12].

Such high-pressure techniques also enable to synthesize novel Mg-based hydrides with transition metal (TM) elements in the IVB group and VB group. For TM = Ti and V, Mg₇TiH_{13–16} [13,14] and Mg₆VH_y [15] with the Ca₇Ge-type FCC structure were reported to be prepared under 8 GPa. Recently, the FCC hydride and the AuTe₂-type monoclinic hydride were reported for Mg–Nb–H system [16]. For TM = Zr, we have showed that a monoclinic hydride was synthesized at 1073 K under pressures of 2–5 GPa [17]. A hydrogen content of the monoclinic Mg–Zr hydride was also evaluated by thermo-gravimetric analysis (TGA) but an accurate value has not been determined. For TM = Ta, few kinds of ternary hydrides were reported [18].

The purpose of this study is to explore new hydrides of the Mg–TM systems (TM = Zr, Nb, Hf and Ta) by using the cubic-anvil-type apparatus and to investigate crystal structures, thermal stabilities and hydrogen contents for newly found hydrides.

2. Experimental procedures

Starting materials were Mg (purity 99.9 mass%), ZrH₂ (purity 98 mass%), Nb (purity 99.9 mass%), Hf (purity 99.5 mass%) and Ta (purity 99.9 mass%)

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powders. From these elements, MgH_2 , NbH , HfH_2 and TaH were prepared in an autoclave filled with hydrogen gas. The powders were mixed and pressed into a pellet. This pellet was placed in a hydrogen-sealer capsule of NaCl . In case of using an additional hydrogen source (a mixture of $\text{Ca}(\text{OH})_2$ and NaBH_4 with a molar ratio of $\text{Ca}(\text{OH})_2:\text{NaBH}_4 = 2:1$), the sample pellet was separated from it by a small container of BN . The NaCl capsule was surrounded by a graphite heater and a pyrophyllite cube. All the manipulations in the sample preparation were conducted in a glovebox filled with Ar gas in order to prevent the samples from oxidizing. The high-pressure synthesis was carried out in the cubic-anvil-type apparatus. The samples were prepared at 1073 K under 5 GPa for 2 h, and then quenched before reducing the pressure. The detailed processing schedules were described elsewhere [7].

Phase identification was carried out by X-ray diffractometry (XRD) with $\text{Cu K}\alpha$ radiation. Compositional analysis was performed by SEM-EDX. Thermal stability of the newly found hydride was measured by using a differential scanning calorimeter (DSC) under Ar atmosphere. Hydrogen contents of the hydrides were investigated by fusion extraction analysis.

3. Results and discussion

3.1. Phase identification and structural analysis

3.1.1. Mg–Zr–H system

Fig. 1 shows the X-ray diffraction patterns of MgH_2 - $x\%$ ZrH_2 ($x = 50, 60$ and 67) samples prepared at 1073 K for 2 h under 5 GPa. For the sample of $x = 60$, monoclinic hydride phase appeared as a single phase. For $x = 50$ or 67 , MgH_2 or ZrH_2 appeared as a secondary phase, respectively. In our previous work [17], a nominal composition of this monoclinic hydride was reported to be $\text{Mg}_2\text{Zr}_3\text{H}_y$. However, the result from SEM-EDX analysis, showed that the molar ratio of metal atoms in this hydride was $\text{Zr}/\text{Mg} = 2$. Thus, we conclude that the hydride can be described as MgZr_2H_y . The new hydride had a C-centered monoclinic unit cell with $a = 5.816(1) \text{ \AA}$, $b = 3.3539(5) \text{ \AA}$, $c = 8.591(1) \text{ \AA}$, $\beta = 103.06(3)^\circ$ and $V = 163.2 \text{ \AA}^3$.

