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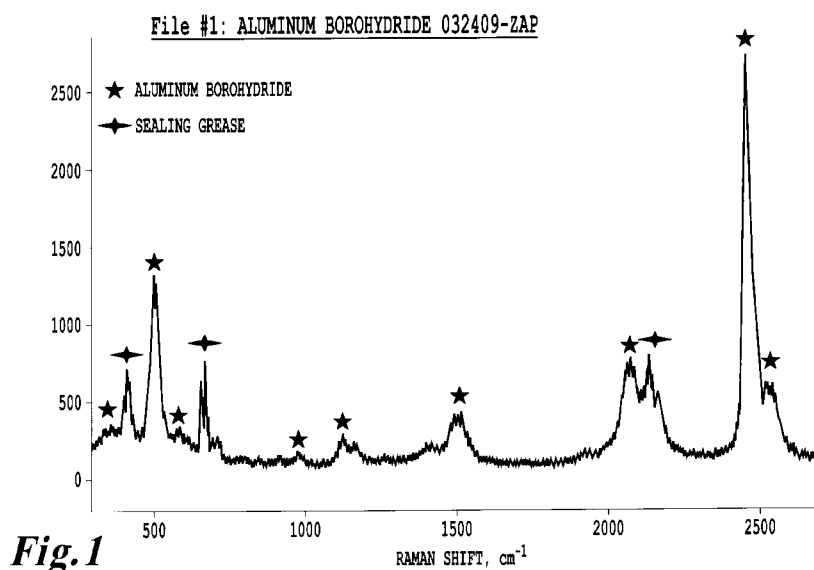
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(54) Title: HIGH CAPACITY STABILIZED COMPLEX HYDRIDES FOR HYDROGEN STORAGE

(57) Abstract: Complex hydrides based on $\text{Al}(\text{BH}_4)_3$ are stabilized by the presence of one or more additional metal elements or organic adducts to provide high capacity hydrogen storage material.

TITLE OF THE INVENTION

5 HIGH CAPACITY STABILIZED COMPLEX HYDRIDES
FOR HYDROGEN STORAGE

This invention was made with government support under Contract No.
DE-AC09-08SR22470 awarded by the U.S. Department of Energy. The government
10 has certain rights in the invention.

REFERENCE TO RELATED APPLICATIONS

This application claims benefit of U.S. provisional application 61/270,511
filed July 9, 2009, the entire contents of which are incorporated herein by reference.
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FIELD OF THE INVENTION

The present invention relates to materials for hydrogen storage. In particular,
the present invention relates to complex hydrides for hydrogen storage. This invention
is also directed towards stabilized high capacity complex hydrides useful for
20 hydrogen storage. The invention is further directed to methods and processes for
making stabilized high capacity complex hydrides, such processes and methodology
lending themselves toward economical and safer techniques of producing stabilized
high capacity complex hydrides.

25 DISCUSSION OF THE BACKGROUND

This invention relates in part to metal hydrides and complex hydrides that may
be used to form a stable hydrogen capacity for hydrogen cycling. There remains a
need for improvements in metal and complex hydrides with respect to hydrogen
storage capacity, dehydriding temperatures, and reversibility of the hydrogen sorption
30 and desorption cycles. For instance, it is known in the art as set forth in U.S. Pat. No.
7,094,387 directed to molten state processes of forming unique metal hydrides and
complex metal hydrides. However, there remains room for improvement and
variation in the art directed to techniques and resulting materials to form stabilized
high capacity complex hydrides.

Currently hydrogen is stored on board a vehicle under 5,000 to 10,000 psi pressure. However, these storage systems are not efficient from a volumetric point of view. For example, the storage density of hydrogen gas at 10,000 psi is only 0.035 g/cm³, which is approximately half the storage density of liquid hydrogen at the 20K boiling point of hydrogen. Despite the higher storage density, liquid hydrogen is an undesirable storage form due to hydrogen liquefaction storage loss and short lived dormancy at 20K due to boil off.

Complex metal hydrides, such as alanates (e.g., LiAlH₄, NaAlH₄ and KAlH₄) and borohydrides (e.g., LiBH₄, NaBH₄ and KBH₄), show promise as materials for solid state storage of hydrogen. For example, the theoretical hydrogen volumetric storage density in lithium borohydride (LiBH₄) is approximately 0.12 g/cm³, more than three times the density of gaseous hydrogen at 10,000 psi.

However, many complex metal hydrides are unsuitable for hydrogen storage applications. For example, Al(BH₄)₃ is an unstable compound, and its vapor ignites spontaneously on exposure to air containing only traces of moisture.

A great deal of research is currently underway with other complex hydride compounds and materials to determine the most efficient and useful hydrogen storage material.

There is a need for solid state hydrogen storage materials having improved chemical stability, stable hydrogen capacity with cycling, and enhanced kinetics compatible with automotive and other portable power source requirements.

SUMMARY OF THE INVENTION

The present invention provides a complex metal hydride compound that has improved chemical stability and thermodynamic characteristics that can be tuned to satisfy the on-board hydrogen storage requirements of various automotive and portable power source applications.

The complex compound of the present invention has a composition in which the normally unstable Al(BH₄)₃ compound is stabilized by the addition at least one BH₄⁻ group and at least one element other than Al selected from the group consisting of metals.

The complex compound can have the composition M^{x+}Al³⁺(BH₄)_{3+x}, where M is an element other than Al selected from the group consisting of metals; and x is a valence number (oxidation number) of 1, 2, 3, 4, 5, 6, 7 or 8.

The complex compound can also have the composition $M1^{x+}M2^{y+}Al^{3+}(BH_4^-)_{3+x+y}$, where M1 and M2 are different elements other than Al selected from the group consisting of metals; x is a valence number of 1, 2, 3, 4, 5, 6, 7 or 8; and y is a valence number of 1, 2, 3, 4, 5, 6, 7 or 8.

5 The complex compound can also have the composition of $Al(BH_4)_3:R$, where R is an organic adduct.

The stabilized aluminum borohydride complex compound of the present invention can be produced by a Lewis base reaction. The complex compound can be stabilized in organic solvent.

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BRIEF DESCRIPTION OF THE DRAWINGS

The preferred embodiments of the invention will be described in detail, with reference to the following figures, where:

FIG. 1 is a Raman spectrum for unsolvated $Al(BH_4)_3$.

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FIG. 2 is an X-ray diffraction pattern showing unsolvated $Al(BH_4)_3$ stabilized using KBH_4 (i.e., $KAl(BH_4)_4$)

FIG. 3 shows the thermal hydrogen storage properties of $KAl(BH_4)_4$ in plots versus temperature of TG and DTA.

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FIG. 4 is an X-ray diffraction pattern following the stabilization of solvated $Al(BH_4)_4$ in toluene with triethylene diamine (TEDA).

FIG. 5 shows the XRD Analysis of $Al(BH_4)_3$ stabilized using KBH_4 using direct synthesis method.

FIG. 6 shows the XRD Analysis of $Al(BH_4)_3$ stabilized with $LiBH_4$ using direct synthesis method.

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FIG. 7 shows the stabilization of $Al(BH_4)_3$ with Triethylene Diamine $C_6N_2H_{12}$ using direct formation and solvent method.

FIGS. 8-18 show various aspects of the present invention.

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DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The complex compound of the present invention is based on $Al(BH_4)_3$, which is a very unstable liquid complex hydride. The present inventors have discovered the addition of one or more metal elements and one or more BH_4^- groups to the $Al(BH_4)_3$

complex results in a new aluminum borohydride complex compound having greater chemical stability and higher hydrogen storage capacity than $\text{Al}(\text{BH}_4)_3$.

In embodiments, the complex compound can have the composition $\text{M}^{x+}\text{Al}^{3+}(\text{BH}_4^-)_{3+x}$, where M is an element other than Al selected from the group consisting of metals; and x is a valence number of 1, 2, 3, 4, 5, 6, 7 or 8. Preferably x is 1 or 2. For example, the complex compound can be $\text{LiAl}(\text{BH}_4)_4$, $\text{NaAl}(\text{BH}_4)_4$, $\text{MgAl}(\text{BH}_4)_5$, for example.

In other embodiments, the complex compound can have the composition $\text{M1}^{x+}\text{M2}^{y+}\text{Al}^{3+}(\text{BH}_4^-)_{3+x+y}$, where M1 and M2 are different elements other than Al selected from the group consisting of metals; x is a valence number of 1, 2, 3, 4, 5, 6, 7 or 8; and y is a valence number of 1, 2, 3, 4, 5, 6, 7 or 8. Preferably x is 1 or 2, and y is 1 or 2. For example, the complex compound can be $\text{LiNaAl}(\text{BH}_4)_5$, $\text{LiMgAl}(\text{BH}_4)_6$, for example.

In still other embodiments, the complex compound can have the composition $\text{M1}^{x+}\text{M2}^{y+}\text{Al}^{3+}(\text{BH}_4^-)_{3+x+y}$, where M1 and M2 are the same element other than Al selected from the group consisting of metals; and x and y are different valence numbers of 1, 2, 3, 4, 5, 6, 7 or 8.

As discussed above, M, M1 and M2 are metal elements other than Al. Metal elements other than Al include alkali metals, alkaline earth metals, transition metals, rare earth elements, Ga, In, Sn, Pb and Bi.

Preferred alkali metals include Li, Na and K.

Preferred alkaline earth metals include Mg, Ca, Ba and Sr.

Preferred transition metals include Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt and Au.

Preferred rare earth elements are the lanthanide series rare earth elements. Lanthanide series rare earth elements include La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

In still yet other embodiments, the complex compound can have the composition $\text{Al}(\text{BH}_4)_3 \cdot \text{R}$, where R is an organic adduct. For example, R can be an amine or a phosphine. Preferred amines include trimethyl amine and triethylene diamine (TEDA). Preferred phosphines include trimethyl phosphine.

The complex compound of the present invention can be produced by reacting unstable aluminum borohydride ($\text{Al}(\text{BH}_4)_3$) with a stabilization agent.

In a first synthetic pathway to the stabilized complex compound of the present invention, unsolvated $\text{Al}(\text{BH}_4)_3$ is synthesized by combining in an inert environment (e.g., a commercial chemical reactor and/or Schlenk line flask) aluminum chloride (AlCl_3) with lithium borohydride (LiBH_4). The LiBH_4 can be premilled to reduce its particle size and enhance the yield of $\text{Al}(\text{BH}_4)_3$.

Reactions and syntheses described herein, including the synthesis of the unsolvated $\text{Al}(\text{BH}_4)_3$, can be carried out, for example, at temperatures in a range of from -50 to 600°C , preferably 0 to 400°C , for a period of time in a range of from 0.1 to 100 hours. The pressure can be maintained in a range of from 0 to 6000 psi, for example.

The unsolvated $\text{Al}(\text{BH}_4)_3$ then undergoes a stabilization reaction with a stabilization agent. For producing the complex compound of the composition $\text{M}^{x+}\text{Al}^{3+}(\text{BH}_4^-)_{3+x}$, the stabilization agent comprises the metal M . For producing the complex compound of the composition $\text{M}_1^{x+}\text{M}_2^{y+}\text{Al}^{3+}(\text{BH}_4^-)_{3+x+y}$, the stabilization agent comprises the metals M_1 and M_2 . The stabilization agent can include one or more metals in metallic form (e.g., metallic Na and metallic K). The stabilization agent can also include one or more compounds of one or more metals. Metals M_1 and M_2 can both be in one of the compounds or can be in separate compounds. The stabilization agent can be a borohydride of a metal (e.g., LiBH_4 , KBH_4 , or $\text{Mg}(\text{BH}_4)_2$) or a halide of a metal (e.g., LiCl), etc.

For producing the complex compound of composition $\text{Al}(\text{BH}_4)_3:\text{R}$, the stabilization agent can comprise an organic compound with electron donor ligands, such as amine compounds and phosphine compounds. Examples of the amine compounds include trimethyl amine ($\text{N}(\text{CH}_3)_3$) and triethylene diamine ($\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$, TEDA). Examples of the phosphine compounds include trimethyl phosphine ($\text{P}(\text{CH}_3)_3$).

Excess unsolvated $\text{Al}(\text{BH}_4)_3$ can be used in the stabilization reaction. The stabilization reaction for the unsolvated $\text{Al}(\text{BH}_4)_3$ can be carried out at temperatures in a range of from 25 to 100°C , for example, for a period of time in a range of from 18 to 24 hours, for example. During the synthesis, the pressure can be maintained in a range of from 0 to 1000 psig, for example.

Preferably the stabilization reaction is carried out in an inert environment.

The inert environments for the unsolvated $\text{Al}(\text{BH}_4)_3$ synthesis and for the stabilization reaction can contain one or more inert gases. Inert gases include He, Ne, Ar, Kr and Xe. Preferably, the inert gas is Ar.

