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Novel Mg–Zr–A–H (A = Li, Na) hydrides synthesized by a high pressure technique and their hydrogen storage properties

Xiao Yang, Nobuhiko Takeichi, Kenji Shida, Hideaki Tanaka, Nobuhiro Kuriyama, Tetsuo Sakai*

Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

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ABSTRACT

It is important to develop the hydrogen storage technology by creating novel metal hydrides. In the present study, the powder mixtures of $6MgH_2 + ZrH_2 + nAH$ (A = Li, Na; n = 0, 0.3, 0.7, 1.0) were reacted to synthesize quaternary hydrides by use of a high pressure technique. The crystal structures of the new hydrides were refined by the Rietveld method based on the synchrotron XRD data. By reacting $6MgH_2 + ZrH_2 + nLiH$, the quaternary hydrides with simple FCC-type structure were formed. In the case of $6MgH_2 + ZrH_2 + nNaH$, novel quaternary hydrides with Ca_7Ge type structure were formed as well as the hydrides with simple FCC structure. The hydrogen storage capacities were around 6 wt.% according to the pressure-composition isotherm measurements. The formation enthalpies of the quaternary hydrides with simple FCC structure were proved to be lower while the enthalpies of the Mg–Zr–Na–H hydrides with Ca_7Ge type structure were higher, than that of the ternary Mg–Zr–H hydride obtained by reacting the basic system $6MgH_2 + ZrH_2$. The hydrogen releasing temperatures of the quaternary Mg–Zr–A–H hydrides were slightly lower than that of the ternary Mg–Zr–H hydride.

1. Introduction

Depletion of fossil-fuel, industrial waste and global warming linked to emission of greenhouse gases have made the development of alternative methods of energy production, conversion and storage popular topics in today's energy-conscious society [1]. These crucial environmental issues, together with the rapid advance and eagerness from the electric automotive industry have combined to make the development of radically improved energy storage systems a worldwide imperative [2].

It is believed that hydrogen will within a few of years become the fuel that powers most vehicles and portable devices. As one of the energy storage methods, storage of hydrogen by absorption as chemical compounds has definite advantages from the capacity and safety perspectives. Light weight magnesium has been regarded as a promising hydrogen storage metal, with a hydrogen capacity as large as 7.6 wt.% when forming MgH_2. However, the comprehensive application of MgH_2 is restricted by its main disadvantages, including the high temperature of hydrogen releasing, slow desorption kinetics and a high reactivity toward air and oxygen [3,4]. Many approaches focused on Mg-based hydrides are being studied aiming to solve these problems.

It has been found that some transition metals can serve as the catalysis well to improve the hydrogen storage properties in the Mg-based hydride system [5]. The present authors have succeeded in creating a series of new ternary hydrides "Mg_7MH_{16}" (M = Ti, [6,7] V, [8] Nb, [9,10] Ta, [11] Hf and Zr [12,13]) with face-centered cubic (FCC) lattice by reacting MgH_2 and transition metal hydrides under gigapascal hydrogen pressure. The hydrogen releasing temperature of the ternary hydride was lowered down sharply compared with that of the pure MgH_2. Quaternary hydrides were also studied. As reported in the previous study [14], addition of alkali metal hydrides into the powder mixture of $MgH_2 + TiH_2$ reacted at high pressure can enhance the yield of FCC Mg_7TiH_{16} phase and improve the kinetics of hydrogen releasing/restoring reactions.

In the present work, novel quaternary Mg–Zr–A–H (A = Li, Na) hydrides were successfully synthesized by the high pressure technique. The crystal structure and hydrogen storage properties of these quaternary hydrides would be reported.

2. Experimental

The commercially available reagents were used as the starting materials to prepare the powder mixture of $6MgH_2 + ZrH_2 + nAH$ (A = Li, Na; n = 0, 0.3, 0.7, 1.0): MgH_2 (Alfa Aesar, purity 98%); ZrH_2 (Aldrich Chemical Company, 90%); LiH (Aldrich Chemical Company, 95%); NaH (Aldrich Chemical Company, 95%). The molar ratio of 6:1 between MgH_2 and ZrH_2 was fixed in order to obtain the highest formation ratio of the FCC phase after reaction, according to the findings in the previous study [13].

The high pressure synthesis technique was developed by Fukai and Okuma [15]. A NaCl capsule placed in an octahedral pyrophyllite cell was used as the reactor

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* Corresponding author. Tel.: +81 72 751 9611; fax: +81 72 751 9623.
E-mail addresses: mryangxiao@yahoo.com.cn (X. Yang), sakai-tetsuo@aist.go.jp (T. Sakai).

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for high pressure synthesis. The admixture pellet was enclosed into the NaCl capsule together with two pellets of internal hydrogen source, consisting of $NaBH_4$ and $Ca(OH)_2$. The sample pellet and hydrogen source were separated by boron nitride (BN) disc which can protect the sample from contamination due to the hydrogen source. The octahedral cell was compressed up to 8 GPa at 873 K by use of a high pressure generating apparatus to induce the formation of new hydrides. After reaction for 1 h, the sample was recovered. More detailed explanation of the high pressure synthesis can be found in the previous papers [6,7].

