Journal of Alloys and Compounds 509S (2011) S719–S723

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Hydrogen release and structural transformations in $LiNH_2$–MgH_2 systems

D. Pottmaier[a], F. Dolci[b], M. Orlova[c], G. Vaughan[c], M. Fichtner[d], W. Lohstroh[d], M. Baricco[a,*]

[a] Dipartimento di Chimica IFM and NIS, Università di Torino – Turin, Italy
[b] Institute for Energy DG, Joint Research Center – Petten, Netherlands
[c] ID11, European Synchrotron Radiation Facility – Grenoble, France
[d] Institute of Nanotechnology, Karlsruhe Institute of Technology – Karlsruhe, Germany

ARTICLE INFO

Article history:
Received 15 August 2010
Received in revised form 11 October 2010
Accepted 27 October 2010
Available online 4 November 2010

Keywords:
Lithium amide
Magnesium hydride
Hydrogen storage
Thermal programmed desorption
Differential scanning calorimetry
In situ synchrotron X-ray diffraction

ABSTRACT

Reactive hydride composites are good candidates for solid hydrogen storage due to their high gravimetric capacity, cyclability, and suitable thermodynamic properties. The $LiNH_2$–MgH_2 system is promising as changes in stoichiometry and milling conditions may result in tailoring of these properties. In this work, $LiNH_2$–MgH_2 with different ratios (Li2:Mg, Li:Mg) and ball milling conditions (100, 600 rpm) were investigated. Thermal desorption profiles shows hydrogen release starting at 125 °C for Li2:Mg 600 sample and at 225 °C for Li:Mg 600 sample, while for Li:Mg 100 sample simultaneous hydrogen and ammonia release at 175 °C is observed. In-situ synchrotron X-ray diffraction shows the related structural transformations, such as formation of $Mg(NH_2)_2$ and allotropic transformation of α into β-$Li_2Mg(NH)_2$ for Li2:Mg 600 sample at 350 °C or direct formation of β-$Li_2Mg(NH)_2$ for Li:Mg 100 sample at 370 °C. Different polymorphs of the LiMgN phase were also observed during cooling for these two samples. For the Li:Mg 600 sample, transformation occurs in a unique reaction from an unknown phase into β-$Li_2Mg(NH)_2$ at 290 °C. The unknown phase is indexed as a *Fm*3*m* cubic similar to the high temperature γ-$Li_2Mg(NH)_2$.

1. Introduction

Reactive hydride composites, obtained by ball milling a metal hydride (A-H, A = Li, Na, Mg, ...) and a complex hydride (A-X-H, X = N, B, Al), have been subject of intense investigation for solid state hydrogen storage. The amide/hydride system was brought to the hydrogen storage field by the pioneer work of Chen et al. [1], demonstrating the suitable sorption reactions of the $LiNH_2$:2LiH composite. Such materials are very attractive for solid state hydrogen storage due to their high storage capacity, good cyclability and good thermodynamic properties [1–8]. The search for means to destabilize $LiNH_2$ leads to the partial substitution of Li by Mg using different approaches [2–5] and the corresponding change in the enthalpy amounts from about 60 KJ/mol H_2 for $LiNH_2$:LiH to about 30 KJ/mol H_2 for $2LiNH_2$:MgH_2 [6]. In agreement with different studies [2,3], the hydrogen exchange reaction of the $2LiNH_2$:MgH_2 system (Li2:Mg), passing or not by metathesis reactions already during ball milling, can be written as:

$$2LiNH_2 + MgH_2 \rightarrow Li_2Mg(NH)_2 + 2H_2 \leftrightarrow Mg(NH_2)_2 + 2LiH \quad (1)$$

On the other hand, fewer studies were performed in the $LiNH_2$:MgH_2 system (Li:Mg) and some controversy exists among theoretical approaches [6,7] suggesting the reaction

$$LiNH_2 + MgH_2 \leftrightarrow LiMgN + 2H_2 \quad (2)$$

and experimental results [9,10], which observed different desorption reactions:

$$LiNH_2 + MgH_2 \rightarrow 1/3Mg_3N_2 + 3LiH + 1/3Li_2Mg_2(NH)_3 + 3/2H_2 \quad (3)$$

$$LiNH_2 + MgH_2 \rightarrow 1/4Mg_3N_2 + 1/4LiH + 1/4Li_2Mg(NH)_2 + 3/2H_2 \quad (4)$$

The system $LiNH_2$–MgH_2 is a promising one, as changes in stoichiometry [11–15] and ball milling conditions [16–19] result in different reaction mechanisms. One expects the former to change the reaction pathway by tailoring thermodynamics and the second to interfere in the kinetics aspects. However, what is observed always in experiments is an interplay of the two effects. In the present work, we analyze both the difference in stoichiometry, considering Li2:Mg and Li:Mg composites, and ball milling preparation, using a rotation speed of 100 and 600 rpm. The desorption behavior and corresponding structural phase transformations of these samples will be discussed.

