Decomposition of LiBH₄-MgH₂-Al

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Abstract

LiBH₄ is an interesting hydrogen storage material, as it has a high gravimetric hydrogen content of 18.5 wt% [1]. However, the utilization is hampered by lack of reversibility and high decomposition temperatures. One way of improving metalaborohydrides, is the utilization of reactive hydride composites (RHC), which can be achieved by adding for instance Al [2] or Mg₄ [3]. The ternary LiBH₄-MgH₂-Al composite further improves the hydrogen release and uptake properties of LiBH₄ [4]. In this study the decomposition reactions of LiBH₄-MgH₂-Al in molar ratios (4:1:1) and (4:1:5) are investigated using in situ Synchrotron Radiation Powder X-ray Diffraction (SR-PXD) and thermal analysis (TGA/DSC) coupled with mass spectroscopy (MS).

Mechanochemical Synthesis: Fritsch Pulverisette no. 4 with main disk speed: 400 rpm. Relative ratio: -2:25. Mill time: 5 min, Pause time: 2 min, Ball-to-Powder mass ratio: 35:1, Repetitions: 24 (Total mill time: 120 min).

LiBH₄·MgH₂·Al (4:1:1) →

During desorption the transformation from α-LiBH₄ to h-LiBH₄ is observed at T = 100 °C. At T = 265 °C diffraction from h-LiBH₄ disappear. MgH₂ decompose at T = 290 °C after which diffraction from the intermediate compounds Mg₄Al₁₂ and Mg₄Al₂₁ are observed. These compounds were not expected from the proposed decomposition reactions [4]. Mg₄Al₁₂ is formed at T = 390 °C and LiAl is observed at T = 460 °C.

Both samples were heated from RT → 500 °C (10 °C/min) and kept at 500 °C for 10 min prior to cooling.

LiBH₄·MgH₂·Al (4:1:5) →

The transformation from α-LiBH₄ to h-LiBH₄ and the disappearance of h-LiBH₄ is observed at T = 100 °C and T = 250 °C respectively. MgH₂ decomposes at T = 290 °C, but unlike the LiBH₄-MgH₂-Al (4:1:1) sample, Mg₄Al₁₂ and Mg₄Al₂₁ are not observed. An unknown intermediate (denoted 1) is however observed, that could be similar to intermediates observed in LiBH₄-Al systems [2]. The formation of Mg₄Al₁₂ and of LiAl is observed at T = 330 °C and 410 °C respectively. Another unknown compound, denoted 2 is observed at T = 450 °C.

TGA/DSC-MS analysis complement the pathway observed from in situ data. The phase transformation and melting of LiBH₄ is observed at 107 °C and 110 °C and 265 °C and 267 °C (peak temp) for the samples. At T = 300 °C the decomposition of MgH₂ is observed in sample LiBH₄-MgH₂-Al (4:1:1), but not in the (4:1:5) sample, although a release of hydrogen is observed in the MS data for both samples. The formation of Mg₄Al₁₂ is observed as a broad endothermic event and the formation of LiAl is revealed at T = 410 °C. No diborane is released during the decomposition of either sample (not shown).

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References: