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## RESEARCH ARTICLE

## Influence of LiH and Ti metal additives on milling LiAlH<sub>4</sub> compound

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### Abstract

Adding LiAlH<sub>4</sub> with Ti-metal as a catalyst and ball-milling in argon atmosphere for 5 and 35 hours results in solid-state transformation of tetrahedral LiAlH<sub>4</sub> into octahedral Li<sub>3</sub>AlH<sub>6</sub> and the transformation is investigated using XRD, FT-IR and the thermal stability of the compounds after milling is measured by thermogravimetric analysis. XRD data reveals partial transformation of LiAlH<sub>4</sub> into Li<sub>3</sub>AlH<sub>6</sub> after 5 hours of milling. After 35 hours almost complete transformation occurs. The data obtained from FT-IR spectra approve the XRD results. The thermal stability of the compounds is significantly affected by increasing temperature over 100°C. Mechanical milling of LiAlH<sub>4</sub> with LiH in argon atmosphere needs 72 hours to transform to Li<sub>3</sub>AlH<sub>6</sub>. Increasing the milling time to 120 hr the compounds are amorphized and its thermal stability deteriorates.

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### Introduction

Synthesis and characterization of complex hydrides with the general formula S<sub>x</sub>M<sub>y</sub>H<sub>z</sub>, at which S is an alkali or alkaline earth metal and M is a non-transition or transition metal, have been studied by different methods (Bronger, 1991; Firman and Landis, 1998; Olofsson-Mårtensson et al., 1999; Wiswall et al., 1978). In general, the family of non-transition complex hydrides consists of S<sup>+</sup>cation and MH<sub>4</sub><sup>-</sup> anion, where the H atoms are tetrahedrally coordinated around the M atom and have a distinct electron-rich character (Lauher et al., 1979). As they contain lightweight elements such as lithium, sodium, and aluminum, non-transition complex hydrides (such as LiAlH<sub>4</sub> (Sklar and Post, 1967) and Li<sub>3</sub>AlH<sub>6</sub> (Ehrlich et al., 1966)) offer the potential of much higher hydrogen capacities than the intermetallic hydrides and since overall hydrogen content of two alkali metal aluminohydrides, LiAlH<sub>4</sub> and NaAlH<sub>4</sub> (10.5 and 7.3 wt% H<sub>2</sub>, respectively), is one of the highest among about 70 known complex hydrides (Yvon, 1998), there has been considerable increase of interest to them as potential ultra-high capacity hydrogen storage solids (Bogdanović and Schwickardi, 1997; Gross et al., 2000; Sandrock, 1995; Zidan et al., 1999). Formation and decomposition of hydrides in these complex hydrides are barely reversible, which in turn making them impractical for industrial applications. Till recently, this situation has been changed by (Bogdanović and Schwickardi, 1997) who pioneered the demonstration that upon doping with certain titanium compounds, the dehydrogenation of NaAlH<sub>4</sub>/Na<sub>3</sub>AlH<sub>6</sub>/Na<sub>2</sub>LiAlH<sub>6</sub> could be kinetically enhanced and rendered reversible under moderate conditions in the solid state.

Further progress devoted for the development of catalysts for the reversible dehydrogenation of NaAlH<sub>4</sub> (Gross et al., 2000; Zidan et al., 1999). Also Balema et al. reported that iron-metal showed good catalytic effect on the decomposition of pure LiAlH<sub>4</sub> (Balema et al., 2000a). It is noteworthy that the hydrogen plateau pressure of the Na<sub>3</sub>AlH<sub>6</sub> into NaH + Al + H<sub>2</sub> equilibrium is less than 1 atm at temperatures below 100°C, which reduces the

available hydrogen content from 5.5 to 3.6 wt%. The recent progress on the preparation of  $\text{Li}_3\text{AlH}_6$ ,  $\text{Na}_3\text{AlH}_6$ , and  $\text{Na}_2\text{LiAlH}_6$  by the ball milling technique (Zaluski et al., 1999) eliminates the need for high temperatures and pressures that were previously required for their syntheses (Ashby and Kobetz, 1966; Claudy et al., 1982). Furthermore, a mechanistic explanation for the catalytic phenomenon is not available and sufficient kinetic enhancement of the rehydriding process is also required.

