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Short Communication

Short communication: High-pressure synthesis and crystal structure of a novel Mg_3CuH_x ternary hydride

B. Torres [a,*], M.J. Martínez-Lope [b], J.A. Alonso [b], D. Serafini [a], M.T. Fernández-Díaz [c], R. Martínez-Coronado [b]

[a] Departamento de Física, Facultad de Ciencias, Universidad de Santiago de Chile, Av. Lib. Bernardo O'Higgins, 3363 Santiago, Chile

[b] Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain

[c] Institut Laue-Langevin, B.P. 156, F-38042 Grenoble Cedex 9, France

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ABSTRACT

A novel ternary hydride in the Mg–Cu–H system has been identified by a new synthesis method based on the direct reaction of simple hydrides under high-pressure and moderate-temperature conditions. A well-crystallized sample was obtained in a piston-cylinder hydrostatic press at moderate pressures of 3.5 GPa and temperatures around 850 °C starting from mixtures of MgH_2 and Cu enclosed in platinum capsules. X-ray and neutron powder diffraction analysis were used to identify the purity of the samples and provide an accurate description of the crystal structure features. The crystal structure of Mg_3CuH_x was determined by ab-initio procedures from neutron powder diffraction (NPD) data in the cubic space group *F-43m* (No. 216), with lattice parameter $a = 6.285$ Å. The hydrogen positions were determined by Fourier synthesis revealing the introduction of hydrogen atoms in the system. A final Rietveld refinement of the structure gives up a $Mg_3CuH_{0.6}$ composition, which is consistent with the Fourier synthesis. Thermogravimetric analysis (TGA) has been carried out to determine the hydrogen desorption temperature, and to confirm the hydrogen contents. A destabilization with respect to MgH_2 hydride, with a reduction of the desorption temperature of approximately 240 °C, suggests that Cu-doping of MgH_2 may find applications in the hydrogen storage field.

1. Introduction

The utilization of hydrogen as energy vector strongly relies on the development of suitable hydrogen storage materials. Metal hydrides are perhaps the most realistic choice for the storage of hydrogen. Magnesium-based alloys are very attractive for hydrogen storage due to their large hydrogen capacity, light weight and low cost.

One of the most attractive hydrides is MgH_2, which presents a high volumetric and gravimetric hydrogen capacity

* *Corresponding author*. Tel.: +56 34 91 334 9000; fax: +56 34 91 372 0623.
E-mail address: jaalonso@icmm.csic.es (B. Torres).

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(~110 kg(H_2) m^{-3} and 7.6 wt.%, respectively) [1]. However, MgH_2 presents serious kinetic and thermodynamic limitations for hydrogen absorption and desorption processes. Many efforts have been done in order to reduce the thermodynamic stability of MgH_2; the most common is by doping with various transition elements (Ni, Fe, Co, Cu) [2–5], via different conventional metallurgy techniques such as melting and sintering [6,7] mechanical alloying [8,9] and mechanical milling [3].

The Mg–Cu system has two intermetallic $MgCu_2$ and Mg_2Cu alloys in the phase diagram. Only Mg_2Cu forms hydrides at pressures of 20 atm H_2, and 300 °C [10]. Although this intermetallic is not hydrided under ambient pressure, the kinetic studies of hydrogenation of the eutectic alloy Mg/Mg_2Cu under milder conditions suggest that the Mg_2Cu phase acts as a catalyst, because probably provides oxide-free penetration sites on the surface of Mg particles [11].

Solid-state high-pressure synthesis is presented as a useful tool to explore the formation of new materials in a variety of research fields. In the field of the hydrogen storage materials, this method has being recently used to obtain new hydrides as a different approach from traditional methods, as shown for Mg_2FeH_6 and $NaMgH_3$ [12,13]. In the present work we have been able to stabilize a new hydride $Mg_3CuH_{0.6}$ under hydrostatic pressure conditions at moderate temperatures. We describe a comprehensive study of the crystal structure, which has been determined by *ab-initio* methods from XRD and NPD data, in complement with thermal analysis (TGA), yielding a scope of the delivery of hydrogen that has been compared to other well-know metal hydrides.

