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Solid state phase transformations in LiAlH_4 during high-energy ball-milling

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Abstract

Mechanochemical processing of polycrystalline LiAlH_4 revealed good stability of this complex aluminohydride during high-energy ball-milling in a helium atmosphere for up to 35 h. The decomposition of lithium aluminohydride into Li_3AlH_6 , Al and H_2 is observed during prolonged mechanochemical treatment for up to 110 h and is most likely associated with the catalytic effect of a vial material, iron, which is introduced into the hydride as a contaminant during mechanical treatment. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

High capacity solid-state storage and delivery of hydrogen at ambient conditions is becoming increasingly important as the most efficient proton exchange membrane (PEM) fuel cell power plants approach broad use in automotive and electrical utility applications. PEM fuel cells use hydrogen as a fuel, and since overall hydrogen content of two alkali metal aluminohydrides, LiAlH_4 and NaAlH_4 (10.5 and 7.3 wt% H_2 , respectively), is one of the highest among about 70 known complex hydrides [1], there has been considerable increase of interest to them as potential ultra-high capacity hydrogen storage solids [2–6].

Unlike complex boron- and magnesium-based hydrides [7,8], little is known about mechanically induced solid-state transformations of complex derivatives of aluminum hydride. Except for a few reports on mechanically induced solid-state reactions between alkali metal aluminohydrides and transition metal halogenides [9,10], and on mechanochemical preparation of complex aluminohydrides of Li, Na, Mg and Sr [11–15], no systematic data about mechanochemistry of this class of materials exists in the literature. Surprisingly, even the stability of pure alkali metal aluminohydrides during mechanochemical process-

ing remains in question. In 1994, Dymova et al. [16] reported a moderate to complete decomposition of LiAlH_4 during its treatment in a vibromill for 1.5–8 h. However, Zaluski et al. [15], reported that ball-milling of lithium aluminohydride for as long as 24 h has no effect on its chemical and phase compositions.

The analysis of the thermodynamic stability of LiAlH_4 indicates that this hydride is quite stable with respect to its decomposition into the elements (Li, Al and H_2): at 25°C the standard Gibbs free energy of this reaction is $\Delta G_{298}^\circ = 35.53 \text{ kJ mol}^{-1}$ [16]. However, the standard Gibbs free energy becomes negative ($\Delta G_{298}^\circ = -27.7 \text{ kJ mol}^{-1}$ [16]) for the transformation of LiAlH_4 into Li_3AlH_6 , Al and H_2 (see Eq. (2), below). The stability of the solid lithium aluminohydride at room temperature is, therefore, restricted by kinetics of the solid-state transformation process in LiAlH_4 rather than by thermodynamics. As a result, the low-temperature decomposition of lithium aluminohydride into lithium hexahydroaluminate, aluminum and hydrogen is generally possible if kinetic restrictions could be eliminated by an appropriate catalyst and/or processing technique.

Various basic processing issues need to be addressed before alkali metal aluminohydrides and their derivatives find practical use as reliable solid-state hydrogen storage media. Therefore, understanding of transformations occurring in pure complex aluminohydrides during mechanical treatment is vitally important for the development of novel

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ultra-high capacity hydrogen storage materials. It is quite obvious that these phase transformation processes may significantly influence mechanochemical behavior of complex aluminohydrides as well as properties of other mechanically produced/processed aluminum-containing hydrogen storage materials.

Here, we report on mechanochemical transformations, which occur in commercially pure LiAlH_4 during high-energy ball-milling in conventional hardened-steel equipment. As a part of this study, we also mechanochemically prepared Li_3AlH_6 from commonly available precursors, and characterized it using X-ray powder diffraction (XRD) and differential thermal analysis (DTA).

2. Experimental

LiAlH_4 (≥ 97 wt% pure) and LiH (95 wt% pure) were purchased from Sigma–Aldrich, and iron powder (99.9 wt% pure) was purchased from Alfa. All operations with lithium aluminohydride, lithium hydride, and iron powder were carried out in a glove box in a helium atmosphere. Ball-milling of various quantities, usually 0.5–0.7 g of LiAlH_4 , was performed in a Spex mill in a hardened-steel vial sealed under helium using 21 g of steel balls. Forced air-cooling of the vial was employed to prevent its heating during ball-milling experiments. Li_3AlH_6 was prepared mechanochemically according to the previously described procedure [15] from 0.80 g (0.1 mol) LiH and 1.90 g (0.05 mol) LiAlH_4 using the same equipment.