Here we study the influence of ball-milling, addition of Ti and LiH and different milling times on pure  $\text{LiAlH}_4$  structure and the reaction products were characterized by X-ray diffraction pattern (XRD), Fourier Transform Infrared spectroscopy (FTIR- spectroscopy) and Thermal gravimetric analysis (TGA).

## 2- Experimental

### 2.1. Materials and methods

$\text{LiAlH}_4$  (95 wt% pure), LiH (97 wt% pure) and Ti-metal powder (99 wt% pure) purchased from Sigma-Aldrich are used.

Due to high sensitivity of all materials to oxygen and water vapor all operations are handled in nearly inert atmosphere using argon as inert gas filling the reaction medium (Ball-mill vial). In order to make sure that the environment inside the reaction medium is filled only with argon, the vial after being filled with stoichiometric mixtures of the reactants was sucked at least three times using a pump and then filled under controlled pressure using pressure gauge with argon and this mechanism is repeated after each taken sample. All reactions were performed in a hardened-steel ball-mill vial using 21 g of steel balls at 600 RPM. Forced air-cooling to the vial was employed to avoid extra heating during ball-milling. Different samples were taken after different time periods and characterized by different techniques.

### 2.2. Characterization

The samples were characterized and identified by using different techniques.

#### 2.2.1. X-ray diffraction pattern (XRD)

The X-ray powder diffraction characterization of the obtained hydride powders was carried out on a Scintag powder diffractometer using  $\text{Cu K}\alpha$  radiation. A full profile Rietveld analysis of the powder diffraction data, which were collected between  $20$  and  $80^\circ$   $2\theta$  at room temperature with a  $0.02^\circ$   $2\theta$  step, was employed for crystal structure refinement and the grain size has been calculated using Scherrer's equation ( $D = \frac{0.9\lambda}{B \cos \theta}$ , where B is the full width at half maximum and  $\lambda$  is the X-ray wavelength). According to Balema et.al. observations, obtained hydride powders were not affected by a short-time exposure (5–10 min) to ambient atmosphere. However, their decomposition became quite apparent if they remained in contact with air for more than 3 h (Balema et al., 2000a).

#### 2.2.2. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed in transmission mode on a Bruker VERTEX 70 FT-IR spectrophotometer using the dry KBr pellet method.

#### 2.2.3. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis using NETZSCH STA 409 Thermogravimetric Analyzer under Helium atmosphere using a heating ramp of  $5^\circ\text{Cmin}^{-1}$  with a sample size of  $\sim 5$  mg.

## 3- Result and discussion

### 3.1. X-ray diffraction section

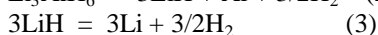
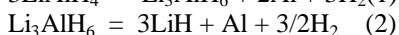
The diffraction patterns of  $\text{LiAlH}_4$  compound before and after different milling times 5 and 35 hours in the presence of Ti as a catalyst are displayed in figure 1. The as-received  $\text{LiAlH}_4$  recorded peaks match with the  $\text{LiAlH}_4$  ICDD card number 73-0461 as shown in figure 1a, the preferred orientations at different angles are shown in table 1. The grain size was found to be 41.5nm of as received  $\text{LiAlH}_4$ .

Table 1. Orientations located at angles ( $2\theta$ ) for as-received  $\text{LiAlH}_4$

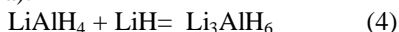
Orientations	Angles (2 $\theta$ )
100	19.7815
020	22.8451
002	24.1873
021	25.7597
048	26.7281
112	27.3446
111	29.2701
121	29.6787
120	30.2616
022	33.4305
121	35.6704

No other peaks belongs to any other phase had been detected which confirms that the as received compound is a single phase.

Significant changes were brought in  $\text{LiAlH}_4$  upon milling in the presence of Ti-metal. General reduction in the peaks intensities and grain size and peaks broadening, are recorded. As observed in figure 1b partial transformation from tetrahedral  $\text{LiAlH}_4$  to octahedral  $\text{Li}_3\text{AlH}_6$  after 5 hours of milling at which  $\text{LiAlH}_4$  intensities decrease and new peaks appear for  $\text{Li}_3\text{AlH}_6$  located at angles  $[2\theta = 21.87, 22.43, 31.64, 35.09 \text{ and } 38.81]$ , these peaks represent the strongest reflections of  $\text{Li}_3\text{AlH}_6$  according to ICDD card number 19-0712. These peaks' intensities reduce by increasing the milling time up to 35 hours as could be observed in the figure 1c. Such reduction could be attributed to the decomposition of  $\text{Li}_3\text{AlH}_6$  by milling as suggested by (Balema et al., 2000b; Blanchard et al., 2004; Brinks and Hauback, 2003; Chen et al., 2001) according to the following equations



