Journal of Alloys and Compounds 509 (2011) 10–14

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Experimental and computational investigations on the AlH_3/AlF_3 system

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ARTICLE INFO

Article history:
Received 26 June 2010
Received in revised form 26 August 2010
Accepted 27 August 2010
Available online 6 September 2010

Keywords:
Energy storage materials
Metal hydrides
Mechanochemical synthesis
Thermodynamic modelling
Thermodynamic properties
Phase diagrams

ABSTRACT

The possibility of changing the thermodynamic properties of AlH_3, alane, by fluorine anion substitution has been investigated by experimental measurements, *ab initio* calculations and thermodynamic modelling. No solid solution phases are observed experimentally. In accordance to this the calculations give a positive free energy of mixing for all compositions, showing that a mixed phase is not thermodynamically favourable. Thus fluorine anion substitution does not seem feasible for the alane system.

1. Introduction

The main challenge for introduction of the “hydrogen economy” is efficient storage of hydrogen, and metal hydrides are potential candidates as solid hydrogen storage materials. Aluminium hydride, alane, is a potential hydrogen storage media because of its high gravimetric content of hydrogen (10.1 wt%) and hydrogen release at moderate temperatures [1,2]. This has led to extensive studies of AlH_3 in the latest years [3–9]. AlH_3 has been found to take at least six different crystal structures, depending on the synthesis route: α, α', β, γ, δ and ε [10]. α-AlH_3 is the most stable polymorph, its dehydrogenation enthalpy has been measured to be positive and equal to 7.6 kJ/mol H_2 [11], giving a very high equilibrium pressure, in the kilobar range even at ambient temperature. Thus, alane is a metastable hydride and not possible to rehydrogenate at non-extreme conditions. α-AlH_3 is kinetically stabilized by an oxide layer of Al_2O_3 and can be stored for years [1,12–14]. The other polymorphs are less stable; γ-AlH_3 is found to release hydrogen at room temperature [10], and both β- and γ-AlH_3 decompose to α-AlH_3 during storage [8]. α'-AlH_3 is reported to release hydrogen at 40 °C [5].

It is well known that many hydrides are isostructural with the corresponding fluorides [15,16]. For alane this is valid as α-AlH_3 takes the same structure as α-AlF_3, a rhombohedral structure with space group R-3c (167) [5]. α'-AlH_3 is isostructural to β-AlF_3, taking an orthorhombic space group Cmcm (63) [6]. The difference in thermodynamic properties between the hydrides and the fluorides leads to the idea of substitution of fluoride into the hydride structure and thereby changing the thermodynamics of the hydride. This effect was experimentally shown in the NaH–Al–F-system both by Brinks et al. [17] and Eigen et al. [18], who prepared a $Na_3AlH_{6-x}F_x$ phase with far lower stability than Na_3AlH_6. Brinks et al. reported the value of x to be approximately 4. The effect of halide anion substitution in alanates and borohydrides has lately been thoroughly investigated for several systems both experimentally and by computational methods [19–24].

Combining experimental investigations and modelling efforts can in many aspects give complementary information. Computational modelling provides valuable information of a wide range of compositions in a material system, while experiments may reveal metastable phases or unforeseen reaction products. With the continuous rapid increase in computational power and the development of robust and reliable first-principles software, *ab initio* data are extensively used as CALPHAD [25] input for calculations of phase diagrams [26]. The scope of the present work is to investigate whether fluorine anion substitution could be achieved in AlH_3 and possibly changing the thermodynamics in a favourable manner with respect to hydrogen storage by stabilization of the compound. A coupled *ab initio*/CALPHAD study has been carried out to investigate the thermodynamic behaviour of the AlH_3–AlF_3 solid solution, and an experimental

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doi:10.1016/j.jallcom.2010.08.147

Table 1
Sample preparation conditions.