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. To protect samples from the atmospheric oxygen and moisture during X-ray powder diffraction experiments, the sample holder containing a hydride powder was covered with an X-ray transparent polymer film in a glove box under helium. According to our observations, obtained hydride powders were not effected 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.

Differential thermal analysis of the prepared powder samples was carried out using Perkin-Elmer DTA 7 between 20 and 350°C with a heating rate of $10^\circ\text{C min}^{-1}$ in an argon atmosphere. Alumina crucibles were used as holders and aluminum oxide was used as a reference material.

Chemical analysis of the hydride powders was performed using an ICP-AES technique on the Thermo Jerrrell Ash IRIS spectrometer. The samples were weighed in a glove box under helium, decomposed with 0.1–0.5 ml of

methanol and 1–2 ml of distilled water, and dissolved in concentrated HNO_3 . After subsequent dilution with distilled water they were analyzed according to a standard ICP-AES procedure [17].

3. Results and discussion

3.1. Mechanochemically prepared Li_3AlH_6

Li_3AlH_6 was prepared with the quantitative yield by ball-milling a stoichiometric mixture of lithium hydride and lithium aluminohydride (taken in 1:2 molar ratio) in a helium atmosphere for 5 h. The obtained product was analyzed using X-ray powder diffraction and differential thermal analysis. The X-ray powder diffraction pattern of the above mentioned reaction product is shown in Fig. 1. As far as we are aware, the crystal structure of Li_3AlH_6 is unknown except for the report by Bastide et al. [18], where the authors suggest a monoclinic crystal structure (space group $P2_1/m$, $a = 7.892$, $b = 8.096$, $c = 5.650$ Å, and $\beta = 91.83^\circ$) for Li_3AlH_6 obtained in organic solution. Based on the observed Bragg peak positions we also were able to perform the indexing of the entire diffraction pattern of the mechanochemically prepared lithium hexahydroaluminat assuming the monoclinic symmetry and primitive Bravais lattice. The space group is $P2_1/c$ with the following lattice parameters $a = 5.667(1)$, $b = 8.107(2)$, $c = 7.917(2)$ Å, $\beta = 92.07(1)^\circ$, $V = 363.5(2)$ Å³. The lattice parameters are in a good agreement with those reported in Ref. [18], indicating that the mechanochemically prepared Li_3AlH_6 has the

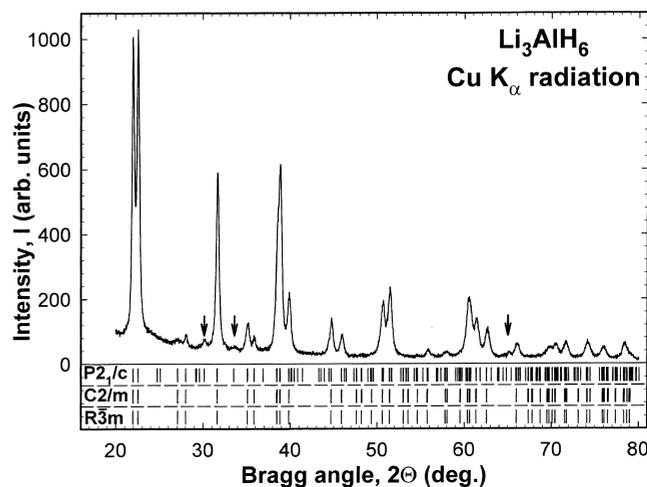


Fig. 1. The X-ray powder diffraction pattern of the mechanochemically prepared Li_3AlH_6 (Eq. (1)). The vertical bars at the bottom of the plot indicate calculated positions of Bragg peaks in three different space groups symmetry. The three low intensity Bragg peaks requiring lowering the symmetry to the primitive Bravais lattice are marked with the vertical arrows.

same crystal structure as the hydride prepared conventionally in organic solution according to the following reaction:



Therefore, our results along with the data reported in Ref. [15], confirm that this chemical transformation also occurs in solid state during mechanochemical treatment.

