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Direct synthesis of $BaAlH_5$ and Ba_2AlH_7 from BaH_2 and Al system and their hydriding/dehydriding characteristics

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ABSTRACT

$BaAlH_5$ and Ba_2AlH_7 were successfully synthesized through reactive ball milling commercially available BaH_2 and Al powders for the first time. The effects of the mole ratios of BaH_2/Al on the phase formation and structural properties were investigated by means of X-ray diffractions and a subsequent Rietveld refinement. For different BaH_2/Al mole ratios (0.5, 1.0 and 2.0) the main phases were $BaAlH_5$, Ba_2AlH_7 and BaH_2, respectively. Ba_2AlH_7 can also be prepared by ball milling BaH_2/Al (1:1) under Ar and a subsequent hydrogenation. The phase transition and hydriding/dehydriding characteristics of the ball milled BaH_2/Al (1:1) system under Ar were investigated using in-situ differential scanning calorimeter (DSC) under H_2 atmosphere and pressure–composition isotherms (PCI). The mechano-chemistry induced phase transformation of the BaH_2/Al (1:1) mixture to a $BaH_2/BaAl_4$ (3:1) mixture during ball milling under Ar was first observed. The hydrogenation enthalpy of $BaH_2/BaAl_4$ (3:1) to form Ba_2AlH_7 was determined to be $-20.0\,kJ\,mol^{-1}$ from a van't Hoff plot. The phase transitions during ball milling under Ar and PCT measurements were proposed as follows:

$$28BaH_2 + 28Al \xrightarrow[Ar]{\text{Ball milling}} 21BaH_2 + 7BaAl_4 \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} 12Ba_2AlH_7 + 4BaAl_4$$

1. Introduction

Hydrogen as a potential alternative energy carrier has received wide concerns in recent years [1–6]. Safe and efficient hydrogen storage is a major technical challenge for the widespread use of hydrogen, especially for the development of on-board vehicular hydrogen storage technology. The current on-board hydrogen storage approaches are mainly focused on compressed hydrogen gas, cryogenic and liquid hydrogen, metal hydrides including interstitial hydride or complex hydrides, high surface area materials (such as nanostructure, porous materials and metal–organic frameworks), chemical hydrogen storage and some new materials (such as inorganic clathrates or polymers) [7–13]. Since Bogdanović and Schwickardi [14] discovered that the dopant of titanium catalyst can make the hydrogenation–dehydrogenation of sodium alanate ($NaAlH_4$) reversible at a moderate temperature the complex hydrides have attracted great interest [15–19]. However, Ti-doped $NaAlH_4$ can not meet the requirement for hydrogen capacity and hydrogen desorption kinetics in the practical on-board application. Now days, many groups pay attentions on non-interstitial hydrides such as boron hydrides [20–22], amides [23,24] and AlH_3 [7] in addition to alanates.

Alkaline earth metals (AE)-based alanates have attracted much interest because of their high hydrogen capacity [25–29]. However, AE-based alanates such as $Mg(AlH_4)_2$ and $Ca(AlH_4)_2$ are usually synthesized through ball milling $MgCl_2$ and $CaCl_2$ with $NaAlH_4$ or $LiAlH_4$ [26]. Dymova and co-workers [30,31] reported the synthesis of $Mg(AlH_4)_2$ and $Ca(AlH_4)_2$ from the mixture of MgH_2 and CaH_2 with $AlCl_3$, respectively. $CaAlH_5$ or $MgAlH_5$ only appeared as an intermediate phase during the decomposition of the corresponding alanates and has not been prepared separately [26,30,31]. Our group has succeeded in synthesizing several novel alkaline earth metal-aluminum hydrides such as $SrAl_2H_2$ [32], Sr_2AlH_7 [33], $BaAlH_5$ [34] and Ba_2AlH_7 [35] through hydriding of suitable AE–Al alloys such as $SrAl_2$ and Ba_7Al_{13} intermetallic compounds and other alloys. The crystal structures of these newly synthesized hydrides were analyzed by the Rietveld method using X-ray and neutron diffractions [32–35]. All of these crystal structures were new types of crystal structures [32–35].