Sample no.	Mixture	Cryo milling time	Theoretical H:F or D:F ratio
1	$3LiAlD_4 + AlCl_3 \rightarrow 4AlD_3 + 3LiCl$	1 h	–
2	$3NaAlH_4 + AlCl_3 \rightarrow 4AlH_3 + 3NaCl$	1 h	–
3	$3LiAlD_4 + AlCl_3 + 12NaF$	1 h	1:1
4	$3LiAlD_4 + AlCl_3 + 4AlF_3$	1 h	1:1
5	$3LiAlD_4 + AlCl_3 + TiF_3$	15, 30 min	4:1
6	$3NaAlH_4 + AlCl_3 + AlF_3$	1 h	4:1
7	$4AlD_3$ (+3LiCl) + 3NaF	5, 10, 15, 30 min	4:1
8	$4AlD_3$ (+3LiCl) + AlF_3	5, 10 min	4:1
9	$4AlD_3$ (+3LiCl) + TiF_3	5, 10, 15 min	4:1
10	$4AlH_3$ (+3NaCl) + AlF_3	15 min	4:1
11	$4AlH_3$ (+3NaCl) + 3NaF	15 min	4:1

screening of adding different fluorides to alane has been performed.

2. Methods

2.1. Synthesis and characterization

The samples were made by mechanochemical synthesis at liquid nitrogen temperatures by cryo milling. AlD_3 was prepared according to reaction (1) [5]:

$$3LiAlD_4 + AlCl_3 \rightarrow 4AlD_3 + 3LiCl \quad (1)$$

Alternatively AlH_3 was obtained through a similar reaction (2) [27]:

$$3NaAlH_4 + AlCl_3 \rightarrow 4AlH_3 + 3NaCl \quad (2)$$

Samples were made from commercial starting materials: $LiAlD_4$ (Armar Chemicals, ≥98% purity), $NaAlH_4$ (Albermarle, >99% purity), $AlCl_3$ (Merck, 98% purity), NaF (Sigma Aldrich, 99.99% purity), TiF_3 (Aldrich), AlF_3 (Alfa Aesar, 99.99% purity), AlF_3 (Fluorsid, single phase). According to reactions (1) and (2) alane was made from either sodium- or lithium alanate. In the case of reaction (1) the deuterated lithium alanate, $LiAlD_4$, was used because high purity $LiAlH_4$ is not commercially available. Thus samples made from reaction (1) contain AlD_3 while samples made from reaction (2) contain AlH_3. The purchased AlF_3-powder from Alfa Aesar showed multiphase diffraction signals, and because of problems analyzing the sample data a batch of single phase AlF_3 was provided from Fluorsid to make some additional samples.

Samples were cryo milled in a Spex 6770 mill, using a stainless steel or polyethylene vial and a stainless steel impactor of 32 g. The study was performed as a screening study, making samples at different conditions. Commercial AlF_3, NaF and TiF_3 were used as sources of fluoride. Two methods were tested to facilitate fluoride substitution. For some samples the additive was present in the synthesis of alane, by including the additive among the starting materials in reaction (1) or (2). In other samples the fluoride was cryo milled with the AlD_3/AlH_3 after the alane synthesis. Sample preparation conditions are listed in Table 1.

All material handling was done under purified argon (<0.1 ppm O_2, <0.1 ppm H_2O) in an MBraun glove box.