When utilizing alkali metals (e.g., metallic Na or metallic K) as stabilization agents, the stabilization reaction can be conducted at temperatures at or higher than the melting point of the alkali metal and lower than the decomposition temperature of the $\text{Al}(\text{BH}_4)_3$. Such conditions can enhance the yield of the stabilized complex compound of the present invention through vapor/liquid-liquid reactions.

The formation of the complex compound of the present invention can be marked by the transformation of a liquid $\text{Al}(\text{BH}_4)_3$ phase into a solid phase of stabilized complex compound.

In a second synthetic pathway to the stabilized complex compound of the present invention, solvated aluminum borohydride ($\text{Al}(\text{BH}_4)_3$) is synthesized by combining in an inert environment (e.g., Schlenk line flask) aluminum chloride (AlCl_3) solvated in an aprotic solvent and lithium borohydride (LiBH_4) premixed with the aprotic solvent.

The solvated $\text{Al}(\text{BH}_4)_3$ then undergoes a stabilization reaction with one of the stabilization agents discussed above to produce the stabilized complex compound of the present invention.

The aprotic solvent can be dimethylformamide, dimethyl sulfoxide, benzene or toluene. Preferably, the aprotic solvent is toluene.

The stabilization reaction of $\text{Al}(\text{BH}_4)_3$ in solvent permits safer handling of unstable $\text{Al}(\text{BH}_4)_3$ reactant, higher yield and greater purity of products. The formation of volatile intermediates that can be difficult and expensive to handle can be avoided.

The stabilized complex compound produced is a solid. Traces of solvent can be separated from the solid product by applying a vacuum.

The stabilized solid aluminum borohydride complex compounds of the present invention can release hydrogen at temperatures of less than 200°C .

It is another aspect of at least one of the present embodiments to provide for a process of combining AlH_4 groups and BH_4 groups, to produce a high capacity hydride for hydrogen storage.

It is a further aspect of at least one embodiment of the present invention to provide for a process and resulting product of reacting $\text{Al}(\text{BH}_4)_3$ which is dissolved in

an organic solvent such as toluene or benzene and then reacted with a fine powder of $M^x(BH_4)_x$ to form $M^xAl(BH_4)_{3+x}$ where M is selected from the group consisting of Li, Na, K, or Mg to produce a high capacity hydride for hydrogen storage.

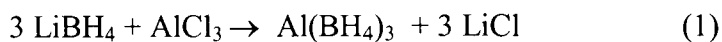
It is a further aspect of at least one embodiment of the present invention to provide for a reaction and a resulting product of combining $Al(BH_4)_3$ in either a liquid or gas form with a molten metal "M" where M is selected from the group of Li, Na, K, or Mg to produce high capacity hydride for hydrogen storage having the general form of $[M^xAl(BH_4)_{3+x}]$.

It is a further object of at least one embodiment of the present invention to provide for a process and resulting reaction product of reacting $Al(BH_4)_3$ dissolved in an organic solvent interacting with a molten metal "M" under elevated pressures and temperatures to form a high capacity hydride hydrogen storage in the form of $M^xAl(BH_4)_{3+x}$.

Complex hydrides described herein are based on an unstable liquid complex hydride of $Al(BH_4)_3$. In accordance with the present invention, it has been found that by adding another element to the $Al(BH_4)_3$ complex a more stable and higher capacity hydride may be formed having a general formula of $M^xAl(BH_4)_{3+x}$ where M is a metal and X is a valence number. It has been found that the resulting complexes offer improvements for hydrogen storage applications. Further, it has been found that new synthesis techniques can avoid the formation of volatile intermediates, thereby reducing the difficulty of production and the expense of handling volatile intermediates.

Direct Formation

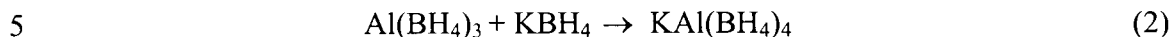
The formation $Al(BH_4)_3$ as starting material is known and occurs by mixing $LiBH_4$ and $AlCl_3$ and stirring and heating.



The $Al(BH_4)_3$ is collected by heating and cold trapping.

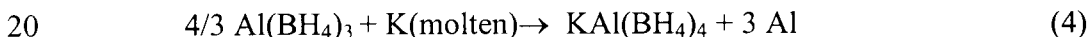
One aspect of the invention is to form $M^xAl(BH_4)_{3+x}$ high hydrogen capacity complexes for hydrogen storage.

The reaction is between $\text{Al}(\text{BH}_4)_3$ and an $\text{M}^x(\text{BH}_4)_x$ (e.g. $\text{M}=\text{Li}, \text{K}, \text{Na}, \text{Mg}$), resulting in $\text{M}^x \text{Al}(\text{BH}_4)_{3+x}$. As an example a balanced equation for the formation of $\text{KAl}(\text{BH}_4)_4$ and $\text{CaAl}(\text{BH}_4)_5$ is as follows:



- 10 The reaction can occur at room temperature but will require a multiple day reaction time. In order to accelerate the reaction, the starting powder such as KBH_4 is finely ground by ball milling. KBH_4 as an example was loaded under inert atmosphere in a pressure vessel. $\text{Al}(\text{BH}_4)_3$ is condensed at low temperature into the pressure vessel from $\text{Al}(\text{BH}_4)_3$ vapor. The starting materials were mixed in the pressure vessel and
- 15 heated up to 70 C where the pressure in the vessel increased. The pressure increase is solely due to $\text{Al}(\text{BH}_4)_3$ going from liquid state to gaseous state.

The same reaction can occur between $\text{Al}(\text{BH}_4)_3$ and molten metal such as K at 70° C as follows:



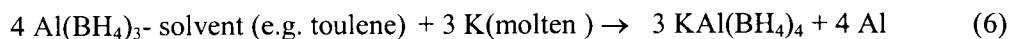
Solvent Method :

The same results of forming $\text{M}^x \text{Al}(\text{BH}_4)_{3+x}$ can be obtained using a similar method which avoids dealing directly with volatile $\text{Al}(\text{BH}_4)_3$ in its pure form.

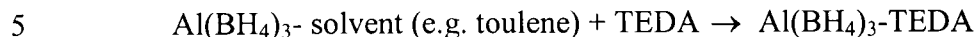
- 25 Reaction 1 is done in solution where the product $\text{Al}(\text{BH}_4)_3$ dissolved in a solvent such as toluene and the LiCl is filtered out. The solution can then be reacted with $\text{M}^x(\text{BH}_4)_x$ (e.g. $\text{M}=\text{Li}, \text{K}, \text{Na}, \text{Mg}$). A reactant such as finely ground KBH_4 is added to the solvent containing $\text{Al}(\text{BH}_4)_3$ resulting in precipitating $\text{KAl}(\text{BH}_4)_4$.

- 30 Reaction 2 can occur in solvents containing $\text{Al}(\text{BH}_4)_3$:





The formation of $\text{Al(BH}_4)_3$ adduct such as $\text{Al(BH}_4)_3\text{-TEDA}$ is similar:



where $\text{Al(BH}_4)_3\text{-TEDA}$ precipitates as a solid and can easily be filtered

10 The products were determined by thermal gravimetric measurements and x-ray.

The above reactions and processes are designed to take advantage that complex metal hydrides offer an opportunity of compressing hydrogen into a lowest form of storage density. For instance, in a chemically bonded format such as a complex metal hydride, hydrogen shows a superior density that is desired for storage purposes. The present invention provides for high storage volume complex metal hydrides which alter and improve the thermodynamic properties of hydrogen rich compounds such as LiBH_4 .

20 The above processes and reaction products take advantage of combining higher thermodynamically stable borohydrides with a lower stability alanate and/or Al-B compounds in order to achieve a thermodynamically tuned intermediate compound. For instance, substitution of a less electronegative Li and LiBH_4 with a more electronegative cation of the form $\text{M} + \text{X}$ equals a lower bond strength of the B-H bond with a resulting T_{des} value being lower. Similarly, substitution of the less stable AlH_4^- with BH_4^- brings about a lowering of the hydrogen T_{des} value.

25

EXAMPLES

Example 1 - Synthesis using unsolvated $\text{Al(BH}_4)_3$

30 Unsolvated $\text{Al(BH}_4)_3$ was synthesized by combining in a Schlenk line flask under an Ar atmosphere 1 mole of aluminum chloride (AlCl_3) with 3 moles of unsolvated lithium borohydride (LiBH_4). The synthesis was carried out at 65°C and under vacuum for 3 hours. The LiBH_4 was premilled to reduce its particle size and enhance the yield of $\text{Al(BH}_4)_3$.

FIG. 1 shows the Raman shifts for the prepared unsolvated $\text{Al}(\text{BH}_4)_3$.

The unsolvated $\text{Al}(\text{BH}_4)_3$ was then reacted with KBH_4 in a closed and evacuated vessel at 65 °C and -14 psig for 72 hours to produce $\text{KAl}(\text{BH}_4)_4$. Excess $\text{Al}(\text{BH}_4)_3$ was utilized such that twice the stoichiometric amount needed was present.

FIG. 2 shows the X-ray diffraction pattern for the unsolvated $\text{Al}(\text{BH}_4)_3$ stabilized using KBH_4 . The X-ray diffraction pattern shows the presence of $\text{KAl}(\text{BH}_4)_4$.

FIG. 3 shows the thermal hydrogen storage properties of the formed $\text{KAl}(\text{BH}_4)_4$. Hydrogen release is evident in the 4.13 wt% weight loss onset at 114.9°C.

Example 2 - Synthesis using solvated $\text{Al}(\text{BH}_4)_3$

Solvated aluminum borohydride ($\text{Al}(\text{BH}_4)_3$) was synthesized by combining in a Schlenk line flask under an Ar atmosphere 1 molar aluminum chloride (AlCl_3) in toluene with 3 molar lithium borohydride (LiBH_4) in toluene.

The stabilized complex compound was then prepared by combining the solvated $\text{Al}(\text{BH}_4)_3$ and a stabilization agent of LiBH_4 or TEDA. Excess solvated $\text{Al}(\text{BH}_4)_3$ was utilized such that 4 times the stoichiometric amount needed was present. The stabilization reactions were carried out under an Ar atmosphere at 25 °C and 0 psig for 8 hours. $\text{LiAl}(\text{BH}_4)_4$ and $\text{Al}(\text{BH}_4)_3\text{:TEDA}$ were produced by the stabilization reactions.

FIG. 4 is an X-ray diffraction pattern following the stabilization of solvated $\text{Al}(\text{BH}_4)_3$ in toluene with triethylene diamine (TEDA). The formation of new crystalline stabilized $\text{Al}(\text{BH}_4)_3\text{:TEDA}$ can be seen marked with #. The product obtained following desorption is marked with *. The results are compared to purchased TEDA marked with @.

FIG. 5 shows the XRD Analysis of $\text{Al}(\text{BH}_4)_3$ stabilized using KBH_4 using direct synthesis method. The formation of new crystalline compound $\text{K}[\text{Al}(\text{BH}_4)_4]$ is confirmed.

FIG. 6 shows the XRD Analysis of $\text{Al}(\text{BH}_4)_3$ stabilized with LiBH_4 using direct synthesis method. The formation of new crystalline compound $\text{Li}[\text{Al}(\text{BH}_4)_4]$ (lower graph) is confirmed.

FIG 7 shows the stabilization of $\text{Al}(\text{BH}_4)_3$ with Triethylene Diamine $\text{C}_6\text{N}_2\text{H}_{12}$ using direct formation and solvent method. X-ray diffraction obtained following the stabilization of $\text{Al}(\text{BH}_4)_3$ with Triethylene Diamine using (A) excess

TEDA using solvent method, (B) 1:1 molar stoichiometric TEDA using direct formation and (C) A mixture of the stoichiometric and excess TEDA stabilized $\text{Al}(\text{BH}_4)_3$. Formation of new crystalline $\text{Al}(\text{BH}_4)_3 \cdot x\text{TEDA}$ compound was obtained, where $x=1$ or 2 molar.

5 FIGS 8-18 describe a number of experimental protocols setting forth the reactants and reaction conditions and characterization protocols showing the formation of useful complex hydrides, the complex hydrides being formed by a variety of different chemical processes. Further, the materials, reactions, and conditions set forth in U.S. Pat. No. 7,094,387, and which is incorporated herein by
10 reference are also useful with the materials and processes of the present invention.

The above written description of the invention provides a manner and process of making and using it such that any person skilled in this art is enabled to make and use the same, this enablement being provided in particular for the subject matter of the appended claims, which make up a part of the original description.

15 As used herein, the phrases “selected from the group consisting of,” “chosen from,” and the like include mixtures of the specified materials. Terms such as “contain(s)” and the like as used herein are open terms meaning ‘including at least’ unless otherwise specifically noted. The term “mentioned” notes exemplary embodiments, and is not limiting to certain species. As used herein the words “a” and
20 “an” and the like carry the meaning of “one or more.”

All references, patents, applications, tests, standards, documents, publications, brochures, texts, articles, etc. mentioned herein are incorporated herein by reference. Where a numerical limit or range is stated, the endpoints are included. Also, all values and subranges within a numerical limit or range are specifically included as if
25 explicitly written out.

