Structures and Thermodynamics of the Mixed Alkali Alanates

J. Graetz, Y. Lee*, J. J. Reilly, S. Park*, T. Vogt*
Department of Energy Sciences and Technology
*Department of Physics
Brookhaven National Laboratory
Upton, New York 11973
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The thermodynamics and structural properties of the hexahydride alanates (M₂MₐAlH₆) with the elpasolite structure have been investigated. A series of mixed alkali alanates (Na₂LiAlH₆, K₂LiAlH₆, K₂NaAlH₆) were synthesized and found to reversibly absorb and desorb hydrogen without the need for a catalyst. Pressure-composition isotherms were measured to investigate the thermodynamics of the absorption and desorption reactions with hydrogen. Isotherms for catalyzed (4 mol% TiCl₃) and uncatalyzed Na₂LiAlH₆ exhibited an increase in kinetics, but no change in the thermodynamics with the addition of a dopant. A structural analysis using synchrotron x-ray diffraction showed that these compounds favor the Fm3m space group with the smaller ion (M⁻) occupying an octahedral site. These results demonstrate that appropriate cation substitutions can be used to stabilize or destabilize the material and may provide an avenue to improving the unfavorable thermodynamics of a number of materials with promising gravimetric hydrogen densities.

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I. INTRODUCTION

There is currently much interest in the development of a sustainable hydrogen storage material for mobile applications. The key requirements for any candidate material for practical on-board hydrogen storage are a high gravimetric hydrogen density and safe, fast, and fully reversible hydrogenation near ambient conditions. Conventional metal hydrides that can readily supply hydrogen at room temperature have storage capacities < 2 wt.% and cannot satisfy this need. However, a number of complex hydrides have appreciable gravimetric hydrogen storage capacities, such as the sodium alanates, which reversibly absorb/desorb hydrogen with the addition of a metal dopant [1, 2]. At present, there is considerable interest in understanding the kinetic enhancements attributed to the transition-metal dopant [3–6] and the mechanism by which the dopant makes the sodium alanates reversible [3–6, 7–9, 10, 11, 12]. The reversible hydrogenation of NaAlH₄ occurs in two steps in the presence of Ti:

3NaAlH₄ ↔ Na₃AlH₆ + 2Al + 3H₂ (3.7 wt.%) (1)

2Na₃AlH₆ ↔ 6NaH + 2Al + 3H₂ (1.9 wt.%). (2)

While the atomic mechanism is not understood, it appears that Ti resides in an under-coordinated environment at or near the surface of the depleted material [10, 11]. Despite the recent attention, sodium aluminum hydride is unlikely to meet the requirements necessary for automotive applications [12]. A few alternatives that exhibit higher hydrogen capacities are LiAlH₄ (7.9 wt.%) and Mg(AlH₄)₂ (6.9 wt.%), which have initial hydrogen desorption temperatures of 453 K and 423 K, respectively [8, 12]. However, these materials have low reaction enthalpies and therefore require extremely high pressures for the absorption of hydrogen.

Despite the unfavorable thermodynamics, it may be possible to change the decomposition temperature and pressure of the high capacity alanates by altering the material composition. The possibility of mixing two different alkali metals (M and M') to form a mixed alanate of MₓMₓ⁻₁AlH₄ or Mₓ−ₓMₓ⁺⁻AlH₆ has been explored by recent computational studies [10, 11]. These efforts suggest that the tetrahydride alanates may be relatively unstable with respect to cation mixing. An ab initio study by de Dompablo and Ceder has shown Na₁₋ₓLiₓAlH₄ favors phase separation at 0 K for 0 < x < 1 [12]. However, there are a number of stable mixed compounds predicted for the hexahydrides, specifically the elpasolites M₂MₐAlH₆ [13]. The mixed alkali elpasolites do not revert, according to reaction 1, to a mixed tetrahydride (MₓMₓ⁻₁AlH₄) or a mixture of monoalkali alanates (2MAIH₄ + M’₋AlH₄). Rather, the absorption/desorption of hydrogen occurs in a single step analogous to reaction 2:

