

# Rapid solid-state transformation of tetrahedral $[\text{AlH}_4]^-$ into octahedral $[\text{AlH}_6]^{3-}$ in lithium aluminohydride

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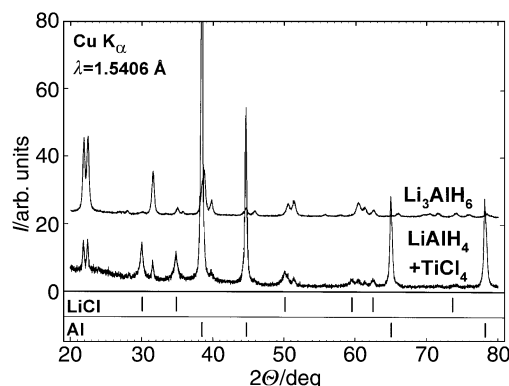
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Polycrystalline  $\text{LiAlH}_4$  transforms into polycrystalline  $\text{Li}_3\text{AlH}_6$  and Al during short time (5 min) ball-milling with 3 mol%  $\text{TiCl}_4$  at room temperature; solid-state rearrangement of tetrahedral  $[\text{AlH}_4]^-$  into octahedral  $[\text{AlH}_6]^{3-}$  at ambient conditions was previously unknown; this transformation does not occur during ball-milling of pure  $\text{LiAlH}_4$  or in the presence of 3 mol%  $\text{TiCl}_4$  without mechanochemical treatment.

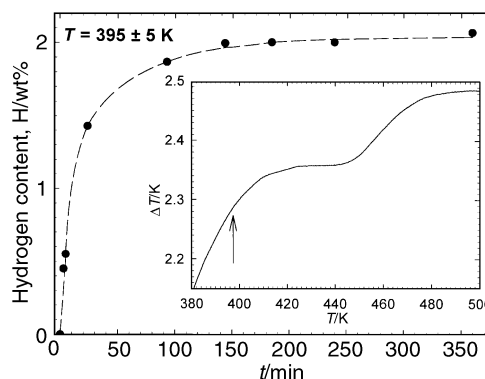
High capacity solid-state storage of hydrogen is becoming increasingly important as fuel cell power plants approach broad use in automotive and electrical utility applications. Overall hydrogen content of two alkali metal aluminohydrides,  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$  (10.5 and 7.3 wt%  $\text{H}_2$ , respectively), is amongst the highest for about 70 known complex hydrides<sup>1</sup> reviving recent interest to them as potential ultra-high capacity hydrogen storage solids.<sup>2–6</sup> Temperature induced transformation of lithium aluminohydride ( $\text{LiAlH}_4$ ) into lithium hexahydroaluminate ( $\text{Li}_3\text{AlH}_6$ ) has been known for almost three decades.<sup>7</sup> However, the processes occurring in pure  $\text{LiAlH}_4$  during its thermal decomposition were understood only recently.<sup>8,9</sup> According to results obtained by Bastide *et al.*<sup>8</sup> and Dymova *et al.*,<sup>9</sup>  $\text{LiAlH}_4$  is quite stable in the solid state below its melting temperature but rapidly transforms in the melt, where rearrangement of the tetrahedral  $[\text{AlH}_4]^-$  ion into the octahedral  $[\text{AlH}_6]^{3-}$  ion<sup>10,11</sup> is easily achieved. The stability of the solid  $\text{LiAlH}_4$  is, therefore, attributed to kinetic restrictions of the solid-state transformation process in the aluminohydride anion rather than to thermodynamic reasons ( $\Delta G$  of the reaction  $\text{LiAlH}_4 = 1/3\text{Li}_3\text{AlH}_6 + 2/3\text{Al} + \text{H}_2$  is  $-27 \text{ kJ mol}^{-1}$ ).<sup>12</sup> Recently, a significant reduction of the decomposition temperatures of alkali metal aluminium hydrides doped with transition metal derivatives has been reported.<sup>3–6</sup> It is, however, unclear, whether transition metal dopants reduce melting points of complex aluminium hydrides or act as catalysts of solid-state transformations near the respective melting temperatures.