Fig. 2 shows the X-ray diffraction pattern of MgH_2 -60% ZrH_2 prepared at 1073 K for 2 h under 5 GPa, and the diffraction pattern simulated by using RIETAN2000 [19]. The structural parameters used for the simulation: atomic sites, space group

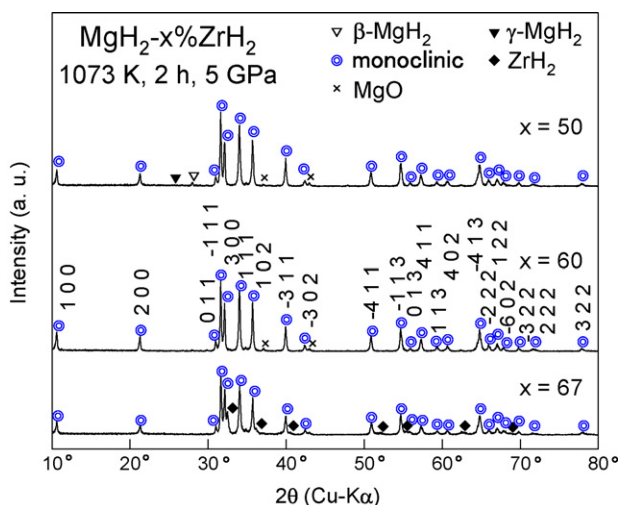


Fig. 1. X-ray diffraction patterns of MgH_2 - $x\%$ ZrH_2 prepared at 1073 K for 2 h under 5 GPa ($x = 50, 60$ and 67).

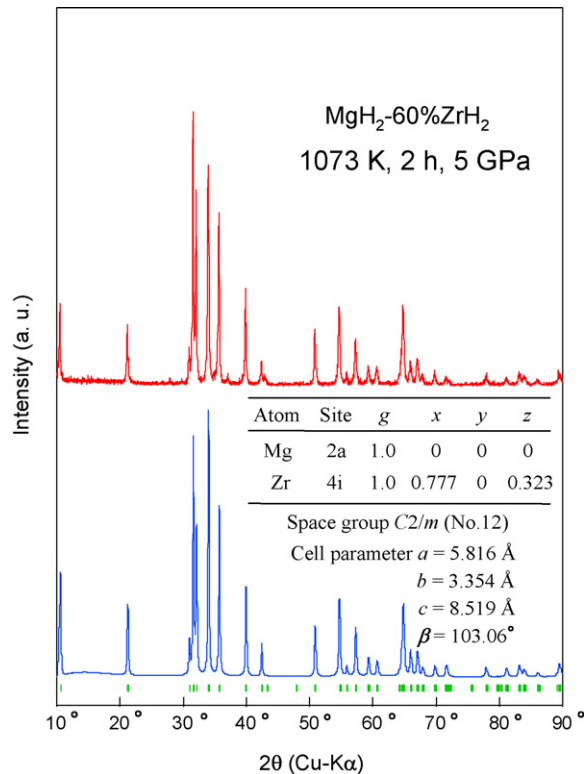


Fig. 2. X-ray diffraction pattern of MgH_2 -60% ZrH_2 prepared at 1073 K for 2 h under 5 GPa, and the diffraction pattern simulated by using structural parameters on the inset table.