M₂M’₋AlH₆ ↔ 2MH + M’⁻H + Al + 3/2H₂. (3)

Despite the number of predicted stable elpasolite phases, Na₂LiAlH₆ is the only composition that has been studied experimentally [11, 13]. The substitution of a Li ion for a Na ion in Na₃AlH₆ to form Na₂LiAlH₆ lowers the equilibrium H₂ pressure by 20 bar at 484 K [11]. However, little else is known about the effects of alkali substitutions in the hexahydrides. In this study, the structural and thermodynamic properties of the elpasolites (MₓMₓ⁻₁AlH₄ where M ≠ M’) were investigated and compared with those of the cryolites (M=M’) to better understand the thermodynamic changes induced by cation mixing. Thermodynamic values were obtained by measuring pressure-composition isotherms and estimating the enthalpy and entropy of the reaction.

II. EXPERIMENTAL

Preparation of the bialkali alanates is accomplished using a number of conventional methods such as dry milling...
or wet chemical techniques. In this study, a tetrahydroxide alanate was mechanically alloyed with the appropriate alkali hydride(s) using either of the following two reactions:

\[ M'\text{AlH}_4 + 2\text{MH} \rightarrow M_2M'\text{AlH}_6 \]  

\[ \text{MAI}_4 + \text{MH} + M'H \rightarrow M_2M'\text{AlH}_6. \]

Precursors of LiAlH\(_4\) (95\%) and LiH (99.4\%) were purchased from Alfa Aesar, while NaH (95\%) and NaAlH\(_4\) (90\%) were obtained from Aldrich. KH was received from Fluka dispersed in mineral oil at a concentration of 33\%. The oil was removed via an octane wash under Ar gas and dried under vacuum. It should be noted that dry KH is extremely pyrophoric and should only be handled in an inert atmosphere. Milling was performed in an Ar atmosphere with a Fritsch Pulverisette 5 planetary mill. The gas pressure and temperature were monitored during milling to ensure that the majority of the hydrogen remained in the solid. The powders (1–2 g) were milled in a 250 mL stainless steel vial with seven 15 mm diameter stainless steel balls (13.7 g) for up to 40 h at 200 rpm. The Ti-doped material was prepared by milling 96 mol\% Na\(_2\)LiAlH\(_6\) with 4 mol\% TiCl\(_4\) (Aldrich) under the same conditions for 1 h.

Structural properties were determined using synchrotron x-ray diffraction (XRD). These experiments were performed on beamline X7A at the National Synchrotron Light Source of Brookhaven National Laboratory. Prior to the diffraction study, each sample was annealed for approximately 20 h under high pressure H\(_2\) gas (160 bar at 510 K for Na\(_2\)LiAlH\(_6\), 40 bar at 570 K for K\(_2\)NaAlH\(_6\) and 150 bar at 480 K for K\(_2\)LiAlH\(_6\)). After annealing, the powders were sieved using a 400 mesh screen (37 \(\mu\)m) and then sealed in 0.5 mm glass capillary tubes under Ar gas. The capillary was mounted on the 2nd axis of the diffractometer. A monochromatic beam was selected using a channel-cut Si(111) monochromator. A gas-proportional position-sensitive detector (PSD), gated at the Kr-escape peak, was employed for high-resolution \((\Delta d/d \sim 10^{-3})\) powder diffraction data measurements. The PSD was stepped in 0.25° intervals between 10° and 70° in 2θ with an increasing counting time at higher angle. The capillary was spun during the measurement to provide better powder averaging.

Pressure-composition isotherms were measured using a Sievert’s-type apparatus. The material was reacted in a stainless steel tube, which was heated using a resistive tape. The internal sample temperature was monitored using a type K thermocouple. The absorption/desorption isotherms were measured by adding/removing an aliquot of H\(_2\), allowing equilibrium to be reestablished, and measuring the pressure change.