Mechanism of formation and decomposition reactions of alanates or inorganic compounds containing Al–H bonding is one of the critical information to develop advanced hydrogen storage

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materials, especially inorganic metal hydrides. In our experience, the Ba–Al–H system is the most suitable to study mechanism of reactions because intermediate phases are stable to isolate compared to Mg–Al–H and Ca–Al–H systems. [26,30,31,34,35] In comparison to the Sr–Al–H system, reaction conditions are milder and reactions were completed in shorter period [34,35]. Therefore, we selected the formation reaction of $BaAlH_5$ and Ba_2AlH_7 from commercially available raw materials.

Up to now, the direct synthesis of the hydrides containing alkaline earth metals and aluminum from AEH_2 and Al has not been achieved as far as we know. This formation reaction was only observed during the process of formation and decomposition of Ba_2AlH_7 but not directly from BaH_2 and Al powders. In this study, we synthesized $BaAlH_5$ and Ba_2AlH_7 from commercially available BaH_2 and Al powders for the first time.

2. Experimental

The commercial BaH_2 (99.7%, Soekawa Chemical Co.Ltd) and Al powders (99.9%, Furuuchi Chemical Corporation) were used as received. About 2 g mixtures of BaH_2/Al with different molar ratios (0.5, 1.0 and 2.0) were weighed in a glove box filled with high purity argon and placed in a stainless steel pot. The milling was performed on a Fritsch Pulverisette-5 planetary under 0.8 MPa H_2 or 0.1 MPa Ar. The ball to powder weight ratio was 40:1 and the rotation speed was 300 rpm. The milling time was 10 h.

The ball milled samples were characterized by X-ray powder diffractions (Rigaku Rint-2500 V diffractometer with CuK_α radiation at 50 kV and 200 mA). To avoid the oxidation a special sample holder filled with Ar was used for XRD measurements. The phase compositions of the ball milled samples were determined through refining the diffraction patterns with FULLPROF program based on the Rietveld method [36].

The DSC measurements were performed on a Rigaku TP-8230HP under 5 MPa H_2 or 0.1 MPa Ar. During the measurements, the temperature was raised from room temperature to 500 °C at a rising rate of 5 °C/min.

Hydrogenation–dehydrogenation characteristics of BaH_2/Al (1:1) ball milled under 0.8 MPa H_2 or 0.1 MPa Ar were measured using a pressure–composition isotherms (PCI) apparatus (Suzuki Shokan Cor.). The largest H_2 pressure was set as 8 MPa, the maximum judging time were 24 h, the minimum time interval was 59 min and the pressure interval pressure was 0.001 MPa. Before measurements the sample was activated by vacuuming for 4 h. In order to calculate the enthalpy of hydrogenation and dehydrogenation the *P–C* isotherms of the ball milled BaH_2/Al (1:1) were measured at 260 °C, 280 °C and 305 °C, respectively.

3. Results and discussion

3.1. Effects of BaH_2/Al mole ratios on the phase formation under reactive ball milling conditions

Fig. 1 shows the XRD patterns of BaH_2/Al systems with different ratios of 2:1, 1:1 and 1:2 ball milled under 0.8 MPa H_2. Rietveld refinement was used to determine the phase compositions. The calculated curve agreed well with the observed XRD pattern as shown in Fig. 2. According to the stoichiometric proportion the mixture of $2BaH_2$/Al was expected to form Ba_2AlH_7 but the calculated proportion of Ba_2AlH_7 in the final product was only 41.7 wt% with a 58.3 wt% excess of BaH_2. BaH_2/Al (1:1) was expected to form $BaAlH_5$ but the real product was composed of Ba_2AlH_7 (84.2 wt%), BaH_2 (11.9 wt%) and Al (3.9 wt%). However, when the ratio of BaH_2/Al was changed to 1:2 the main phase was $BaAlH_5$ (83.2 wt%) accompanied by a 16.8 wt% excess of Al. The results show that $BaAlH_5$ and Ba_2AlH_7 can be directly prepared by ball milling the mixture of BaH_2 and Al under a mild H_2 pressure, which is quite different from what's observed in Mg–Al [27] system. In previous studies, MgH_2 formed by ball milling Mg–Al system under H_2 while $Mg(AlH_4)_2$ or other hydrides cannot be successfully prepared.

