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Synthesis and crystal structure of β-AlD_3

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Abstract

β-AlD_3 was synthesized from $LiAlD_4$ and $AlCl_3$ via thermal decomposition of aluminum hydride etherate in presence of $LiBH_4$ and excess $LiAlD_4$. β-AlD_3 was determined by powder neutron diffraction and synchrotron X-ray diffraction to take the pyrochlore structure and it crystallizes in space group $Fd\bar{3}m$. The cubic structure has unit-cell dimension $a = 9.0037(1)$ Å and consists of corner-sharing AlD_6 octahedra where each hydrogen is shared between two octahedra. Each of the six octahedra surrounding an octahedron is interconnected to two of the other surrounding octahedra. The octahedra are forming a 3D network with about 3.9 Å channels. There is one Al and one D crystallographic site and the Al-D distance is 1.712(1) Å.

Keywords: Powder neutron diffraction; Synchrotron radiation; Metal hydrides; Alane

1. Introduction

AlH_3 (alane) is one of the solid compounds with the largest hydrogen content (10.1 wt.%) and is therefore of interest for hydrogen storage applications. AlH_3 has been found to take at least six different crystal structures depending on the synthesis route [1]: α, α′, β, γ, δ and ε. The two latter structure modifications have not been synthesized reproducibly and been suspected to be caused by impurities [1].

α-AlH_3 is the most stable phase [1]. In accordance with its small dehydrogenation enthalpy of 7.6 kJ/mol H_2 [2], it has an equilibrium pressure of more than 10^4 bar at room temperature. β-AlH_3 and γ-AlH_3 were determined by differential scanning calorimetry to be less stable [3–5]. Nevertheless, α-AlH_3 is kinetically stable and can be stored for several years [6].

Powder X-ray diffraction fingerprints for the different AlH_3 phases were given by Brower et al. [1], but until recently, α-AlH_3 was the only alane phase with a complete crystal structure determination [7]. α-AlD_3 crystallizes in space group $R\bar{3}c$ with AlD_6 octahedra sharing all corners with one other octahedron. For α′-AlD_3, all AlD_6 octahedra share all corners with one other octahedron, but in a different way than α-AlD_3, giving rise to a β-AlF_3 related structure with space group *Cmcm* [8].

AlH_3 has typically been synthesized from $LiAlH_4$ and $AlCl_3$ in diethyl ether resulting in an adduct with 0.25–0.30 Et_2O per AlH_3. By adding $LiAlH_4$ or $LiBH_4$, the ether is removed and AlH_3 crystallizes usually in the α, β or γ structure depending on the conditions [1]. α′-AlH_3 is formed by heating an ethereal solution under pressure.

In the present work, β-AlD_3 was synthesized by the method described by Brower et al. [1] β-AlD_3 was obtained in about 90% purity, the balance of material being mainly γ-AlD_3. The crystal structure was determined by synchrotron-radiation powder X-ray diffraction (SR-PXD) and powder neutron diffraction (PND).

2. Experimental

$LiAlD_4$ (≥98 wt.% purity) and $LiBH_4$ (≥95 wt.% purity) were purchased from Aldrich. $AlCl_3$ (≥99 wt.% purity) was purchased from Alfa. The $LiAlD_4$ was purified via Soxhlet extraction.

Diethyl ether (Fischer Scientific, certified ACS, 99.9% purity) solutions of $LiAlD_4$ (2.500 g, 90 ml Et_2O), $LiBH_4$ (0.647 g, 60 ml Et_2O) and $AlCl_3$ (2.000 g, 18.75 ml Et_2O) were prepared. The $LiAlD_4$ solution was added to the $AlCl_3$

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Table 1
Refined structural parameters for β-AlD_3

Atom	x	y	z	B (Å^2)
Al	½	0	0	1.19(6)
D	0.4301(1)	1/8	1/8	1.83(2)

The space group is $Fd\bar{3}m$, $Z = 16$, and the unit-cell dimension is 9.0037(1) Å. Reliability factors are $R_{wp} = 7.27\%$ and $\chi^2 = 2.69$ for the SR-PXD data and $R_{wp} = 5.85\%$ and $\chi^2 = 2.34$ for the PND data. Estimated standard deviations in parentheses.

solution in a 4:1 molar ratio at room temperature and stirred for 2–3 min. LiCl was filtered by a medium grade glass filter, and the $LiBH_4$ solution was added to the filtrate. The molar ratio between $LiBH_4$ and the original amount of $LiAlD_4$ was 1:2. Diethyl ether was removed overnight under vacuum at 35 °C. The product was ground to a fine powder and heated at 65 °C in a pre-heated oil bath for 2 h. The final β-AlD_3 was obtained by washing with diethyl ether with subsequent drying at room temperature overnight under vacuum. β-AlH_3 has been reported to be soluble in Et_2O [9], but at least at the time scale of the present washing with Et_2O, this is not a significant effect.

PND data at 22 °C were collected with the PUS instrument at the JEEP II reactor at Kjeller (Norway) [10]. Neutrons with λ = 1.5553 Å were obtained from a Ge(5 1 1) focussing monochromator. The detector unit consists of two banks of seven position-sensitive ^{3}He detectors, each covering 20° in 2θ (binned in steps of 0.05°). The sample was placed in a rotating cylindrical vanadium sample holder with 6 mm diameter.