Replacing the Ti-catalyst by LiH, the XRD patterns after 72 and 120 hours of milling are shown in figure 2. The data of as received  $\text{LiAlH}_4$  is the same in figure 1 while milling for 72 hours reveals new peaks are related to  $\text{Li}_3\text{AlH}_6$  located at angles  $[2\theta = 22.6014 \text{ and } 38.3441]$ , another peaks are related to LiH are observed located at angles  $[2\theta = 44.33 \text{ and } 64.49]$  as shown in figure 2b, peaks of LiH represent the strongest reflections of LiH according to JCPDS card number (89-4072). Such observation suggests a slower decomposition rate than the Ti-metal catalyst and this attributed to reaction of LiH-powder with  $\text{LiAlH}_4$  to form  $\text{Li}_3\text{AlH}_6$  according to equation (4), then further milling causes  $\text{Li}_3\text{AlH}_6$  decomposition according to equation (2) as reported by Balema et.al. (Balema et al., 2000a).



Not as in Ti-metal case, where peaks hold their position by increasing the milling time from 5 to 35 hours. Peaks at 2-theta equals 44.17 and 21.76 appeared after 72 hours, disappeared in the 120 hours pattern which may be attributed to reduction in the grain size and amorphization occurred after long time of milling as shown in figure 2c.

### 3.2. Fourier transform infrared (FTIR) spectroscopy section

Figure 3 shows transmission mode FT-IR spectra have been recorded for  $\text{LiAlH}_4$  milled in the presence of Ti-metal for 5 and 35 hours in the range of 500 to 4000  $\text{cm}^{-1}$ . Two absorption peaks at 3487  $\text{cm}^{-1}$  and 885  $\text{cm}^{-1}$  correspond to O-H stretching mode and Li-Al-H bending mode respectively. The latter is usually indexed to  $\text{LiAlH}_4$  phase by other authors (Ares et al., 2008; Rather et al., 2009; Zhang et al., 2010), while the former could be attributed to moisture exist in the examined powder as shown in figure 3a. These two peaks are recorded in all powders after milling which confirms the incomplete decomposition of  $\text{LiAlH}_4$  to  $\text{Li}_3\text{AlH}_6$  even after long period of milling. These results are in agreement with the X-ray diffraction data.

Third peak centered at 1470  $\text{cm}^{-1}$  is also recorded, see figure 3a. Such peak is not usually recorded for  $\text{LiAlH}_4$ . In the work of (Graetz et al., 2008) all peaks in the range of 1500 – 1900  $\text{cm}^{-1}$  are indexed to  $\text{LiAlH}_4$  phase. The small shift in the peak position could be attributed to the strain inside the material.

After 5h of milling in the presence of Ti-metal powder two absorption peaks centered at 1440 and 1510  $\text{cm}^{-1}$  are observed see figure 3b. Increasing the time of milling time to 35h results in 2  $\text{cm}^{-1}$  shift in the second peak position (1510  $\text{cm}^{-1}$ ). While the first peak position (1440  $\text{cm}^{-1}$ ) remains unchanged as shown in figure 3c. According to the work of (Li et al., 2012) peak centered at (1440  $\text{cm}^{-1}$ ) has been attributed to Al-H stretching mode of  $\text{Li}_3\text{AlH}_6$ , this peak is an evidence for the formation of  $\text{Li}_3\text{AlH}_6$  phase.

Figure 4 shows the IR-spectra results for the as received  $\text{LiAlH}_4$  milled with LiH powder for 72 and 120 hours. The broad peak related to O-H stretching mode appears nearly at the same wavelength ( $3500\text{ cm}^{-1}$ ), but sharper than in case of Ti-metal.

Table 1 lists all recorded peaks and their indexing. The peaks recorded at  $1436.89$ ,  $864.06$  and  $1004.85\text{ cm}^{-1}$  could be attributed to Al-H stretching mode and Li-Al-H bending mode of the octahedral form  $(\text{AlH}_6)^{-3}$  as reported by (Ares et al., 2008), which in turns confirms the transformation of  $\text{LiAlH}_4$  into  $\text{Li}_3\text{AlH}_6$ , and this results are in agreement with X-ray diffraction pattern of the same samples.