3.2. DSC measurements of BaH_2/Al system

Differential scanning calorimeter (DSC) was used to measure the thermal behavior of the hydrides. Fig. 3 shows DSC curves

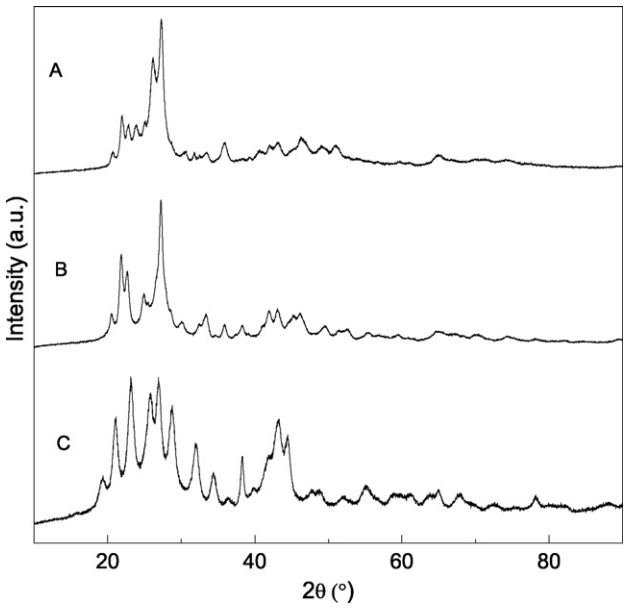

Fig. 1. XRD patterns of BaH_2/Al systems with different ratios (A: 2:1; B: 1:1; C: 1:2) ball milled under 0.8 MPa H_2.

of BaH_2/Al system (BaH_2:Al = 0.5 and 1.0) ball milled under 0.8 MPa H_2. For BaH_2:Al = 0.5 the onset temperature of the endothermal transition was about 315 °C which can be attributed to the decomposition of $BaAlH_5$. For BaH_2:Al = 1.0 there also appeared an endothermal peak and the onset transition temperature was about 330 °C representing decomposition reaction of Ba_2AlH_7. The DSC results also indicated that the hydrides formed during the reactive ball milling process.

To study the H_2-induced phase transition and H_2 absorption behavior of BaH_2/Al system in-situ DSC measurements under 5 MPa H_2 atmosphere were performed. BaH_2/Al system (BaH_2:Al = 1.0) was first ball milled under 0.1 MPa Ar. Fig. 4 shows in-situ DSC curves of BaH_2/Al system (BaH_2:Al = 1.0) ball milled under 0.1 MPa Ar (Measurement conditions: 5 MPa H_2, 30–500 °C, 5 °C/min). As shown in Fig. 4, for BaH_2:Al = 1.0 there appeared one broad exothermal peak at 350 °C which is attributed to the H_2 absorption reaction

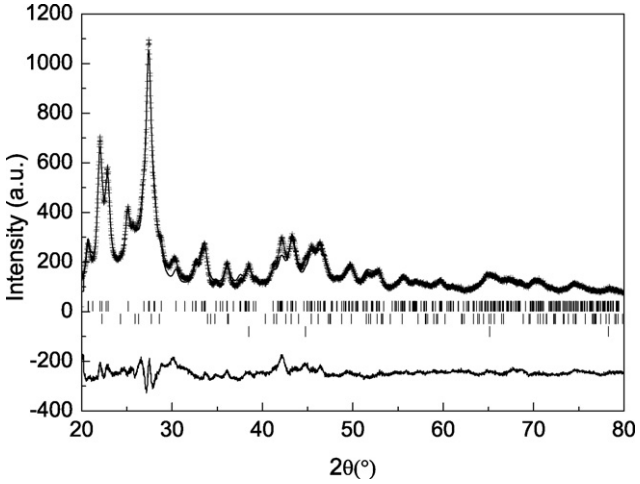

Fig. 2. Rietveld refinement results of BaH_2/Al system with molar ratio of 1:1. The plus signs (+) represent the observed data. The solid line represents the calculated profile. Vertical bars (from above) correspond to the position of Bragg peaks for Ba_2AlH_7, BaH_2 and Al, respectively. The lowest curve is the difference between the observed and calculated patterns. R_w = 8.38%, R_p = 6.43%, R_{exp} = 7.48%, χ^2 = 1.26.