SR-PXD data at 22 °C were collected at the Swiss-Norwegian beam line (station BM01B) at the European synchrotron radiation facility (ESRF) in Grenoble, France. The samples were kept in rotating 0.8 mm boron-silica-glass capillaries. Intensities were measured in steps of $\Delta(2\theta) = 0.0035°$. The wavelength 0.50059 Å was obtained from a channel-cut Si(1 1 1) monochromator.

Rietveld refinements were carried out using the program Fullprof (version 2.8) [11]. The neutron scattering lengths and the X-ray form factors were taken from the Fullprof library. Thompson-Cox-Hastings pseudo-Voigt profile functions were used, and the background was modelled by interpolation between manually chosen points. The instrumental resolution of SR-PXD was found by a LaB_6 standard.

3. Results and discussion

Based on the SR-PXD and PND data, β-AlD_3 was indexed to be cubic with a unit-cell dimension of ~9 Å. F-centering was determined from the systematic extinctions of reflections. A structure type that is in line with this is the pyrochlore-type structure (space group $Fd\bar{3}m$), as e.g. FeF_3 takes. Recently, Ke et al. [12] optimised such an alane modification by density functional theory. This model was taken as a starting point for the present Rietveld refinements of β-AlD_3.

Combined Rietveld refinement of PND and SR-PXD data (Fig. 1), measured less than 2 weeks after the synthesis of the sample, was carried out and the results of the refinements are given in Table 1. Table 2 contains selected distances and angles.

The sample contained, according to Rietveld refinements, 89.5 mol% β-AlD_3, 9.4 mol% γ-AlD_3, 0.9 mol% α-AlD_3 and 0.1 mol% Al. The structural model of γ-AlD_3 was taken from Ref. [13]. Brower et al. [1] reported that, even with extensive synthesis over a long period, they did never succeeded in preparation of phase-pure β-AlH_3. On this background, the present sample is considered of high purity, and it is reliable for crystal structure determination. Furthermore, the crystallinity is very

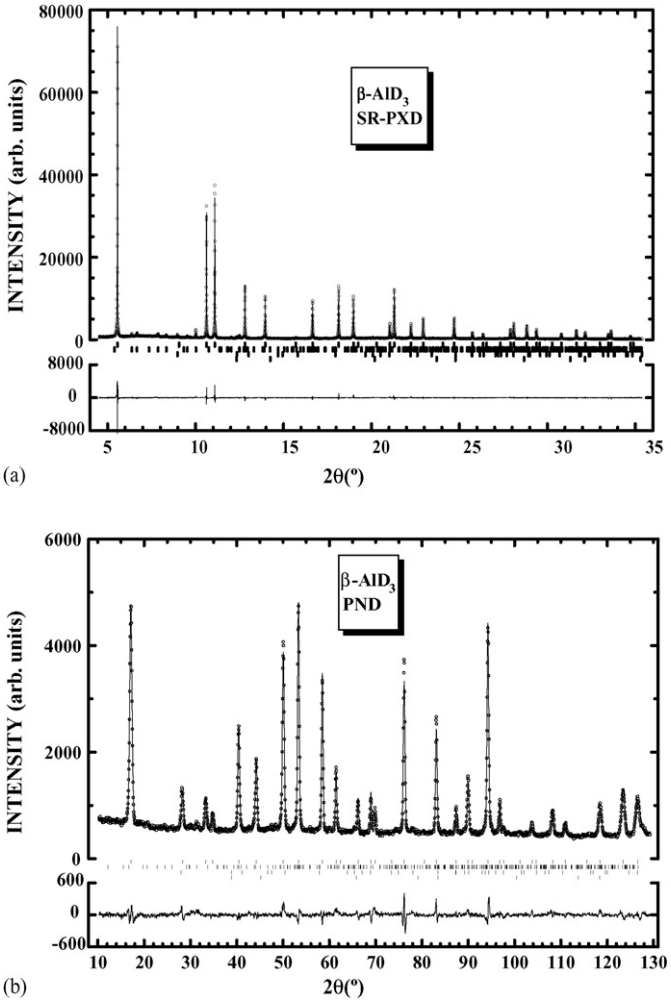

Fig. 1. Observed intensities (circles) and calculated intensities from Rietveld refinements (upper line) of for β-AlD_3 at 22 °C for (a) SR-PXD (BM01B, ESRF) and (b) PND (PUS, Kjeller) data. Positions of Bragg reflections are shown with bars for β-AlD_3, γ-AlD_3, α-AlD_3 and Al (from top). The difference between observed and calculated intensity are shown with the bottom line.

good with an estimated crystallite size, based on broadening of SR-PXD reflections, of 175 nm and with an isotropic strain of 0.04%.

The atomic arrangement is shown in Fig. 2. The structure consists of corner-sharing AlD_6 octahedra. There is only one

Table 2
Selected inter-atomic distances (Å) and angles (°) in the crystal structure of β-AlD_3

Atoms	Distances			
Al-D	1.712(1)			
D-D	2.358(1)	2.482(1)		
Al-Al	3.183(1)			
Atoms	**Angles**			
D-Al-D	87.07(2)	92.93(2)	179.99(2)	180.00(2)
Al-D-Al	136.83(3)			

Estimated standard deviations in parentheses.