Our attempts to solve the crystal structure of Li_3AlH_6 based on the X-ray powder diffraction data were unsuccessful because of the strong pseudosymmetry found in this compound. As also shown in Fig. 1, the entire powder diffraction pattern except three very weak diffraction peaks marked by vertical arrows, can be indexed assuming either the base-centered monoclinic [space groups $C2/m$, Cm , or $C2$, $a = 7.917(2)$, $b = 8.107(2)$, $c = 5.667(1)$ Å, $\beta = 92.07(1)^\circ$, $V = 363.5(2)$ Å³], or even rhombohedral [$R\bar{3}m$, $R3m$, $R\bar{3}$, or $R3$, $a = 8.113(1)$, $c = 9.570(1)$ Å, $V = 545.5(2)$ Å³] symmetry. The unit cell volume of the rhombohedral lattice is 1.5 times greater than that of both primitive and base centered monoclinic lattices. We believe that the weak Bragg peaks (Fig. 1) requiring the lowering of the symmetry from a rhombohedral to a primitive monoclinic lattice are intrinsic to Li_3AlH_6 since they do not belong to either the LiH or LiAlH_4 structures, nor they can be assigned to pure Al, which could have formed during mechanical treatment. The detailed study of the crystal structure of lithium hexahydroaluminate using both single crystal X-ray diffraction and neutron powder diffraction techniques is underway and results will be reported elsewhere.

The DTA trace of Li_3AlH_6 between 20 and 300°C is shown in Fig. 2. It contains only one endothermic peak (207–260, minimum 230), which corresponds to thermal decomposition of Li_3AlH_6 into LiH, Al and H_2 . The location of the peak is in a good agreement with the data

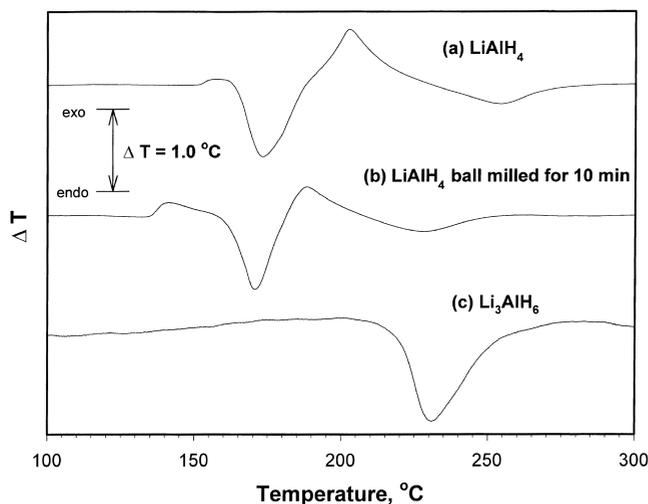


Fig. 2. The DTA traces of the starting LiAlH_4 (a), LiAlH_4 after ball-milling for 10 min (b), and the mechanochemically prepared Li_3AlH_6 (c).

published for conventionally prepared lithium hexahydroaluminate [19,20].

3.2. Transformations of LiAlH_4 during high-energy ball-milling

To resolve the inconsistencies mentioned above about the stability of lithium aluminum hydride during mechanochemical processing, we sealed the commercially pure LiAlH_4 in a hardened-steel vial in a helium atmosphere, then ball-milled for 10 min, 35, 75 and 110 h. Samples for XRD and DTA experiments were extracted from the vial in a glove box under helium at each time interval, then the vial was sealed again, and ball-milling continued.