The phase components of the as-prepared sample were characterized by use of XRD data obtained at synchrotron radiation facility SPring-8, Japan, at beam line BL19B2. A large Debye-Scherrer camera was used to detect the fine diffraction patterns. The wavelength was calibrated to 0.700053 Å using CeO_2 as a standard. The exposure time of X-rays was 5 min for each sample. The sample powders were contained in glass capillaries (ϕ0.3 mm) and sealed with glue in an Ar-filled glove box to prevent oxygen or moisture. The structural refinements were made by use of the Rietveld program RIETAN-2000 [16].

Pressure–composition isotherms (PCI curves) were measured by a Sieverts volumetric system (LESCA PCI-A08-01). Before the isotherm measurements, hydrogen stored in the sample was released in evacuation (below 10^{-4} MPa). The sample container was heated in a band-heater up to 523 K, 548 K, and 573 K, and held during the isotherm measurements. The PCI measurements were conducted in the pressure range of 10^{-4} to 0.8 MPa.

Hydrogen releasing and restoring properties were measured by a differential scanning calorimeter (Rigaku DSC8230HP) under hydrogen pressure of 0.5 MPa. The heating/cooling rates were 10 K/min.

3. Results and discussion

3.1. High pressure synthesis

Fig. 1 shows the synchrotron XRD patterns of the as-prepared samples after reaction at high pressure: (a) basic = $6MgH_2 + ZrH_2$; (b) basic + 0.3LiH; (c) basic + 0.7LiH; (d) basic + 1.0LiH. For the basic system $6MgH_2 + ZrH_2$, new peaks corresponding to the simple FCC phase can be observed clearly, in accordance with the previous studies [6,7]. The addition of different amount of LiH into the basic system results in the formation of simple FCC phase as well. The starting powder α-MgH_2, γ-MgH_2, and impurities MgO, ZrN, ZrB_2 et al. were also found. It is considered that LiH participated into the reaction between the MgH_2 and ZrH_2 resulting in the formation of simple FCC-type quaternary Mg–Zr–Li–H phases. The influence of the LiH addition on the crystal structures of the newly formed hydrides will be discussed in the following section.

Fig. 2 shows the synchrotron XRD patterns of the as-prepared $6MgH_2 + ZrH_2 + n$NaH samples. In the case of adding 0.3NaH into the basic system ($6MgH_2 + ZrH_2$), simple FCC phase was formed. Similar to the addition of LiH, small amount of NaH also participated into the reaction between the MgH_2 and ZrH_2 to form simple FCC-type quaternary Mg–Zr–Na–H phases. When adding 0.7 or 1.0 NaH, the XRD patterns were rather different. The peaks corresponding to the new phase other than simple FCC can be noticed. This new phase was proved to be a Ca_7Ge type superlattice structure according to the structural refinement, as explained latter.

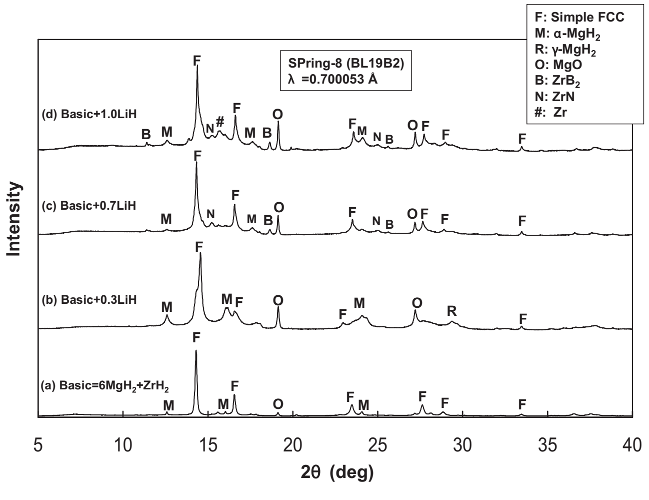

Fig. 1. Synchrotron XRD patterns for the as-prepared $6MgH_2 + ZrH_2 + n$LiH samples.

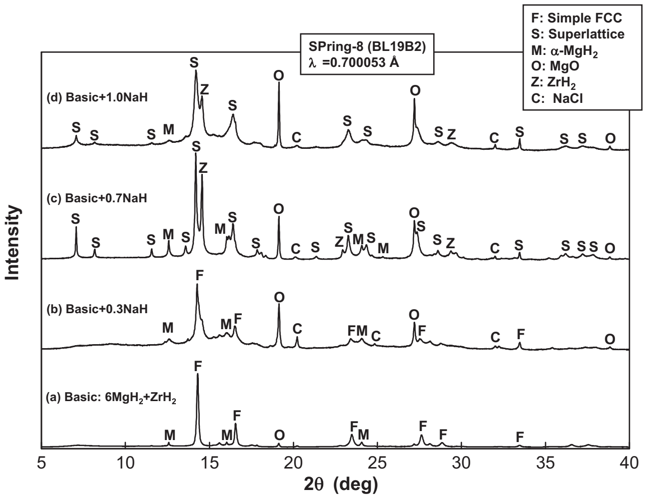

Fig. 2. Synchrotron XRD patterns for the as-prepared $6MgH_2 + ZrH_2 + n$NaH samples.