Powder X-ray diffraction (PXD) was performed with a Bruker-AXS D8 advance diffractometer equipped with a Göbbel mirror and a LynxEye^{TM} 1D silicon strip detector. Sample powders were contained in sealed, rotating glass capillaries, and pure Si powder (ABCR, 99.999% purity) was added as an internal standard. Some samples were investigated by synchrotron radiation powder X-ray diffraction (SR-PXD) at the Swiss-Norwegian beam line (SNBL) at the European synchrotron radiation facility (ESRF) in Grenoble, France. High resolution SR-PXD-data were collected at station BM01B. The samples were kept in rotating 0.5 mm boron–silica–glass capillaries. Intensities were measured in steps of $(2\theta) = 0.0035^\circ$ with 6 scintillation detectors with secondary monochromators mounted with 1.1° separation. The wavelength of $\lambda = 0.50271151$ Å was obtained from a channel-cut Si (1 1 1) monochromator. Some data were also collected at station BM01A (SNBL, ESRF). Two-dimensional powder data were collected using an imaging plate system (MAR345) with an exposure time of 30 s. The samples were kept in 0.5 mm boron–silica–glass capillaries and rotated 30° during the exposure. The wavelength was $\lambda = 0.65478$ Å. The two-dimensional data were converted into one-dimensional powder diffraction patterns with the program Fit2d [28]. Data were collected in the 2θ range of 1–34.5° and were rebinned with a step size of 0.02°.

Rietveld refinements were done using the programs Fullprof [29], GSAS [30] and EXPGUI [31]. The X-ray form factor coefficients were taken from the Fullprof or GSAS libraries. A pseudo-Voigt profile function was used to describe the peak shapes, and the background was described by interpolation between manually selected points or refined with a polynomial. Structural parameters were taken from the published structural data of the individual phases and only refined when appropriate.

2.2. Computational investigations

Ab initio calculations based on DFT GGA Hamiltonian (PBE [32]) were carried out with the periodic CRYSTAL06 [33,34] code and localized basis set functions of polarized double-ζ quality.

To simulate the formation of the AlH_3/AlF_3 solid solution, the pure compound structures in their most stable phases at room temperature (α-phase, trigonal lattice, space group R-3CH, n.167) were first fully optimized (both lattice parameters and internal coordinates), using X-ray and neutron powder diffraction data as a starting point [35,36]. Phonons at gamma point in the harmonic approximation were computed to derive the thermodynamic functions (for details on the computational procedure see Refs. [37,38]). Calculation of phase diagram has been carried out with Thermo-Calc software [39].

3. Results and discussion

Hydrides and corresponding fluorides that take the same crystal structure usually have significantly different unit cell parameters. As an example, LiH has $a = 4.0750$ Å while for LiF $a = 4.027$ Å. For α-AlH_3 $a = 4.436$ Å while for α-AlF_3 $a = 4.93$ Å. For α′-AlH_3 $a = 6.470$ Å and the corresponding β-AlF_3 has $a = 6.963$ Å. Anion substitution of fluoride in the hydride will therefore change the unit cell parameters. Such changes should be clearly detectable by changes in positions of the Bragg peaks in a diffraction experiment. All samples were therefore investigated by PXD. The two approaches of adding fluoride to the samples, described above, gave different results.

3.1. Fluorides present in the initial mix of reactants

To possibly directly synthesize fluoride substituted alane, selected fluorides were included among the starting materials in reactions (1) and (2). No AlD_3 was observed after the synthesis of sample 3 made from $LiAlD_4$, $AlCl_3$ and NaF. According to reaction (1) LiCl would be expected in the sample, but the presence of NaF in the cryo milling gave formation of $NaAlD_4$ and NaCl instead of LiCl. In addition some Na_3AlF_6 was present after synthesis. In situ SR-PXD of the sample during heating at a rate of 2 K/min showed that the content of Na_3AlF_6 increased at 90 °C, and the decomposition of $NaAlD_4$ at around 150 °C gave a further increase in the intensities of the Na_3AlF_6 peaks.

In sample 4 made from $LiAlD_4$, $AlCl_3$ and AlF_3, no AlD_3 was observed. In sample 5 with $LiAlD_4$, $AlCl_3$ and TiF_3, no AlD_3 was formed, but AlF_3 was observed indicating a reaction between $AlCl_3$ and TiF_3 to form AlF_3. For sample 6 prepared from $NaAlH_4$, $AlCl_3$ and AlF_3, AlH_3 was formed, but no change in the unit cell parameters was observed. The AlF_3 stayed unreacted. There was a significant content of Al, indicating that a larger amount of AlH_3 has possibly formed and partly decomposed in the synthesis.