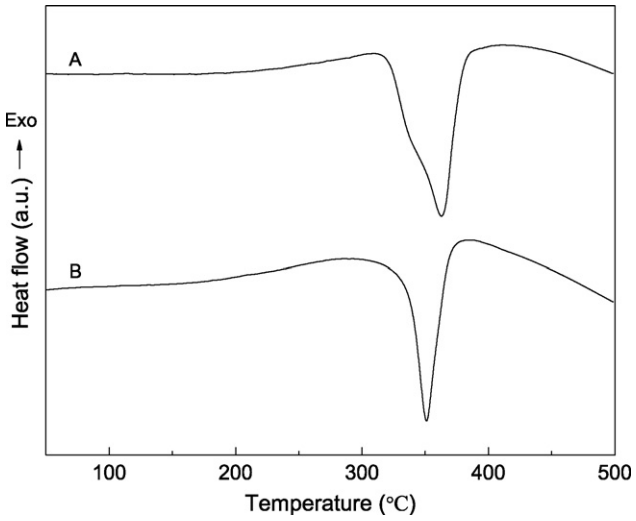

Fig. 3. DSC curves of BaH_2/Al system (A: 1:2; B: 1:1) ball milled under 0.8 MPa H_2. (hearting rate: 5 °C/min, atmosphere: 0.1 MPa Ar).

and the formation of Ba_2AlH_7 hydride. The DSC results show that the milled BaH_2/Al system (BaH_2:Al = 1.0) under Ar absorbed H_2 and transformed into hydrides during in-situ DSC measurement under H_2 atmosphere.

3.3. Pressure–composition isotherms (PCI) measurements

Fig. 5 shows the *P–C* isotherm of the mixture of BaH_2/Al (1:1) ball milled under 0.8 MPa H_2. The measurement temperature was 260 °C. The mixture with a composition of Ba_2AlH_7 (84.2 wt%), BaH_2 (11.9 wt%) and Al (3.9 wt%) analyzed in Section 3.1 did not absorb H_2 during hydriding process. The actual amount of desorbed hydrogen at 260 °C was only 0.2 wt%. According to the above XRD analysis, the sample contains 84.2 wt% Ba_2AlH_7 and the theoretical H_2 content is about 1.9 wt% much higher than the amount of actually desorbed H_2, which indicates that the desorption of H_2 at 260 °C is incomplete and only a part of Ba_2AlH_7 can desorb H_2 under this condition.

Fig. 6 shows the *P–C* isotherms of the mixture of BaH_2/Al (1:1) ball milled under 0.1 MPa Ar. In order to study the thermodynamic behavior and calculate the enthalpy of hydrogenation and dehydrogenation, the *P-C* isotherms of the ball milled mixture of

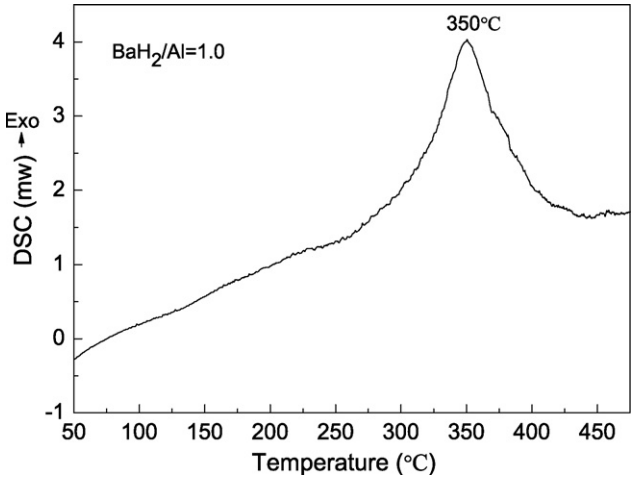

Fig. 4. In-situ DSC curve of BaH_2/Al system (BaH_2:Al = 1.0) ball milled under 0.1 MPa Ar (hearting rate: 5 °C/min, atmosphere: 5 MPa H_2).