Table 2. FT-IR data of  $\text{LiAlH}_4$  after milling with LiH

Sample after 72 hours of milling		Sample after 120 hours of milling	
Wave Length $\text{cm}^{-1}$	Index	Wave Length $\text{cm}^{-1}$	Index
864.06	Li-Al-H bending mode $(\text{AlH}_6)^{-3}$	858.27	Li-Al-Hbending mode $(\text{AlH}_6)^{-3}$
1004.85	Li-Al-Hbending mode $(\text{AlH}_6)^{-3}$	1008.71	Li-Al-Hbending mode $(\text{AlH}_6)^{-3}$
1436.89	Al-H stretching mode $(\text{AlH}_6)^{-3}$	1429.17	Al-Hstretching mode $(\text{AlH}_6)^{-3}$
1492.82	AL-Hstretching mode $(\text{AlH}_4)^{-1}$	1510.18	AL-Hstretching mode $(\text{AlH}_4)^{-1}$
1577.68	Al-Hstretching mode $(\text{AlH}_4)^{-1}$	1581.54	Al-Hstretching mode $(\text{AlH}_4)^{-1}$
3568.11	OH <sup>-</sup>	3570.04	OH <sup>-</sup>

By increasing the milling time up to 120 hours the only difference observed slight shift in peak position, which could be attributed to variation of bond length.

### 3.3. Thermal gravimetric analysis (TGA) section

Figure (5) presents thermal gravimetric analysis (TGA) of as-received  $\text{LiAlH}_4$  before and after ball milling in the presence of Ti and LiH for different time periods. Two decomposition steps are recognized for all samples. The overall weight loss for as-received sample is about 8% which in line with the recorded result by (Rather et al., 2009) in the same temperature range as shown in figure 5a. Ball-milling the as-received  $\text{LiAlH}_4$  with Ti-metal for 5 hours enhances the kinetics of the material since the first decomposition step started at  $70^\circ\text{C}$  instead of  $119^\circ\text{C}$  in case of the as-received  $\text{LiAlH}_4$ , while the second decomposition step started at  $160^\circ\text{C}$  instead of  $182^\circ\text{C}$  and the total weight loss reached 6wt.% for the two decomposition steps see figure 5b, this value is lower than the theoretical value 7.9 wt%(Chen et al., 2001). Such difference could be attributed to the following reason; losing of some hydrogen content during milling as mentioned previously for doped  $\text{LiAlH}_4$  (Hanada et al., 2007).

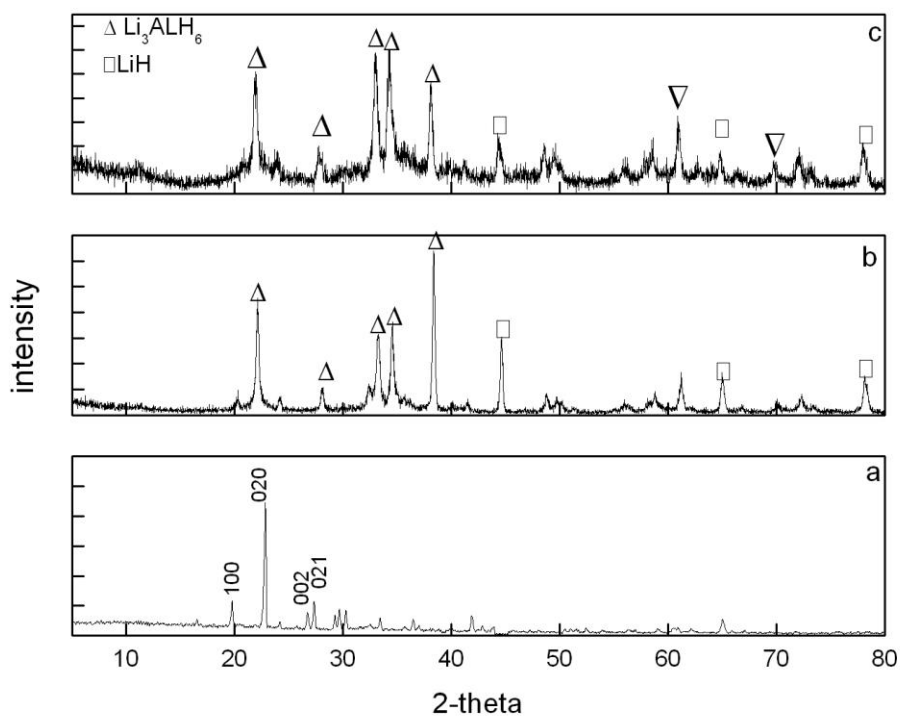
Further milling in the presence of Ti-metal up to 35 hours resulted in more enhancement in the kinetics of the material since more reduction in the decomposition temperature occurred, the firstdecomposition step started at

