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Hydrogen-induced phase decomposition of Ba₇Al₁₃ and the crystal structure of Ba₂AlH₇

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Abstract

The hydrogenation characteristics of Ba_7AI_{13} have been studied under a hydrogen pressure of 7 MPa at different temperatures for 5 days. Ba_7AI_{13} reacts with hydrogen to form $BaAIH_5$ and Al between 373 and 553 K. When the temperature is in the range from 553 to 603 K, Ba_7AI_{13} is hydrogenated to Ba_2AIH_7 and Al. However, further increasing the temperature leads to the hydrogen-induced decomposition of Ba_7AI_{13} into Ba_2AIH_7 and $BaAI_4$. The crystal structure of Ba_2AID_7 was also studied by neutron powder diffraction. Ba_2AID_7 is isostructural to Sr_2AID_7 , crystallizing with a monoclinic structure in space group I2/a. The lattice parameters were determined as a = 13.197(3) Å, b = 10.237(2) Å, c = 8.509(2) Å, $\beta = 101.290(9)^\circ$.

Keywords: Hydrogen absorbing materials; Gas-solid reaction; Crystal structure; Neutron diffraction

1. Introduction

For the on-board storage of hydrogen in fuel-cell-powered vehicles, it is desirable to develop hydrogen storage materials which can absorb and desorb a large amount of hydrogen under moderate conditions of pressure and temperature. Recently, the alkali metal aluminum hydrides (alanates) NaAlH₄ and LiAlH₄ have been studied extensively for this purpose because they have hydrogen contents of 7.4 and 10.5 wt%, respectively [1–6]. It was found that the kinetic and thermodynamic properties of the dehydriding process can be improved by the assistance of surface catalysts [7–10]. Thus alkali metal aluminum hydrides can be considered as possible candidates for reversible hydrogen storage.

Alkaline earth metal aluminum hydrides have also attracted attention recently [11,12]. It was confirmed that $SrAl_2$ can be hydrogenated to $SrAl_2H_2$ at about 463 K. $SrAl_2$ is a Zintl phase alloy with a three-dimensional Al network and $SrAl_2H_2$ is a Zintl hydride with a twodimensional Al–H network [11]. On increasing the temperature to 513 K, $SrAl_2H_2$ further absorbs hydrogen to form Sr_2AlH_7 and Al. Sr_2AlH_7 has a new structure type that consists of $[AlH_6]$ octahedra and $[HSr_4]$ tetrahedra [12]. As the temperature is increased to about 563 K, Sr_2AlH_7 decomposes to SrH_2 , Al and H_2 .

In the Ba–Al binary system, a BaAl₂ intermetallic compound does not exist, but Ba_7Al_{13} exists in the equilibrium state [13]. This is a remarkable difference between the Sr–Al and Ca–Al binary systems. In our latest work [14], we also found that BaAlH₅ can be synthesized by hydrogenation of Ba_7Al_{13} . BaAlH₅ is structurally constructed from [AlH₆] octahedra, which share one corner and form one-dimensional zig-zag chains. Because of this interesting arrangement of the hydrogenation behavior of Ba_7Al_{13} has not been clarified. Thus the purpose of the present study was to obtain more extensive information in order to understand the hydrogenation characteristics of Ba_7Al_{13} .

2. Experimental

The Ba_7Al_{13} alloy was prepared by arc melting Ba and Al metals. Before the preparation, the loss of Ba during arc melting was determined to be about 3 wt%. On the basis of the stoichiometric amounts of starting materials, an extra 3

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wt% of Ba was added to compensate for the loss of Ba during arc melting. The ingot was remelted four times in the arc melt furnace to ensure homogeneity. The alloy was then ground to a powder of particle size smaller than 45 µm. Powder samples of 1-2 g were loaded into stainless steel containers and placed in stainless steel autoclaves. Hydrogenation experiments were carried out under a hydrogen pressure of 7 MPa at different temperatures for 5 days. After hydrogenation, XRD measurements of the hydrogenated samples were performed using a Rigaku RINT-2500V diffractometer with Cu Kα radiation at 50 kV and 200 mA. The XRD profiles were analyzed with the Rietveld refinement program RIETAN-97 [15]. A deuteride sample was prepared under a deuterium pressure of 7 MPa at 613 K for 10 days. Neutron powder diffraction data of the deuteride sample were collected at room temperature using the backward bank of the time-of-flight (TOF) diffractometer Vega [16] at the Neutron Science Laboratory of the High Energy Accelerator Research Organization of Japan. The neutron diffraction profiles were analyzed by the program RIETAN-2001T [17].

