**In situ hydrogenation of intermetallic phases in the system Li-Al**

C. Reichert, H. Kohlmann
Saarland University, Inorganic Solid State Chemistry, Saarbrücken, Germany

**Introduction**

A major issue in solid state chemistry is hydrogen storage materials. A promising system due to its availability, non-toxicity and low weight is Li-Al. In this system there are 3 different intermetallic phases known. Two of these have been investigated towards their reactivity with hydrogen. The first, LiAl (NaTl type), is a zintl type intermetallic [1]. Despite this, it has a phase width of approximately 0.45 to 0.54 mol% Li in Al. Two different defect variations are known: Li may occupy Al positions and there may be vacancies on Li sites. Both defect types appear together, whereas in LiAl with Li excess LiAl defects overwhelm, in an Al-lean Li, V Li defects are more dominant.[2,3]

The second phase is LiAlH2, a trigonal structure of its own type [4]. According to [5] LiAlH2 is a line phase.

Essential in investigating hydrogenation reactions is neutron diffraction. As we are also interested in reaction mechanics of the formation of hydrides out of intermetallics, we utilise a self-developed gas phase cell, consisting of a sapphire single crystal. With this device we were able to carry out in situ measurements of the solid gas reaction between the intermetallics of the Li-Al system and hydrogen.

**Synthesis of intermetallics and ex situ hydrogenation**

LiAl phases were synthesized in ranges from Li2Al to LiAl3 by the 30 bar hydrogenation reactions or solid state reactions from the elements

LiAlH2 was synthesized stoichiometric form the elements via solid state reaction

Ex situ hydrogenation (50 to 190 bar hydrogen pressure) of LiAl leads to LiAlH2 with a decreased unit cell and LiH and Al. Temperature (ranging from 100 to 300°C) and time have the largest influence on the scale of unit cell reduction.

LiAlH2 decomposes under moderate pressures (50bar) and high temperatures (400°C) into LiH, Li2H and elemental Al.

**The sapphire gas phase cell for in situ neutron diffraction**

A novel gas phase cell for in situ neutron diffraction has been developed which provides:

- no hydrogen embrittlement
- no hydrogen storage pressure: stability tested up to 160 bar hydrogen pressure, Fig. 4
- temperature stability tested up to 700 K using lead metal seals: unobstructed pathway for the neutron beam (Fig. 4)
- free optical access for visual reaction control
- low incoherent scattering
- low neutron absorption
- low background with little or no contribution of the crystal (Fig. 4)
- heating by 24 W diode lasers ($\lambda \approx 808$ nm, Fig. 4)
- accurate temperature monitoring via pyrometry (Fig. 3)

The new sapphire gas phase cell provides high-quality powder diffraction data under in situ conditions. This enables us to study the reaction mechanism of the hydrogenation of intermetallics and determine crystal structures of eventual metastable compounds.

**In situ investigation of the hydrogenation of LiAlH2**

Ex situ:

LiAlH2 + H2 → LiAl + 2LiH

Instant of the formation of LiAl yet unclear, but not before several hours

Cell Volume decreases only by 0.620 Å

Lesser, but similar effect as in LiAl

LiAlH2 and LiD are obtained. The resulting Li defects contradict LiAlH2 being a line phase

**Summary and Outlook**

**In situ characterisation of the hydrogenation of LiAl and LiAlH2**

**Concluded**

Mechanism of the hydrogenation proposed

**Hydrogenation Products** are LiAlH2/LiAl with a decreased unit cell and LiD and Al

**Discovery of a new phase LiAl-H**

**yet unknown structure**

**Solving the above mentioned structure**

in situ experiments on Lithiumaluminate and their reaction with Hydrogen

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**References**