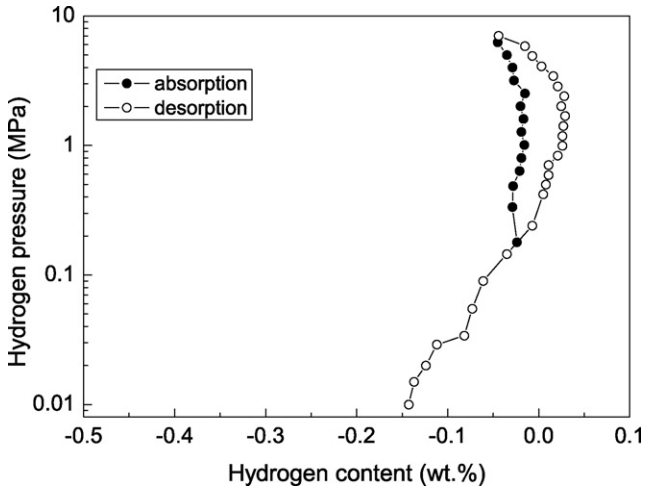

Fig. 5. *P–C* isotherm of the mixture of BaH_2/Al (1:1) after ball milling under 0.8 MPa H_2 measured at 260 °C.

BaH_2/Al (1:1) were measured at 260 °C, 280 °C and 305 °C, respectively. Similar to most of hydrogen storage materials there appeared obvious absorption pressure plateau region. With the increase of measurement temperature the plateau region became broader and the plateau pressure increased. The total H_2 absorption amounts at 260 °C, 280 °C and 305 °C were 0.583 wt%, 0.723 wt% and 0.732 wt%, respectively. There existed an obvious plateau pressure difference between the absorption and the desorption curves. In addition, it is noticed that the absorbed hydrogen can not release completely but more H_2 releases with the increase of measurement temperature.According to the *P–C* isotherms measured at different temperatures a van't Hoff plot ($\ln p_{H_2} \sim 1/T$) was made as show in Fig. 7 The enthalpy of hydrogenation can be calculated using the slope of the van't Hoff plot according to the following equations.

$$\ln p_{H_2} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

The enthalpy of hydrogenation was determined to be $-20.0\,kJ\,mol^{-1}$.

The phase transition of the mixture of BaH_2/Al (1:1) during ball milling under Ar and after *P–C* isotherms measurement was investigated by XRD and subsequent Rietveld refinements. Fig. 8 shows the

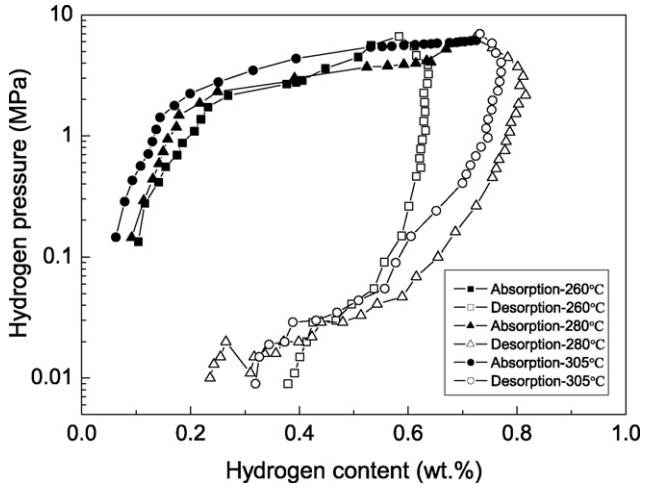

Fig. 6. *P–C* isotherms of the mixture of BaH_2/Al (1:1) ball milled under 0.1 MPa Ar. Measurement temperatures are 260 °C, 280 °C and 305 °C, respectively.

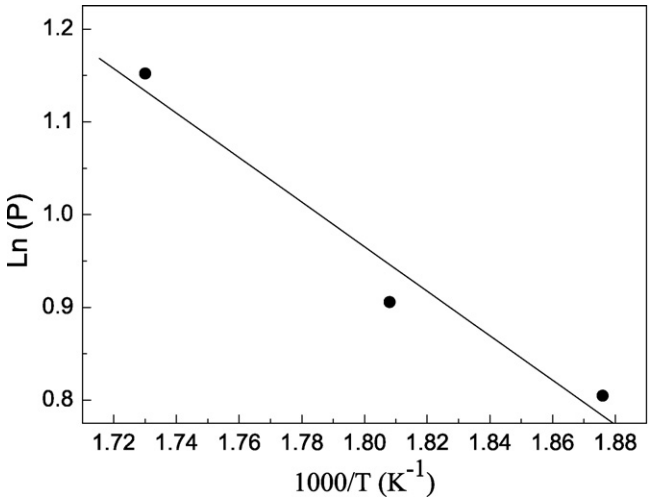

Fig. 7. Van't Hoff plot (ln $p_{H_2} \sim 1/T$) for the mixture of BaH_2/Al ball milled under 0.1 MPa Ar during hydriding process.