3. Results

Fig. 1 shows the calculated and observed XRD patterns for the Ba_7Al_{13} alloy sample. It can be seen that the sample contains the major phase Ba_7Al_{13} and an impurity phase Ba_3Al_5 . We attempted to prepare a single-phase Ba_7Al_{13} sample, but all efforts were unsuccessful under the present experimental conditions. From the Rietveld analysis, we found that the amounts of Ba_7Al_{13} and Ba_3Al_5 were about 80 and 20 wt%, respectively. Ba_7Al_{13} has trigonal symmetry in space group $P\bar{3}m1$ [18]. In the present case, the lattice parameters were calculated as a = 6.1006(2) Å and c = 17.2697(5) Å by the Rietveld method.

Fig. 2a presents the XRD pattern for the sample hydrogenated at 333 K for 5 days. The diffraction peaks are only from Ba_7Al_{13} and Ba_3Al_5 , indicating that no other phase was formed during hydrogenation. However, additional weak peaks can be seen in the XRD pattern for the sample hydrogenated at 373 K (Fig. 2b). When the temperature was increased to 413 K, the diffraction peaks from the reaction product can clearly be observed and were indexed to be $BaAlH_5$ and Al, as shown in Fig. 2c. From these results, we found that Ba_7Al_{13} can react with hydrogen to form $BaAlH_5$ and Al starting at about 373 K.

The structure of BaAlH₅ was studied in our latest work [14]. It crystallizes with a new orthorhombic structure in space group $Pna2_1$. Using this structure model, we refined the XRD pattern for the sample hydrogenated at 513 K. As shown in Fig. 3, the calculated pattern is in good agreement with the measured pattern. The lattice parameters of BaAlH₅ were calculated to be a = 9.187(1) Å, b = 7.047(1)Å and c = 5.1238(4) Å, which compare well with those of BaAlD₅ [14]. This sample also contained 3 wt% of unreacted Ba₇Al₁₃ with lattice parameters a = 6.099(3) Å and c = 17.272(5) Å. Compared with those of the as-cast sample, the lattice parameters of the unreacted Ba₇Al₁₃ do not change. This indicates that the solubility of hydrogen in Ba₇Al₁₃ is very small and a small amount of hydrogen absorption readily leads to the decomposition and hydrogenation of Ba₇Al₁₃.

Fig. 4 compares the XRD patterns of the samples hydrogenated at 553, 603 and 653 K for 5 days. We found that a second hydride was formed besides $BaAlH_5$, Al and unreacted Ba_7Al_{13} when the hydrogenation temperature



Fig. 1. Rietveld refinement (_____) of the observed XRD pattern (+) for the Ba_7Al_{13} alloy sample. Reflection markers are for Ba_7Al_{13} and Ba_3Al_5 (from above), respectively. $R_{wp} = 14.68\%$, $R_p = 11.20\%$, S = 3.37.





Two Theta (degree)

Fig. 2. XRD patterns for the sample hydrogenated at (a) 333, (b) 373 and (c) 413 K for 5 days.

Fig. 4. XRD patterns for the samples hydrogenated at (a) 553, (b) 603 and (c) 653 K for 5 days.