3.2. Fluorides added to pre-made alane

AlD_3 and AlH_3 were synthesized according to reaction (1) and (2), respectively, as earlier reported by Brinks et al. [5] and Sartori et al. [27]. These mixtures were also used as reference samples.

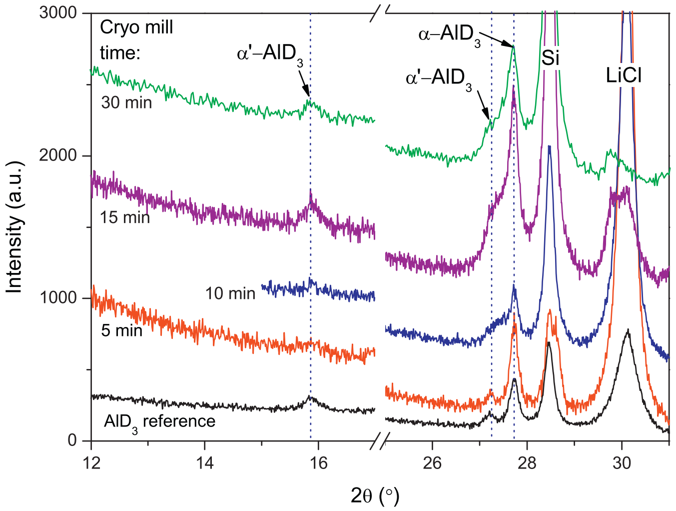

Fig. 1. AlD_3 cryo milled with NaF (sample 7) for varying milling times. No change in position of the reflections is seen. The label Si corresponds to the Bragg peaks for the Si standard.

Upon mixing AlD_3, LiCl and NaF (sample 7) the PXD-data showed no change in the unit cell parameters of AlD_3 compared to a reference sample, see Fig. 1. Formation of NaCl was seen after cryo milling, and even in spite of overlap with the stronger reflections of Al some diffraction peaks could be attributed to LiF. The intensities of the LiCl reflections decreased while the NaCl reflections increased by increasing the milling time. This indicates a reaction between LiCl and NaF to form NaCl and LiF. Weak diffraction peaks attributed to Li_3AlF_6 were also observed after cryo milling for 15 and 30 min.

Neither sample 7, 8 nor 9 showed any change in the positions of the Bragg peaks from AlD_3 after addition of fluorides at any milling time. PXD patterns after 10 min of milling are shown in Fig. 2. Diffraction peaks of both α-AlH_3 and α′-AlH_3 are seen, but no change of peak positions can be detected. A PXD measurement of sample 8 after 4 months of storage showed an increased content of Al, indicating partly decomposition of AlD_3 during storage.

For AlH_3 made from $NaAlH_4$ there was NaCl present in the mixture, according to reaction (2). Upon mixing with AlF_3 (sample 10) there was no change in unit cell parameters of AlH_3, and AlF_3 stayed unreacted. Mixing of AlH_3 and NaF (sample 11) led to decomposition of AlH_3 giving a significant content of Al in the sample.