The above description is presented to enable a person skilled in the art to make and use the invention, and is provided in the context of a particular application and its requirements. Various modifications to the preferred embodiments will be readily apparent to those skilled in the art, and the generic principles defined herein may be
30 applied to other embodiments and applications without departing from the spirit and scope of the invention. Thus, this invention is not intended to be limited to the embodiments shown, but is to be accorded the widest scope consistent with the principles and features disclosed herein. In this regard, certain embodiments within the invention may not show every benefit of the invention, considered broadly.

WHAT IS CLAIMED IS:

1. A complex compound having the composition $M^{x+}Al^{3+}(BH_4^-)_{3+x}$, where M is an element other than Al selected from the group consisting of metals; and
x is a valence number of 1, 2, 3, 4, 5, 6, 7 or 8.
2. The complex compound according to Claim 1, wherein the metals are selected from the group consisting of alkali metals.
3. The complex compound according to Claim 2 wherein the alkali metals are selected from the group consisting of Li, Na and K; and x is 1.
4. The complex compound according to Claim 1, wherein the metals are selected from the group consisting of alkaline earth metals.
5. The complex compound according to Claim 4, wherein the alkaline earth metals are selected from the group consisting of Mg, Ca, Sr and Ba; and
x is 2.
6. A method of making a complex compound, the method comprising reacting $Al(BH_4)_3$ with a stabilization agent comprising an element other than Al selected from the group consisting of metals; and
producing the complex compound of Claim 1.
7. The method according to Claim 6, wherein the $Al(BH_4)_3$ is unsolvated $Al(BH_4)_3$; and
the unsolvated $Al(BH_4)_3$ is synthesized by reacting $AlCl_3$ with $LiBH_4$ in an inert environment.

8. The method according to Claim 6, wherein
the $\text{Al}(\text{BH}_4)_3$ is solvated $\text{Al}(\text{BH}_4)_3$; and
the solvated $\text{Al}(\text{BH}_4)_3$ is synthesized by reacting AlCl_3 with LiBH_4 in an aprotic solvent.
9. A complex compound having the composition $\text{M1}^{x+}\text{M2}^{y+}\text{Al}^{3+}(\text{BH}_4^-)_{3+x+y}$,
where
M1 and M2 are different elements other than Al selected from the group consisting of metals;
x is a valence number of 1, 2, 3, 4, 5, 6, 7 or 8; and
y is a valence number of 1, 2, 3, 4, 5, 6, 7 or 8.
10. The complex compound according to Claim 9, wherein the metals are selected from the group consisting of alkali metals.
11. The complex compound according to Claim 10, wherein
the alkali metals are selected from the group consisting of Li, Na and K;
x is 1; and
y is 1.
12. The complex compound according to Claim 9, wherein the metals are selected from the group consisting of alkaline earth metals.
13. The complex compound according to Claim 12, wherein
the alkaline earth metals are selected from the group consisting of Mg, Ca, Sr and Ba;
x is 2; and
y is 2.
14. A method of making a complex compound, the method comprising
reacting $\text{Al}(\text{BH}_4)_3$ with a stabilization agent comprising an element other than Al selected from the group consisting of metals; and
producing the complex compound of Claim 9.

15. A complex compound having a composition $\text{Al}(\text{BH}_4)_3\cdot\text{R}$, where R is an organic adduct.
16. The complex compound according to Claim 15, wherein R is selected from the group consisting of amines and phosphines.
17. The complex compound according to Claim 15, wherein R is selected from the group consisting of trimethyl amine, trimethyl phosphine and triethylene diamine.
18. A method of making a complex compound, the method comprising reacting $\text{Al}(\text{BH}_4)_3$ with a stabilization agent comprising an organic adduct; and producing the complex compound of Claim 15.
19. The method according to Claim 18, wherein the $\text{Al}(\text{BH}_4)_3$ is unsolvated $\text{Al}(\text{BH}_4)_3$; and the unsolvated $\text{Al}(\text{BH}_4)_3$ is synthesized by reacting AlCl_3 with LiBH_4 in an inert environment.
20. The method according to Claim 18, wherein the $\text{Al}(\text{BH}_4)_3$ is solvated $\text{Al}(\text{BH}_4)_3$; and the solvated $\text{Al}(\text{BH}_4)_3$ is synthesized by reacting AlCl_3 with LiBH_4 in an aprotic solvent.
21. A compound selected from the following group of compounds:
a compound of the formula $\text{K}[\text{Al}(\text{BH}_4)_4]$ having the XRD spectrum shown in Figure 5,
a compound of the formula $\text{Li}[\text{Al}(\text{BH}_4)_4]$ having the XRD spectrum shown in Figure 6,
a compound of the formula $\text{Al}(\text{BH}_4)_3\cdot x\text{TEDA}$ where $x=1$ or 2 having the X-ray diffraction spectrum shown in Figure 7.

1/21

File #1: ALUMINUM BOROHYDRIDE 032409-ZAP

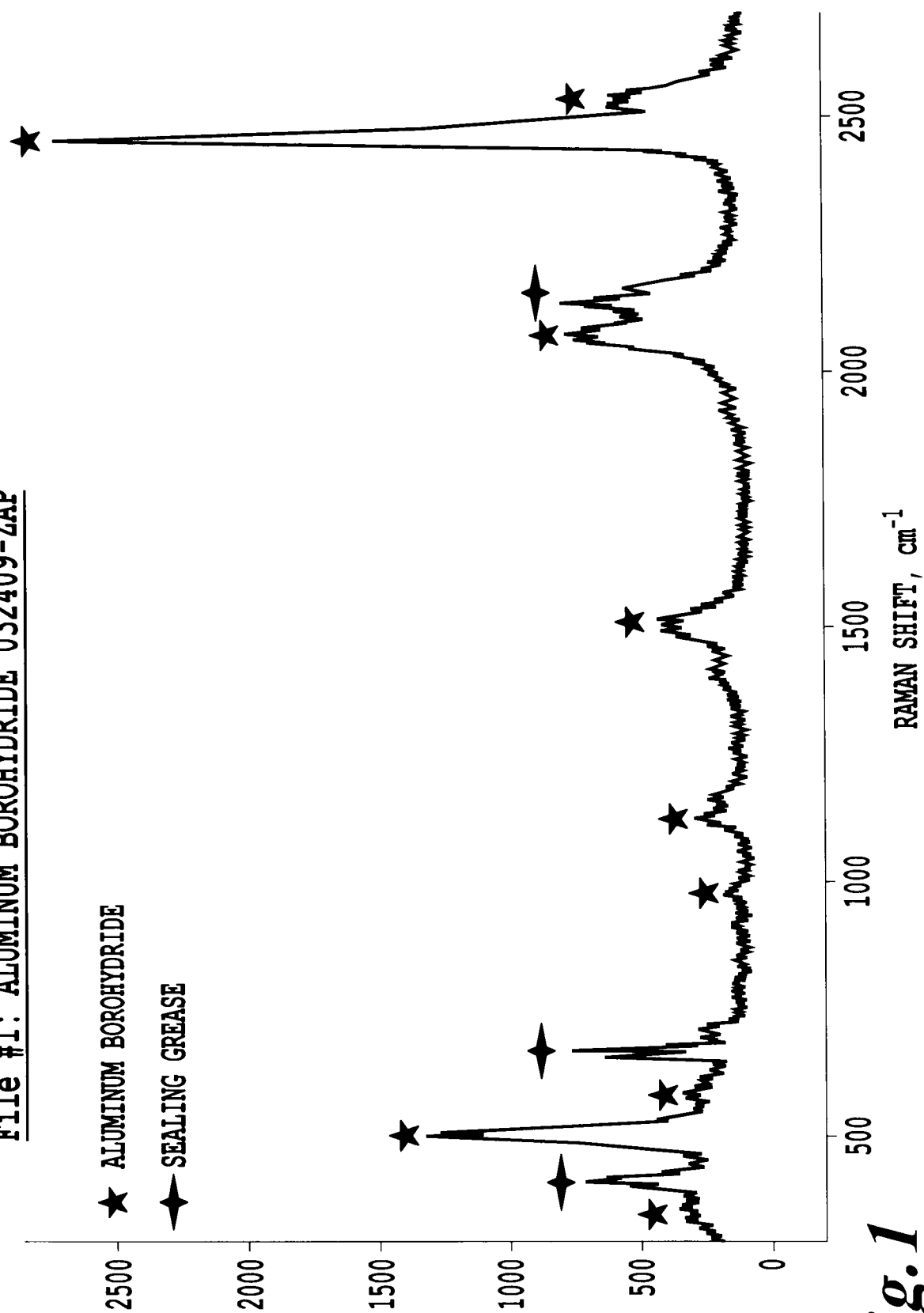
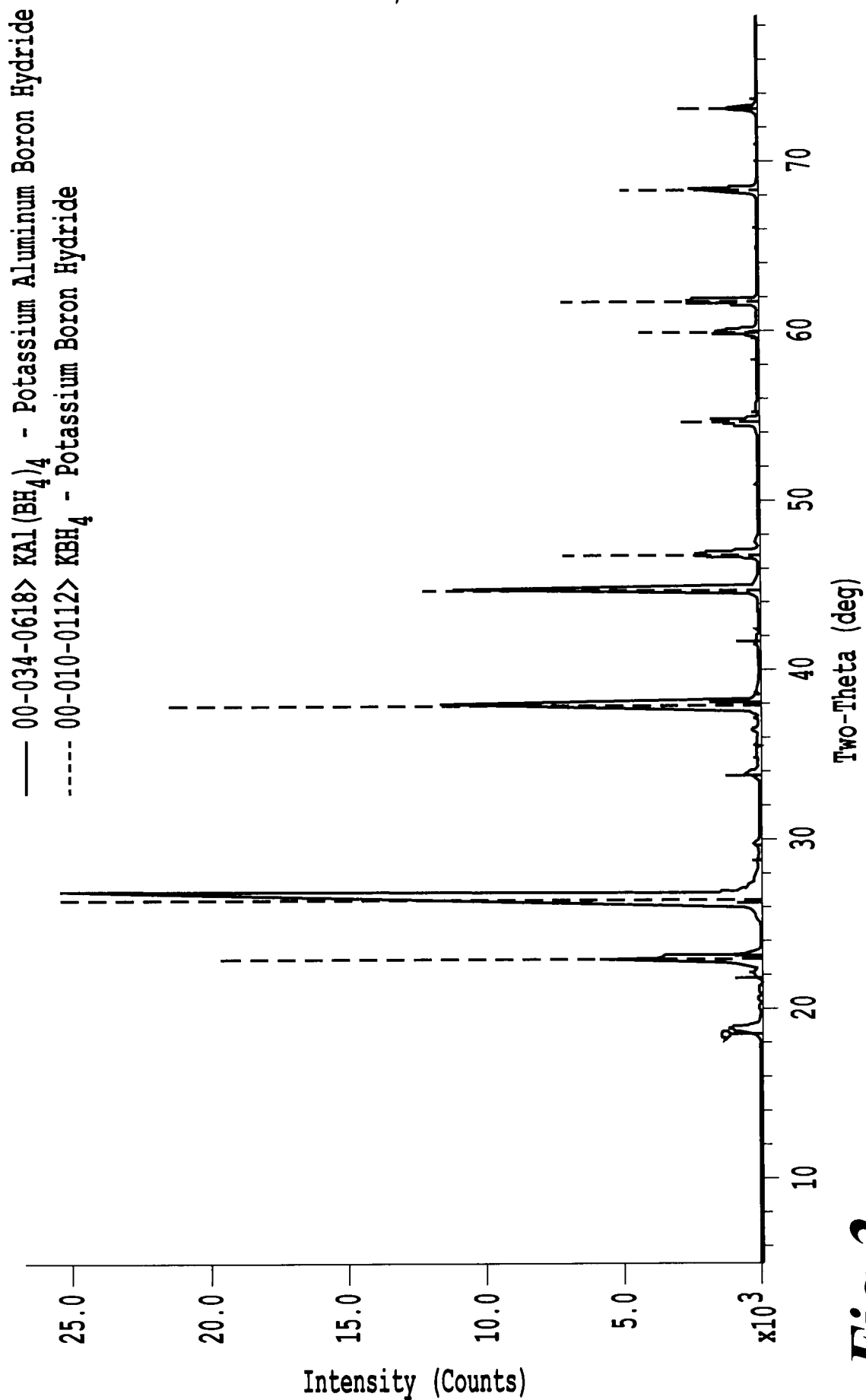
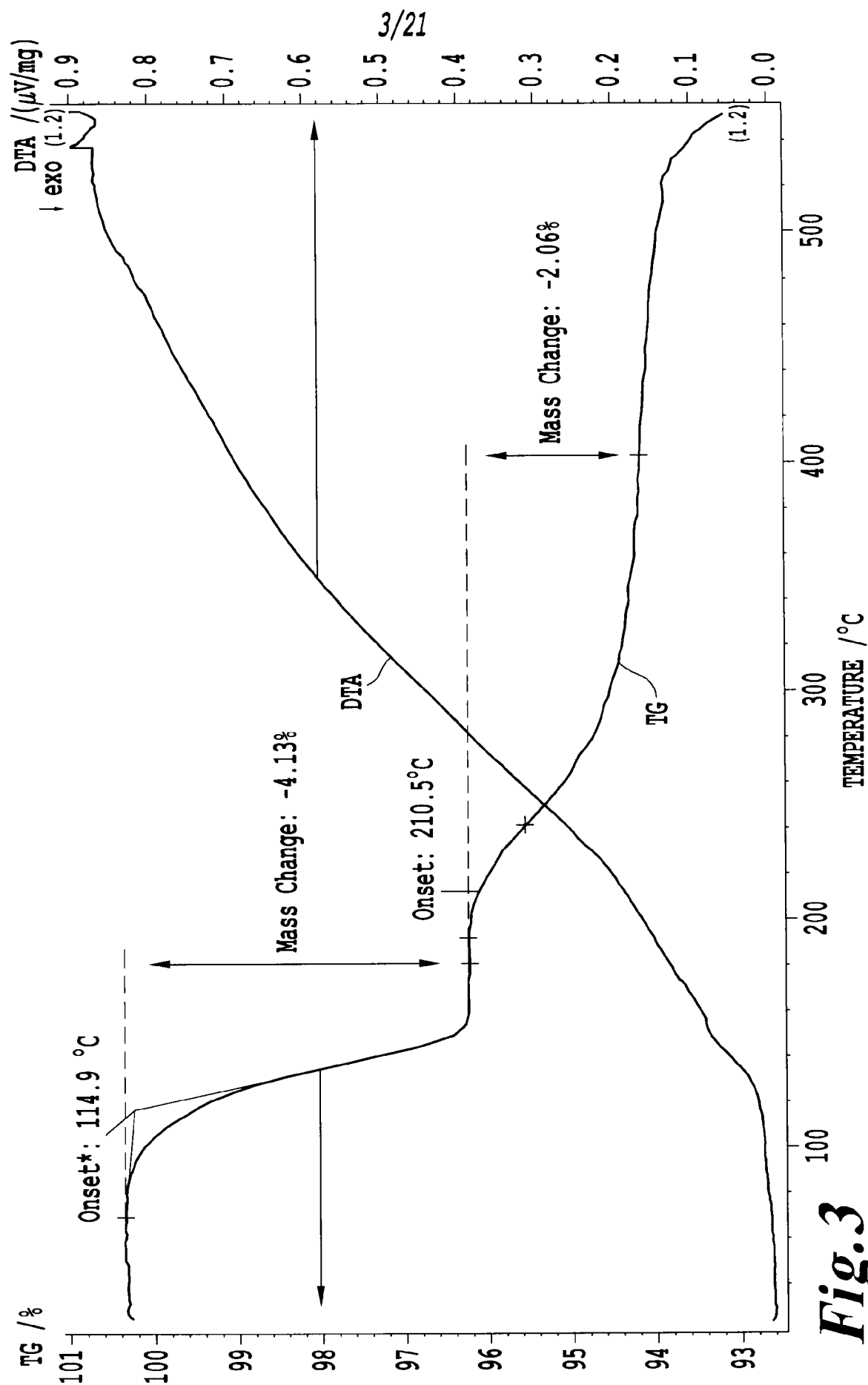