Fig. 3. Rietveld refinement (------) of the observed XRD pattern (+) for the sample hydrogenated at 513 K for 5 days. Reflection markers are for BaAlH₅, Al and Ba₇Al₁₃ (from above), respectively. $R_{wp} = 9.81\%$, $R_p = 7.81\%$, S = 2.50.

was 553 K. As the temperature was raised to 603 K, BaAlH₅ disappeared entirely and the second hydride was observed together with Al and BaAl₄. The diffraction peaks from the second hydride were indexed to be a monoclinic unit cell isostructural to Sr_2AlH_7 [12]. Thus we can conclude that Ba_7Al_{13} is hydrogenated to Ba_2AlH_7 and Al when the temperature exceeds 553 K. It should be noted that the increase of temperature resulted in the precipitation of $BaAl_4$ as well as Al accompanying the formation of Ba_2AlH_7 (Fig. 4b). On further increasing the temperature to 653 K, as shown in Fig. 4c, only $BaAl_4$ precipitated instead of Al, while Ba_3AlH_7 was formed.

In order to confirm the structure of Ba_2AlH_7 , a deuteride sample was prepared under a deuterium pressure of 7 MPa at 613 K for 10 days. The structure refinement was first carried out from the XRD data of the deuteride sample. For the refinement, the metal atom coordinates of Sr_2AlD_7 [12] were used as a starting model for Ba₂AlD₇. Fig. 5 shows the calculated and measured XRD patterns for the deuteride sample. It can be seen that the calculated pattern fits the measured pattern very well. The refined Ba and Al atom coordinates were then fixed during refinement of the deuterium positions in the neutron diffraction data. The neutron diffraction data were analyzed by the Rietveld refinement program RIETAN-2001T [17]. The deuterium positions were initially located by using those of Sr₂AlD₇. The occupation factors of the deuterium positions were refined to be close to 1 (the differences were smaller than 3σ), thus they were fixed at unity during the final refinement. The observed and calculated neutron powder diffraction patterns are shown in Fig. 6. Tables 1 and 2 list the final refinement results and selected inter-atomic distances of Ba₂AlD₇, respectively.

Isostructural to Sr₂AlD₇ [12], Ba₂AlD₇ crystallizes with a monoclinic structure in the I2/a (No. 15) space group (Z=8). The lattice parameters were determined to be a = 13.197(3) Å, b = 10.237(2) Å, c = 8.509(2) Å, $\beta =$ $101.290(9)^{\circ}$. Similarly, the crystal structure of Ba₂AlD₇ can be built up from isolated $[AID_6]$ units and infinite one-dimensional chains of edge-sharing [DBa₄] tetrahedra. The Al–D bond lengths in the $[AlD_6]$ octahedra are from 1.67 to 1.85 Å, and thus the octahedra are rather distorted compared with those in Sr_2AlD_7 (1.71–1.76 Å [12]). However, similar distorted [AlD₆] octahedra were also found in BaAlD₅ (1.69–1.85 Å [14]). Therefore, we suggest that the distortion of the $[AlD_6]$ octahedra is related to the larger size of Ba. The Ba-D bond lengths (2.59-2.86 Å) in the [DBa₄] tetrahedra of Ba₂AlD₇ are in good agreement with those in binary BaD₂ (2.57-2.98 Å [19]). As far as we are aware, $[DBa_4]$ tetrahedra also exist in Ba₅Ga₆D₂ [20], but the twisted chain of edge-sharing [DBa₄] tetrahedra is an interesting feature of the present

4. Discussion

structure.

4.1. Decomposition of Ba_7Al_{13} under hydrogen atmosphere

As reported above, Ba_7AI_{13} is transformed into $BaAIH_5$ and Al during hydrogenation at 373–553 K. Prior to decomposition, the lattice parameters of Ba_7AI_{13} do not change, indicating that only a small amount of hydrogen can dissolve in it. When the temperature exceeds 553 K,







Fig. 6. Calculated (——) and measured (+) neutron powder diffraction patterns of Ba_2AlD_7 prepared under a deuterium pressure of 7 MPa at 613 K for 10 days. Reflection markers are for Ba_2AlD_7 and $BaAl_4$ (from above), respectively. $R_{wp} = 2.88\%$, $R_p = 2.27\%$, S = 2.23.