XRD patterns and phase components of BaH_2/Al (1:1) system after ball milling under 0.1 MPa Ar (before PCI) and after PCI measurement at 280 °C. Fig. 9 shows the refinement results of XRD patterns of ball milled BaH_2/Al (1:1) and after PCT measurements at 280 °C. The calculated data agreed well with the observed. After ball milled the mixture of BaH_2/Al (1:1) was composed of BaH_2 (65.4%) and $BaAl_4$ (34.6%) indicating that the mixture of BaH_2/Al first transformed into a mixture of BaH_2 and $BaAl_4$ (molar ratio is about 3:1) during ball milling process under Ar. However, as discussed in Section 3.1 the phase compositions of the reactive ball milling BaH_2/Al (1:1) system under 0.8 MPa H_2 was composed of Ba_2AlH_7 (84.2 wt%), BaH_2 (11.9 wt%) and Al (3.9 wt%) and no $BaAl_4$ formed during the process of reactive ball milling under 0.8 MPa H_2, which indicate that BaH_2 and $BaAl_4$ exist under Ar or very low H_2 while Ba_2AlH_7 are stable at high hydrogen pressure. This is the reason why BaH_2 and $BaAl_4$ were found in ball milled BaH_2/Al (1:1) sample under Ar and $BaAlH_5$ or Ba_2AlH_7 was present in the ball milled samples under H_2. After PCI measurements, the sample was composed of BaH_2 (41.4 wt%), $BaAl_4$ (29.1 wt%) and Ba_2AlH_7 (29.5 wt%). Based on the results of XRD analyses and PCI measurements it can

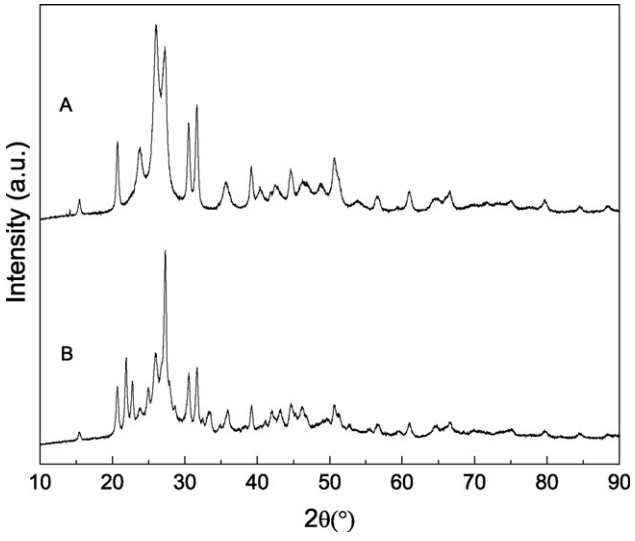

Fig. 8. XRD patterns and phase changes of BaH_2/Al (1:1) system ball milled under 0.1 MPa Ar before PCI measurement (A) and after PCI measurement at 280 °C (B).