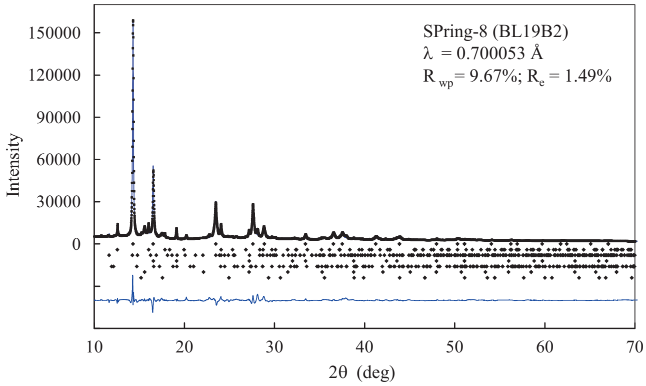

Fig. 3. Rietveld refinements of the synchrotron XRD data for the as-prepared $6MgH_2 + ZrH_2$. The phases from top to bottom are: the FCC phase, α-MgH_2, γ-MgH_2, MgO, ZrH, Zr and ZrN.

3.2. Crystal structural refinement

3.2.1. Mg–Zr–H system

According to the synchrotron XRD data, the structure of the as-prepared sample $6MgH_2 + ZrH_2$ was refined by use of the Rietveld method as shown in Fig. 3. The composition $Mg_{0.86}Zr_{0.14}H_2$ and simple FCC-type structure in space group Fm-3m used to describe the newly formed phase leads to the best fitting in Rietveld refinement. The crystal parameters for $Mg_{0.86}Zr_{0.14}H_2$ are listed in Table 1. In the new FCC phase, Mg and Zr are sharing the 4a site while H occupies the 8c site. The phase components determined from the Rietveld refinements and the numerical criteria of fit are summarized in Table 2. Such results are basically in accordance with the previous study [6,7].

Table 1
Crystallographic parameters for $Mg_{0.86}Zr_{0.14}H_2$ in space group Fm-3m (No. 225).

Atom	Site	Occupancy	*x*	*y*	*z*	*B* (Å^2)
Mg	4a	0.86	0	0	0	3.5
Zr	4a	0.14	0	0	0	0.25
H	8c	1	0.25	0.25	0.25	1.19

Table 2
Phase components and numerical criteria of fit from the Rietveld refinements of the synchrotron XRD data for the as-prepared $6MgH_2 + ZrH_2$.

Phases	R_B(%)	R_F(%)	wt.%	Space group	Cell parameters (Å)
FCC phase	2.31	1.31	77.5	Fm-3m (No. 225)	$a = 4.85859$
α-MgH_2	2.59	1.65	8.5	P42/mnm	$a = 4.50964$
					$c = 3.01515$
γ-MgH_2	2.11	1.34	5.6	Pbcn	$a = 4.43906$
					$b = 5.43068$
					$c = 4.94279$
MgO	2.35	1.21	3.2	Fm-3m	$a = 4.20640$
ZrH	2.90	1.62	2.5	P42/n	$a = 4.66622$
					$c = 4.83862$
Zr	2.70	1.50	2.2	Im-3m	$a = 3.64411$
ZrN	2.67	1.60	0.5	Fm-3m	$a = 3.57826$

3.2.2. Mg–Zr–Li–H system

According to the structural refinement of the as-prepared $6MgH_2 + ZrH_2 + n$LiH samples, it is understood that Mg–Zr–Li–H hydrides with simple FCC-type structure in space group Fm-3m (No. 225) were formed. The crystallographic parameters for the quaternary hydrides are listed in Table 3. Due to the similar ion radius, Li can partly replace Mg or Zr in the lattice. As a result, Mg, Zr and Li atoms are sharing the 4a site and the occupancy of Li increases with the increase of LiH ratio in the starting powder.

The phase components determined from the rietveld refinements for the Mg–Zr–Li–H system and the numerical criteria of fit are summarized in Table 4. Compared with the results for the basic system as shown in Table 2, the formation ratios of the new hydrides in all the three cases with LiH addition (around 50 wt.%) were not as high as that for the basic system (77.5 wt.%), and much MgH_2 did not participate into the reaction at high pressure. Therefore, it is considered that the addition of LiH into the basic system ($6MgH_2 + ZrH_2$) makes MgH_2 excessive in the reaction at high pressure. Regarding to the cell volume of the new hydride, the addition of LiH showed little influence on the cell parameter.

3.2.3. Mg–Zr–Na–H system

With the addition of 0.3NaH into the Mg–Zr–H system, quaternary hydride was formed with simple FCC-type structure, the same as the previous systems. As listed in Table 5, Mg, Zr and Li atoms are sharing the 4a site in the cell. However, in the cases of adding 0.7 or 1.0 NaH, Ca_7Ge type superlattice phases in space group Fm-3m (No. 225) were formed instead of simple FCC type. The atomic arrangement of the superlattice phase can be illustrated in Fig. 4.

Table 3
Crystallographic parameters of the quaternary hydrides in the as-prepared $6MgH_2 + ZrH_2 + n$LiH samples.

Atom	Site	Occupancy	x	y	z	B (Å^2)
(a) $6MgH_2 + ZrH_2 + 0.3$LiH						
Mg	4a	0.79	0	0	0	1.2
Zr	4a	0.12	0	0	0	0.1
Li	4a	0.09	0	0	0	0
H	8c	1	0.25	0.25	0.25	1
(b) $6MgH_2 + ZrH_2 + 0.7$LiH						
Mg	4a	0.75	0	0	0	1.02
Zr	4a	0.12	0	0	0	2.5
Li	4a	0.13	0	0	0	3
H	8c	1	0.25	0.25	0.25	9
(c) $6MgH_2 + ZrH_2 + 1.0$LiH						
Mg	4a	0.65	0	0	0	0.98
Zr	4a	0.14	0	0	0	1.06
Li	4a	0.18	0	0	0	0
H	8c	1	0.25	0.25	0.25	0

Table 4
Phase components and numerical criteria of fit from the Rietveld refinements of the synchrotron XRD data for the as-prepared $6MgH_2 + ZrH_2 + n$LiH samples.

