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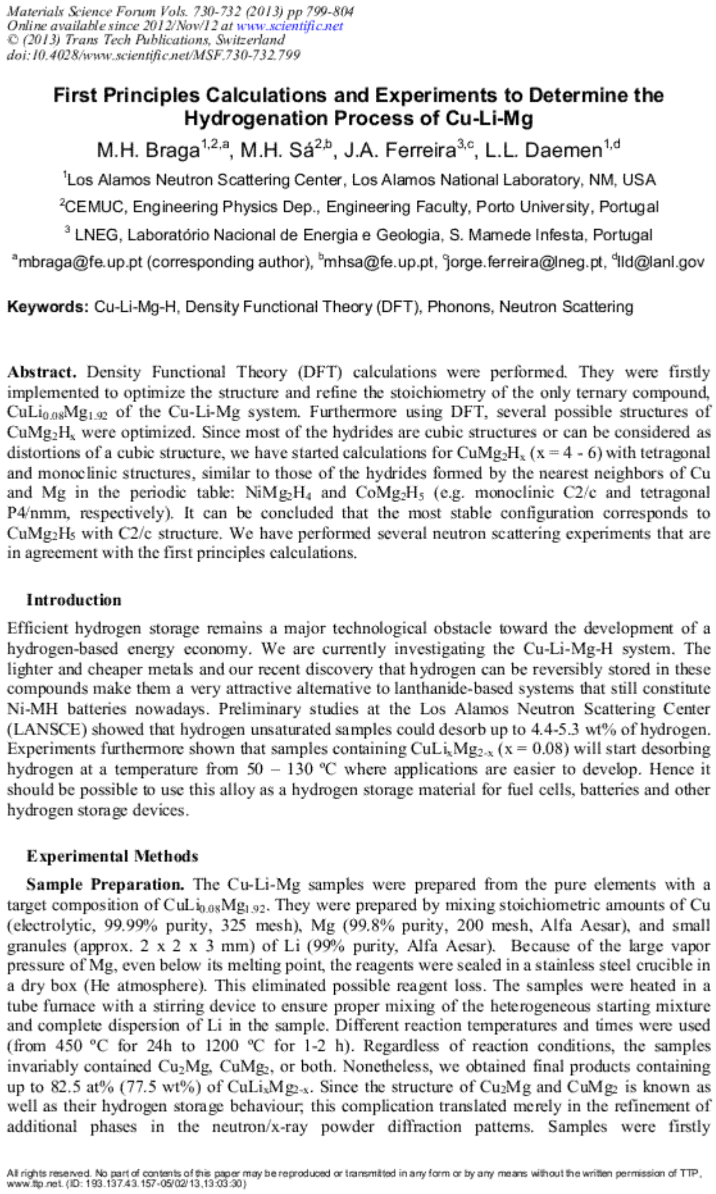

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First Principles Calculations and Experiments to Determine the Hydrogenation Process of Cu-Li-Mg

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Abstract. Density Functional Theory (DFT) calculations were performed. They were firstly implemented to optimize the structure and refine the stoichiometry of the only ternary compound, $CuLi_{0.08}Mg_{1.92}$ of the Cu-Li-Mg system. Furthermore using DFT, several possible structures of $CuMg_2H_x$ were optimized. Since most of the hydrides are cubic structures or can be considered as distortions of a cubic structure, we have started calculations for $CuMg_2H_x$ ($x = 4 - 6$) with tetragonal and monoclinic structures, similar to those of the hydrides formed by the nearest neighbors of Cu and Mg in the periodic table: $NiMg_2H_4$ and $CoMg_2H_5$ (e.g. monoclinic C2/c and tetragonal P4/nmm, respectively). It can be concluded that the most stable configuration corresponds to $CuMg_2H_5$ with C2/c structure. We have performed several neutron scattering experiments that are in agreement with the first principles calculations.

Introduction

Efficient hydrogen storage remains a major technological obstacle toward the development of a hydrogen-based energy economy. We are currently investigating the Cu-Li-Mg-H system. The lighter and cheaper metals and our recent discovery that hydrogen can be reversibly stored in these compounds make them a very attractive alternative to lanthanide-based systems that still constitute Ni-MH batteries nowadays. Preliminary studies at the Los Alamos Neutron Scattering Center (LANSCE) showed that hydrogen unsaturated samples could desorb up to 4.4-5.3 wt% of hydrogen. Experiments furthermore shown that samples containing $CuLi_xMg_{2-x}$ ($x = 0.08$) will start desorbing hydrogen at a temperature from 50 – 130 ºC where applications are easier to develop. Hence it should be possible to use this alloy as a hydrogen storage material for fuel cells, batteries and other hydrogen storage devices.

Experimental Methods

Sample Preparation. The Cu-Li-Mg samples were prepared from the pure elements with a target composition of $CuLi_{0.08}Mg_{1.92}$. They were prepared by mixing stoichiometric amounts of Cu (electrolytic, 99.99% purity, 325 mesh), Mg (99.8% purity, 200 mesh, Alfa Aesar), and small granules (approx. 2 x 2 x 3 mm) of Li (99% purity, Alfa Aesar). Because of the large vapor pressure of Mg, even below its melting point, the reagents were sealed in a stainless steel crucible in a dry box (He atmosphere). This eliminated possible reagent loss. The samples were heated in a tube furnace with a stirring device to ensure proper mixing of the heterogeneous starting mixture and complete dispersion of Li in the sample. Different reaction temperatures and times were used (from 450 ºC for 24h to 1200 ºC for 1-2 h). Regardless of reaction conditions, the samples invariably contained Cu_2Mg, $CuMg_2$, or both. Nonetheless, we obtained final products containing up to 82.5 at% (77.5 wt%) of $CuLi_xMg_{2-x}$. Since the structure of Cu_2Mg and $CuMg_2$ is known as well as their hydrogen storage behaviour; this complication translated merely in the refinement of additional phases in the neutron/x-ray powder diffraction patterns. Samples were firstly