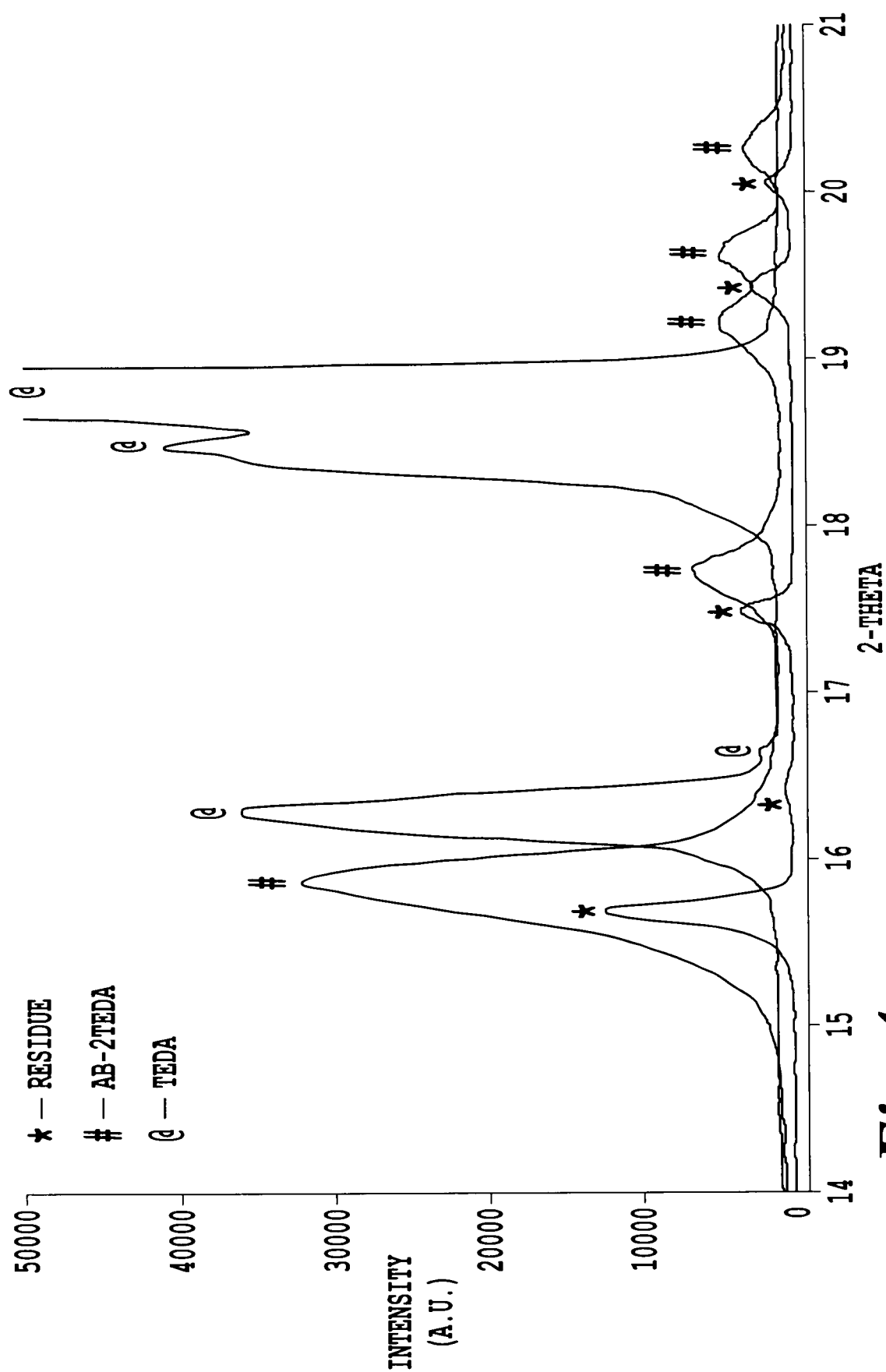
Fig. 1

2/21

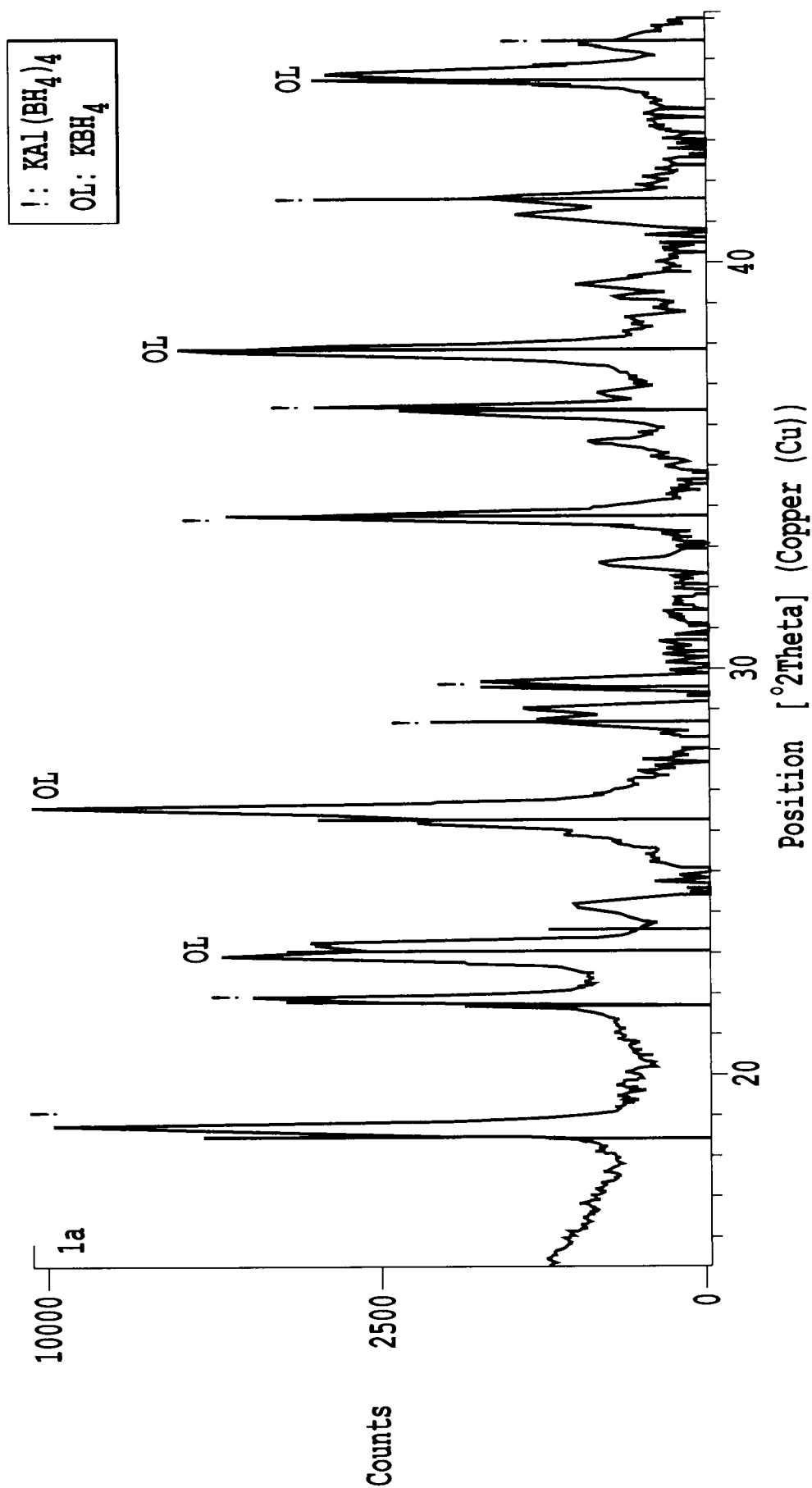
**Fig. 2**



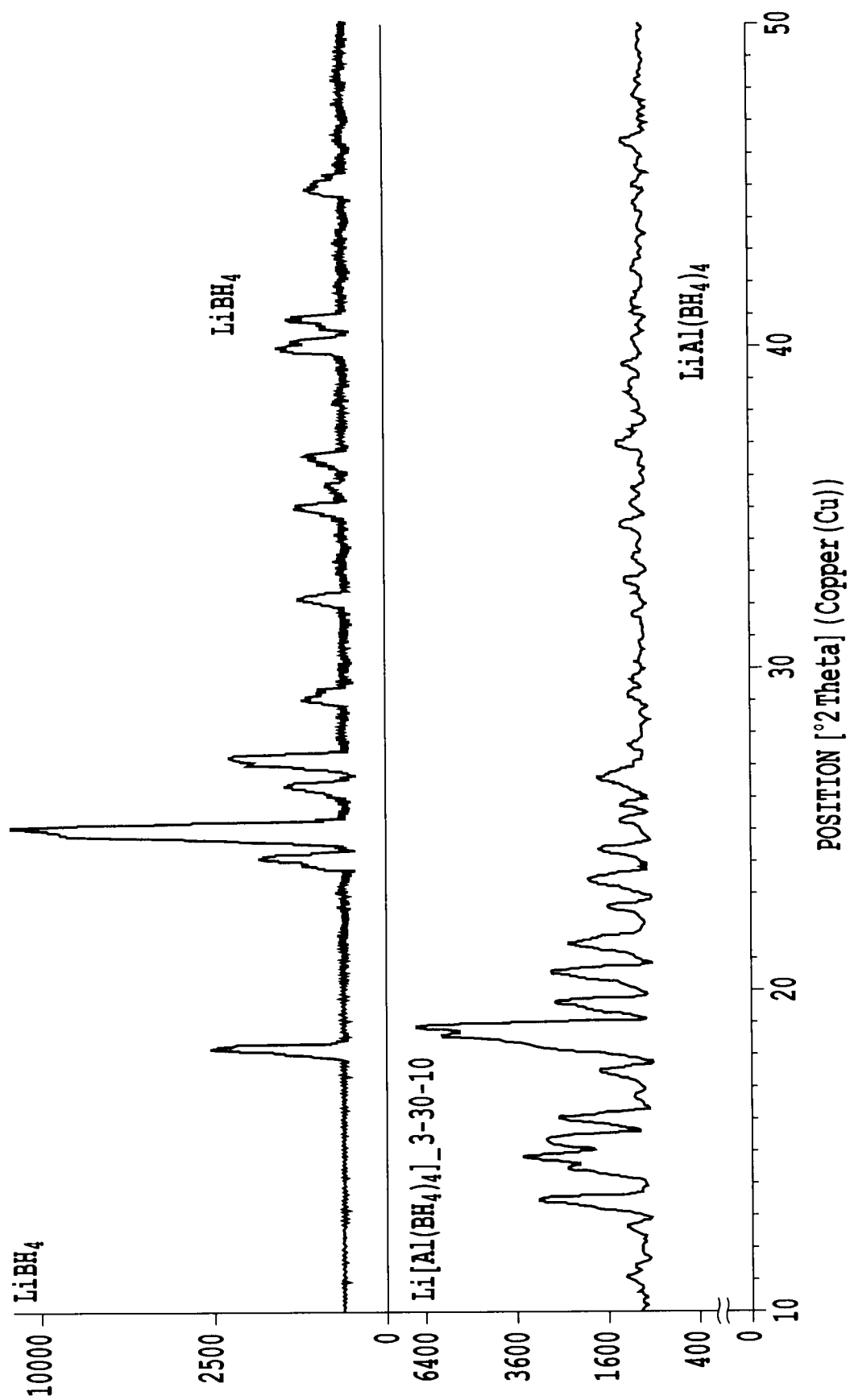
4/21

**Fig.4**

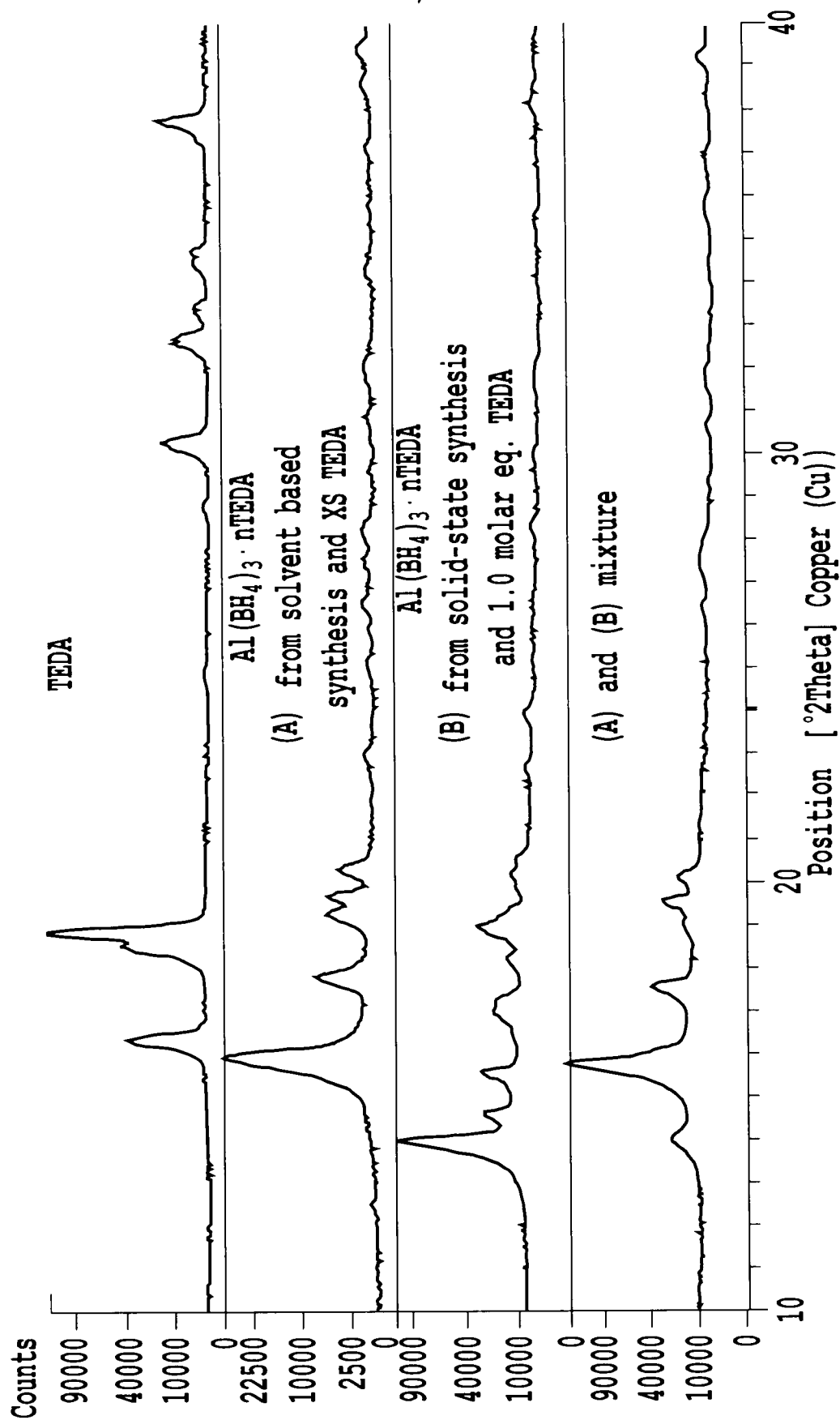
5/21

**Fig. 5**

6/21

**Fig. 6**

7/21

**Fig. 7**

8/21

Experimental

(1) Reactants

Alanates:

- NaAlH_4 , $\Delta H_f = -115 \text{ kJ/mol}$
- $\text{MgCl}_2:\text{LiAlH}_4^*$, $\Delta H_f \text{ Mg}(\text{AlH}_4)_2 = -63 \text{ kJ/mol}$
- $\text{CaCl}_2:\text{LiAlH}_4^{**}$, $\Delta H_f \text{ Ca}(\text{AlH}_4)_2 = -82.97 \text{ kJ/mol}$