The X-ray powder diffraction patterns of the starting LiAlH_4 and the powders obtained during its ball-milling for 35, 75 and 110 h are shown in Fig. 3. Since mechanical treatment for 10 min did not cause observable changes in the lithium aluminum hydride, the X-ray powder diffraction pattern of this material is not included in Fig. 3. It is easy to see that ball-milling for 35 h causes only minor changes in the lithium aluminum hydride. In addition to the expected broadening of Bragg peaks, the X-ray diffraction pattern of LiAlH_4 ball-milled for 35 h contains only weak additional peaks of micro-crystalline aluminum, confirming the rather high stability of lithium aluminum hydride during mechanochemical treatment. Prolonged ball-milling for 75 and 110 h, however, leads to a gradual increase of aluminum content in the hydride samples indicating slow decomposition of LiAlH_4 into Li_3AlH_6 , Al and H_2 according to Eq. (2):

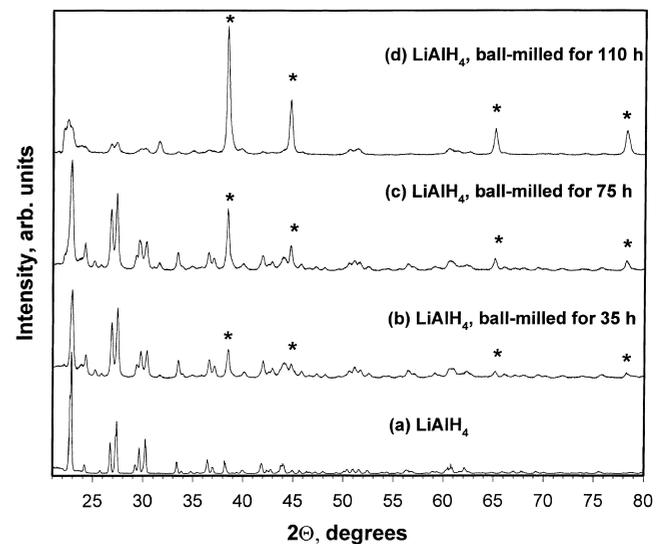


Fig. 3. The X-ray powder diffraction patterns of the starting LiAlH_4 (a), and of the LiAlH_4 after ball-milling during 35 (b), 75 (c) and 110 (d) h. Asterisks indicate Bragg peaks corresponding to micro-crystalline aluminum.

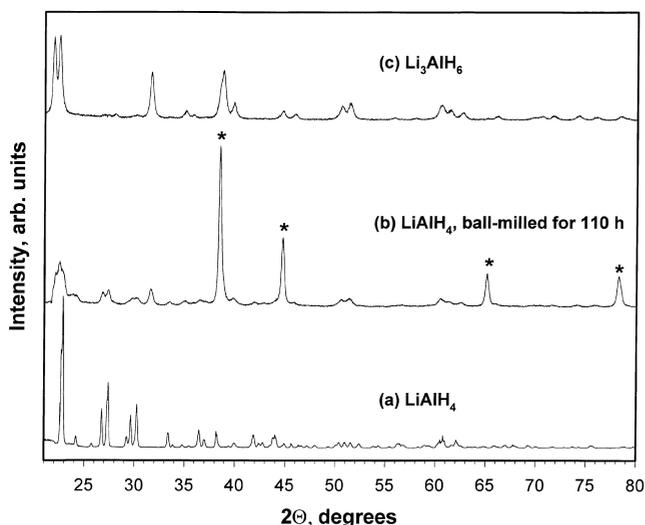
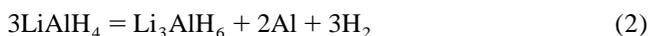


Fig. 4. The X-ray powder diffraction patterns of the starting LiAlH_4 (a), LiAlH_4 after ball-milling for 110 h (b) and the mechanochemically prepared Li_3AlH_6 (c). Asterisks indicate Bragg peaks corresponding to micro-crystalline aluminum.



The formation of lithium hexahydroaluminat during long-term ball-milling of the commercially pure LiAlH_4 is evident from the comparison of the X-ray powder diffraction patterns of the hydride material ball-milled for 110 h with the X-ray powder diffraction pattern of Li_3AlH_6 prepared mechanochemically (Fig. 4).