51 °C resulting in 9 wt.% as a total weight loss figure 5c. The kinetics enhancement of the material not only occurred in the presence of Ti-metal, but also in the presence of LiH powder, the first decomposition step of as-received material milled with LiH for 72 hours started at 71°C, while the 2<sup>nd</sup> step started at 139 °C with total weight loss 9 wt.% see figure 5d

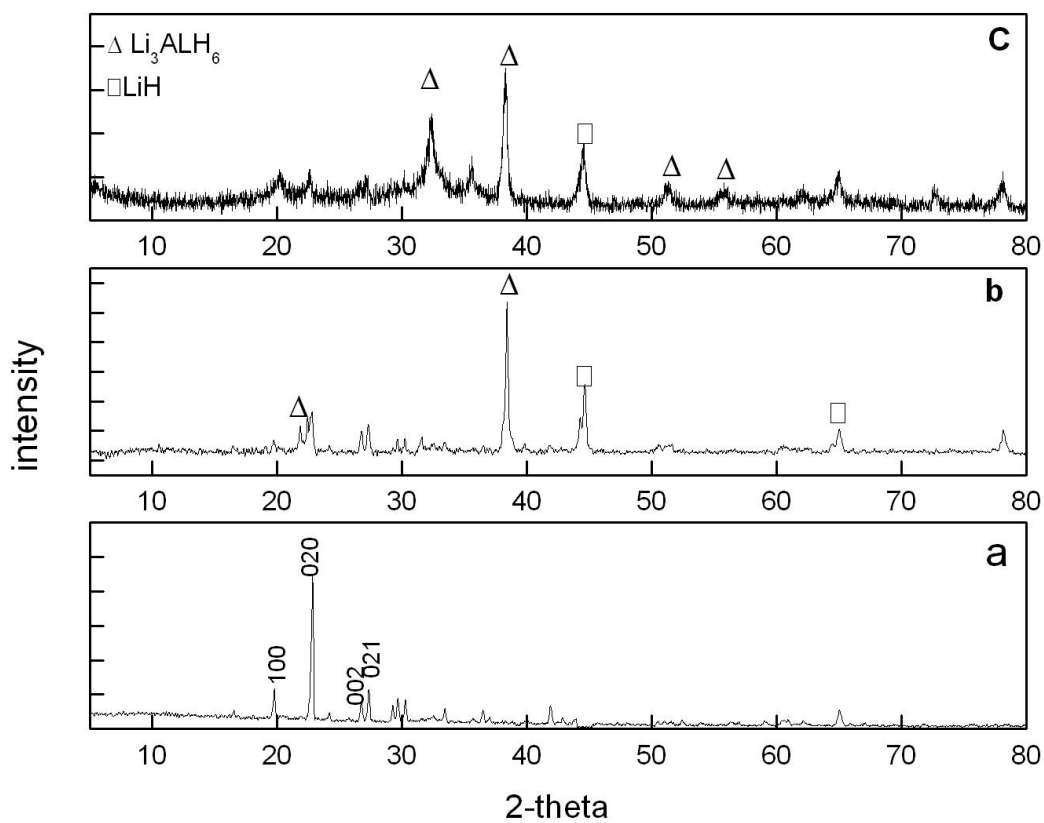
Further milling up to 120 hours causes amorphization which deteriorates its thermal stability as shown in figure 5e.