Phases	R_B(%)	R_F(%)	wt.%	Space group	Cell parameters (Å)
(a) $6MgH_2 + ZrH_2 + 0.3$LiH ($R_{wp} = 5.49\%$; $R_e = 4.05\%$)					
FCC phase	0.88	0.72	47.8	Fm-3m	$a = 4.83215$
α-MgH_2	0.77	0.75	28.6	P42/mnm	$a = 4.50677$
					$c = 3.03521$
γ-MgH_2	0.51	0.43	4.9	Pbcn	$a = 4.08138$
					$b = 5.85085$
					$c = 4.85077$
MgO	0.99	0.68	9.4	Fm-3m	$a = 4.20454$
ZrH_2	0.87	0.7	9.3	I4/mmm	$a = 3.50312$
					$c = 4.45289$
(b) $6MgH_2 + ZrH_2 + 0.7$LiH ($R_{wp} = 8.46\%$; $R_e = 1.56\%$)					
FCC phase	1.83	1.30	53.9	Fm-3m	$a = 4.86095$
α-MgH_2	2.00	1.63	26.1	P42/mnm	$a = 4.44062$
					$c = 3.12994$
γ-MgH_2	2.23	1.67	9.2	Pbcn	$a = 4.55838$
					$b = 5.40590$
					$c = 4.94454$
MgO	2.03	1.41	6.0	Fm-3m	$a = 4.21313$
ZrN	2.24	1.63	3.8	Fm-3m	$a = 4.57572$
Zr	1.85	1.09	1.0	Im-3m	$a = 3.65682$
(c) $6MgH_2 + ZrH_2 + 1.0$LiH ($R_{wp} = 7.72\%$; $R_e = 4.27\%$)					
FCC phase	0.68	0.53	50.7	Fm-3m	$a = 4.83748$
α-MgH_2	0.95	0.75	32.0	P42/mnm	$a = 4.46531$
					$c = 3.10108$
MgO	0.65	0.55	7.7	Fm-3m	$a = 4.20525$
ZrH_2	0.95	0.69	0.9	I4/mmm	$a = 3.54535$
					$c = 4.53623$
ZrB_2	0.95	0.74	0.9	P6/mmm	$a = 3.15927$
					$c = 3.52274$
ZrN	1.11	0.70	3.5	Fm-3m	$a = 4.56378$
Zr	0.79	0.59	4.3	Im-3m	$a = 3.65682$

These Mg–Zr–Na–H hydrides can be described by the atomic positions in the lattice: Na at 4a (0, 0, 0), Zr at 4b (0.5, 0.5, 0.5), Mg and Zr at 24d (0, 0.25, 0.25), and H at two 32f sites.

Since Na is next to Mg in the periodic table and the ion radius of Na^+ is slightly larger than that of Mg^{2+}, it is considered that small amount of NaH added into the basic system resulted the formation of simple FCC-type hydride at high pressure reaction due to

Table 5
Crystallographic parameters of the quaternary hydrides in the as-prepared $6MgH_2 + ZrH_2 + n$NaH samples.

Atom	Site	Occupancy	x	y	z	B (Å^2)
(a) $6MgH_2 + ZrH_2 + 0.3$NaH						
Mg	4a	0.82	0	0	0	5.2
Zr	4a	0.04	0	0	0	5.4
Na	4a	0.14	0	0	0	0
H	8c	1	0.25	0.25	0.25	1.6
(b) $6MgH_2 + ZrH_2 + 0.7$NaH						
Na-1	4a	1	0	0	0	0.1
Zr-1	4b	0.82	0.5	0.5	0.5	0.4
Na-2	4b	0.09	0.5	0.5	0.5	0.4
Mg	24d	0.81	0	0.25	0.25	1.4
Zr-2	24d	0.14	0	0.25	0.25	2.5
H-1	32f	0.86	0.086	0.086	0.086	4.1
H-2	32f	0.68	0.417	0.417	0.417	0
(c) $6MgH_2 + ZrH_2 + 1.0$NaH						
Na	4a	1	0	0	0	3.3
Zr-1	4b	0.76	0.5	0.5	0.5	4.2
Mg	24d	0.86	0	0.25	0.25	2.3
Zr-2	24d	0.14	0	0.25	0.25	0.6
H-1	32f	0.6	0.136	0.136	0.136	6.6
H-2	32f	0.5	0.42	0.42	0.42	6.4

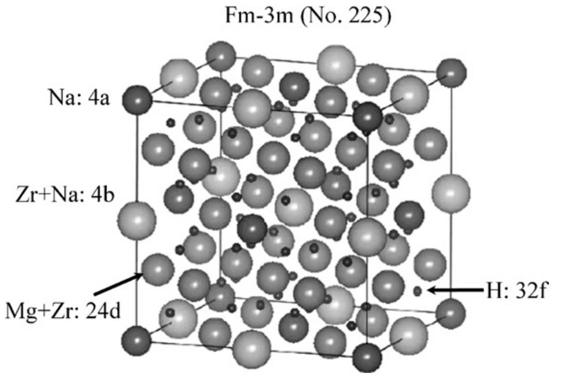

Fig. 4. Atomic arrangement in the lattice of the Ca_7Ge type Mg–Zr–Na–H hydride.