The DTA traces of the starting LiAlH_4 together with those of the hydride powders ball-milled for 10 min, 75 and 110 h, and the mechanochemically prepared Li_3AlH_6 are shown in Figs. 2 and 5. The DTA plot of the starting lithium aluminohydride between 20 and 300°C consists of

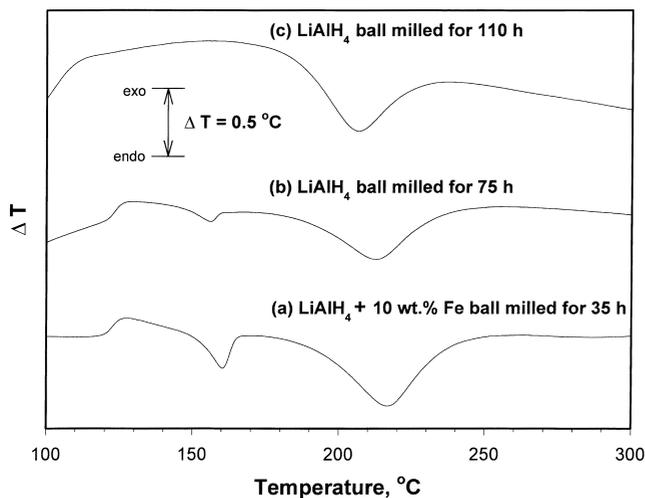


Fig. 5. The DTA traces of LiAlH_4 after ball-milling with 10 wt% of iron powder for 35 h (a), and LiAlH_4 after ball-milling during 75 h (b), and 110 h (c).

two exothermic (153–165°C, maximum at 155°C and 190–220°C, maximum at 203°C) and two endothermic (165–188°C, minimum at 175°C and 220–280°C, minimum at 255°C) peaks. The locations of the anomalies are in excellent agreement with the literature data [19–21].

The ball-milling of LiAlH_4 for 10 min does not cause significant changes in its DTA trace (Fig. 2), except all thermal events shift by 5–25°C towards lower temperatures. It should be noted, however, that the position of the endothermic peak corresponding to the melting of LiAlH_4 ball-milled for 10 min (156–180°C, minimum at 171°C) [20,21] is only slightly influenced, and the position of the second endothermic peak (205–255°C, minimum at 227°C) becomes almost identical to the location of the endothermic effect (207–260°C, minimum at 230°C) on the DTA plot of the mechanochemically prepared Li_3AlH_6 , which corresponds to the decomposition of the latter hydride (Fig. 2).

Prolonged ball-milling, however, causes significant changes in the thermochemical properties of lithium aluminum hydride (Fig. 5). The intensity of the peaks corresponding to the melting and subsequent transformation of LiAlH_4 into Li_3AlH_6 significantly decreases after 75 h of milling, and the endothermic effect that accompanies decomposition of Li_3AlH_6 increases accordingly. After 110 h of mechanical treatment, only one broad endothermic peak between 165 and 235°C with the minimum at 206°C is distinguishable on the DTA trace of the ball-milled lithium aluminohydride. The fact that according to the X-ray powder diffraction this hydride powder consists mainly from Li_3AlH_6 and Al, explains the obtained thermochemical data quite well. It should be expected that the mechanochemical transformation of LiAlH_4 into Li_3AlH_6 would lead to the reduction, and further, to the disappearance of the thermal events corresponding to the melting and decomposition of LiAlH_4 in the ball-milled hydrides. At the same time, the endothermic effect corresponding to the decomposition of Li_3AlH_6 would gradually increase with the increasing Li_3AlH_6 content.

Recent investigations of the decomposition of alkali metal hydrides in the presence of transition metal derivatives have shown that transition metals can significantly reduce their decomposition temperatures [3–6,22,23]. Therefore, we analyzed the starting lithium aluminohydride and hydride powders obtained after ball-milling of LiAlH_4 for 75 and 110 h for iron, which could be introduced into the samples during long-term ball-milling in a steel equipment [24]. Indeed, iron content in the hydride powders gradually increases from 0.002 wt% in the initial lithium aluminum hydride to 0.3 wt% in the hydride after ball-milling for 75 h and, finally, to 1 wt% in the powder obtained after ball-milling for 110 h. To determine whether iron contamination in the LiAlH_4 samples was responsible for the mechanochemical transformation of the commercially pure lithium