* Corresponding author. Tel.: +39 011 6707569; fax: +39 011 6707855.
E-mail address: marcello.baricco@unito.it (M. Baricco).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.10.166

2. Experimental

Starting materials, $LiNH_2$ (99%) and MgH_2 (95%), were purchased from Sigma Aldrich and used as received without any further purification. Composite samples were prepared by ball milling in different ratios of Li:Mg using a Fritsch P6 planetary equipment with vial and balls of silicon nitride, under an argon atmosphere, for 12 h each, and a powder to ball ratio of 1:20. Milling rotation speeds of 100 and 600 rpm were used. Mass spectroscopy (MS) was performed using a quadropole mass spectrometer (Catlab Hiden) with a helium flow of 50 mL/min for identification of gaseous species. Thermal programmed desorption (TPD) was performed with a volumetric instrument (Advanced Materials) under initial static vacuum of 10^{-4} mbar for hydrogen release quantification. High pressure differential scanning

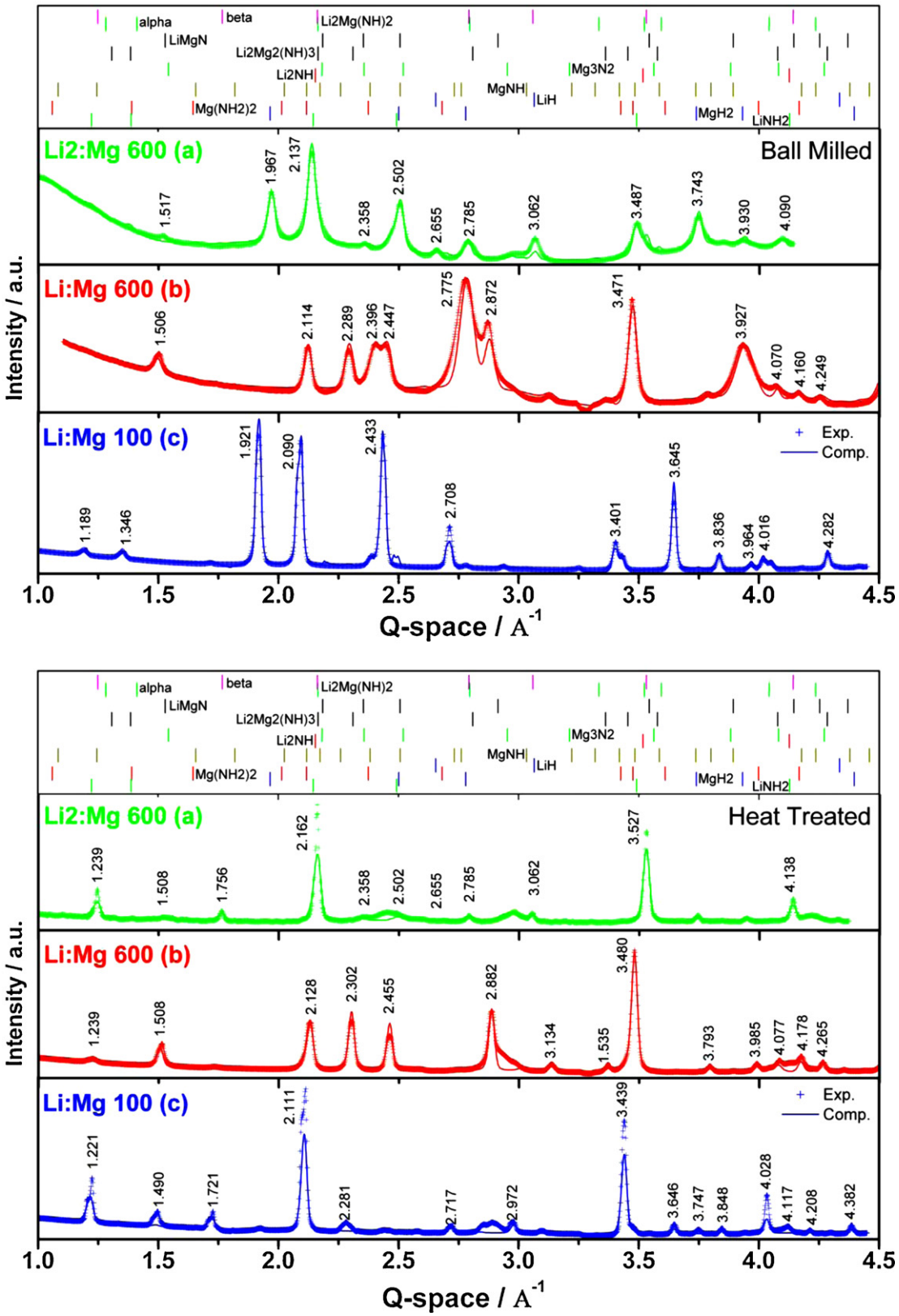

Fig. 1. SXRD patterns at room temperature top and bottom heat treatment of samples: Li2:Mg 600 (a), Li:Mg 600 (b), and Li:Mg 100 (c). Symbols: experimental points; lines: calculated from Rietveld refinement.