Boron hydrides:

- LiBH_4 , $\Delta H_f = -190.46 \text{ kJ/mol}$

**, **: Ca and Mg alanate halide with LiAlH_4 used as substitute for separate synthesis of Ca and Mg alanate*

2) Reaction vessels (synthesis)

- Planetary ball mill, Fritsch P.7, 316L jars, milled 3 hr @500 rpm
- High pressure (up to 4500 psi)/temperature (up to 350 °C) manifold

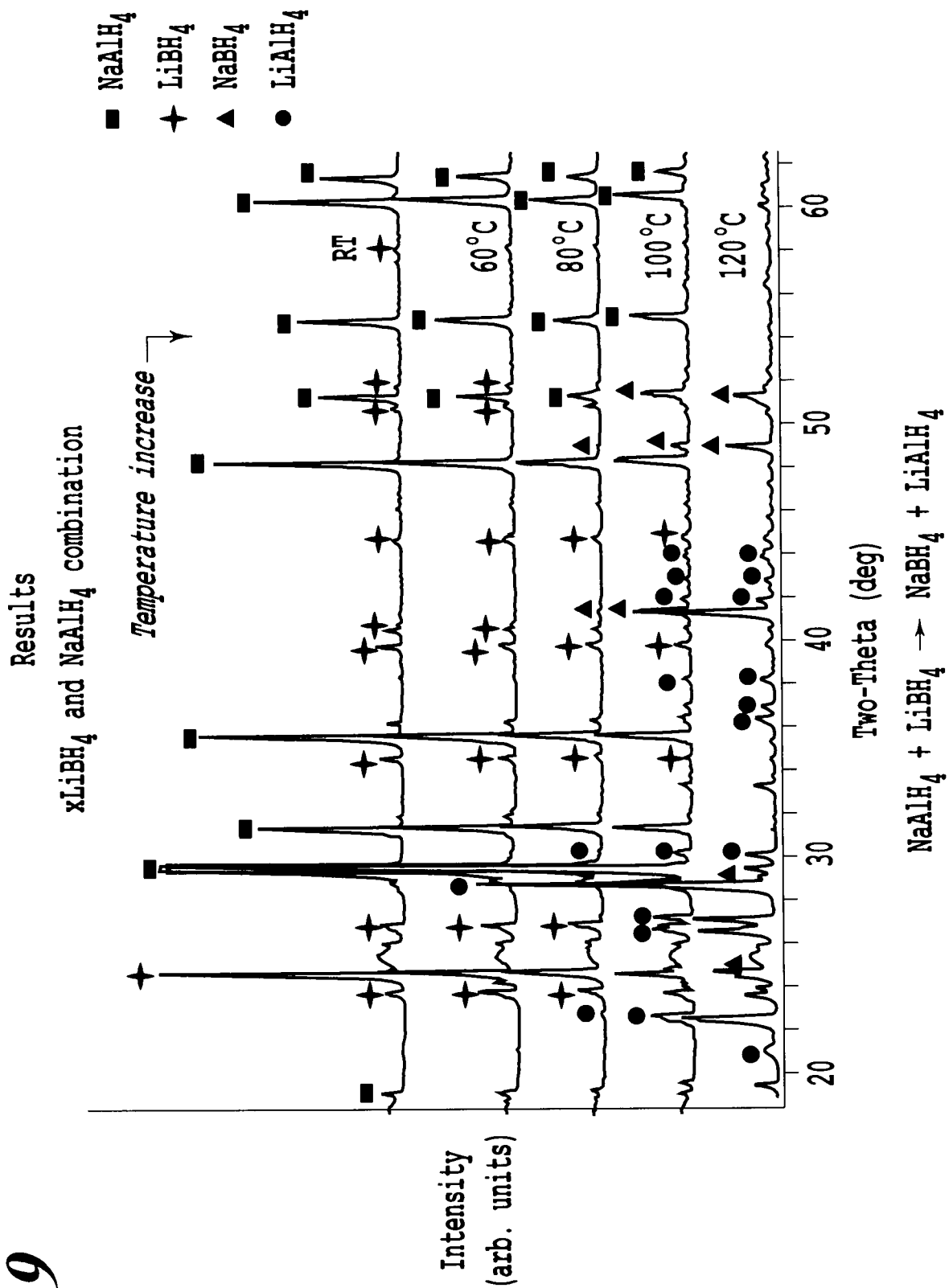
3) Characterization

- X ray diffraction PXRD
- Thermal analysis, TPD, TG-DTA; heating rate 2 °C/min
- Magic angle spinning MAS NMR