aluminumhydride during long-term ball-milling, LiAlH_4 was ball-milled in the presence of 10 wt% of iron powder for 20 and 35 h. The DTA trace of the reaction mixture obtained after ball-milling for 35 h, and the X-ray powder diffraction patterns of the ball-milled samples are shown in Figs. 5 and 6, respectively. It is easy to see from the X-ray powder diffraction data (Fig. 6) that the decomposition of LiAlH_4 in the presence of iron is already evident after 20 h of mechanical treatment. Ball-milling for additional 15 h leads to further significant increase in the aluminum content in the hydride powder. Semi-quantitative analysis based on the relative intensities of the resolved Al and strongest LiAlH_4 Bragg peaks indicate that the phase composition of the sample processed with 10 wt% iron powders during 35 h resembles that of the commercially pure lithium aluminumhydride ball-milled during 75 h. The DTA traces of both materials also correlate quite well (Fig. 5).

The results presented above indicate that commercially pure lithium aluminumhydride is rather stable during mechanochemical treatment in an inert-gas atmosphere. Most likely, its transformation into Li_3AlH_6 , Al, and H_2 observed during long-term ball-milling in a conventional hardened-steel equipment should be attributed to the catalytic effect of iron, which is introduced into the sample as a contaminant during mechanochemical processing. Our experiments on ball-milling of LiAlH_4 containing 10 wt% of iron powder support this conclusion. We believe that the most feasible explanation for the role of iron in promoting mechanochemical transformation of LiAlH_4 during long-term ball-milling is the amorphization and subsequent mechanical alloying of small amounts of iron into the crystal lattice of LiAlH_4 . The destabilization of the host

crystal lattice caused by the presence of iron atoms can lead to the formation of metastable nano-crystalline or amorphous hydride phases, where low-temperature transformation of lithium aluminumhydride into lithium hexahydroaluminate, aluminum and hydrogen becomes possible. The high surface area and accumulation of numerous defects in the crystal lattice of mechanochemically treated materials [25] can provide the necessary conditions for the mentioned mechanical alloying of Fe with LiAlH_4 .

4. Conclusions

As a result of mechanochemical processing experiments we have confirmed that Li_3AlH_6 can be obtained from LiH and LiAlH_4 via solid state reaction. It has monoclinic symmetry, however, its crystal structure with atomic resolution remains unknown due to rhombohedral pseudo-symmetry. Investigation of the products obtained during mechanochemical processing of LiAlH_4 revealed rather high stability of this hydride during high-energy ball-milling in a helium atmosphere for up to 35 h. The decomposition of lithium aluminumhydride during prolonged mechanochemical treatment for up to 110 h is attributed to the catalytic effect of a vial material, iron, which is introduced into the hydride as a contaminant during prolonged ball-milling. The control experiments on the ball-milling of LiAlH_4 containing 10 wt% of iron powder support this conclusion.

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References

- [1] K. Yvon, *Chimia* 52 (1998) 613.
- [2] G. Sandrock, in: Y. Yürüm (Ed.), *Hydrogen Energy Systems*, Kluwer, Dordrecht, 1995, p. 135.
- [3] B. Bogdanovic, M.J. Schwickardi, *J. Alloys Comp.* 253 (1997) 1.
- [4] R.A. Zidan, S. Takara, A.G. Hee, C.M. Jensen, *J. Alloys Comp.* 285 (1999) 119.
- [5] C.M. Jensen, R.A. Zidan, N. Mariels, A.G. Hee, C. Hagen, *Int. J. Hydrogen Energy* 24 (1999) 461.
- [6] K.J. Gross, S. Guthrie, S. Takara, G. Thomas, *J. Alloys Comp.* 297 (2000) 270.
- [7] V.V. Volkov, K.G. Myakishev, *Inorg. Chim. Acta* 289 (1999) 51.
- [8] I.G. Kostanchuk, E.Yu. Ivanov, V.V. Boldyrev, *Russ. Chem. Rev.* 67 (1998) 69.
- [9] V.V. Volkov, A.I. Golovanova, N.N. Maltseva, K.G. Myakishev, N.T.