## III. RESULTS AND DISCUSSION

### A. Li\(_2\)NaAlH\(_6\) and Li\(_2\)KAlH\(_6\)

The preparation of Li\(_2\)NaAlH\(_6\) was attempted using two different synthesis routes: reactions 1 and 5. In both cases, a characterization of the reaction products using x-ray diffraction showed the formation of a small amount Na\(_2\)LiAlH\(_6\), but no other compositional changes. Similarly, attempts to synthesize Li\(_2\)KAlH\(_6\) using reaction 5 were also unsuccessful. X-ray diffraction after milling revealed a reaction product consisting of KAlH\(_4\) and LiH. These results suggest that Li\(_2\)NaAlH\(_6\) and Li\(_2\)KAlH\(_6\) are thermodynamically less stable than other competing cryolite or elpasolite phases. Lovvik et al. have predicted the enthalpy changes associated with mixing different alkali metals to form a biaxial alanate at 0 K using density functional theory (DFT). The large, positive mixing enthalpies associated with Li\(_2\)NaAlH\(_6\) and Li\(_2\)KAlH\(_6\) (10.9 and 20.8 kJ/mol, respectively) are additional evidence that these compounds are thermodynamically unstable.

### B. Na\(_2\)LiAlH\(_6\) and Na\(_2\)KAlH\(_6\)

Na\(_2\)LiAlH\(_6\) was prepared by both reaction 1 and 5. A characterization of the material at different stages of alloying using XRD showed that in reaction 5 intermediate phases of NaAlH\(_4\) and LiH are formed before the final product (Na\(_2\)LiAlH\(_6\)), while pathway 1 leads to Na\(_2\)LiAlH\(_6\) directly. The structure of Na\(_2\)LiAlH\(_6\) was determined by x-ray powder diffraction using a wavelength of 0.7149 Å (Fig. 1). An elemental analysis, measured with an inductively coupled plasma - mass spectrometer (ICP-MS), confirmed a near-stoichiometric composition of 2.02:1.06:1.00 for Na:Li:Al. A Rietveld refinement using GSAS was performed with the constrained stoichiometry (Na2LiAlH6) and revealed the best fit in the Fm\(\overline{3}m\) space group with a lattice constant of 7.4064(1) Å. This is in contrast with the room temperature phases of the pure cryolites Li\(_3\)AlH\(_6\) and Na\(_3\)AlH\(_6\), which crystallizes in the R\(\overline{3}\) and P\(\overline{2}_1/n\) space groups, respectively. The Rietveld fit along with a difference plot are shown in Fig. 1. The results of the Rietveld analysis, displayed in Table 1, demonstrate that the Na ions are in a 12-fold coordination while the Li ions oc-
TABLE I: Interatomic distances and coordination numbers for Na$_2$LiAlH$_6$.

| Neighbors | Distance (Å)    | Coordination |
|-----------|-----------------|--------------|
| Na-H      | 2.6205(3)       | 12           |
| Na-Al     | 3.2071(1)       | 4            |
| Na-Li     | 3.2071(1)       | 4            |
| Na-Na     | 3.7032(1)       | 6            |
| Li-H      | 1.952(8)        | 6            |
| Li-Na     | 3.2071(1)       | 8            |
| Li-Al     | 3.7032(1)       | 6            |

FIG. 2: Pressure-composition absorption (●) and desorption (○) isotherms for (a) Ti-doped Na$_2$LiAlH$_6$ and (b) uncatalyzed Na$_2$LiAlH$_6$. The arrows indicate the direction of hydrogen transfer.

ocupy octahedral sites. These values are consistent with the predictions of Lovvik et. al and are also in agreement with the space group and lattice constant reported by Claudy et. al using conventional x-ray diffraction.