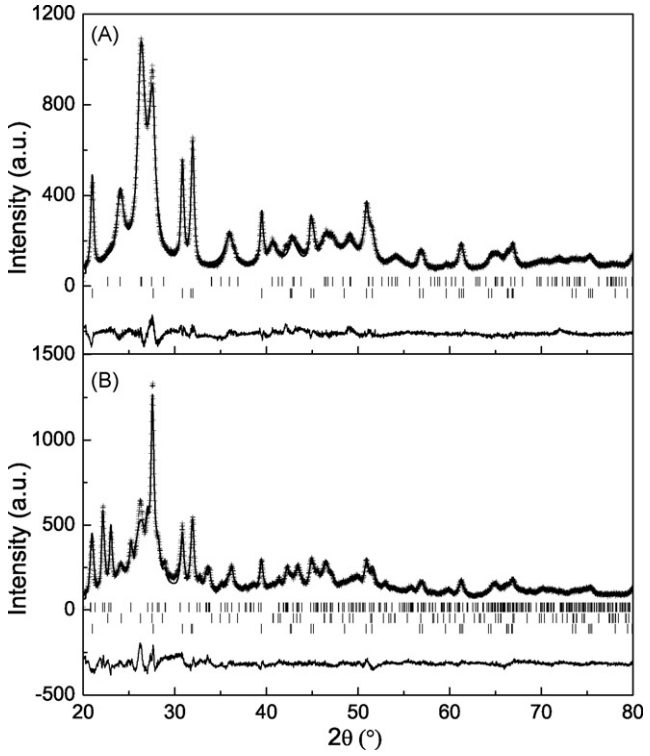

Fig. 9. Rietveld refinement results of BaH_2/Al (1:1) system ball milled under 0.1 MPa Ar before PCI measurement (A) and after PCI measurement at 280 °C (B). The plus signs (+) represent the observed data. The solid line represents the calculated profile. Vertical bars (from above) correspond to the position of Bragg peaks. The lowest curve is the difference between the observed and calculated patterns.

be concluded that the mixture of BaH_2/Al (1:1) first transformed into BaH_2/$BaAl_4$ (3:1) after ball milling under Ar and then the mixture of BaH_2 and $BaAl_4$ reacted with H_2 to form Ba_2AlH_7 during the PCI absorption process. These phase transformation behaviors from BaH_2/Al (1:1) to BaH_2 /$BaAl_4$ (3:1) during ball milling under Ar and the mixture of $BaAl_4$ and BaH_2 to Ba_2AlH_7 after hydrogenation were observed for the first time, which is quite different from what's observed in NaH/Al system, where no phase transformation was reported during the ball milling under Ar [15]. During the dehydriding process Ba_2AlH_7 hydride desorbed H_2 to regenerate into BaH_2 and $BaAl_4$ indicating this is a reversible process. This desorbtion behavior was also different from what's observed in other alanates, where Al usually formed during the decomposition process [37]. This process was demonstrated as follows.

$$28BaH_2 + 28Al \xrightarrow[Ar]{\text{Ball milling}} 21BaH_2 + 7BaAl_4 \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} 12Ba_2AlH_7 + 4BaAl_4$$

For the dehydrogenation of Ba_2AlH_7, there exists the possibility that Ba_2AlH_7 first partly dehydrogenates to form a mixture of BaH_2 and Al and then the latter further dehydrogenates to form BaH_2 and $BaAl_4$.

4. Conclusions

$BaAlH_5$ and Ba_2AlH_7 were successfully obtained through ball milling the mixture of commercially available BaH_2 and Al powder under H_2. With different mole ratios of BaH_2/Al (0.5, 1.0 and 2.0) the main phases were $BaAlH_5$, Ba_2AlH_7 and BaH_2, respectively. The ball milled BaH_2/Al system (1:1) under Ar first transformed into $3BaH_2$/$BaAl_4$. The mixture of BaH_2/$BaAl_4$ absorbed H_2 to form Ba_2AlH_7 during hydrogenation process and Ba_2AlH_7 released H_2 during the dehydrogenation process. With the increase of mea-

surement temperature from 260 °C to 305 °C the plateau pressure increases from 2.2 MPa to 3.2 MPa. The hydrogenation enthalpy of $BaH_2/BaAl_4$ (3:1) to form Ba_2AlH_7 was determined to be $-20.0\,kJ\,mol^{-1}$ from a van't Hoff plot.