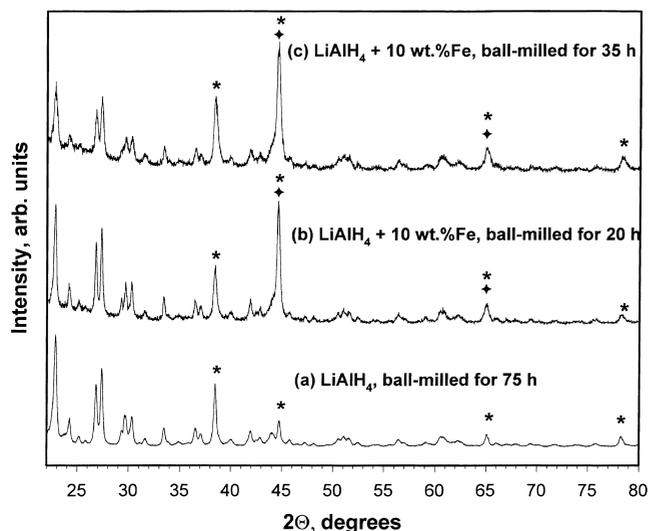


Fig. 6. The X-ray powder diffraction patterns of the pure LiAlH_4 after ball-milling for 75 h (a) and LiAlH_4 after ball-milling with 10 wt% of iron powder for 20 h (b), and 35 h (c). Asterisks indicate Bragg peaks corresponding to micro-crystalline aluminum, and filled diamonds indicate Bragg peaks corresponding to iron which overlap with aluminum.

- Kusnetsov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* 1 (1988) 67.
- [10] N.N. Maltseva, K.G. Myakishev, A.I. Golovanova, V.V. Volkov, N.T. Kusnetsov, *Zh. Neorg. Khim.* 34 (1989) 40.
- [11] T.N. Dymova, V.N. Konoplev, A.S. Sizareva, D.P. Aleksandrov, *Russ. J. Coord. Chem.* 25 (1999) 312.
- [12] T.N. Dymova, V.N. Konoplev, A.S. Sizareva, D.P. Aleksandrov, N.T. Kusnetsov, *Dokl. Akad. Nauk.* 359 (1998) 200.
- [13] T.N. Dymova, D.P. Aleksandrov, V.N. Konoplev, T.A. Silina, N.T. Kusnetsov, *Russ. J. Coord. Chem.* 19 (1993) 491.
- [14] J. Hout, S. Boily, V. Güther, R. Schultz, *J. Alloys. Comp.* 283 (1999) 304.
- [15] L. Zaluski, A. Zaluska, J.O. Ström-Olsen, *J. Alloys. Comp.* 290 (1999) 71.
- [16] T.N. Dymova, D.P. Aleksandrov, V.N. Konoplev, T.A. Silina, A.S. Sizareva, *Russ. J. Coord. Chem.* 20 (1994) 263.
- [17] S.J. Hill (Ed.), *Inductively Coupled Plasma Spectrometry and Its Applications*, Sheffield Academic Press, Sheffield, UK, 1999.
- [18] J.P. Bastide, B.M. Bonnetot, J.M. Letoffe, P. Claudy, *Stud. Inorg. Chem.* 3 (1983) 785.
- [19] J.A. Dilts, E.C. Ashby, *Inorg. Chem.* 11 (1972) 1230.
- [20] T.N. Dymova, V.N. Konoplev, D.P. Aleksandrov, A.S. Sizareva, T.A. Silina, *Russ. J. Coord. Chem.* 21 (1995) 165.
- [21] J.P. Bastide, B.M. Bonnetot, J.M. Letoffe, P. Claudy, *Mater. Res. Bull.* 20 (1985) 999.
- [22] B. Bogdanovic, R.A. Brand, A. Marjanovic, M. Scheickardi, J. Tölle, *J. Alloys. Comp.* 302 (2000) 36.
- [23] V.P. Balema, K.W. Dennis, V.K. Pecharsky, *Chem. Commun.* (2000) 1665.
- [24] V.P. Balema, A.O. Pecharsky, V.K. Pecharsky, *J. Alloys Comp.* 307 (2000) 184.
- [25] V.V. Boldyrev, *Solid State Ionics* 63–65 (1993) 537.