The pressure-composition isotherms for catalyzed and uncatalyzed Na$_2$LiAlH$_6$ are displayed in Figs. 2a and 2b, respectively. Desorption isotherms are shown at various temperatures between 476 K and 518 K. The isotherms exhibit a sharp transition upon desorption indicating the emergence of a new phase with little or no solid solution region. Another sharp transition appears at the end of desorption, indicating the depletion of the Na$_2$LiAlH$_6$ phase. A complete absorption/desorption isotherm taken at 486 K is also displayed in Fig. 3a. The complete absorption/desorption isotherm exhibits little hysteresis as previously reported by Bogdanovic et. al. The measured hydrogen capacities for the catalyzed material are approximately 3.0 wt.% (85% of theoretical) for the first cycle (496 K) and 2.6 wt.% (75% of theoretical) for subsequent cycles. The hydrogen capacity for the uncatalyzed material is 3.2 wt.% (91% of theoretical) for the first cycle (518 K) and 2.8 wt.% (80% of theoretical) for subsequent cycles. In both cases, the capacity loss after the first cycle is attributed to incomplete absorption, which was confirmed by the presence of NaH, LiH and Al in XRD patterns after rehydriding.

The thermodynamic parameters of the decomposition reaction were calculated from the van’t Hoff equation:

$$\ln P = \frac{1}{T} \left( \frac{\Delta H}{R} \right) + \frac{\Delta S}{R},$$

where $P$ is the equilibrium H$_2$ pressure at temperature $T$ and $R$ is the universal gas constant. Using a plot of lnP vs. 1/T, known as a van’t Hoff plot, the enthalpy ($\Delta H$) and entropy ($\Delta S$) are determined from the slope and intercept, respectively. The van’t Hoff plots for Ti-doped Na$_3$AlH$_6$ and Na$_2$LiAlH$_6$ (doped and undoped) are shown in Fig. 3. The equilibrium pressure values were taken from the midpoint of the plateau in Fig. 2. The plateau pressure of Na$_3$AlH$_6$ is approximately 20 bar higher than that of Na$_2$LiAlH$_6$ at 486 K and 30 bar higher at 518 K. The measured decomposition enthalpy, $\Delta H = 53.5 \pm 1.2$ kJ/mol H$_2$, is slightly more positive than the decomposition enthalpy of Na$_3$AlH$_6$ (47 kJ/mol H$_2$). The entropy change, $\Delta S = 132.1 \pm 2.4$ J/mol K of H$_2$, is approximately equivalent to the entropy associated with the formation of molecular hydrogen ($S(H_2) = 130.7$ kJ/mol K).

The addition of a catalyst (4 mol% TiCl$_3$) significantly improves the reaction kinetics. In the uncatalyzed state, Na$_2$LiAlH$_6$ begins slowly desorbing hydrogen at approximately 490 K, while the catalyzed material exhibits a desorption temperature of less than 470 K. Similarly, the...
time required for the system to return to equilibrium is substantially decreased by the addition of a catalyst. Equilibrium times ranged from 1–2 days for the Ti-doped samples to approximately 1 week for the undoped material.

Although the kinetics of reaction 4 are clearly enhanced by the addition of Ti, the thermodynamics remain unaffected. This is demonstrated in Figure 3, which illustrates that the data for the catalyzed and uncatalyzed material fall on the same line in the van’t Hoff plot. The dopant has no measurable affect on the enthalpy or entropy of the desorption reaction. This supports a number of recent studies that suggest that the Ti acts as a true catalyst (possibly in the form of a Ti-Al alloy) and does not alter the reaction thermodynamics.

The preparation of Na$_2$KAlH$_6$ was attempted using reaction 5. X-ray diffraction of the reaction product revealed phases of K$_2$NaAlH$_6$ and Na$_3$AlH$_6$. This is consistent with predicted mixing enthalpies, which suggest that Na$_2$KAlH$_6$ is considerably less stable than K$_2$NaAlH$_6$ (by 40 kJ/mol) at 0 K. Therefore, Na$_2$KAlH$_6$ should favor phase separation into equal parts K$_2$NaAlH$_6$ and Na$_3$AlH$_6$, as empirically observed.