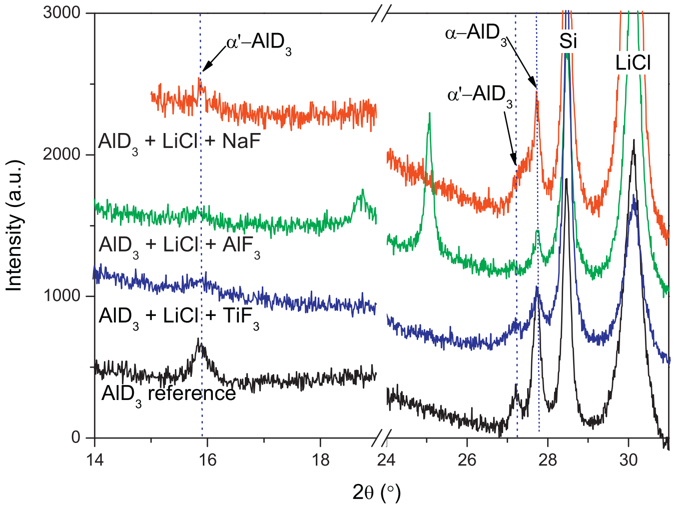

Fig. 2. AlD_3 cryo milled with NaF (sample 7), AlF_3 (sample 8) or TiF_3 (sample 9) for 10 min. No change in peak positions of AlD_3 is seen. The label Si corresponds to the Bragg peaks for the Si standard.

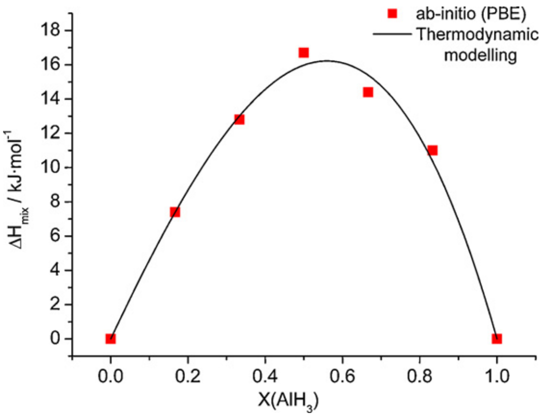

Fig. 3. Calculated enthalpy of mixing in the trigonal solid solution at 298 K and 1 bar in comparison with the results from first-principle calculations.

For the computational studies, as a simple reaction to test the reliability of computed values, the fluorination of aluminium hydride has been chosen,

$$2/3AlH_3(s) + F_2(g) \rightarrow 2/3AlF_3(s) + H_2(g)$$

at $T = 298$ K and $p = 1.01325 \times 10^5$ Pa. The *ab inito* data of ΔH, ΔS and ΔG of the reaction (−914.6 kJ/mol H_2, −42.0 J/mol H_2 K and −902.1 kJ/mol H_2, respectively) have been compared to those calculated by thermodynamic data taken from database [40] (−999.3 kJ/mol H_2, −47.8 J/mol H_2 K and −965.2 kJ/mol H_2, respectively), showing a reasonable agreement.

Because the hydride and fluoride share the same lattice and space group, the formation of the AlH_3/AlF_3 solid solution has been modelled by considering the hydrogen substitution by fluorine inside the unit cell of pure AlH_3, which is composed by two formula units. For instance, in case of mono-substitution, six symmetry equivalent configurations arise ($Al_2H_5F = AlH_{2.5}F_{0.5}$). For the double-substitution ($Al_2H_4F_2 = AlH_2F$), the situation gets more complicated because it results in 15 configurations. By the use of a newly implemented algorithm within the CRYSTAL code [41,42] each configuration is automatically screened on a symmetry base, so that the quantum-mechanical calculations are reduced only to the irreducible configurations. For this latter case, only 3 irreducible classes arise upon the total of 15. Five compositions for the solid solutions were computed, starting from $AlH_{2.5}F_{0.5}$ to $AlH_{0.5}F_{2.5}$, and the corresponding thermodynamic values have been used to calculate ΔH, ΔS and ΔG of mixing for the reaction:

$$(1-a)AlH_3 + aAlF_3 \rightarrow AlH_{3-3a}F_{3a}$$

with $a = 1/6$, $1/3$, $1/2$, $2/3$ and $5/6$ at $T = 298$ K and $p = 1.01325 \times 10^5$ Pa.