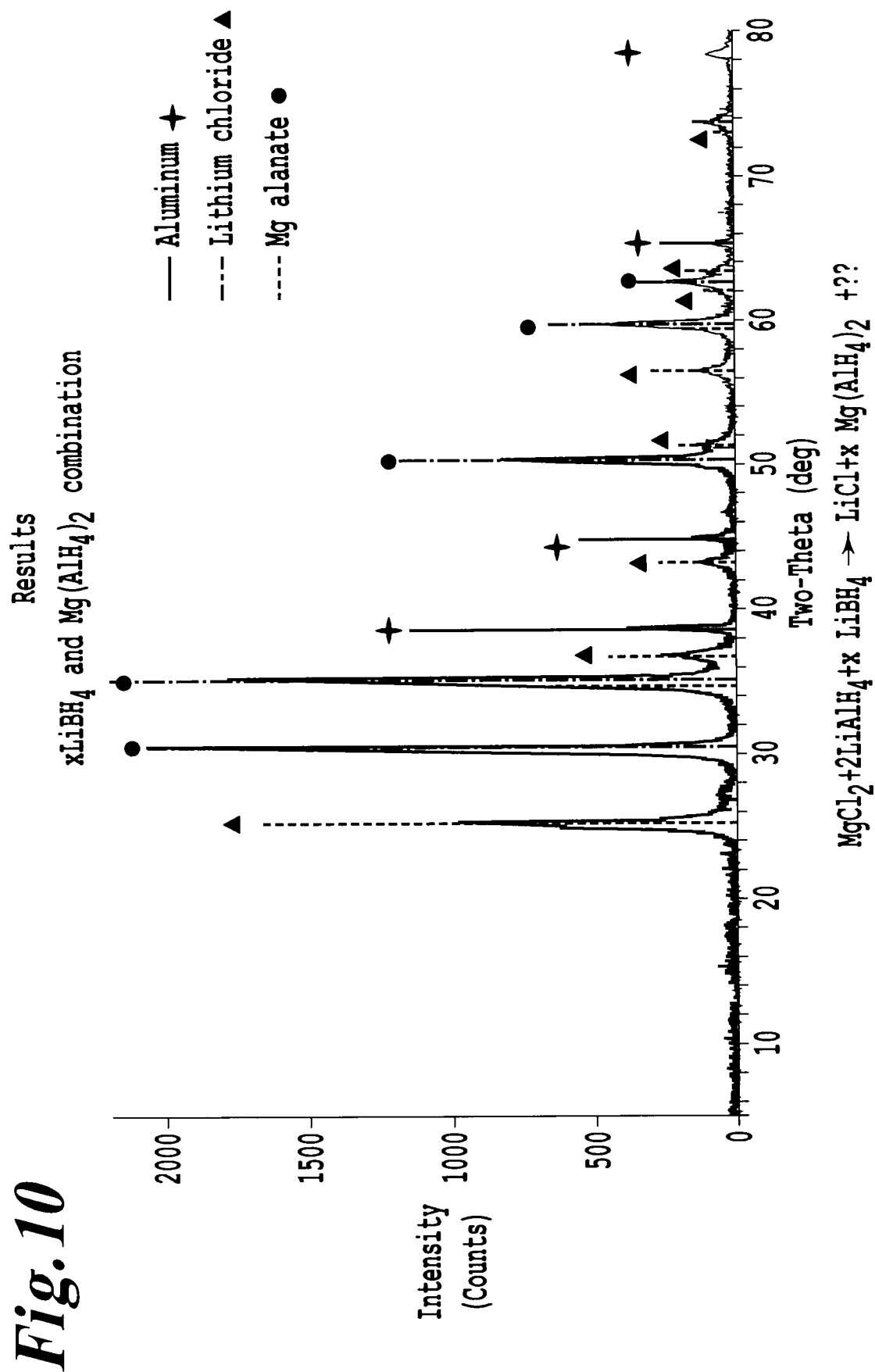
Fig.8

9/21

Fig. 9

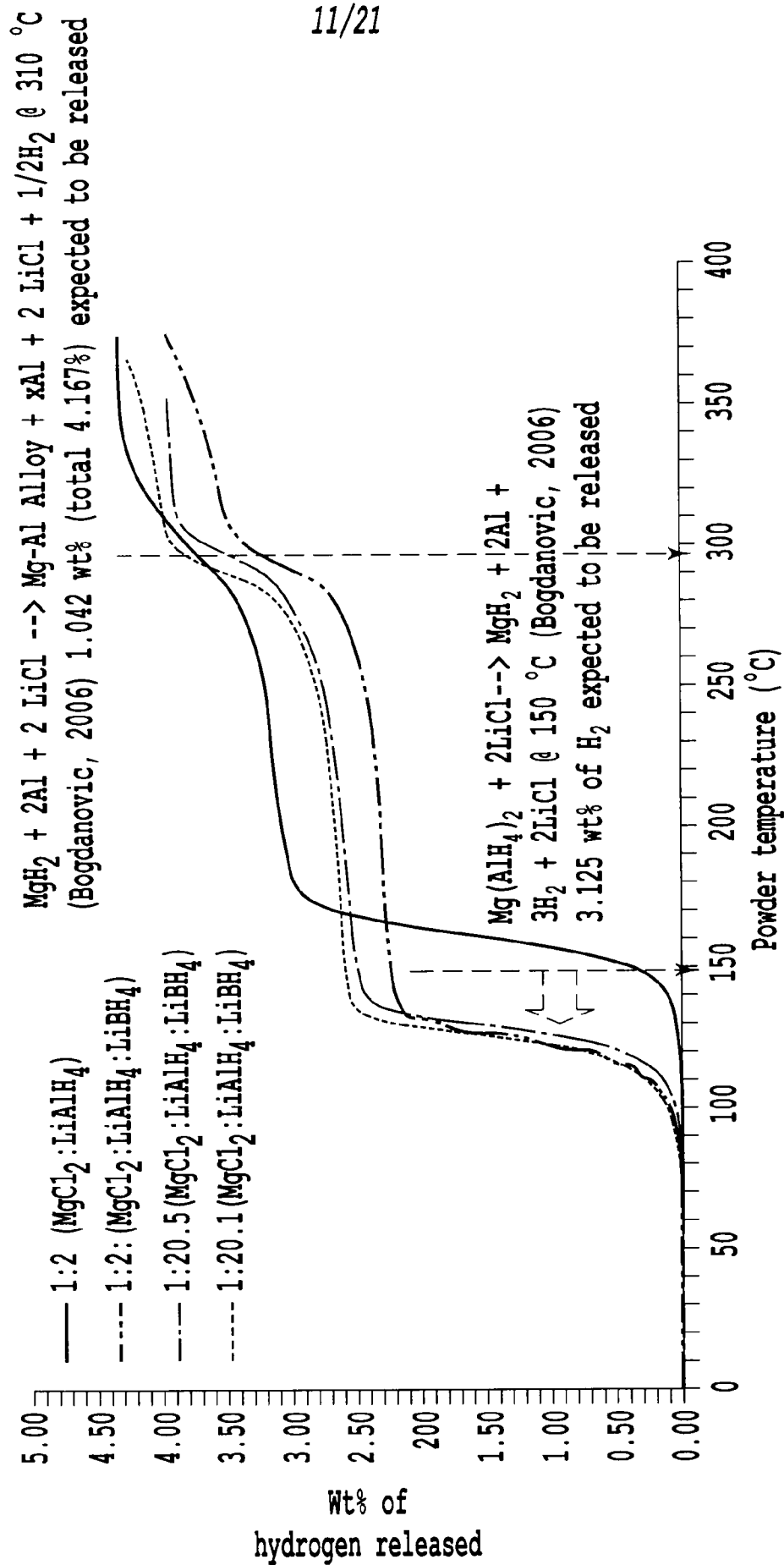


10/21



11/21

Thermal Analysis:

*Fig. 11*

12/21

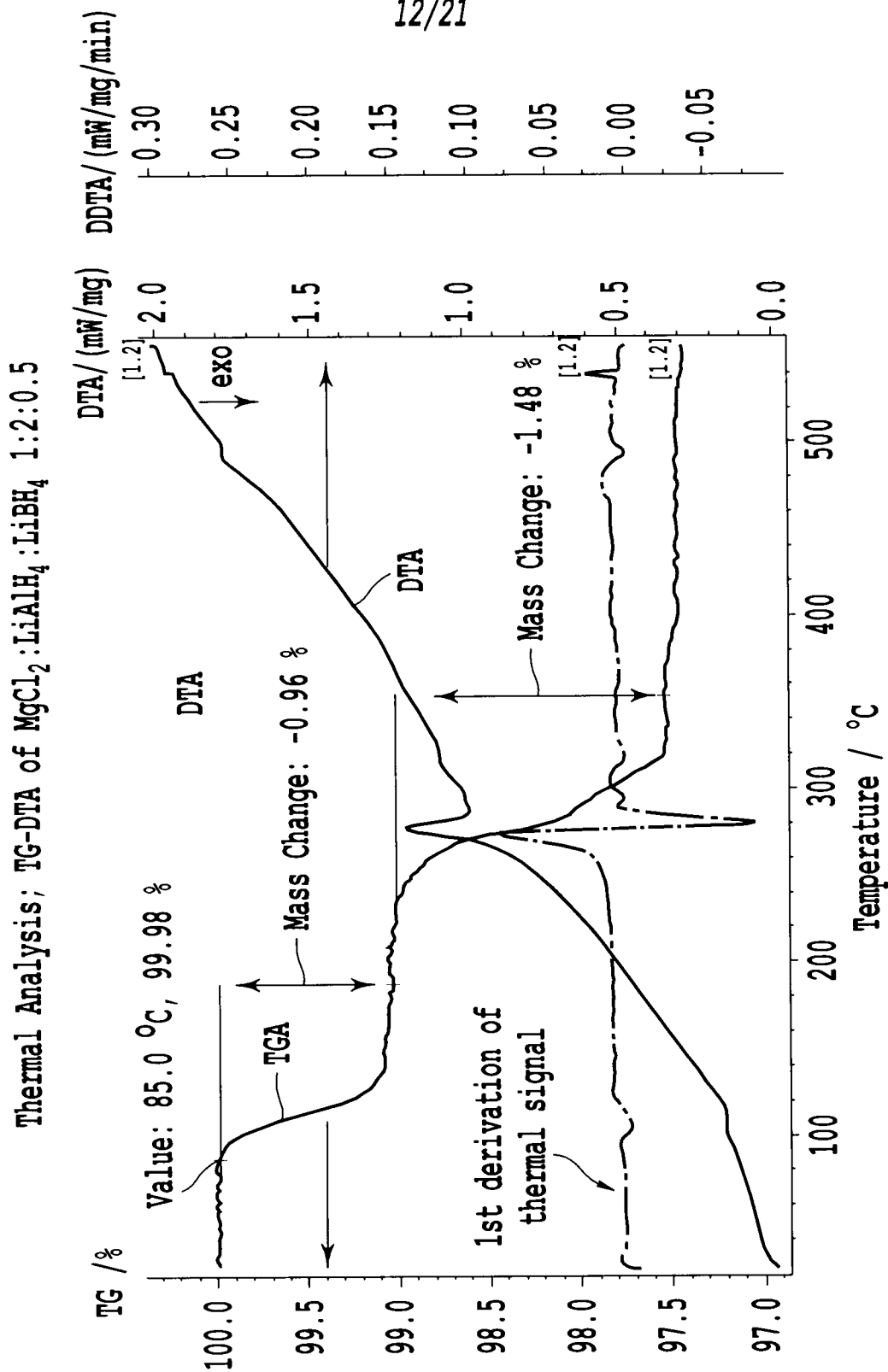
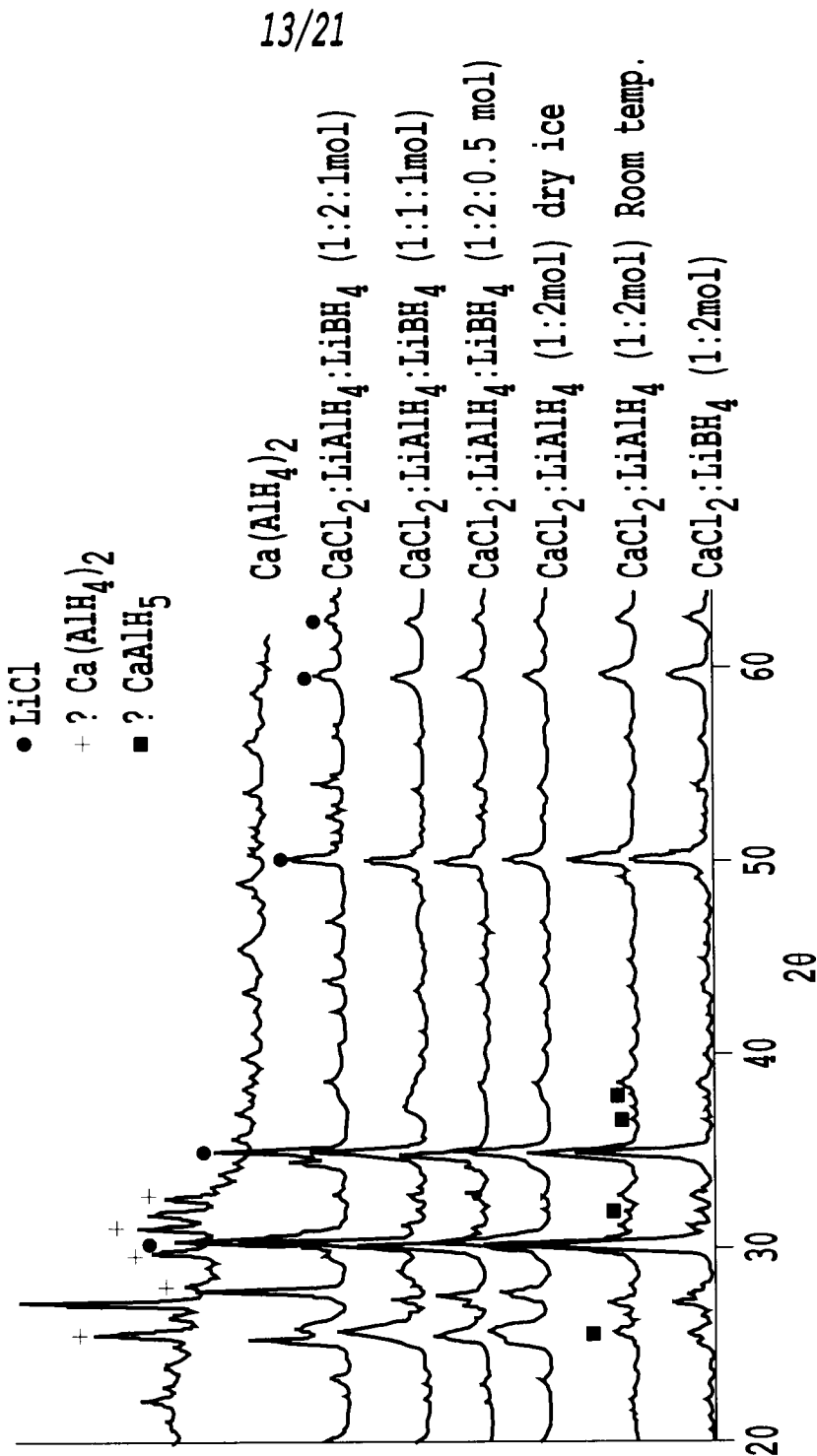
**Fig. 12**