### C. K$_2$LiAlH$_6$ and K$_2$NaAlH$_6$

A new alanate was prepared by mixing K and Li ions in reaction 4 to form K$_2$LiAlH$_6$. An elemental analysis of the product (ICP-MS) revealed a near-stoichiometric composition of 2.04:1.10:1.00 for K:Li:Al. The powder diffraction results, using x-rays of wavelength 0.7329 Å, are shown in Fig. 4. This pattern was not suitable for a Rietveld analysis due to a number of additional broad peaks attributed to KH impurities. However, a full profile fit to the data demonstrated the best fit in the $Fm3m$ space group with a lattice parameter of 7.9383(5) Å. As observed for Na$_2$LiAlH$_6$, the mixed potassium/lithium elpasolite crystallizes in a different space group than the pure cryolite phases Li$_3$AlH$_6$ and K$_3$AlH$_6$, which have rhombohedral ($R$) and tetragonal ($T$) symmetries, respectively. The full profile fit along with a difference pattern are displayed in Fig. 4. The $Fm3m$ space group is consistent with the structure predicted by DFT for K$_2$LiAlH$_6$.

K$_2$NaAlH$_6$ was prepared by both synthesis routes (reaction 4 and 5). The structural characterization was performed by XRD using a wavelength of 0.6985 Å (Fig. 5). An elemental analysis (ICP-MS) gave a composition of 1.54:0.97:1.00 for K:Na:Al. A small amount of NaH was detected in the diffraction pattern indicating that the product was probably stoichiometric K$_2$NaAlH$_6$ with a NaH impurity (~20 mol%). A sample prepared with excess KH (~25 mol%) resulted in a similar diffraction pattern with the exception of small amounts of KH impurities. Therefore, the Rietveld refinement using the data presented in Fig. 5 was performed with a fixed stoichiometry of K$_2$NaAlH$_6$ (impurities were ignored). The Rietveld fit, in the $Fm3m$ space group, along with a difference plot are shown in Fig. 5. The measured lattice parameter is $a = 8.1209(1)$ Å. The nearest-neighbor distances and coordination numbers are listed in Table II.

The first, and only other reported synthesis of K$_2$NaAlH$_6$ used reaction 4 in an organic medium under high pressure (25 kbar) H$_2$ gas. An XRD structural char-
The initial desorption occurs at approximately 500 K for the system to reach equilibrium after the sorption reaction proceeds slowly in both samples. The capacity for K2LiAlH6 is 2.0 wt.%, respectively. This capacity is 90% of the theoretical value and the loss is attributed to an impurity of KOH in the KH precursor.

Due to the impractically slow reaction kinetics, it was not feasible to measure a series of desorption isotherms at different temperatures. Therefore, the reaction enthalpies for K2LiAlH6 and K2NaAlH6 were approximated from equation 4. The equilibrium pressures were taken from the midpoint of the isotherms shown in Fig. 6. The entropy was estimated, \( \Delta S_{T \to \infty} \approx 130.7 \text{ kJ/mol K} \), using the change in entropy associated with the transition of hydrogen from an ordered solid to a gas. The estimated decomposition enthalpies (reaction 3) for K2LiAlH6 and K2NaAlH6 are 82 kJ/mol H2 and 97 kJ/mol H2, respectively.

A summary of the structural and thermodynamic data for the hexahydride alanates is presented in Table III. The bialkali alanates have a face centered cubic structure in the Fm3m space group, similar to the high temperature (525 K) sodium alanate phase, \( \beta\text{-NaAlH}_6 \).