Na replacing Mg or Zr, while too much NaH addition led to the formation of Ca_7Ge type super lattice phase.

The phase components determined from the Rietveld refinements for the Mg–Zr–Na–H system and the numerical criteria of fit are summarized in Table 6. When 0.3NaH was added, the formation ratio of simple FCC phase was lowered down, while the cell parameter increased due to the entering of Na with larger ionic radius into the lattice, compared with those for the basic system. In the cases of 0.7 and 1.0 NaH addition, the formation ratios of super lattice phase were around 50 wt.%. Since a large amount of starting powder was remained for all three cases, it is considered that the addition of NaH into $6MgH_2 + ZrH_2$ may lower down the reactivity or kinetics of both MgH_2 and ZrH_2 at high pressure.

3.3. Hydrogen storage properties of the Mg–Zr–A–H hydrides (A = Li, Na)

3.3.1. PCI measurements

The pressure-composition isotherms (PCI curves) for the as-prepared samples $6MgH_2 + ZrH_2 + 0.3LiH$ and $6MgH_2 + ZrH_2 + 0.3NaH$ at different temperatures (523, 548 and 573 K) are compared in Fig. 5. As can be seen, the quantity of hydrogen for releasing and restoring was about 2.5–2.8 wt.%. The value is a little bit lower than that of the basic system $6MgH_2 + ZrH_2$ [13] in the range of 3–3.5%. The reason is attributed to the influence from the addition of alkali hydride that the formation ratios of the new hydrides were decreased. The actual hydrogen capacities of the quaternary Mg–Zr–A–H hydrides were calculated to be in the range of 5–7 wt.%.

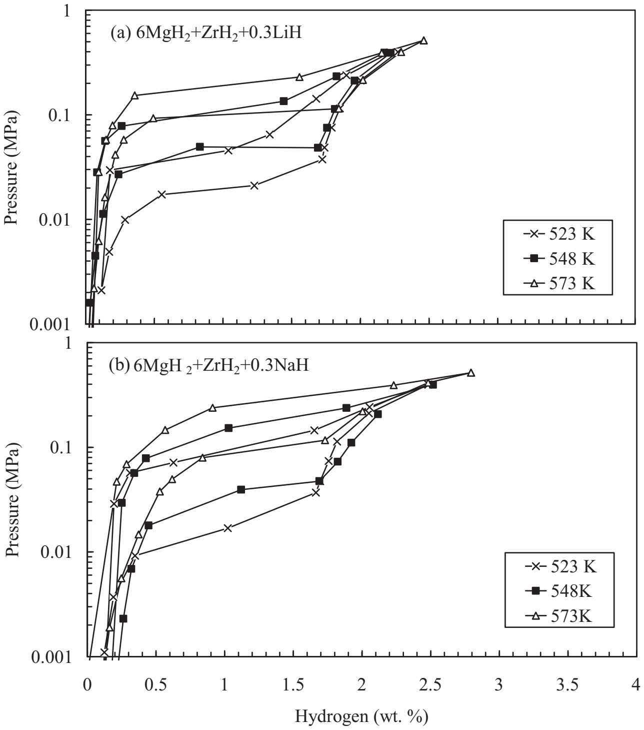

Fig. 5. Pressure-composition isotherms (PCI curves) at different temperatures for the as-prepared $6MgH_2 + ZrH_2 + 0.3LiH$ and $6MgH_2 + ZrH_2 + 0.3NaH$.

From the plateau pressures at different temperatures in the PCI curves, the van't Hoff equation can be applied to determine forma-

Table 6
Phase components and reliable factors from the Rietveld refinements of the synchrotron XRD data for the as-prepared $6MgH_2 + ZrH_2 + n NaH$ samples.

Phases	R_B(%)	R_F(%)	wt.%	Space group	Cell parameters (Å)
(a) $6MgH_2 + ZrH_2 + 0.3NaH$ ($R_{wp} = 5.55\%$; $R_e = 3.94\%$)					
FCC phase	0.60	0.52	42.1	Fm-3m	$a = 4.87367$
α-MgH_2	0.85	0.68	11.7	P42/mnm	$a = 4.51214$ $c = 3.01597$
MgO	0.75	0.66	18.6	Fm-3m	$a = 4.20469$
ZrH_2	0.85	0.74	19.8	I4/mmm	$a = 3.43811$ $c = 4.51756$
Zr	0.65	0.54	2.3	Im-3m	$a = 3.67406$
NaCl	1.03	0.72	5.5	Fm-3m	$a = 5.63347$
(b) $6MgH_2 + ZrH_2 + 0.7NaH$ ($R_{wp} = 8.03\%$; $R_e = 4.25\%$)					
Super lattice phase	1.42	0.95	50.8	Fm-3m	$a = 9.81612$
α-MgH_2	1.92	0.99	18.6	P42/mnm	$a = 4.51002$ $c = 3.01942$
MgO	1.83	0.94	15.2	Fm-3m	$a = 4.20712$
ZrH_2	1.60	0.99	15.3	I4/mmm	$a = 3.51656$ $c = 4.45497$
NaCl	1.86	0.94	0.1	Fm-3m	$a = 5.67293$
(c) $6MgH_2 + ZrH_2 + 1.0NaH$ ($R_{wp} = 5.62\%$; $R_e = 4.02\%$)					
Super lattice phase	1.03	1.17	46.0	Fm-3m	$a = 9.81066$
α-MgH_2	1.05	1.12	22.6	P42/mnm	$a = 4.54080$ $c = 3.20270$
MgO	1.60	1.25	14.6	Fm-3m	$a = 4.20654$
ZrH_2	1.20	1.29	13.8	I4/mmm	$a = 3.51479$ $c = 4.48534$
NaCl	0.60	0.71	3.0	Fm-3m	$a = 5.64078$

