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New Alkaline Earth Aluminum Hydride with One-Dimensional Zigzag Chains of [AlH_6]: Synthesis and Crystal Structure of $BaAlH_5$

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The title hydride and its deuteride were successfully synthesized. The crystal structure of the deuteride was determined by time-of-flight neutron powder diffraction. $BaAlD_5$ crystallizes with a new orthorhombic structure in space group $Pna2_1$ (No. 33), cell parameters $a = 9.194(1)$ Å, $b = 7.0403(9)$ Å, and $c = 5.1061(6)$ Å, $Z = 4$. $BaAlH_5$ is the first example that contains one-dimensional zigzag chains of [AlH_6] along the crystallographic *c* axis.

Metal hydrides have been extensively studied concerning hydrogen storage applications. Recently alanates have attracted increasing attention because of their high hydrogen storage capacities.[1] Apart from AlH_3[2] and the alkali metal aluminum hydrides $LiAlH_4$,[3] $NaAlH_4$,[4] and Na_3AlH_6,[5] however, only a few alanates are known. Thus synthesis of new alanates is considered as a promising path to find potential candidates for hydrogen storage applications. Taking account of the fact that the alkaline earth metals show a richer chemistry with aluminum[6] and the compounds of alkaline earth metals are easily stabilized by hydrogen,[7] our studies have concentrated on alkaline earth metal aluminum hydrides. In the previous work, a Zintl hydride $SrAl_2H_2$[8] was synthesized by hydrogenating $SrAl_2$ under a hydrogen pressure of 5 MPa at about 473 K. This structure contained a two-dimensional polymer Zintl anion, in which one H atom is covalently bonded to each Al atom. In this paper we present the synthesis and structural characterization of a new barium aluminum hydride $BaAlH_5$ with high hydrogen capacity, which is the first example that contains one-dimensional zigzag chains of [AlH_6].

All steps of synthesis and sample preparation for X-ray and neutron diffraction were carried out under a dry argon atmosphere. Ba_7Al_{13} alloy was prepared by arc melting of Ba (Furuuchi Chemical, 99.9%) and Al (Furuuchi Chemical, 99.99%) metals. Before preparation, the loss of Ba during arc melting was determined to be about 3 wt %. On the basis of stoichiometric amounts of starting materials, thus, an extra 3 wt % of Ba was added to compensate the loss of Ba during arc melting. The alloy was remelted four times to ensure homogeneity in the arc melt furnace. The ingot was ground to powders with particle size smaller than 45 μm. The powder samples (∼2 g for preparing hydride and ∼6 g for preparing deuteride) were loaded into stainless steel containers and placed in stainless steel autoclaves. Initially, hydrogenation reaction was carried out under a hydrogen pressure of 7 MPa at 513 K for 5 days and the deuteride sample was prepared under a deuterium pressure of 7 MPa at 473 K for 10 days. The X-ray diffraction patterns for the samples showed that a novel hydride (or deuteride) along with Al was formed during the reactions. However, the neutron diffraction profiles for the deuteride sample showing significant background and peak broadening because of poor crystallization were unsuitable for structural determination. In order to obtain the neutron powder diffraction data with a higher quality, the deuteride sample was finally prepared under a deuterium pressure of 7 MPa at 473 K for 30 days. The reaction product was dark gray and sensitive to air. The deuterium content was measured to be 2.56 wt % using a hydrogen determinator LECO RH-402.

X-ray powder diffraction data of the final deuteride sample were obtained using a Rigaku RINT-2500V diffractometer equipped with a rotating anode generator of Cu Kα under the conditions of 50 kV and 200 mA. The X-ray diffraction pattern also showed that the sample contained the new phase and Al. After subtraction of the diffraction peaks of Al, the X-ray diffraction pattern was indexed by TREOR90[9] to an orthorhombic unit cell with $a = 9.19$ Å, $b = 7.04$ Å, and

