

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/ijhydene](http://www.elsevier.com/locate/ijhydene)

## Metal aluminum amides for hydrogen storage – Crystal structure studies

Satoshi Hino<sup>a</sup>, Hilde Grove<sup>a</sup>, Takayuki Ichikawa<sup>b</sup>, Yoshitsugu Kojima<sup>b</sup>, Magnus H. Sørby<sup>a,\*</sup>, Bjørn C. Hauback<sup>a</sup>

<sup>a</sup> Physics Department, Institute for Energy Technology, P.O. Box 40, NO-2027 Kjeller, Norway

<sup>b</sup> Institute for Advanced Materials Research, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan

### ARTICLE INFO

#### Article history:

Received 18 December 2014

Accepted 1 May 2015

Available online 27 May 2015

#### Keywords:

Hydrogen storage materials

Powder neutron diffraction

Powder X-ray diffraction

Ball-milling

### ABSTRACT

Crystal structure of metal aluminum amides has been investigated by synchrotron radiation powder X-ray diffraction (SR-PXD) and powder neutron diffraction (PND). Alkali and alkaline-earth metal aluminum amides  $M[Al(NH_2)_4]_x$  desorb ammonia during thermal decomposition and have recently been studied as possible hydrogen storage system by making composites with metal hydrides. In this work, deuterated metal aluminum amides  $M[Al(ND_2)_4]_x$  with  $M = Li, Na, K, Mg$  and  $Ca$  were synthesized by ball-milling of  $M$  (or  $MD_x$ ) +  $Al$  (or  $AlD_3$ ) under liquid  $ND_3$ . The crystal structures of  $MAl(ND_2)_4$  phases with  $M = Li, Na, K$  ( $\alpha$ -phase) have been refined by simultaneous Rietveld refinement using PND and SR-PXD data. Structure determination was successful for  $\beta$ - $KAl(ND_2)_4$  and  $Ca[Al(ND_2)_4]_2$ . The structures are composed of  $[Al(ND_2)_4]^-$  tetrahedra and  $M$  cations, and the unit cells are:  $M = Li$ ; monoclinic space group  $P2_1/n$ ,  $a = 9.5075(3)$  Å,  $b = 7.3610(2)$  Å,  $c = 7.4076(2)$  Å,  $\beta = 90.165(3)^\circ$ ,  $Na$ ; monoclinic space group  $P2_1/c$ ,  $a = 7.3317(9)$  Å,  $b = 6.0447(8)$  Å,  $c = 13.151(2)$  Å,  $\beta = 94.110(9)^\circ$ ,  $K$  ( $\alpha$ -phase); orthorhombic space group  $C222_1$ ,  $a = 10.17258(7)$  Å,  $b = 5.78762(5)$  Å,  $c = 9.98651(7)$  Å,  $K$  ( $\beta$ -phase); orthorhombic space group  $Pnma$ ,  $a = 11.4183(4)$  Å,  $b = 8.8588(2)$  Å,  $c = 6.1696(2)$  Å, and  $Ca$ ; monoclinic space group  $Pc$ ,  $a = 6.4321(2)$  Å,  $b = 6.4377(2)$  Å,  $c = 12.2939(3)$  Å,  $\beta = 90.612(2)^\circ$ . The structural features of metal aluminum amides have been compared with the corresponding alanates.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

### Introduction

Utilization of hydrogen as an energy carrier is one of the key challenges in developing a carbon-neutral energy economy. Compact and safe way to store hydrogen is necessary [1], and one of the candidates is hydrogen storage in solid materials which possess high volumetric hydrogen capacity. Complex

hydrides, e.g., metal alanates  $M(AlH_4)_x$  where hydrogen is covalently bonded with  $Al$  to make complex anion, have high gravimetric hydrogen capacity and have been studied as one of the most promising hydrogen storage materials [2]. For example,  $LiAlH_4$  can store 10.5 mass% hydrogen, however the irreversibility of the hydrogen desorption reaction is challenging.  $NaAlH_4$  with transition metal additives shows good

\* Corresponding author. Tel.: +47 6380 6000; fax: +47 6381 0920.

E-mail address: [magnuss@ife.no](mailto:magnuss@ife.no) (M.H. Sørby).