Table 7
The values of equilibrium pressure, formation enthalpy (ΔH^{θ}) and entropy (ΔS^{θ}) for the as-prepared samples $6MgH_2 + ZrH_2 + n$AH (A = Li, Na; n = 0.3, 0.7, 1.0).

Sample	Equilibrium pressure (MPa)			Structure of new hydride	ΔH^{θ} (kJ/mol H_2)	ΔS^{θ} (J/mol H_2)
	523 K	548 K	573 K			
$6MgH_2 + ZrH_2 + 0.3LiH$	0.0192	0.0488	0.1036	Simple FCC type	−84.1	−147.2
$6MgH_2 + ZrH_2 + 0.7LiH$	0.0155	0.0382	0.0894		−87.3	−151.4
$6MgH_2 + ZrH_2 + 1.0LiH$	0.0294	0.0663	0.2148		−98.7	−177.9
$6MgH_2 + ZrH_2 + 0.3NaH$	0.0126	0.0434	0.0981		−102.5	−179.2
$6MgH_2 + ZrH_2 + 0.7NaH$	0.0261	0.0478	0.0826	Ca_7Ge type	−57.4	−98.7
$6MgH_2 + ZrH_2 + 1.0NaH$	0.0304	0.0469	0.0648		−37.8	−62.57

tion enthalpy (ΔH^{θ}) and entropy (ΔS^{θ}) of the hydride. The plateau pressures and the calculated thermodynamic data for all the as-prepared samples are summarized in Table 7. As can be noticed, the enthalpies for the as-prepared samples: $6MgH_2 + ZrH_2 + n$LiH and $6MgH_2 + ZrH_2 + 0.3NaH$ were lowered down compared with that of the basic system $6MgH_2 + ZrH_2$ ($\Delta H^{\theta} = -73$ kJ/mol H_2) [13], while for the cases of $6MgH_2 + ZrH_2 + 0.7NaH$ and $6MgH_2 + ZrH_2 + 1.0NaH$ the enthalpies were increased. This result suggests that the formation enthalpies of the quaternary hydrides with simple FCC structure were lower while the enthalpies of the Mg–Zr–Na–H hydrides with Ca_7Ge type structure were higher, than that of the ternary Mg–Zr–H hydride obtained by reacting the basic system $6MgH_2 + ZrH_2$.

3.3.2. DSC measurements

The differential scanning calorimeter (DSC) spectra for all the as-prepared samples was measured under 0.5 MPa of hydrogen pressure with the heating and cooling for 3 cycles. Fig. 6 shows the DSC spectra for the reagent grade MgH_2 and the as-prepared sample $6MgH_2 + ZrH_2$. In the case of $6MgH_2 + ZrH_2$, an endothermic peak denoting the hydrogen releasing during heating and an exothermic one denoting hydrogen restoring when cooling can be detected apparently, indicating that the newly formed hydride exhibit the property of reversible hydrogen releasing and restoring. The starting temperature of hydrogen releasing read from the figure is about 627 K. For the reagent grade MgH_2, apparent an endothermic peak was detected during heating whereas the exothermic one during cooling was comparatively very small. Such result indicates the truth that metallic Mg is difficult to restore hydrogen owing to the slow reaction kinetics.

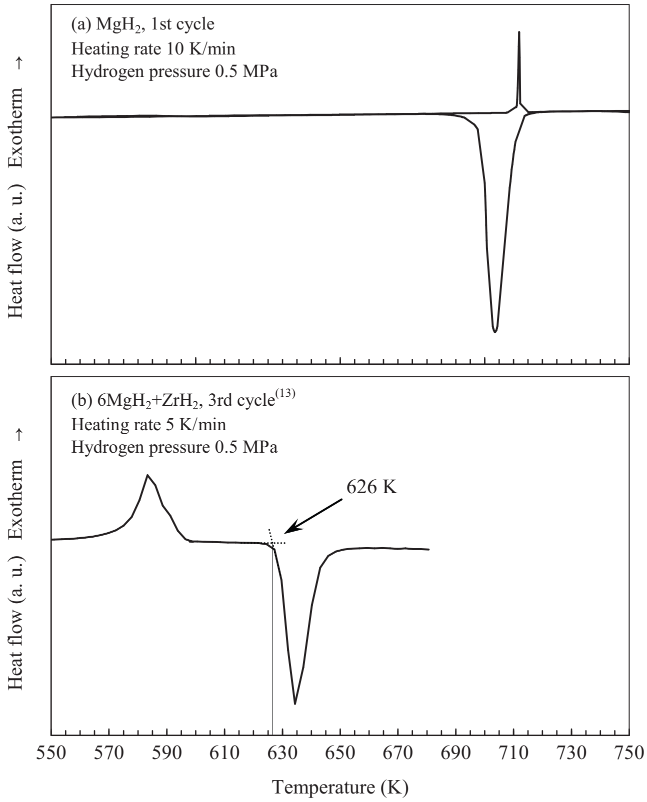

Fig. 6. The DSC spectra for MgH_2 and the as-prepared $6MgH_2 + ZrH_2$.