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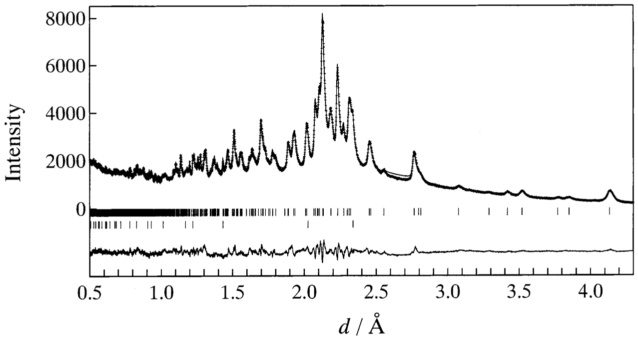

Figure 1. Observed and calculated neutron powder diffraction patterns of $BaAlD_5$. Reflection markers are for $BaAlD_5$ and Al (from above), respectively.

$c = 5.10$ Å. The reflection conditions ($0kl$, $k + l = 2n$; $h0l$, $h = 2n$; $h00$, $h = 2n$; $0k0$, $k = 2n$, and $00l$, $l = 2n$) led to the possible space groups $Pna2_1$ (No. 33) and $Pnam$ (No. 62). The structure was solved by the EXPO program[10,11] in space group $Pnam$ with the content BaAl ($Z = 4$), in which Ba and Al atoms occupied the special position 4c (x, y, $^1/_4$). Using this structural model, the Ba and Al positions were successfully refined from the X-ray diffraction data with the program RIETAN-97,[12] but all attempts to subsequently refine the deuterium positions from the neutron diffraction data were unsuccessful. Thus, the general position 4a (x, y, z) in the space group $Pna2_1$ was considered for the Ba and Al atoms. After refinement, the calculated and measured X-ray diffraction patterns were in good agreement.

Neutron powder diffraction data were collected at room temperature using a backward bank of a time-of-flight (TOF) diffractometer Vega[13] at the Neutron Science Laboratory of the High Energy Accelerator Research Organization, Tsukuba, Japan. The structure of the deuteride was refined in the space group $Pna2_1$ from the neutron diffraction data using the Rietveld refinement program RIETAN-2001T.[14] For the refinement, the initial Ba and Al atom coordinates were taken from those refined on the X-ray diffraction data and the deuterium positions were located by placing the atoms in the tetrahedral and octahedral holes formed by Ba and Al atoms. The occupation factors were also refined initially, but all the refined occupation factors were close to 1 (the differences were smaller than 3σ). Thus the occupation factors were fixed at unity for the final refinement. Figure 1 shows the observed and calculated neutron powder diffraction patterns of the deuteride sample. It can be seen that the refined pattern fits the observed data points very well ($R_{wp} = 4.95\%$, $R_p = 3.85\%$, $R_I = 6.97\%$, and $S = 3.10$).

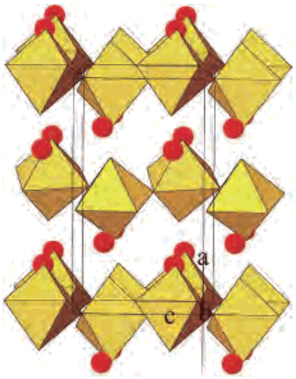

Figure 2. Crystal structure of $BaAlD_5$ viewed approximately along the b axis (a is vertical). The Ba atoms are represented as spheres, and the deuterium octahedra are centered by Al.

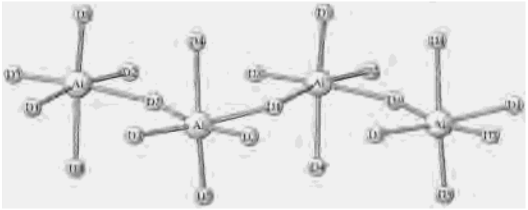

Figure 3. Zigzag chain of $[AlD_6]$ viewed along the b axis (a is vertical) in $BaAlD_5$.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) in $BaAlD_5$