Here we report on the first observation of the rapid solid-state transformation of lithium aluminohydride into lithium hexahydroaluminate in the presence of a catalytic amount of titanium tetrachloride ( $\text{TiCl}_4$ ) during mechanochemical activation at ambient conditions.<sup>†</sup> A reaction mixture containing 97 mol%  $\text{LiAlH}_4$  and 3 mol%  $\text{TiCl}_4$  was ball-milled in a Spex mill under helium for 5 min and then investigated using X-ray powder diffraction (XRD), differential thermal (DTA) and gas-volumetric analyses. According to XRD data,  $\text{LiAlH}_4$  was completely transformed during the short mechanochemical treatment with a catalytic quantity of  $\text{TiCl}_4$ . Only Bragg peaks corresponding to the crystalline  $\text{Li}_3\text{AlH}_6$ ,<sup>13a</sup> Al and LiCl are seen in the X-ray powder diffraction pattern of the reaction mixture (Fig. 1). The DTA trace of the reaction mixture in the temperature range between 380 and 500 K contains one broad endothermic peak between approximately 395 and 485 K with a minimum at 445 K (inset in Fig. 2). The endothermic process occurs at lower temperatures when compared to that observed in the pure mechanochemically prepared  $\text{Li}_3\text{AlH}_6$ <sup>13a</sup> (ca. 480–535 K, minimum at 505 K). This lowering of the hydrogen release

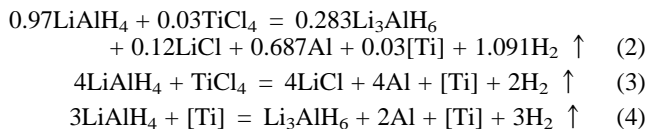
temperature is, however, in good agreement with previously reported data on reduction of decomposition temperature of transition metal-doped alkali metal aluminohydrides.<sup>3–5</sup> The gas-volumetric analysis of the reaction mixture between 295 and 675 K in vacuum revealed a slow one-step hydrogen evolution at  $395 \pm 5 \text{ K}$  (Fig. 2), *i.e.* at the onset temperature of the endothermic effect observed in the DTA experiment. The amount of released hydrogen, 2.08 wt%, agrees well with the decomposition of  $\text{Li}_3\text{AlH}_6$  [eqn. (1)], which was formed according to eqn. (2) (the theoretical hydrogen content in the mixture is 2.1 wt%). The intensities of Bragg peaks (Fig. 1) are in quantitative agreement with the amounts of reaction products. Eqn. (2) summarizes transformations of  $\text{LiAlH}_4$  and  $\text{TiCl}_4$  during ball-milling [eqns. (3) and (4)]:



**Fig. 1** The X-ray powder diffraction pattern of the reaction mixture obtained during 5 min ball-milling of 97 mol%  $\text{LiAlH}_4$  and 3 mol%  $\text{TiCl}_4$  compared with the X-ray powder diffraction pattern of  $\text{Li}_3\text{AlH}_6$  prepared mechanochemically.<sup>13</sup> Vertical bars at the bottom of the chart indicate positions of Bragg peaks of pure LiCl and Al.



**Fig. 2** The results of gas-volumetric analysis at  $395 \pm 5 \text{ K}$  of the reaction mixture obtained during 5 min ball-milling of 97 mol%  $\text{LiAlH}_4$  with 3 mol%  $\text{TiCl}_4$ . The inset shows the DTA trace of the same reaction mixture. The vertical arrow on the inset indicates the onset of the endothermic process.



The formation of lithium chloride, aluminium and a Ti-containing micro-crystalline phase with unknown composition during 5 min ball-milling of lithium aluminohydride and titanium tetrachloride was confirmed by mechanochemical treatment of stoichiometric amounts (4:1) of LiAlH<sub>4</sub> and TiCl<sub>4</sub> [eqn. (3)].<sup>13b</sup> No Bragg peaks corresponding to either LiAlH<sub>4</sub> or Li<sub>3</sub>AlH<sub>6</sub> were detected from XRD data. Furthermore, the gas-volumetric analysis of the obtained reaction mixture [eqn. (3)] did not reveal observable hydrogen gas evolution up to 925 K.