<http://dx.doi.org/10.1016/j.ijhydene.2015.05.012>

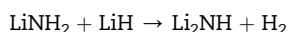
0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

**Table 1 – Crystal structure data of metal aluminum amides and related compounds. Lattice constants (*a*, *b*, *c* and  $\beta$ ), unit cell volume (*V*) and formula units per unit cell (*Z*). “\*” denotes compounds where atomic positions have been reported. Estimated standard deviations are given in parentheses when reported.**

Compound	Space group	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	$\beta$ (°)	<i>V</i> /Å <sup>3</sup>	<i>Z</i>	Ref.
LiAl(NH <sub>2</sub> ) <sub>4</sub>	P2 <sub>1</sub> /n	9.478(1)	7.351(1)	7.398(1)	90.26(1)	519.39	4	[11]*
NaAl(NH <sub>2</sub> ) <sub>4</sub>	P2 <sub>1</sub> /c	7.328(2)	6.047(2)	13.151(3)	94.04(1)	581.3	4	[12]*
Na <sub>2</sub> Al(NH <sub>2</sub> ) <sub>5</sub>	Cmma or Abm2	23.56	19.36	6.78	90	3092.5	16	[17]
$\alpha$ -KAl(NH <sub>2</sub> ) <sub>4</sub>	C222 <sub>1</sub>	10.00(1)	5.80(1)	10.14(1)	90	588.12	4	[13]*
$\beta$ -KAl(NH <sub>2</sub> ) <sub>4</sub>	Pnma	11.37(1)	8.85(1)	6.146(6)	90	618.44	4	[10]
RbAl(NH <sub>2</sub> ) <sub>4</sub>	P4/n	7.406(4)	7.406(4)	5.386(4)	90	295.42	2	[14]*
CsAl(NH <sub>2</sub> ) <sub>4</sub>	P4/n	7.563(3)	7.563(3)	5.354(1)	90	306.24	2	[14]*
Mg[Al(NH <sub>2</sub> ) <sub>4</sub> ] <sub>2</sub>	Hexagonal	12.1	12.1	7.95	90	1008.02	N/A	[5]
Ca[Al(NH <sub>2</sub> ) <sub>4</sub> ] <sub>2</sub>	Monoclinic	12.27	6.44	6.43	90.7	508.05	N/A	[5]
Ca[Al(NH <sub>2</sub> ) <sub>4</sub> ] <sub>2</sub> ·NH <sub>3</sub>	I2/c	10.189(9)	9.897(11)	12.151(12)	98.60(15)	1211.54	4	[18]*
CaAl(NH <sub>2</sub> ) <sub>5</sub>	P4 <sub>2</sub> 22	6.471(5)	6.471(5)	12.244(9)	90	512.70	4	[19]
Sr[Al(NH <sub>2</sub> ) <sub>4</sub> ] <sub>2</sub>	P6 <sub>2</sub> , P6 <sub>4</sub> , P6 <sub>2</sub> 22, or P6 <sub>4</sub> 22	17.49(1)	17.49(1)	28.17(2)	90	7462.72	36	[15]
Ba[Al(NH <sub>2</sub> ) <sub>4</sub> ] <sub>2</sub> ·2NH <sub>3</sub>	R-3c	15.7370(17)	15.7370(17)	28.840(6)	90	6177.71	18	[16]*

cyclability, however the practical reversible capacity is only around 4 wt% H [3].

Metal aluminum amides (tetra-amido-aluminates), M [Al(NH<sub>2</sub>)<sub>4</sub>]<sub>x</sub>, consist of complex ion of Al tetrahedrally coordinated by four NH<sub>2</sub><sup>-</sup>, Al(NH<sub>2</sub>)<sub>4</sub><sup>-</sup> and balancing alkali or alkaline-earth metal cations, M<sup>x+</sup>. They can thus be regarded as metal alanates where the hydrogen atoms have been substituted by NH<sub>2</sub>. The compounds desorb NH<sub>3</sub> during thermal decomposition and the NH<sub>3</sub> desorption properties have been investigated with temperature-programmed-desorption coupled with a mass spectrometer (TPD-MS), revealing that the main NH<sub>3</sub> release occurs in the range 50–150 °C for M [Al(NH<sub>2</sub>)<sub>4</sub>]<sub>x</sub> (M = Li, Na, K, Mg and Ca) [4,5]. Analogously to the amide-imide system [6], NH<sub>3</sub> desorption in metal aluminum amides can be replaced by H<sub>2</sub> desorption by making composites with alkali metal hydrides, therefore the compounds have recently been studied as hydrogen storage materials. The lithium amide-imide system desorbs ~6.5 mass% H<sub>2</sub> at 255 °C through the following reaction [6].



For more unstable amides the H<sub>2</sub> desorption temperature is decreased, e.g., the composite LiH–LiAl(NH<sub>2</sub>)<sub>4</sub> can desorb up to 6.2 mass% hydrogen at 130 °C [7].

