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Investigation on structural and magnetocaloric properties of $LaFe_{13-x}Si_x(H,C)_y$ compounds

M. Phejar, V. Paul-Boncour, L. Bessais *

CMTR, ICMPE, CNRS – UPEC, UMR7182, 2-8 rue Henri Dunant, F-94320 Thiais, France

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ABSTRACT

The first part of this study is devoted to $LaFe_{13-x}Si_xH_y$ hydrides. The parent intermetallic alloys were synthesized by high energy ball milling. The insertion of H atoms was carried out by solid/gas reaction using a Sievert apparatus. Their thermodynamic properties show a very fast kinetic absorption at 298 K under 10 bars depending on Si content. The structural results combined with magnetic measurements allow to explain the magnetovolumic effect on the Curie temperature. The second part of this study is dedicated to $LaFe_{13-x}Si_xC_y$ carbides. They were synthesized by solid/solid reaction between the intermetallic powder and the anthracene. Their structural as well as magnetocaloric properties were investigated. Further structural and magnetic results were carried out by neutron diffraction. A complete crystallographic characterization was made. The cell parameter and the Fe magnetic moments versus temperature were determined. Moreover, the misunderstanding on interstitial site was clear up.)

1. Introduction

The magnetocaloric effect (MCE) is an intrinsic property of magnetic materials which was originally discovered in nickel by Weiss and Piccard [1]. This effect can be used in many magnetocaloric devices like magnetic heat pumps, magnetic energy conversion machines or magnetic refrigerators [2]. In the latter, the MCE was related to an isothermal magnetic entropy change as well as an adiabatic temperature change of a magnetic material upon application of a magnetic field.

Since the discovery of the giant magnetocaloric effect in magnetic materials showing a first-order metamagnetic transition such as $Gd_5Ge_2Si_2$ [3] much research have been carried out on iron rich compound because of its possible applications in domestic appliances at room temperature [4]. The interesting magnetocaloric properties of intermetallic compound $LaFe_{13-x}Si_x$ with $1.56 \leq x \leq 1.82$ have been shown by Fujita et al. [5] since the research on these compounds increase and the existence of the giant magnetocaloric effect has been shown. Effectively, $LaFe_{13-x}Si_x$ compound with $x=1.6$ showed a large magnetic entropy variation higher than that of the $Gd_5Ge_2Si_2$ under the same magnetic field change [6]. The point is that the Curie temperature, even if it can be adjusted by Si content is lower than ambient temperature what is no suitable for room temperature application. For a Si content in the range of $1.3 \leq x \leq 2.2$, these materials exhibit a large entropy magnetic variation around 200 K which is caused by an itinerant electron metamagnetic (IEM) transition [7,8]. Many studies have been carried out in order to increase the Curie temperature of these materials by substituting La and Fe respectively by another rare-earth or transition metal such as Co or by the insertion of interstitial atoms like hydrogen or carbon [7].

Recently we have studied structural and magnetic properties for $LaFe_{13-x}Si_x$ compounds [9]. An almost single 1:13 phase was obtained after only a 30 min heat treatment at 1393 K for ball-milled samples. This means a gain of time, therefore a gain in energy which is very interesting for industrial application.

The present work relates the investigations which were made on thermodynamical and magnetic properties of $LaFe_{13-x}Si_x$ hydrides as well as carbides. Their metallurgical properties were studied in function of various external synthesis parameters. Neutron powder diffraction analysis were carried out for further magnetic and structural characterizations.

2. Experimental procedures

The LaSi as-cast ingot was ground to powder in an agate mortar. Fe and Si powders were added to the precursor in order to reach the appropriate composition, $LaFe_{13-x}Si_x$ ($x=1.2$, 1.4, 1.5, 1.6, 1.8, 2.0 and 2.2). The starting materials were pure elements (99.9%). To prevent any loss of lanthanum caused by the large

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* Corresponding author.
E-mail address: bessais@icmpe.cnrs.fr (L. Bessais).

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amount of powder stuck on the vial wall and its possible oxidation, an excess of 20 wt% of La was systematically added. All powders were mixed in an agate mortar and loaded into a stainless steel vial under high-purity Ar atmosphere inside a glove box. Before sealing the vial, five stainless steel balls of 15 mm diameter were added. The powder to ball weight ratio was 1:14. The ball-milling was performed in a planetary crushing Fritsch Pulverisette 7. A low energy 30 min ball-milling at 200 rpm was done before the high energy ball-milling at 600 rpm during 5 h [9,10]. These milling conditions correspond to a kinetic shock energy, a shock frequency and an injected shock power values respectively equal to 0.81 J/hit, 62 Hz and 19.5 W/g. The as-milled alloys were sealed under argon in a silica tube and annealed at 1423 K for 30 min followed by a quenching in water.

The composition and homogeneity of the alloys were investigated by X-ray diffraction (XRD) using a Bruker D8 diffractometer (Cu Kα radiation) and electron microprobe analysis (EPMA). The analysis revealed that the samples were almost single phase with $NaZn_{13}$-type structure with a small quantity of α-(Fe, Si) (≃2 wt%) and La_2O_3 (≃2 wt%).

The $LaFe_{13-x}Si_xH_y$ hydrides were prepared by solid/gas reaction using a Sievert apparatus. The intermetallic powder (0.5–1 g for hydride and 5 g for deuteride) was introduced into a stainless steel container, connected to the hydrogenation device and outgased one night under primary vacuum (10^{-2} bar) at 473 K. The sample was then submitted to an hydrogen (deuterium) pressure ($P_{max}=10$ bar) at temperatures between 298 K and 473 K. The hydrogen (deuterium) content was obtained using a volumetric method.