In these compounds (\( \beta\text{-M}_2\text{M}'\text{AlH}_6 \)), the smaller \( \text{M}' \) is octahedrally coordinated while \( \text{M} \) has a 12-fold coordination. A diagram of the general elpasolite structure is shown in Fig. 7. In the monoclinic (\( P2_1/n \)) polymorph, \( \alpha\text{-M}_2\text{M}'\text{AlH}_6 \), the M ion is coordinated by 8 atoms [34]. Ab initio calculations have predicted \( \alpha\text{-Na}_2\text{LiAlH}_6 \) to be slightly more stable than the \( \beta \)-phase at 0 K [17]. However, at 300 K the experimental data suggests that the \( \beta \) polymorph is preferred for all of the stable bialkali alanates. It is interesting to note that when two different alkali metals are present, the octahedral site is always occupied by the smaller ion. The compounds Li2NaAlH6, Li3KAlH6, and Na2KAlH6 tend to phase separate, suggesting that the substitution of the smaller ion into the 12-fold coordinated site is thermodynamically unfavorable. This trend also seems to apply to the "true" elpasolites, \( \beta\text{-M}_2\text{M}'\text{AlF}_6 \). Each of the stable bialkali aluminum hydrides (\( \text{M}, \text{M}' = \text{Li}, \text{Na} \) or \( \text{K} \)) has a corresponding fluoride compound with a similar lattice constant (\( \pm 0.2 \text{ Å} \)) [35, 36, 37] in the \( \text{Fm}3\text{m} \) space group. Analogous to the hydrides, there are no reported fluorides where \( \text{M}' \) is greater than \( \text{M} \).

The decomposition temperature (\( T_d \)) and enthalpy are also dependent upon the size of the alkali metals \( \text{M} \) and \( \text{M}' \). The substitution of Li for Na to form \( \text{Na}_2\text{LiAlH}_6 \) increases \( \Delta H \) and \( T_d \) by 6.5 kJ/mol and 20 K, respectively. This case is an exception to the general rule that the decomposition temperature and enthalpy increase with the size of the alkali metal. This trend is well documented for the monoalkali alanates, as shown in Table III. The tendency for greater hydride stability with a larger alkali metal also applies when only a partial substitution of the metal is involved. For example in the K-M' alanates, K2NaAlH6 is 14.6 kJ/mol more stable than K2LiAlH6 and 38.5 kJ/mol less stable than K2KAlH6.
TABLE III: Structural and thermodynamic properties based upon experimental data for alanates of the form M₂M’AlH₆.
The parameters listed include the structure (space group or symmetry), lattice constants, decomposition enthalpy (∆H) and
decomposition temperature (Tₜ). The data for the cryolite phases were obtained from the references listed.

| M    | M’   | Structure | Lattice Constants (Å) | ∆H (kJ/mol H₂) | Tₜ (K) | References |
|------|------|-----------|-----------------------|----------------|--------|------------|
| Li   | Li   | R3        | a = 8.07(2)(1) c = 9.51(3)(2) | 43.5 | 453 | [28], [29], [15] |
| Li   | Na   | unstable  | -                     | -              | -      |            |
| Li   | K    | unstable  | -                     | -              | -      |            |
| Na   | Na   | Fm3m     | a = 7.40(4)(1)         | 53.5(12)       | 490    |            |
| Na   | K    | unstable  | -                     | -              | -      |            |
| K    | Li   | Fm3m     | a = 7.93(5)            | 82             | 500    |            |
| K    | Na   | Fm3m     | a = 8.12(9)(1)         | 97             | 530    | [31], [32], [27] |
| K    | K    | tetragonal| a = 8.445 b = 8.584    | 135            | 593    |            |

IV. CONCLUSION

Novel elpasolite phases of the complex alanates were synthesized using conventional mechanical alloying tech-
niques. Each of these compounds reversibly absorbs and desorbs hydrogen without a catalyst. The addition of a
catalyst to Na₂LiAlH₆ shows improved kinetics, but no change in the bulk thermodynamics. Structural analyses
of the bialkali alanates demonstrates that the preferred space group is Fm3m with the larger ion in a 12-fold
coordination and the smaller occupying an octahedral site. In general, a smaller alkali ion (M or M’) reduces
the reaction enthalpy of the hexahydride. These results demonstrate that the temperature of hydrogen evolution
and the equilibrium gas pressure can be tailored by appropriate substitutions of the alkali metals.

V. ACKNOWLEDGEMENTS

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