#### **4- Conclusion**

Mechanochemical transformation of  $\text{LiAlH}_4$  into  $\text{Li}_3\text{AlH}_6$  using ball-mill technique in argon atmosphere is achieved by doping  $\text{LiAlH}_4$  with Ti-metal and milling for 5 and 35 hours and the reaction products are investigated using XRD, FT-IR and TGA. XRD data reveals transformation of  $\text{LiAlH}_4$  into  $\text{Li}_3\text{AlH}_6$  after 5 hours of milling, further milling results in more peaks which is related to the new form  $\text{Li}_3\text{AlH}_6$ . Data obtained from FT-IR are in agreement with XRD data since there is observed occurrence of the new form  $\text{Li}_3\text{AlH}_6$  after milling. The decomposition observed from TGA data confirms our conclusions about  $\text{LiAlH}_4$  transformation. Replacing Ti-metal with LiH and milling for 72 and 120 hours results in formation of  $\text{Li}_3\text{AlH}_6$  after 72 hours of milling and this conclusion is confirmed by XRD, FT-IR and TGA, further milling up to 120 hours results in amorphization in the material



**Figure 1: X-ray diffraction spectra of as received LiAlH<sub>4</sub> (a) compound and after milling in the presence of Ti-metal for 5(b) and 35(c) hours**



**Figure 2: X-ray diffraction spectra of as received  $\text{LiAlH}_4$  compound (a) and after milling in the presence of  $\text{LiH}$  for 72(b) and 120(c) hours**

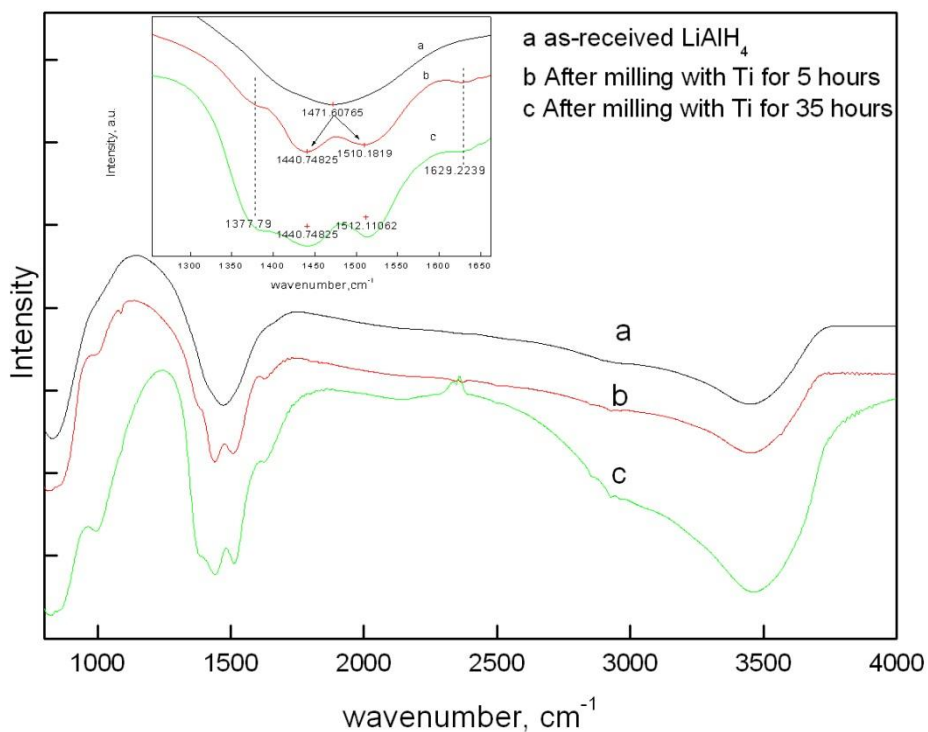


Figure 3 : FT-IR spectra of as received  $\text{LiAlH}_4$  (a) before and after milling with Ti-metal