 Ba_7Al_{13} is hydrogenated to Ba_2AlH_7 and Al. Although our hydrogenation experiments were carried out at constant temperature, we suggest that the procedure for the hydrogen-induced phase decomposition of Ba_7Al_{13} proceeds in two steps. In the first step starting at about 333 K, Ba_7Al_{13} reacts with hydrogen to form $BaAlH_5$ and Al. As the temperature is raised to 553 K, $BaAlH_5$ becomes unstable thermodynamically. Thus the decomposition of $BaAlH_5$ into Ba_2AlH_7 , Al and H_2 takes place as the second step.

It is interesting to note that $BaAl_4$ appears together with Al when Ba_2AlH_7 is formed at 603 K, as shown in Fig. 4b. When the temperature increases to 653 K, however, $BaAl_4$ entirely replaces Al during decomposition (Figs. 4c and 5). These results are probably related to the diffusibility of metal atoms. Phase decomposition is a process of atom

Table 1 Atomic coordinates and isotropic thermal parameters for Ba_2AID_7 refined from neutron powder diffraction data^a

Atom	Site	g	x	у	z	$B(\text{\AA}^2)$
Ba1	8 <i>f</i>	1	0.3459	0.5848	0.3249	3.1(6)
Ba2	8 <i>f</i>	1	0.1084	0.3247	0.0852	0.2(4)
Al1	8 <i>f</i>	1	0.927	0.096	0.235	2.6(7)
D1	8f	1	0.004(1)	0.116(1)	0.077(2)	1.6(4)
D2	8 <i>f</i>	1	0.846(1)	0.974(1)	0.135(2)	1.6(5)
D3	8 <i>f</i>	1	0.023(1)	0.999(2)	0.325(2)	2.2(5)
D4	8f	1	0.844(1)	0.104(2)	0.387(2)	2.9(6)
D5	8 <i>f</i>	1	0.983(1)	0.249(2)	0.324(2)	2.4(5)
D6	8 <i>f</i>	1	0.832(1)	0.207(1)	0.115(2)	0.5(4)
D7	8 <i>f</i>	1	0.693(1)	0.864(1)	0.322(2)	1.5(4)

^a Space group *I2/a* (No. 15); cell parameters: a = 13.197(3) Å, b = 10.237(2) Å, c = 8.509(2) Å, $\beta = 101.290(9)^{\circ}$, V = 1127.2(4) Å³, *Z* = 8; $R_{wp} = 2.88\%$, $R_p = 2.27\%$, $R_1 = 6.28\%$, S = 2.23. The Ba and Al atom coordinates were fixed as those refined from the X-ray diffraction data.

diffusion and, therefore, temperature is a key factor in controlling it. The diffusion behavior of metal atoms is responsible for the decomposition products at different temperatures.

4.2. Structural comparison of Ba_2AlH_7 with fluorides

The structural analogies between hydrides and fluorides have been studied in a systematic way [21]. First, Messer [22] found structural analogies between the binary hydrides and fluorides of the alkali metals, the alkaline earth metals and aluminum. He also suggested that ternary hydrides might be analogous to the corresponding ternary fluorides, at least in those cases where both binary hydride-fluoride pairs have similar compositions and structures. For example, ternary alkaline earth hydrides Ba2Mg3H10 [23] and Ba6Mg7H26 [24], and alkali-alkaline earth hydrides KMgH₃ and ALiH₃ (A=Sr, Ba) [25] are related to the corresponding fluorides. Recently, an alkali metal aluminum hydride Na₃AlH₆ [26] was also found to be isostructural to Na_3AlF_6 [27]. So far, however, we have not found any fluoride analogous to Ba₂AlH₇. In the Ba-Al-F system [28], five ternary fluorides, namely trimorphic BaAlF₅, Ba₃Al₂F₁₂, Ba₅Al₃F₁₉, polymorphic Ba_3AlF_9 and Ba_5AlF_{13} , were found, but nobody reported the compound ' Ba_2AlF_7 '. Even though ' Sr_2AlF_7 ' was reported by Ravez [29], it was recently suggested to be $Sr_5Al_2F_{16}$ with an orthorhombic structure [30]. Moreover, the existence of Ca_2AlF_7 (*Pnma*) [31] and Sr_2InF_7 (*P*2₁/*c*) [32] was confirmed, but their structures are quite different from that of Ba₂AlH₇. Therefore, further work is necessary to clarify whether the structural analogy concept is suitable for alkaline earth metal aluminum hydrides and fluorides.