The reactions between Al and solution of alkali metals (Li, Na, K, Rb and Cs) in liquid NH<sub>3</sub> result in single crystals of the alkali metal aluminum amides and the unit cell parameters of these compounds have been investigated by powder and single crystal diffraction [8–10]. The crystal structures of LiAl(NH<sub>2</sub>)<sub>4</sub>, NaAl(NH<sub>2</sub>)<sub>4</sub>,  $\alpha$ -KAl(NH<sub>2</sub>)<sub>4</sub>, RbAl(NH<sub>2</sub>)<sub>4</sub> and CsAl(NH<sub>2</sub>)<sub>4</sub> have been

reported from single crystal X-ray diffraction measurements [11–14]. The structure models included hydrogen positions, but they are regarded as uncertain due to their low X-ray scattering power. The space groups and unit cell parameters of MAl(NH<sub>2</sub>)<sub>4</sub> for M = Li, Na,  $\alpha$ -K, Rb and Cs respectively, are P2<sub>1</sub>/n, *a* = 9.478(1) Å, *b* = 7.351(1) Å, *c* = 7.398(1) Å,  $\beta$  = 90.268(1)°; and P2<sub>1</sub>/c, *a* = 7.328(2) Å, *b* = 6.047(2) Å, *c* = 13.151(3) Å,  $\beta$  = 94.04°; and C222<sub>1</sub>, *a* = 10.00(1) Å, *b* = 5.80(1) Å, *c* = 10.14(1) Å; and P4/n, *a* = 7.406(4) Å, *c* = 5.386(4) Å; and P4/n, *a* = 7.563(3) Å, *c* = 5.354(1) Å. The crystal structure data are summarized in Table 1 together with those of other known metal aluminum amides and related compounds. Brec and Rouxel [10] have reported the space group and unit cell parameters of  $\beta$ -KAl(NH<sub>2</sub>)<sub>4</sub>: Pnma, *a* = 11.37(1) Å, *b* = 8.85(1) Å, *c* = 6.146(6) Å but without atomic positions. Recently, a study on structures and bonding of alkali metal aluminum amides investigated by IR spectroscopy supported by DFT calculations has been reported [4]. For group 2 elements, the crystal structures of Mg[Al(NH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> and Ca[Al(NH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> are unknown except for their unit cell parameters: hexagonal (*a* = 12.10 Å and *c* = 7.95 Å) and monoclinic (*a* = 12.27 Å, *b* = 6.44 Å, *c* = 6.43 Å, and  $\beta$  = 90.7°) unit cells, respectively [5]. Furthermore Sr[Al(NH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> and Ba[Al(NH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> have been synthesized [15]. The unit cell parameters of Sr [Al(NH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> were determined (hexagonal, *a* = 17.49(1) Å, *c* = 28.17(2) Å), but Ba[Al(NH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> was unstable at ambient conditions without ammonia pressure. Recently, low-temperature single crystal measurement has revealed the crystal structure of Ba[Al(NH<sub>2</sub>)<sub>4</sub>]<sub>2</sub>·2NH<sub>3</sub> synthesized by an ammonothermal method [16].

In the present work, deuterated metal aluminum amides M [Al(ND<sub>2</sub>)<sub>4</sub>]<sub>x</sub>, with M = Li, Na, K, Mg and Ca, were synthesized,

**Table 2 – Summary of experimental conditions for the ball-milling to synthesize the metal aluminum amides.**

Milled materials	Molar ratio	Milling atmosphere	Milling time <sup>a</sup>	Additional treatment
LiAl(ND <sub>2</sub> ) <sub>4</sub>	LiD + Al	Ar (1 MPa)	20 h	Annealing under liq. ND <sub>3</sub> at 100 °C for 2 weeks
NaAl(ND <sub>2</sub> ) <sub>4</sub>	NaD + AlD <sub>3</sub>	Liq. ND <sub>3</sub>	4 h	Kept for 1 week under liq. ND <sub>3</sub> at RT
KAl(ND <sub>2</sub> ) <sub>4</sub>	KD + AlD <sub>3</sub>	Liq. ND <sub>3</sub>	4 h	Kept for 1 week under liq. ND <sub>3</sub> at RT
Mg[Al(ND <sub>2</sub> ) <sub>4</sub> ] <sub>2</sub>	Mg + Al	Liq. ND <sub>3</sub>	8 h	Kept for 1 week under liq. ND <sub>3</sub> at RT
Ca[Al(ND <sub>2</sub> ) <sub>4</sub> ] <sub>2</sub>	CaD <sub>2</sub> + Al	Liq. ND <sub>3</sub>	10 h	Kept for 1 week under liq. ND <sub>3</sub> at RT

<sup>a</sup> Active milling time (without pauses).

Download English Version:

<https://daneshyari.com/en/article/1278391>

Download Persian Version:

<https://daneshyari.com/article/1278391>

[Daneshyari.com](https://daneshyari.com)