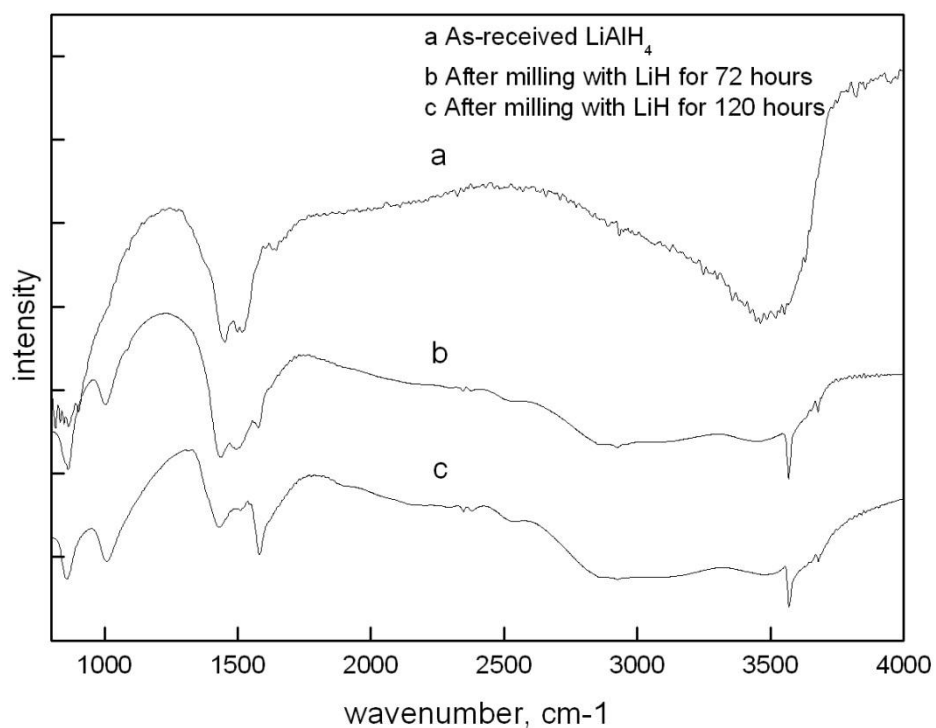


Figure 4 : FT-IR spectra of as received  $\text{LiAlH}_4$  (a) before and after milling with LiH for 72 (b) and 120 hours (c)





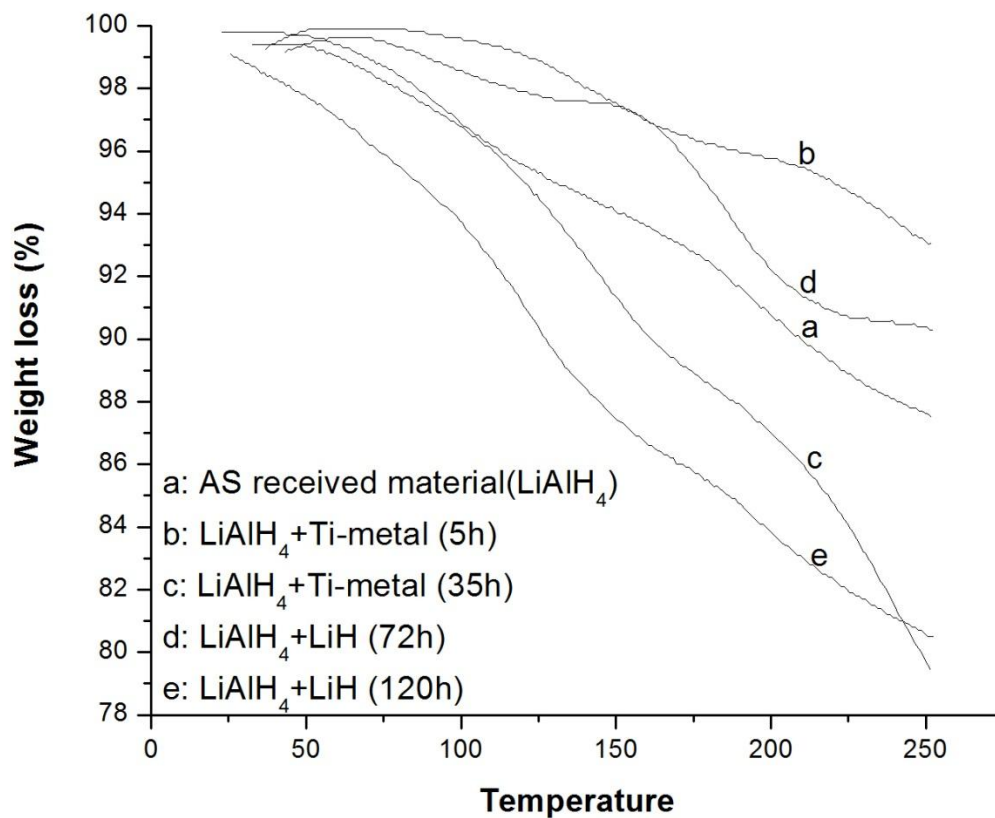


Figure 5 TGA curves of (a) as-received material, (b)  $\text{LiAlH}_4$  + Ti milled for 5 hours, (c)  $\text{LiAlH}_4$  + Ti milled for 35 hours (d)  $\text{LiAlH}_4$  + LiH milled for 72 hours and (e)  $\text{LiAlH}_4$  +

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