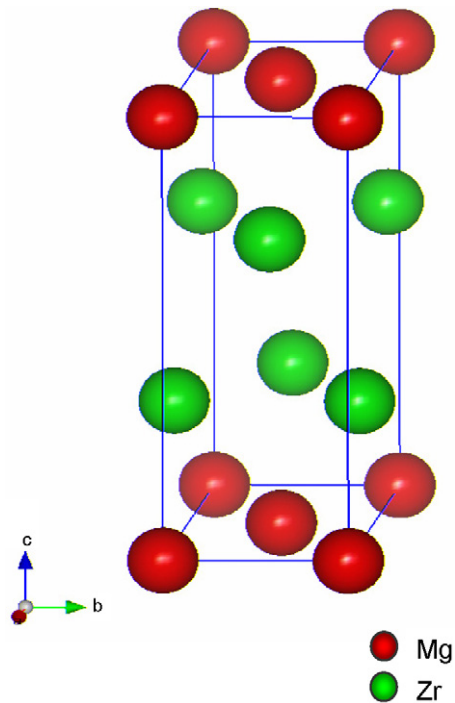
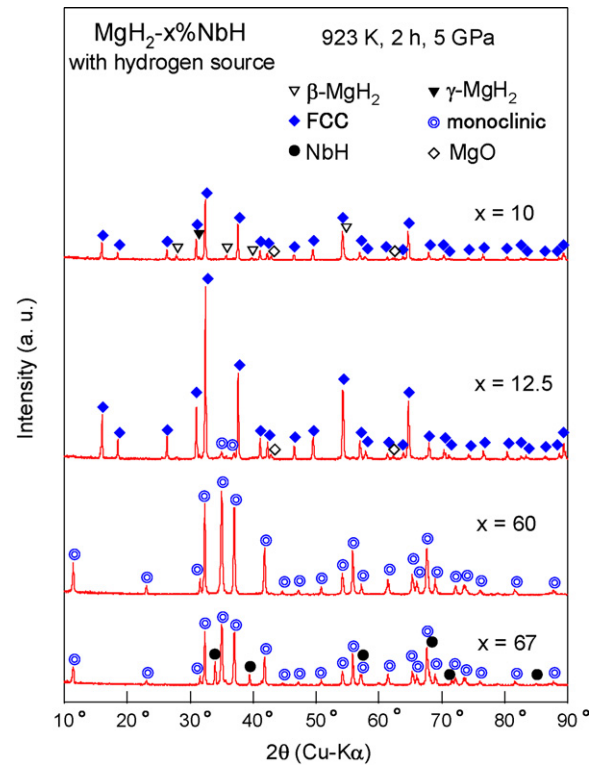
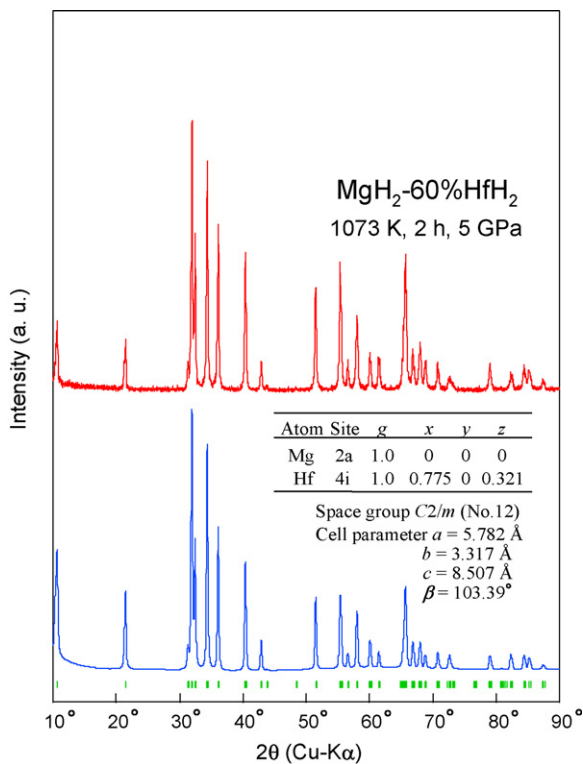
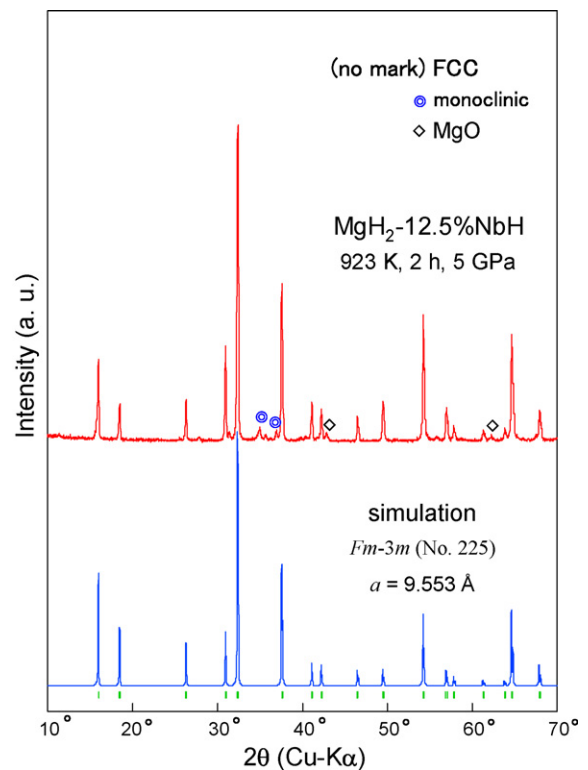
and cell parameters are shown in the inset table. The simulated diffraction pattern has good agreement with the observed one. It implies that the new hydride MgZr_2H_y would have the crystal structure which is shown in Fig. 3.