Fig. 13

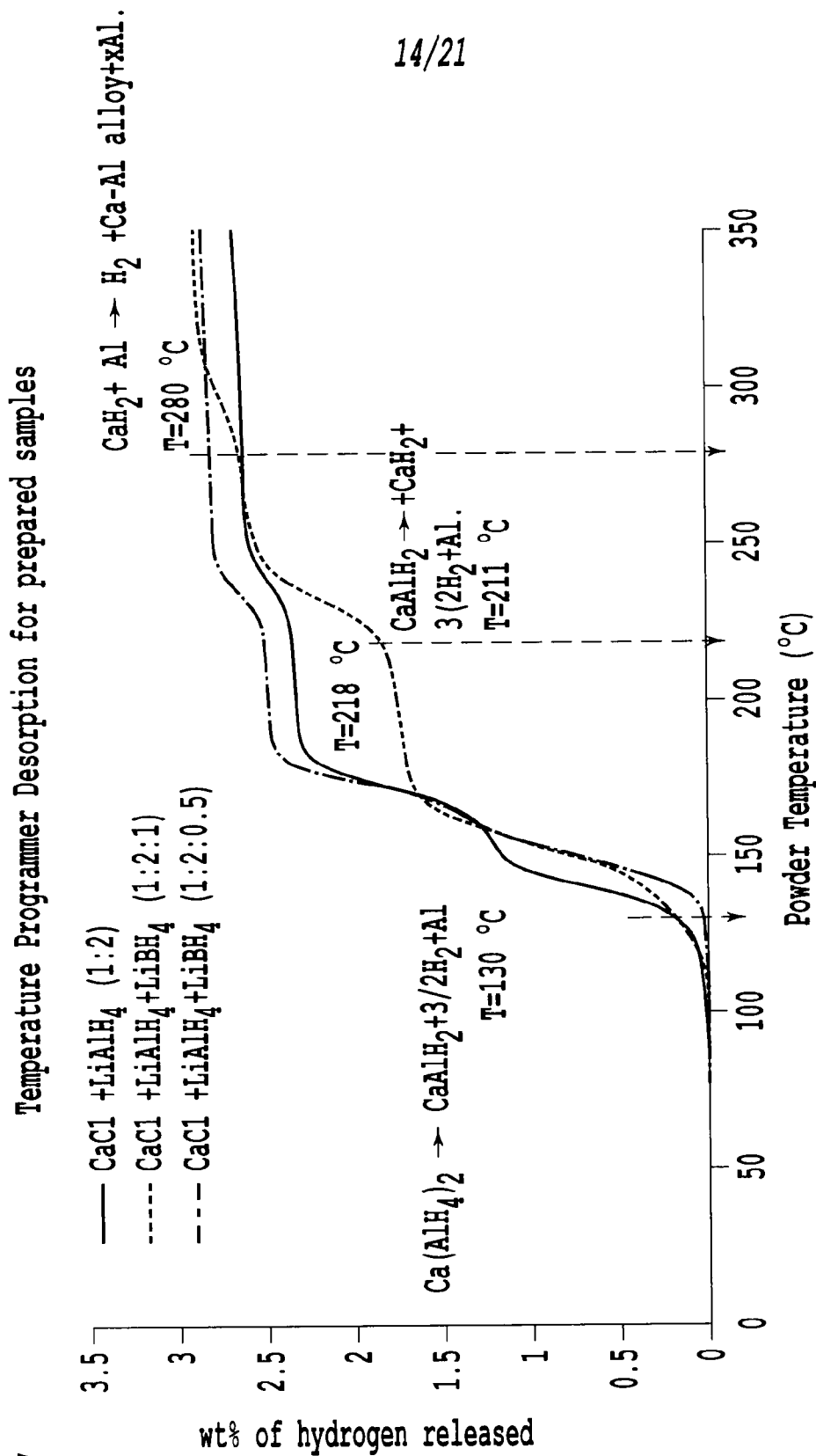
Ca-alanate ($\text{CaCl}_2:\text{LiAlH}_4$)
-x LiBH_4 systems

XRD for "as synthesized" samples as indicated-Samples prepared using Ball milling
 $\text{CaCl}_2:\text{LiAlH}_4:\text{LiBH}_4$ (1:2:0.5 molar)



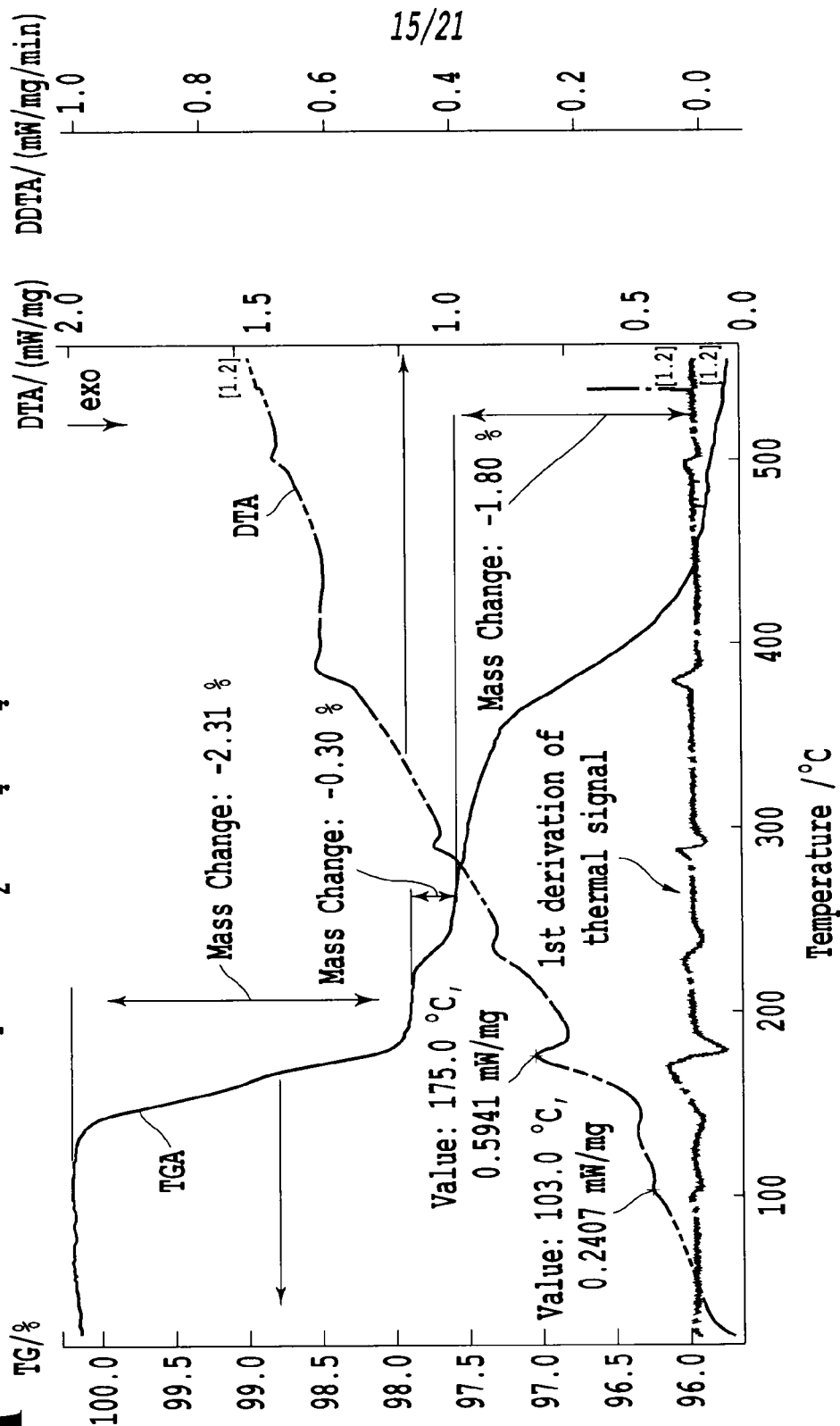
- 1) Formation of LiCl
- 2) Absence of LiBH_4
- 3) Absence of $\text{Ca}(\text{AlH}_4)_2$ clean XRD in literature; $\text{Ca}(\text{AlH}_4)_2$ ID peaks makes analysis inappropriate



Fig. 14

14/21

- 1) Onset temperature and decomposition set modification as LiBH_4 content was increased
- 2) wt% H_2 released $\uparrow$ in LiBH_4 presence @ $T < 200^\circ\text{C}$

Fig. 15AThermal analysis: $\text{CaCl}_2\text{:LiAlH}_4\text{:LiBH}_4$ 1:2:0.5 molar

- 1) 1st decomposition step is endothermic decomposition step $\rightarrow \text{Ca(AlH}_4)_2$ is not present in the sample (exothermic, see DTA comparison) - Reversibility potential
- 2) LiBH_4 presence in the sample is indicated based on phase transformation and melting

16/21

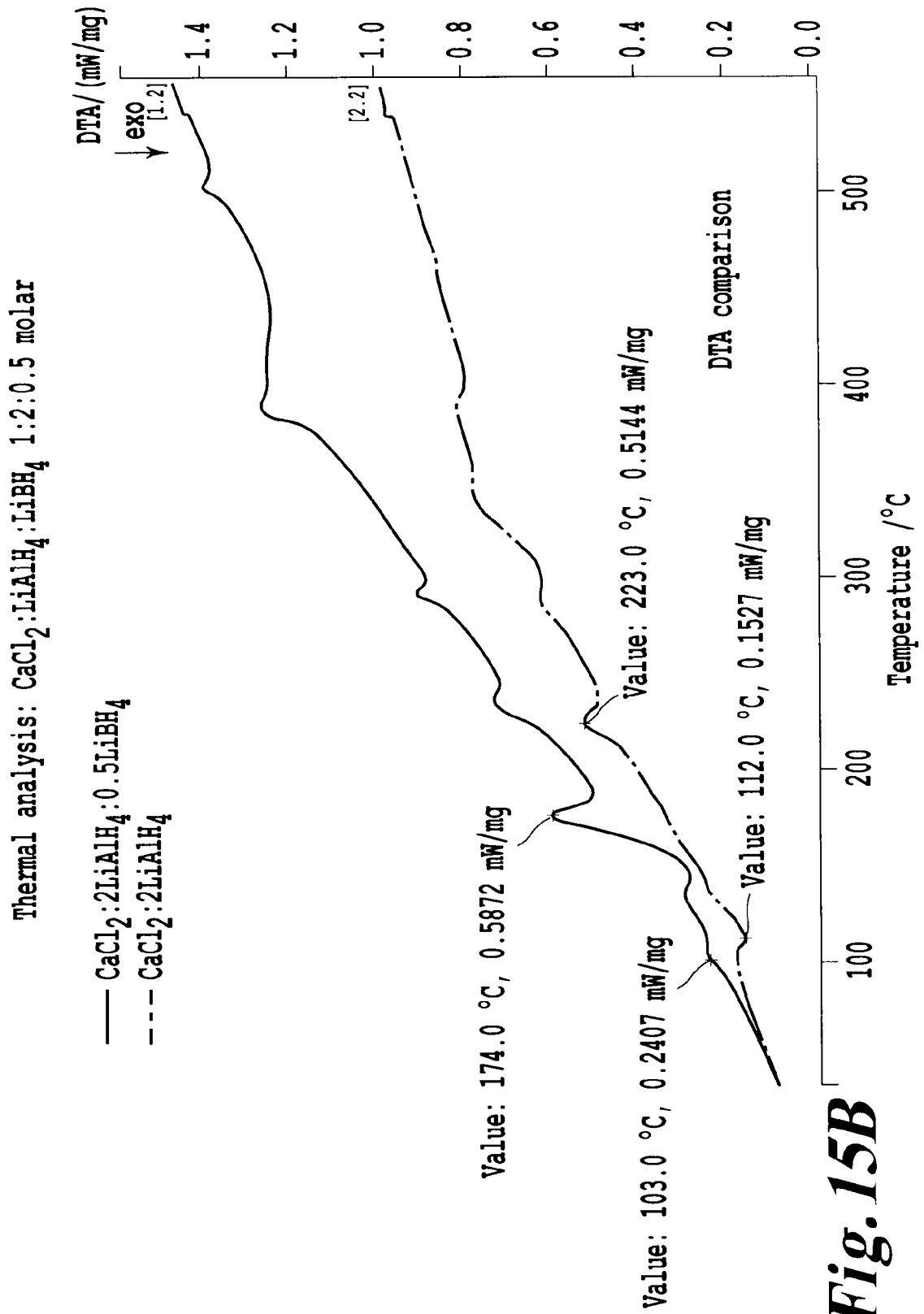


Fig. 15B

17/21

Fig. 16A

MAS NMR results

As synthesized
samples ^{11}B MAS NMR $\omega_r = 14 \text{ kHz}$ $\text{CaCl}_2 + 2\text{LiAlH}_4 + \text{LiBH}_4$ $\text{CaCl}_2 + 2\text{LiAlH}_4 + 0.5\text{LiBH}_4$ $\text{MgCl}_2 + 2\text{LiAlH}_4 + 0.5\text{LiBH}_4$