When more than one configuration was present for the same composition only the most stable one was considered in the thermodynamic assessment. The ΔH of reaction are 11.0, 14.4, 16.7, 12.8 and 7.40 kJ/mol, respectively, for the a values listed above. For all cases, the solid solution is unfavourable due to the computed positive enthalpy of mixing, as shown in Fig. 3, where *ab initio* data have been fitted with the Redlich–Kister (RK) polynomial described further in the text. The contributions coming from ΔS (both thermal and configurational) when combined with the ΔH gave positive free energies ΔG for all cases, indicating that the solid solution does not form spontaneously. For the thermodynamic modelling, the pure elements in their stable phases at 298.15 K and 101,325 Pa were chosen as reference state (SER, standard element reference). The Gibbs energies of the pure elements "phase stabilities" vs temperature have been represented by:

$$G_{\mathrm{i}}^{0}(T) = a + bT + cT\ \ln(T) + dT^2 + eT^{-1} + fT^3 \tag{3}$$

The G_{i} expressions can be given for several temperature ranges where the coefficients *a*, *b*, *c*, *d*, *e* and *f* have different values. The values of these coefficients for Al were taken from the compilation of Dinsdale [43] while those for H_2 and F_2 were obtained from JANAF tables [40].

Seven phases of the Al–H–F-system were considered: trigonal solid solution between α-AlH_3 and α-AlF_3, β-AlF_3, fcc-Al, β-AlH_3, γ-AlH_3, liquid and gas, and were treated with different thermodynamic models. These models describe the Gibbs energy for each phase as a function of temperature, composition and pressure (only for the gaseous phase as $RT \ln p$).

β-AlH_3, γ-AlH_3 and β-AlF_3 were treated as stoichiometric compounds. No compositional dependence is considered for these phases, and thus the Gibbs energy of formation for one mole of formula unit was expressed as a function of temperature similar to Eq. (3). The gas phase containing: Al, H_2, H, F_2, F, HF, AlF_3 and AlH_3 was considered as an ideal mixture. The fcc-Al phase was modelled with two sublattices: the first occupied by Al and the second occupied by H and vacancies to take into account the small solubility of H in fcc-Al. The liquid phase is a regular solution between Al and H described by an interaction parameter with a linear dependence from temperature as reported by Palumbo et al. [44].

The solid solution between α-AlH_3 and α-AlF_3 has been described with two sublattices: the first occupied by Al and the second occupied by H and F so that a single atom of hydrogen can be substituted by an atom of fluorine. The excess Gibbs energy of this phase has been modelled with two terms of the Redlich–Kister (RK) series [45] in order to describe the asymmetry of the free energy as a function of composition.

The first term $L_0 = a_0 + b_0T$ has a linear dependence from temperature and the second $L_1 = a_1$ is constant. Accordingly the free energy of the solid solution is expressed as follows:

$$G = {}^{\mathrm{ref}}G + {}^{\mathrm{id}}G + {}^{\mathrm{exc}}G$$

$${}^{\mathrm{ref}}G = xG(AlH_3) + (1 - x)G(AlF_3)$$

$${}^{\mathrm{id}}G = 3RT(x\ \ln(x) + (1 - x)\ \ln(1 - x))$$

$${}^{\mathrm{exc}}G = x(1 - x)(a_0 + Tb_0) + x(1 - x)(x - (1 - x))a_1$$

where $G(AlH_3)$ and $G(AlF_3)$ are the Gibbs energies of α-AlH_3 and α-AlF_3, *x* is the molar fraction of AlH_3, and $1 - x$ is the molar fraction of AlF_3. ${}^{\mathrm{ref}}G$, ${}^{\mathrm{id}}G$, ${}^{\mathrm{exc}}G$ are the reference Gibbs energies, the ideal mixing and the excess contribution to the free energy, respectively.

As reported previously, *ab initio* calculations have been performed to evaluate the parameters $a_0 = 63{,}923$ J/mol and $a_1 = -16{,}058$ J/mol and $b_0 = 28.7$ J/(mol K).