3.1.2. Mg–Hf–H system

For the sample of MgH_2 -60% HfH_2 prepared at 1073 K for 2 h under 5 GPa, a new phase appeared as an almost single phase. From an EDX analysis, the composition of the unidentified phase was confirmed to be Mg -67% Hf . Fig. 4 shows the X-ray diffraction pattern of the sample of MgH_2 -60% HfH_2 prepared at 1073 K for 2 h under 5 GPa, and the diffraction pattern simulated with an assumption that the unidentified phase would have a similar structure to that of MgZr_2H_y . As can be seen in Fig. 4, the simulation showed good agreement with observation. Thus, the new hydride was found to have a C-centered monoclinic unit cell with $a = 5.782(3) \text{ \AA}$, $b = 3.317(1) \text{ \AA}$, $c = 8.507(4) \text{ \AA}$, $\beta = 103.39(9)^\circ$ and $V = 158.7 \text{ \AA}^3$.

3.1.3. Mg–Nb–H system

In our previous work [17], it was shown that a new hydride Mg_4NbH_y was prepared at 1073 K under 5 GPa from a mixture of MgH_2 and Nb . In this work, NbH was used as the starting material instead of Nb . Fig. 5 shows the X-ray diffraction patterns of MgH_2 - $x\%$ NbH ($x = 10, 12.5, 60$ and 67) samples prepared at 923 K for 2 h with the hydrogen source under 5 GPa. For the sample of MgH_2 -12.5% NbH , an FCC phase appeared as an almost single phase. Fig. 6 shows the X-ray diffraction

Fig. 3. Crystal structure of MgZr_2H_y .Fig. 5. X-ray diffraction patterns of MgH_2 - $x\%$ NbH prepared with the hydrogen source at 923 K for 2 h under 5 GPa ($x = 10, 12.5, 60$ and 67).Fig. 4. X-ray diffraction pattern of MgH_2 -60% HfH_2 prepared at 1073 K for 2 h under 5 GPa, and the diffraction pattern simulated by using structural parameters on the inset table.Fig. 6. X-ray diffraction patterns of MgH_2 -12.5% NbH prepared with the hydrogen source at 923 K for 2 h under 5 GPa, and the simulated diffraction pattern with assumption of the same structure as $\text{Mg}_7\text{TiH}_{13-16}$ [13].

pattern of this sample and the diffraction pattern simulated by assuming the FCC structure similar to $\text{Mg}_7\text{TiH}_{13-16}$ [13]. The simulated diffraction pattern has good agreement with the observed one. The hydride phase would have the FCC unit cell with $a = 9.5526(8)$ Å. From an EDX analysis, the ratio of metal atoms in the FCC hydride (Mg/Nb) was optimized to be 6.2, indicating that this hydride can be described as $\text{Mg}_{6.2}\text{NbH}_y$. The structure and composition of $\text{Mg}_{6.2}\text{NbH}_y$ are close to those of the reported $\text{Mg}_{6.5}\text{NbH}_{14}$ [16].