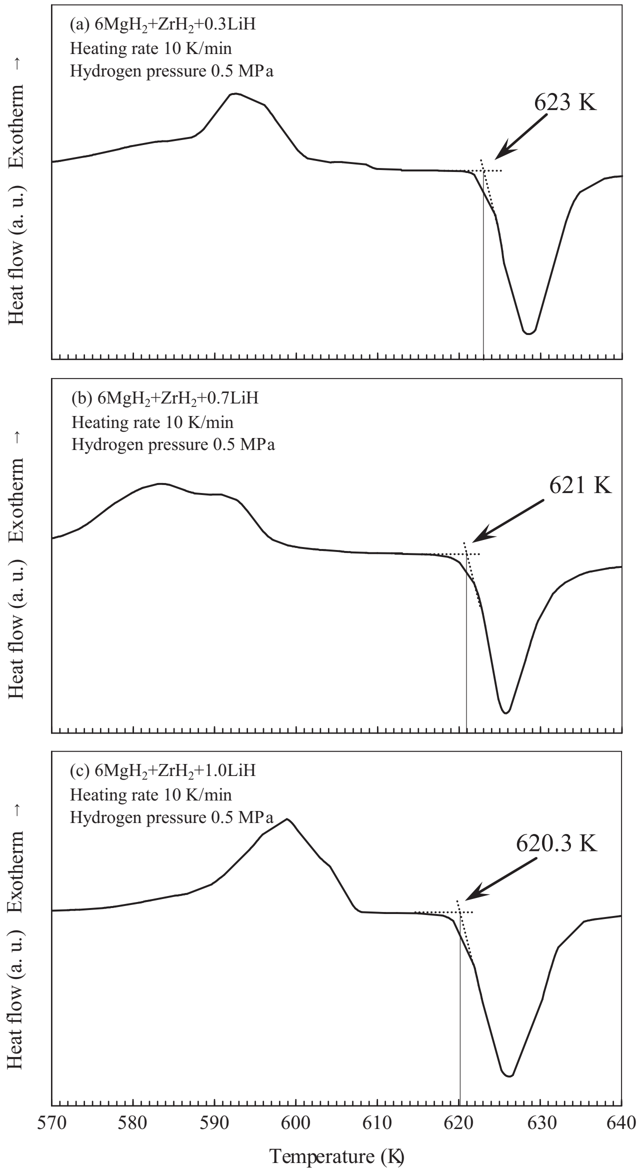

Fig. 7. The DSC spectra (3rd heating/cooling cycle) for the as-prepared $6MgH_2 + ZrH_2 + n$LiH samples.

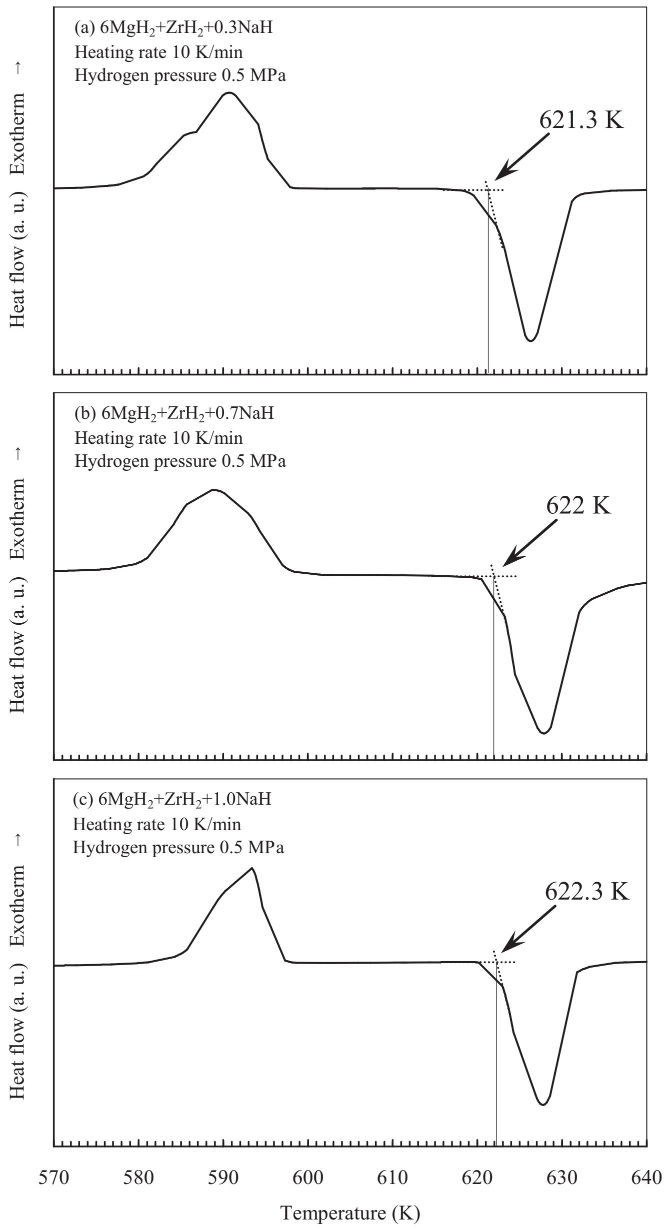

Fig. 8. The DSC spectra (3rd heating/cooling cycle) for the as-prepared $6MgH_2 + ZrH_2 + nNaH$ samples.