2. Experimental procedure

Polycrystalline samples of $Mg_3CuH_{0.6}$ were prepared from stoichiometric mixtures of MgH_2 and Cu. The reactants were intimately mixed and ground in a glove box under N_2 atmosphere. These mixtures were placed into gold or platinum capsules (5 mm diameter, 10 mm length), sealed inside the glove box and then set into a cylindrical graphite heater (6 mm internal diameter). The reactions took place in a piston-cylinder press (Rockland Research Co.), at moderate reaction pressures (2–3.5 GPa) and temperatures (750–850 °C), for short reactions times of less than 1 h. Then, the product was quenched under pressure. The ramp-up for the material synthesis is rather fast, near 150 °C min^{-1}; we reached 750–850 °C in approximately 5 min. The ramp-down is a quenching process; in a matter of seconds the sample is quenched to RT. We have performed several experiments at different conditions (temperature, synthesis time, pressure…) in order to optimise the synthesis process.

The initial characterization was carried out by X-ray diffraction (XRD) with a Bruker- axs D8 Advanced diffractometer (40 kV, 30 mA), controlled by a DIFFRACTPLUS software, in Bragg-Brentano reflection geometry with Cu Kα radiation ($\lambda = 1.5418$ Å) and a PSD (Position Sensitive Detector). A filter of nickel allows the complete removal of Cu Kβ radiation. For the study of the crystal structure, a neutron powder diffraction (NPD) experiment was carried out in the high-resolution powder diffractometer D2B at the Institut Laue-Langevin at Grenoble, with a wavelength of 1.594 Å. The pattern was collected at room temperature. About 0.8 g of sample was contained in a vanadium can, and a time of 2 h was required to collect a full diffraction pattern. The NPD data were analyzed by the Rietveld method [14] with the FULLPROF program [15]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The following parameters were refined in the final run: scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates and isotropic thermal factors for all the atoms. The coherent scattering lengths for Mg, Cu and H were 5.20, 7.60 and −3.72 fm, respectively.

Thermal analysis was carried out in a Mettler TA3000 system equipped with a TC10 processor unit. Thermogravimetric (TGA) curves were obtained in a TG50 unit, working at a heating rate of 10 °C min^{-1}, in a reducing H_2(5%)/N_2(95%) flow of 0.3 L min^{-1}. About 50 mg of sample were used for each experiment.

3. Results and discussion

Six samples were prepared by high-pressure synthesis. The purity of the samples depends on the reaction temperature, reaction time and pressure and on the nature of the capsule. Table 1 summarizes the conditions for the six obtained samples (A–F). The structural evolution of the samples prepared, by shifting some conditions, is illustrated in the XRD patterns in Fig. 1. We used the Rietveld method to determine the structure and proportion of the different phases. All of the samples present a very high crystallinity, in contrast with the compounds obtained by the traditional ball-milling method [16]. The diffraction peaks of unreacted MgH_2, $MgCu_2$, $AuMg_3$ and $AuMg_2$ were detected in the sample (x, *, ◆ and □ symbols in Fig. 1, respectively). The samples from A to E were prepared under an external hydrostatic pressure of 3.5 GPa, while sample F was prepared at 2 GPa.

Sample A was prepared at 750 °C for 40 min. The XRD pattern for sample A, Fig. 1, shows a minor amount of $Mg_3CuH_{0.6}$, but also some impurities such as $MgCu_2$ and MgH_2. Sample B was obtained increasing the reaction temperature up to 800 °C and keeping constant the remaining experimental conditions; Fig. 1 shows an increase in the amount of $Mg_3CuH_{0.6}$ with the consequent decrease of $MgCu_2$ and MgH_2 phases. The continued increase of temperature up to 850 °C, Sample C, demonstrated the increase of the $Mg_3CuH_{0.6}$

Table 1 – Summary of the synthesis conditions of the six $Mg_3CuH_{0.6}$ samples.

Samples	Temp. (°C)	Time (min)	Capsule material	Pressure (Gpa)
A	750	40	Pt	3.5
B	800	40	Pt	3.5
C	850	40	Pt	3.5
D	850	60	Pt	3.5
E	850	40	Au	3.5
F	850	40	Pt	2.0