To verify that the titanium catalyzed solid state transformation of LiAlH<sub>4</sub> into Li<sub>3</sub>AlH<sub>6</sub> proceeds only during mechanochemical activation, the mixture containing 97 mol% of lithium aluminohydride and 3 mol% of titanium tetrachloride was thoroughly ground in a mortar under helium for 10 min. Although slight changes of the reaction mixture color from grayish-white to gray were observed, XRD did not indicate the formation of detectable amounts (*i.e.* 5 vol% or more) of Li<sub>3</sub>AlH<sub>6</sub> during grinding. Weak Bragg peaks corresponding to polycrystalline LiCl and Al were found in the X-ray diffraction pattern of the reaction mixture after grinding, and therefore, the observed color changes were likely associated with the reduction of TiCl<sub>4</sub> by LiAlH<sub>4</sub> according to eqn. (3). Furthermore, our experiments with pure LiAlH<sub>4</sub> revealed that this complex hydride is stable during ball-milling without TiCl<sub>4</sub> for up to 35 h.

Currently, several different models describing the observed rapid solid-state rearrangement of LiAlH<sub>4</sub> (*i.e.* tetrahedral [AlH<sub>4</sub>]<sup>-</sup> ion) into Li<sub>3</sub>AlH<sub>6</sub> (*i.e.* octahedral [AlH<sub>6</sub>]<sup>3-</sup> ion) in the presence of TiCl<sub>4</sub> during mechanochemical treatment at ambient conditions are being considered. One of the most likely mechanisms explaining the catalytic effect of TiCl<sub>4</sub> can be its reduction to a highly reactive nanocrystalline or amorphous titanium phase [eqn. (3)], which subsequently mechanically alloys into the crystal lattice of LiAlH<sub>4</sub>. The following destabilization of the host crystal lattice caused by the presence of titanium leads to the formation of metastable 'melt-like' hydride phases, where the rearrangement of the tetrahedral [AlH<sub>4</sub>]<sup>-</sup> ion into the octahedral [AlH<sub>6</sub>]<sup>3-</sup> ion becomes kinetically possible. Although the nature of intermediate phase(s) is presently unclear, it is feasible that they are similar to the metastable high-pressure  $\gamma$ -LiAlH<sub>4</sub> with hexa-coordinated [AlH<sub>6</sub>]<sup>3-</sup> ion,<sup>10,15</sup> and their formation becomes possible due to mechanically induced strain in the presence of titanium catalyst.

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## Notes and references

† All experiments described in this communication were carried out in a glove box in a purified helium atmosphere and in a hardened-steel vial sealed under helium. The X-ray diffraction experiments were performed under helium in a sample holder covered by X-ray transparent polymer film. The differential thermal analysis was carried out in an argon atmosphere at ambient pressure using commercially available equipment. The heating rate during DTA measurements was 10 K min<sup>-1</sup>. The gas-volumetric experiments were performed using a standard Sievert's type apparatus.

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- 13 (a) Solvent free Li<sub>3</sub>AlH<sub>6</sub> was prepared by ball-milling of 0.80 g (0.1 mol) LiH and 1.90 g (0.05 mol) LiAlH<sub>4</sub> in a helium atmosphere for 5 h. *Crystal data*: for Li<sub>3</sub>AlH<sub>6</sub> monoclinic, space group *P2<sub>1</sub>/c*, *a* = 5.667(1), *b* = 8.107(2), *c* = 7.917(2) Å,  $\beta$  = 92.17(1)°, *V* = 363.5(2) Å<sup>3</sup>, *M* = 53.8, *Z* = 4, *T* = 298 K. The obtained lattice parameters are in excellent agreement with the previously reported data<sup>14</sup> for conventionally prepared Li<sub>3</sub>AlH<sub>6</sub>; (b) ball-milling of stoichiometric amounts of LiAlH<sub>4</sub> and TiCl<sub>4</sub> was carried out in a Spex mill in a hardened-steel vial sealed under helium. According to XRD, the reaction mixture contains polycrystalline LiCl, Al and an unidentified intermetallic Ti<sub>1-x</sub>Al<sub>x</sub> phase.
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