The $LaFe_{13-x}Si_xC_y$ carbides were prepared by solid/solid reaction between the anthracene and the intermetallic powder [11].

The appropriate mass of intermetallic compound and antracene powder was mixed in a mortar into an argon glove box. The mixture was introduced into a silica tube which was sealed under secondary vacuum and heated at 923 K for 24 h. Some pieces of magnesium were also introduced into the silica tube to absorb the hydrogen originating from the decomposition of anthracene upon heating.

Their crystallographic and magnetic structures were checked by XDR measurements and Neutron powder diffraction (NPD) respectively. The NPD analysis was performed at 400 K on 3T2 spectrometer ($\lambda=1.225$ Å) in order to study the crystallographic structure of the $LaFe_{13-x}Si_x(H,C)_y$ compound. The magnetic structure and the evolution of magnetic parameters versus temperature were determined by using the G4-1 spectrometer ($\lambda=2.43$ Å) in the range of temperatures between 1.5 K and 300 K at the Laboratoire Léon Brillouin (LLB), Saclay. The XRD and NPD patterns were refined using the Fullprof code with the assumption of a peak-line profile of Thompson–Cox–Hasting allowing multiple-phase refinement of each of the coexisting phases [12].

The magnetic and magnetocaloric properties were determined using a physical property measurement system (PPMS) magnetometer from Quantum Design operating up to 9 T and from 1.9 to 350 K.

3. Results and discussion

3.1. Hydride compounds

3.1.1. Hydrogenation properties

$LaFe_{13-x}Si_x$ hydrides were prepared under a maximum pressure of 10 bars and temperatures ranging between 298 and 423 K. It was observed that the maximum H content was reached after only 30 min for $x=1.6$, whereas a period of 60 min was necessary for alloys with $x=2$ ($T=298$ K, $P=10$ bars). The increase of absorption time versus Si content can be related to the repulsive interactions between p-elements and H atoms observed by Rundqvist et al. [13]. The kinetic of absorption becomes faster as the temperature increases, due to better diffusion of H atoms in the metallic matrix. The maximum H content obtained at 10 bars and 298 K decreases versus the Si content (Table 1). This can be explained by a diminution of the number of electron holes in the conduction band versus Si content, which limit the maximum number of H atoms than can be added to keep a stable phase.

Table 1
Maximal hydrogen capacity of $LaFe_{13-x}Si_x$ hydrides at 298 K under 10 bar. H/M means number of hydrogen atom per metal atom.

Nominal composition	Content (H/f.u.)	Content (H/M)
$LaFe_{11.5}Si_{1.5}$	1.75(5)	0.13(1)
$LaFe_{11.4}Si_{1.6}$	1.35(5)	0.10(1)
$LaFe_{11.0}Si_{2.0}$	1.22(5)	0.09(1)

In the following part hydrogenated compounds with $x=1.5$ and 1.6 have been selected as their parent alloys give larger entropy variation than those with $x=1.8$, 2 and 2.2; hydrides are therefore more interesting in view of MCE effects [9].

Fig. 1 shows hydrogen desorption PCT isothermal curves measured at 298 K, 363 K and 413 K for $LaFe_{11.5}Si_{1.5}$. The plateau pressure is not observed for all $LaFe_{13-x}Si_x$ hydrides. This fact was noticed by Wang et al. [14]. It means that $NaZn_{13}$-type hydrides are forming an hydrogen solid solution. H desorption under vacuum is not complete up to 413 K ($y=1.55$, 1.46 and 0.68 H/f.u. respectively at 298, 363 and 413 K). Therefore $LaFe_{11.5}Si_{1.5}$ hydrides are thermodynamically stable at room temperature, and the sample should be heated above 413 K to observe a full H desorption.

3.1.2. Structural properties

The refinement of the XRD data of hydride compounds was proceeded at room temperature. They show a doubling of the peaks related to the $NaZn_{13}$-type structure. The new peaks were shifted toward low angle indicating that a certain amount of hydrogen was dissolved in the compound. It means that there is the coexistence of a hydride with the parent intermetallic phase. The structural results from XRD analysis are shown in Table 2.

The XRD patterns of hydrides synthesized at temperatures above 473 K (Fig. 2) contain only one $NaZn_{13}$ phase with a cell volume increase compared to the parent compound. Some Fe and La_2O_3 impurities present in the starting materials are also

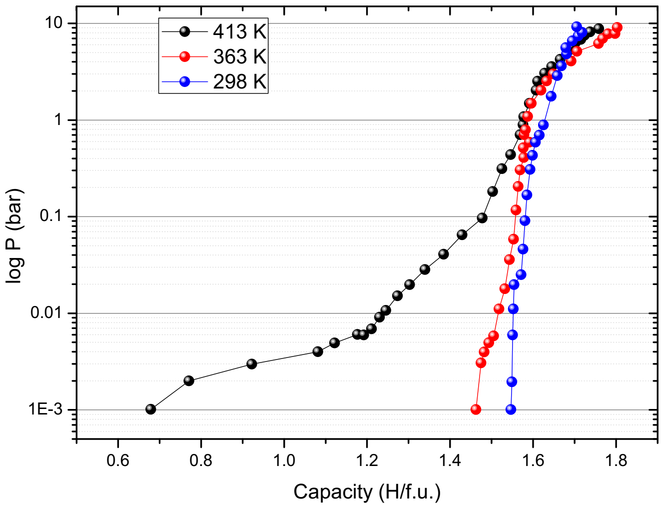

Fig. 1. Hydrogen desorption PCT isothermal curves measured at 298 K, 363 K and 413 K for $LaFe_{11.5}Si_{1.5}$ hydride.