The AlH_3–AlF_3 pseudo-binary phase diagram has been calculated using the Thermo-Calc [39] software and it is shown in Fig. 4. At low temperature the high positive enthalpy of mixing prevents the formation of the solid solution. AlH_3 is metastable at ambient pressure, and therefore it decomposes to Al-fcc and H_2. The trigonal solid solution is AlF_3 with a negligible amount of H inside.

At higher temperatures the phase transformation from trigonal α-AlF_3 to orthorhombic β-AlF_3, the melting of Al and the sublimation of β-AlF_3 are shown.

There is a good agreement between the experimental data and computational results. The modelling results show that the formation of solid solution fluoride in alane is not favourable, and this is confirmed by the experimental data. The experimental results show no signs of fluorine anion substitution or mixed solid solution phases $AlD_{3-x}F_x$, as no change in the unit cell parameters of alane is observed. In samples where fluoride additives were present in the synthesis of reaction (1) or (2) this led to formation of new phases instead of AlD_3/AlH_3, while adding fluorides to pre-made alane gave no changes in the alane phases. A quantitative explanation can be found by considering the differences in unit cell volumes. By comparison with the Na_3AlH_6–Na_3AlF_6-system, where fluoride substitution actually is observed, some notable differences are seen. Even though the corresponding hydrides and fluorides take the same structure, the unit cell parameters can be quite different, as the fluorides has larger unit cells. This difference is much more pronounced for the AlH_3–AlF_3 system. A comparison of the unit cell volumes of the two systems shows that the difference in unit cell volume is only 2.8% for Na_3AlH_6 vs Na_3AlF_6, while for AlH_3 vs AlF_3 the difference is 22.9%. This might explain why the mixing of these compounds is much less likely than the mixing of Na_3AlH_6 and Na_3AlF_6.

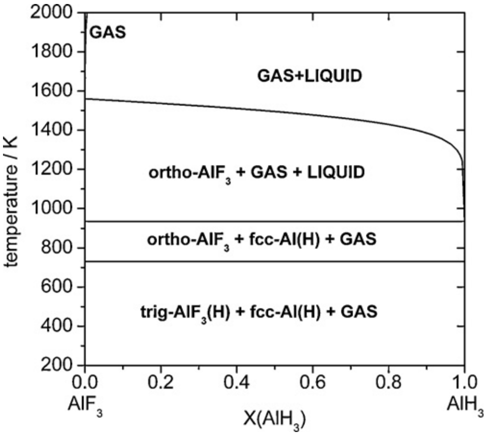

Fig. 4. AlH_3–AlF_3 pseudo-binary phase diagram.

4. Conclusions

No solid solution mixed phases $AlD_{3-x}F_x$ are observed experimentally. For samples where fluoride additives were present in the reaction to form alane this led to formation of other phases instead of AlD_3/AlH_3. For samples of AlD_3/AlH_3 mixed with fluorides the synthesis gave no fluorine mixing or led to decomposition of the alane.

In accordance with the experimental results the computational study shows that a mixed phase is not favourable. *Ab initio* calculations of the trigonal solid solution at 298 K give a positive enthalpy of mixing for all values of substitution. The AlH_3–AlF_3 pseudo-binary phase diagram has been calculated by thermodynamic modelling, showing that the high positive enthalpy of mixing prevents the formation of the solid solution. Thus a mixed phase is not thermodynamically favourable and fluorine anion substitution is not feasible for tailoring the thermodynamics of alane.

Acknowledgements

This work was supported from the FLYHY project (contract no. 226943) under the FP7 Program in the European Commission and by the RENERGI program of the Research Council of Norway. The skilful assistance of the project team at the Swiss-Norwegian beam line (ESRF) is gratefully acknowledged. Fluorsid is acknowledged for providing single phase AlF_3.

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