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References

[1] F. Schüth, B. Bogdanović, M. Felderhoff, Chem. Commun. 20 (2004) 2249.
[2] L. Schlapbach, A. Züttel, Nature 414 (2001) 353.
[3] W. Grochala, P.P. Edwards, Chem. Rev. 104 (2004) 1283.
[4] K. Yvon, B. Bertheville, J. Alloys Compd. 425 (2006) 101.
[5] P. Chen, Z.T. Xiong, W.Z. Luo, K. Lin, K.L. Tan, Nature 420 (2002) 302.
[6] D. Chandra, J.J. Reilly, R. Chellappa, JOM 58 (2006) 26.
[7] J. Graetz, J.J. Reilly, J. Alloys Compd. 424 (2005) 262.
[8] S. Satyapal, J. Petrovic, C. Read, G. Thomas, G. Ordaz, Catal. Today 120 (2007) 246.
[9] T. Ichikawa, S. Isobe, N. Hanada, H. Fujii, J. Alloys Compd. 365 (2004) 271.
[10] V. Ozolins, E.H. Majzoub, T.J. Udovic, J. Alloys Compd. 375 (2004) 1.
[11] K.A. Lokshin, Y.S. Zhao, Appl. Phys. Lett. 88 (2006) 131909.
[12] L.C.J. Rowsell, O.M. Yaghi, J. Am. Chem. Soc. 128 (2006) 1304.
[13] H.W. Brinks, C.M. Jensen, S.S. Srinivasan, B.C. Hauback, D. Blanchard, K. Murphy, J. Alloys Compd. 376 (2004) 215.
[14] B. Bogdanović, M. Schwickardi, J. Alloys Compd. 253 (1997) 1.
[15] P. Wang, C.M. Jensen, J. Phys. Chem. B 108 (2004) 15827.
[16] K.J. Gross, G.J. Thomas, C.M. Jensen, J. Alloys Compd. 330 (2002) 683.
[17] B.C. Hauback, H.W. Brinks, C.M. Jensen, K. Murphy, A.J. Maeland, J. Alloys Compd. 358 (2003) 142.
[18] S. Chaudhuri, J. Graetz, A. Ignatov, J.J. Reilly, J.T. Muckerman, J. Am. Chem. Soc. 128 (2006) 11404.
[19] P. Canton, M. Fichtner, C. Frommen, A. Léon, J. Phys. Chem. B 110 (2006) 3051.
[20] G. Barkhordarian, T. Klassen, M. Dornheim, R. Bormann, J. Alloys Compd. 440 (2007) L18.
[21] Y. Nakamori, S. Orimo, T. Tsutaoka, Appl. Phys. Lett. 88 (2006) 112104.
[22] P. Vajeeston, P. Ravindran, R. Vidya, H. Fjellvag, A. Kjekshus, Cryst. Growth Des. 4 (2004) 471.
[23] H.Y. Leng, T. Ichikawa, S. Hino, N. Hanada, S. Isobe, H. Fujii, J. Phys. Chem. B 108 (2004) 8763.
[24] P. Chen, Z.T. Xiong, L.F. Yang, G.T. Wu, W.F. Luo, J. Phys. Chem. B 110 (2006) 14221.
[25] O.M. Løvvik, Phys. Rev. B 71 (2005) 144111.
[26] M. Mamatha, B. Bogdanović, M. Felderhoff, A. Pommerin, W. Schmidt, F. Schüth, C. Weidenthaler, J. Alloys Compd. 407 (2006) 78.
[27] R.A. Varin, C. Chiu, T. Czujiko, Z. Wronski, Nanotechnology 16 (2005) 2261.
[28] C. Weidenthaler, T.J. Frankcombe, M. Felderhoff, Inorg. Chem. 45 (2006) 3849.
[29] A. Klaveness, P. Vajeeston, P. Ravindran, H. Fjellvag, A. Kjekshus, Phys. Rev. B 73 (2006) 094122.
[30] T.N. Dymova, N.N. Mal'tseva, V.N. Konoplev, A.I. Golovanova, D.P. Aleksandrov, A.S. Sizareva, Russ. J. Coord. Chem. 29 (2003) 385.
[31] N.N. Mal'tseva, A.I. Golovanova, T.N. Dymova, D.P. Aleksandrov, Russ. J. Inorg. Chem. 46 (2001) 1793.
[32] F. Gingl, T. Vogt, E. Akiba, J. Alloys Compd. 306 (2000) 127.
[33] Q.A. Zhang, Y. Nakamura, K. Oikawa, T. Kamiyama, E. Akiba, Inorg. Chem. 41 (2002) 6547.
[34] Q.A. Zhang, Y. Nakamura, K. Oikawa, T. Kamiyama, E. Akiba, Inorg. Chem. 41 (2002) 6941.
[35] Q.A. Zhang, Y. Nakamura, K. Oikawa, T. Kamiyama, E. Akiba, J. Alloys Compd. 361 (2003) 180.
[36] J. Rodriguez-Carjaval, An Introduction to the Program FULLPROF2000, Version, July 2001, France.
[37] S. Orimo, Y. Nakamori, J.R. Eliseo, A. Züttel, C.M. Jensen, Chem. Rev. 107 (2007) 4111.