Table 2 Selected inter-atomic distances (Å) and angles (deg) in Ba_3AID_7

Ba1–D5	2.48(2)	D1-Al1	1.85(1)
D3	2.49(1)	Ba2	2.54(1)
D7	2.59(1)	Ba1	2.70(1)
D1	2.70(1)	Ba1	2.86(1)
D6	2.76(1)		
D6	2.79(1)	D2-Al1	1.75(1)
D4	2.79(1)	Ba2	2.79(1)
D6	2.81(1)	Ba1	2.86(2)
D2	2.86(2)	Ba1	2.87(1)
D1	2.86(1)	Ba2	3.70(1)
D2	2.87(1)	Ba1	4.06(2)
D4	3.23(2)		
D4	3.73(1)	D3-Al1	1.67(2)
D2	4.06(2)	Ba1	2.49(1)
		Ba2	2.70(2)
Ba2–D1	2.54(1)	Ba2	2.91(2)
D5	2.61(2)		
D7	2.62(1)	D4-Al1	1.85(1)
D3	2.70(2)	Ba1	2.79(1)
D7	2.72(1)	Ba2	2.93(2)
D2	2.79(1)	Ba1	3.23(2)
D7	2.86(1)	Ba2	3.64(1)
D3	2.91(2)	Ba1	3.73(1)
D4	2.93(2)		
D5	2.96(2)	D5-Al1	1.83(2)
D4	3.64(1)	Ba1	2.48(2)
D2	3.70(1)	Ba2	2.61(2)
		Ba2	2.96(2)
Al1-D3	1.67(2)		()
D2	1.75(1)	D6-A11	1.85(1)
D5	1.83(2)	Ba1	2.76(1)
D6	1.85(1)	Ba1	2.79(1)
D1	1.85(1)	Ba1	2.81(1)
D4	1.85(1)		
		D7–Ba1	2.59(1)
D1-Al1-D2	95.5(7)	Ba2	2.62(1)
D1-Al1-D3	85.6(7)	Ba2	2.72(1)
D1-Al1-D4	170.7(6)	Ba2	2.86(1)
D1-Al1-D5	88.4(7)		()
D1-Al1-D6	86.6(6)	Ba1-D7-Ba2	111.9(3)
D2-Al1-D3	97.7(7)	Ba1-D7-Ba2	116.9(3)
D2-Al1-D4	89.0(8)	Ba1-D7-Ba2	103.7(3)
D2-Al1-D5	165.7(8)	Ba2–D7–Ba2	106.1(3)
D2-Al1-D6	83.5(6)	Ba2–D7–Ba2	108.3(3)
D3-Al1-D4	101.8(7)	Ba2–D7–Ba2	109.8(3)
D3-Al1-D5	96.3(8)		. /
D3-Al1-D6	172.2(7)		
D4-Al1-D5	85.4(7)		
D4-Al1-D6	85.9(7)		
D5-Al1-D6	83.0(7)		

5. Conclusions

The hydrogen-induced phase decomposition of Ba_7Al_{13} has been studied at different temperatures. Ba_7Al_{13} can react with hydrogen to form $BaAlH_5$ and Al in the temperature range between 373 and 553 K. As the temperature increases to about 553–603 K, Ba_7Al_{13} decomposes into Ba_2AlH_7 and Al under a hydrogen atmosphere. Further increasing the hydrogenation temperature leads to the decomposition of Ba_7Al_{13} into Ba_2AlH_7 and

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