-41.6 ppm

 LiBH_4 Fate

11B MAS shows LiBH_4 presence in the
sample based on signature shift at -41.6 ppm

LiBH_4 from the same samples could not be seen
in the PXRD for samples containing Mg, Ca alanates

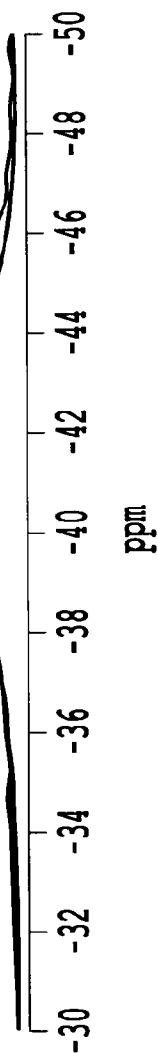


Fig. 16B
MAS NMR results*

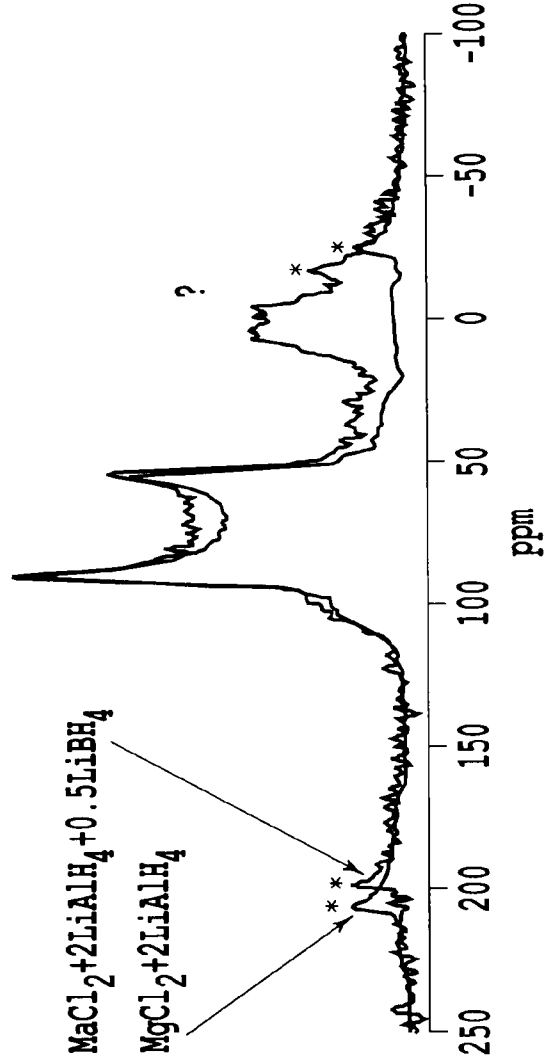
Mg based systems
Shifts show $\text{Mg}(\text{AlH}_4)$ presence consistent with
XRD and thermal analysis

Description	Al_M	$\text{Mg}(\text{AlH}_4)_2$	Residual LiAlH_4	0 ppm $(\text{AlH}_3 \text{ ??})$
$\text{MgCl}_2 + 2\text{LiAlH}_4 + 0.5\text{LiBH}_4$	68	24	1	7
$\text{MgCl}_2 + 2\text{LiAlH}_4$	7.3%	91.7%	1	0

As synthesized
samples

Is LiBH_4 promoting $\text{Mg}(\text{AlH}_4)_2$ decomposition,
or is it $\text{Mg}(\text{AlH}_4)_x(\text{BH}_4)_y$?

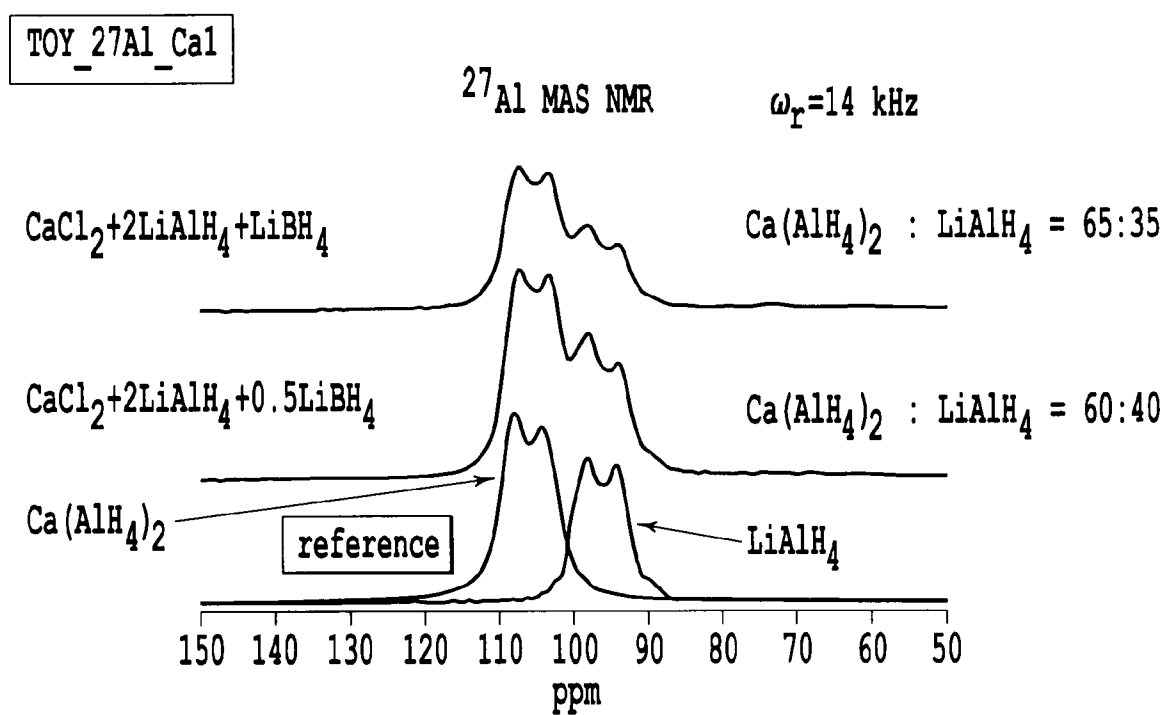
^{27}Al MAS NMR
 $\omega_r = 14\text{-}15 \text{ kHz}$



19/21

Fig. 17A

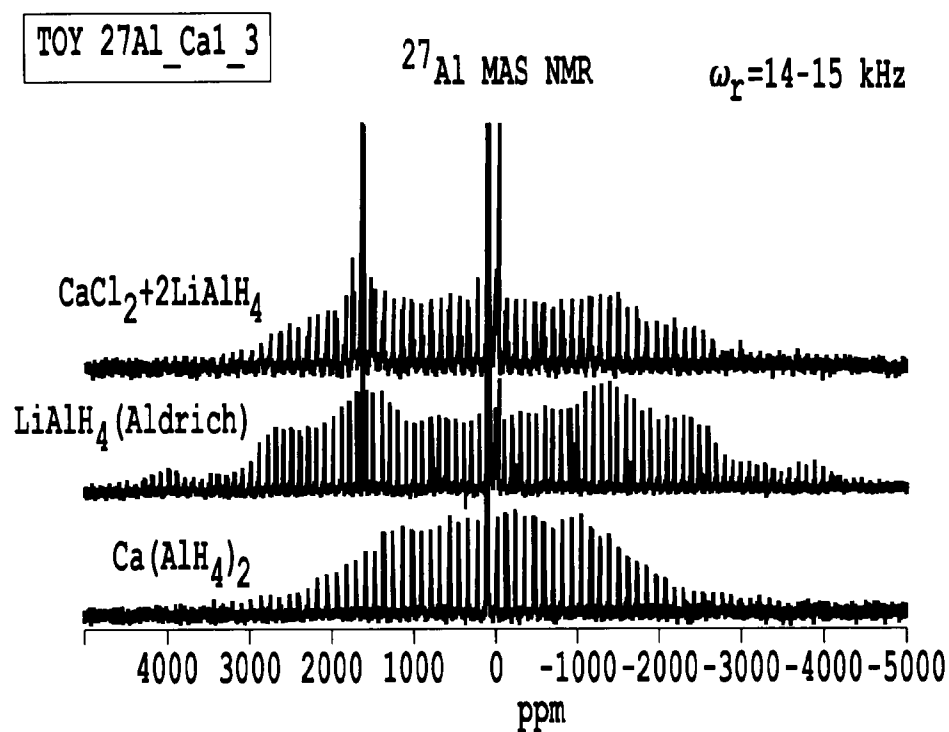
Ca based systems



20/21

Fig. 17B

Ca based systems



Sample	Description	Al _M	Ca(AlH ₄) ₂ ??	Residual LiAlH ₄	Li ₃ AlH ₄ (-34.7 ppm)
TOY-5	CaCl ₂ + 2LiAlH ₄	14.9	42.9	37.2	5.0
TOY-2	CaCl ₂ + 2LiAlH ₄ + 0.5LiBH ₄	5%	57%	38%	-
TOY-3	CaCl ₂ + 2LiAlH ₄ + LiBH ₄	21%	47%	25%	7%

21/21

SUMMARY

- Ionic exchanges observed showed that hydrides chemical reactions are driven by the system thermodynamics
- LiBH_4 promoter effects clearly observed:
 - 1) Rate and onset decomposition lowered by 50°C for Mg alanate: $x\text{LiBH}_4$ system
 - 2) Rate and onset decomposition modified for Ca alanate: $x\text{LiBH}_4$ system-Endothermic decomposition in the presence of LiBH_4 observed
 - 3) LiBH_4 present as amorphous following milling for Mg and Ca alanates systems and was observed in MAS NMR

Formation of $\text{Ca}(\text{AlH}_4)(\text{BH}_4)$ or $\text{Mg}(\text{AlH}_4)(\text{BH}_4)$ ☐ ☐

Fig. 18

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/41533

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C01B 6/24 (2010.01)

USPC - 423/286; 423/648.1; 423/644

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

USPC - 423/286; 423/648.1; 423/644

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PubWest: PGPB,USPT,USOC,EPAB,JPAB; Google; borohydride, BH4, tetrahydroborate, aluminum, alkali, basic, base, lithium, sodium, potassium, alkaline, alkalinity, magnesium, calcium, strontium, barium, unsolvated, aluminum chloride, lithium borohydride, solvate, aprotic, stabilize

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HUMMELSHOJ et al. Density Functional Theory Based Screening of Ternary Alkali-Transition Metal Borohydrides: A Computational Material Design Project. J. Chem. Phys. 01 July 2009, 131, 014101, pages 1-9.	1-3, 6 ----- 4-5 and 7-8
Y	US 2006/0013753 A1 (VAJO et al.) 19 January 2006 (19.01.2006) para [0052].	4-5
Y	EP 1,867,602 A2 (ZANELLA et al.) 19 December 2007 (19.12.2007) para [0031]-[0032].	7-8

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 September 2010 (28.09.2010)

Date of mailing of the international search report

18 OCT 2010

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/41533

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 21
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 21 is considered unsearchable because it is a claim that is not drafted in accordance with PCT Rule 6.2(a).

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-8 directed to a complex compound.

Group II: claims 9-14 directed to a complex compound having the composition $M1_{sup.x} + M2_{sup.y} + Al_{sup.3} + (BH4)_{sub.3+x+y}$ where M1 and M2 are different elements other than Al selected from the group consisting of metals; x is a valence number of 1, 2, 3, 4, 5, 6, 7 or 8; and y is a valence number of 1, 2, 3, 4, 5, 6, 7 or 8.

Group III: claims 15-20 directed to a complex compound having a composition $Al(BH4)_3R$, where R is an organic adduct.

---See Additional Sheet---

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-8

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/41533

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding technical features for the following reasons:

Groups I and II do not include the organic adduct of Group III.

Groups I and III do not include the M2 element of group II.

The common feature of groups I, II and III of a complex compound of $\text{MAl}(\text{BH}_4)_{\text{sub.}3+x}$ is taught by US 6,251,349 B1 issued to Zaluska et al. on 26 July 2001 (col 1, ln 43; ' $\text{K}(\text{Al}(\text{BH}_4)_4)$ ' K is M with a valence number of 1); therefore the common feature is not an improvement over the prior art.

None of these technical features are common to the other groups, nor do they correspond to a special technical feature in the other groups. Therefore, unity of invention is lacking.