For the sample of MgH_2 -60% NbH, a monoclinic phase also appeared as an almost single phase. The composition of this monoclinic phase was confirmed to be Mg-67% Nb from an EDX analysis, indicating that this hydride can be described as MgNb_2H_y . The structural simulation for MgNb_2H_y by assuming the structure similar to MgZr_2H_y has good agreement with the observation. This hydride would have a C-centered monoclinic unit cell with $a = 5.70(1)$ Å, $b = 3.2888(5)$ Å, $c = 7.927(1)$ Å, $\beta = 103.92(2)^\circ$ and $V = 144.2$ Å³. This structure is close to that of the reported $\text{MgNb}_2\text{H}_{\sim 4}$ [16]. It was found that the Mg-Nb monoclinic phase was formed only in the case of use of the starting materials of NbH and additional hydrogen source. This also suggests that the hydrogen concentration y in MgNb_2H_y could be over 4.

3.1.4. Mg-Ta-H system

In the Mg-Ta-H system, samples were prepared with the hydrogen source at 873 K for 2 h under 5 GPa, and phase present was investigated. As the result, a hydride phase which had the FCC unit cell with $a = 9.5373(9)$ Å was observed, although raw materials also remained. A structural simulation implies that the new hydride would have a similar structure to that of $\text{Mg}_7\text{TiH}_{13-16}$ [13]. However, the composition of the Mg-Ta FCC hydride could not be identified in this work.

3.2. Hydrogen contents and thermal stability

3.2.1. Monoclinic Mg-TM hydrides (TM = Zr, Nb and Hf)

Hydrogen contents of the prepared samples, in which new C-centered monoclinic hydrides formed as an almost single phase, were investigated by the fusion extraction analysis. As the results, the hydrogen contents of the prepared samples of MgH_2 -60% ZrH_2 , MgH_2 -60% NbH and MgH_2 -60% HfH_2 were 3.0, 2.8 and 1.7 mass%, respectively. The compositions of the new monoclinic hydrides can be represented by $\text{MgZr}_2\text{H}_{5.9}$, $\text{MgNb}_2\text{H}_{5.9}$ and $\text{MgHf}_2\text{H}_{5.9}$, which are close to a nominal composition of MgTM_2H_6 (TM = Zr, Nb and Hf).

Fig. 7 shows the DSC curves of the prepared samples containing each of MgTM_2H_6 (TM = Zr, Nb and Hf). These curves were obtained with a heating rate of 10 K/min. The prepared sample in the Mg-Zr system exhibited an endothermic peak at 720 K with small endothermic peak around 660 K due to decomposition of MgH_2 . From X-ray diffraction after the DSC measurement, the endothermic reaction at 720 K was found to be due to partial dehydrogenation reaction represented by $\text{MgZr}_2\text{H}_6 \rightarrow \text{Mg} + 2\text{ZrH}_2 + \text{H}_2$. In the Mg-Nb system, two endothermic peaks were observed at about 650 and 715 K. After the DSC measurement, Mg and Nb metallic phases were con-

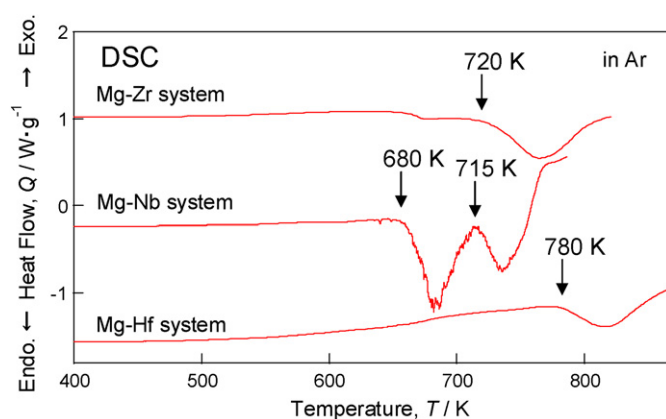


Fig. 7. DSC curves of the prepared samples in the Mg-Zr, Mg-Nb and Mg-Hf systems containing the C-centered monoclinic hydrides.