Ba−D5	2.65(1)	D3−Al	1.73(3)
−D2	2.68(1)	−Ba	2.73(1)
−D3	2.73(1)	−Ba	2.77(1)
−D5	2.73(1)	−Ba	2.97(1)
−D4	2.74(2)	D4−Al	1.82(1)
−D3	2.77(1)	−Ba	2.74(2)
−D2	2.78(1)	−Ba	2.83(2)
−D1	2.81(1)	−Ba	2.91(1)
−D4	2.83(2)	D5−Al	1.69(1)
−D2	2.90(1)	−Ba	2.65(1)
−D4	2.91(1)	−Ba	2.73(1)
−D3	2.97(1)	−Ba	3.03(1)
−D1	3.02(1)	D1−Al−D1	96.1(5)
−D5	3.03(1)	D1−Al−D2	75.7(5)
−D1	3.71(1)	D1−Al−D3	162.8(7)
−D1	3.71(1)	D1−Al−D4	81.9(4)
Al−D5	1.69(1)	D1−Al−D5	87.8(4)
−D3	1.73(3)	D1−Al−D2	169.9(6)
−D2	1.76(2)	D1−Al−D3	97.9(4)
−D1	1.77(3)	D1−Al−D4	81.7(6)
−D4	1.82(1)	D1−Al−D5	84.2(5)
−D1	1.85(2)	D2−Al−D3	89.4(3)
D1−Al	1.77(3)	D2−Al−D4	91.3(5)
−Al	1.85(2)	D2−Al−D5	101.0(4)
−Ba	2.81(1)	D3−Al−D4	90.2(5)
−Ba	3.02(1)	D3−Al−D5	103.7(6)
−Ba	3.71(1)	D4−Al−D5	161.5(5)
−Ba	3.71(1)		
D2−Al	1.76(2)		
−Ba	2.68(1)		
−Ba	2.78(1)		
−Ba	2.90(1)		

From the Rietveld analysis, the deuteride can be determined to be $BaAlD_5$ with cell parameters $a = 9.194(1)$ Å, $b = 7.0403(9)$ Å, and $c = 5.1061(6)$ Å. The phase abundances of $BaAlD_5$ and Al were 88.8 and 11.2 wt %, respectively. Thus the deuterium content of the sample can be calculated as 2.62 wt %, which is in good agreement with the measured value 2.56 wt % by the volumetric method.

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The crystal structure of $BaAlD_5$ (Figure 2) contains Al-centered deuterium octahedra [AlD_6], which share one corner and form one-dimensional zigzag chains along the crystallographic *c* axis. Figure 3 shows the zigzag chain of [AlD_6], which exhibits the coordination environments around the Al atoms. As listed in Table 1, the Al−D bond lengths range from 1.69 to 1.85 Å. The average Al−D length (1.77 Å) is in good agreement with that in Na_3AlD_6 (1.75−1.77 Å).[5] By comparison, the octahedra in $BaAlD_5$ are rather distorted, which may be related to the larger size of Ba. The deuterium atoms exist in the tetrahedral and octahedral holes formed by Ba and Al atoms. In the former case the Ba−D distances (2.65−3.03 Å) compare well with those in binary BaD_2 (2.57−2.98 Å).[15] In the latter condition the Ba−D distances (2.81−3.71 Å) are in agreement with those in $Ba_7Cu_3D_{17}$ (2.59−3.68 Å).[16]

In conclusion, $BaAlH_5$ is structurally built up from [AlH_6] octahedra, which share one corner and form one-dimensional zigzag chains. Because of this interesting arrangement of hydrogen atoms, $BaAlH_5$ has a larger H/M ratio (where H and M indicate hydrogen and metals, respectively) than $NaAlH_4$ and Na_3AlH_6. If some light elements can be used as substitutes for Ba, the weight percent of hydrogen will increase considerably. Further investigations are in progress.

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Supporting Information Available: Description of the structural refinement of $BaAlD_5$. Tables listing detailed atomic coordinates and isotropic thermal displacement parameters for $BaAlD_5$. This material is available free of charge via the Internet at http://pubs.acs.org.

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