In Figs. 7 and 8, the hydrogen releasing temperatures for the as-prepared samples $6MgH_2 + ZrH_2 + nAH$ (A = Li, Na; n = 0.3, 0.7, 1.0) are compared. It can be seen that the hydrogen releasing temperature is lowered down sharply by formation of ternary Mg–Zr–H hydride. The addition of LiH into the basic system $6MgH_2 + ZrH_2$ can further lower down the hydrogen releasing temperature gradually, even though the variation is very tiny. It is considered that the partly replacement of Mg or Zr in the lattice of the simple FCC phase by Li to form the Mg–Zr–Li–H quaternary hydride is favorable for easier hydrogen releasing. In the case of $6MgH_2 + ZrH_2 + nNaH$ samples, the addition of NaH can also decrease the hydrogen releasing temperature. However, 0.3NaH addition shows better effect than 0.7 and 1.0 NaH addition. Such tendency indicates that formation of simple FCC-type Mg–Zr–Na–H hydride can lower down the hydrogen releasing temperature more than the formation of superlattice structure.

4. Conclusion

Novel Mg–Zr–A–H (A = Li, Na) based hydrides were synthesized by high pressure technique to improve the hydrogen storage properties. By reacting $6MgH_2 + ZrH_2 + nLiH$, quaternary hydrides with simple FCC-type structure were formed. Li atom would substitute Mg or Zr in the lattice of the simple FCC phase. In the case of $6MgH_2 + ZrH_2 + nNaH$, novel quaternary hydrides with Ca_7Ge type structure were formed as well as the hydrides with simple FCC-type structure. Reversible hydrogen storage behaviors of the newly formed hydrides were observed. The hydrogen releasing temperatures of the quaternary Mg–Zr–A–H hydrides were proved to be slightly lower than that of the Mg–Zr–H hydride. Formation of simple FCC-type Mg–Zr–A–H hydride with addition of LiH or small amount of NaH into the basic system $6MgH_2 + ZrH_2$ can decrease the hydrogen releasing temperature more than the formation of superlattice phase by addition of 0.7 or 1.0 NaH. The formation enthalpies of the quaternary hydrides with simple FCC structure were proved to be lower while the enthalpies of the Mg–Zr–Na–H hydrides with Ca_7Ge type structure were higher, than that of the ternary Mg–Zr–H hydride obtained by reacting the basic system $6MgH_2 + ZrH_2$.

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References

[1] R.W. Bentley, Energy Policy 30 (2002) 189–205.
[2] M. Asif, T. Muneer, Renewable Sustainable Energy Rev. 11 (2007) 1388–1413.
[3] A Zaluska, L. ZalusKi, J.O. Strom-Olsen, J. Alloy Compd. 288 (1999) 217–225.
[4] G. Barkhordarian, T. Klassen, R. Bormann, J. Alloy Compd. 364 (2004) 242–246.
[5] G. Liang, J. Huot, S.A. Boily, A.V. Neste, R. Schulz, J. Alloy Compd. 292 (1999) 247–252.
[6] D. Kyoi, T. Sato, E. Ronnebro, N. Kitamura, A. Ueda, M. Ito, S. Katsuyama, S. Hara, D. Noreus, T. Sakai, J. Alloy Compd. 372 (2004) 213–217.
[7] E. Rönnebro, D. Kyoi, A. Kitano, Y. Kitano, T. Sakai, J. Alloy Compd. 404 (2005) 68–72.
[8] D. Kyoi, T. Sato, E. Ronnebro, Y. Tsuji, N. Kitamura, A. Ueda, M. Ito, S. Katsuyama, S. Hara, D. Noreus, T. Sakai, J. Alloy Compd. 375 (2004) 253–258.
[9] D. Kyoi, N. Kitamura, H. Tanaka, A. Ueda, S. Tanase, T. Sakai, J. Alloy Compd. 428 (2007) 268–273.
[10] T. Sato, D. Kyoi, E. Ronnebro, N. Kitamura, T. Sakai, D. Noreus, J. Alloy Compd. 417 (2006) 230–234.
[11] D. Kyoi, T. Sakai, A. Ueda, S. Tanase, J. Alloy Compd. 463 (2008) 306–310.
[12] D. Kyoi, T. Sakai, N. Kitamura, A. Ueda, S. Tanase, J. Alloy Compd. 463 (2008) 311–316.
[13] T. Takasaki, D. Kyoi, N. Kitamura, S. Tanase, T. Sakai, J. Phys. Chem. B 111 (2007) 14102–14106.
[14] T. Takasaki, et al., J. Alloys (2010), doi:10.1016/j.jallcom.2010.01.072.
[15] Y. Fukai, N. Okuma, Jpn. J. Appl. Phys. 32 (1993) 1256–1261.
[16] F. Izumi, T. Ikeda, Mater. Sci. Forum 198 (2000) 321–324.