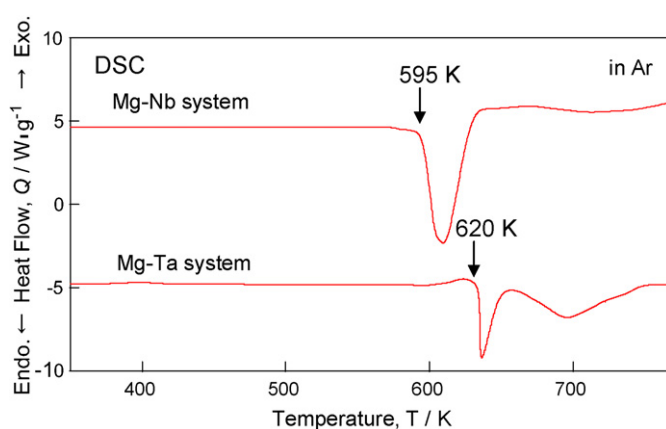


Fig. 8. DSC curves of the prepared samples in the Mg-Nb and Mg-Ta systems containing the FCC hydrides.

firmed to appear. In the Mg-Hf system, an endothermic peak was observed around 780 K.

3.2.2. Mg-TM-H FCC hydrides (TM = Nb and Ta)

In order to determine a hydrogen content of the Mg-Nb FCC hydride $\text{Mg}_{6.2}\text{NbH}_y$, the prepared sample of MgH_2 -12.5% NbH was investigated by the fusion extraction analysis. As the result, the hydrogen content of $\text{Mg}_{6.2}\text{NbH}_y$ was 5.8 mass%, which corresponds to a chemical formula of $\text{Mg}_{6.2}\text{NbH}_{14}$. This hydrogen composition is close to the estimated one in the recent report [16]. The hydrogen content of the Mg-Ta FCC hydride could not be determined in this work.

Fig. 8 shows the DSC curves of the prepared samples containing each of the Mg-TM FCC hydride (TM = Nb and Ta). The prepared sample MgH_2 -12.5% NbH exhibited an endothermic peak around 595 K. While, the prepared sample MgH_2 -12.5% TaH exhibited an endothermic peak around 620 K due to FCC hydride with a continuous endothermic peak due to MgH_2 .

4. Conclusions

The phase present, crystal structure and thermal stability of the new hydrides in the Mg-TM-H systems (TM = Zr, Nb, Hf and Ta), which were synthesized under high pressure,

were studied. In the Mg–Zr–H and Mg–Hf–H systems, the new hydrides $\text{MgZr}_2\text{H}_{\sim 6}$ and $\text{MgHf}_2\text{H}_{\sim 6}$ were synthesized at 1073 K for 2 h under the pressure of 5 GPa, and structurally characterized by X-ray powder diffractions to have the monoclinic structure (space group $C2/m$, $Z=2$) with $a=5.816(1)$ Å, $b=3.3539(5)$ Å, $c=8.591(1)$ Å, $\beta=103.06(3)^\circ$ and $a=5.782(3)$ Å, $b=3.317(1)$ Å, $c=8.507(4)$ Å, $\beta=103.39(9)^\circ$, respectively. In the Mg–Nb–H system, a similar hydride $\text{MgNb}_2\text{H}_{\sim 6}$ was synthesized at 923 K under 5 GPa in the case of using the hydrogen source and the starting material of MgH_2 and NbH. The lattice parameters of $\text{MgNb}_2\text{H}_{\sim 6}$ were $a=5.70(1)$ Å, $b=3.2888(5)$ Å, $c=7.927(1)$ Å, $\beta=103.92(2)^\circ$. These Mg–TM monoclinic hydrides (TM=Zr, Nb and Hf) were thermally stable up to 720, 650 and 780 K, respectively. In the Mg–Nb–H and Mg–Ta–H systems, the new hydrides, $\text{Mg}_{6.2}\text{NbH}_{14.4}$ ($a=9.5526(8)$ Å) and Mg_xTaH_y ($a=9.5373(9)$ Å), with the FCC unit cell similar to $\text{Mg}_7\text{TiH}_{13-16}$ and Mg_6VH_y were found. These Mg–TM FCC hydrides (TM=Nb and Ta) were thermally stable up to about 595 and 620 K, respectively. The results imply that the transition metals in the IVB group (Ti, Zr and Hf) are resemble to those in the VB group (V, Nb, Ta) under high pressure.

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