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Magnetocaloric effect and H gradient in bulk $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_y$ magnetic refrigerants obtained by HDSH

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Abstract

Results are reported on the preparation of bulk parts of $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_y$ via the Hydrogen-Decrepiation-Sintering-Hydrogenation (HDSH) process. Net shape parts for application in room-temperature magnetic refrigeration have been produced in only 8 h of heat treatment which is considerably faster than the conventional ingot homogenization heat treatment of 7 days. The samples produced by HDSH showed higher amounts of hydrogen than the parts hydrogenated by the conventional method of thermal homogenization (20 h at 1423 K), milling to fine powder and subsequent hydrogenation. Hydrogenation parameters play an important role for the stability of the desired $\text{La}(\text{Fe},\text{Si})_{13}$ phase during the process. Hydrogen desorption was seen to occur at two temperature ranges as a result of internal gradients. Dissimilar amounts of α -Fe were precipitated for different hydrogenation times. As a result, parts produced via HDSH with 2 and 4 h of hydrogenation exhibited different magnetocaloric behaviours. For a hydrogenation step of 4 h, parts with a demagnetization factor of 0.49 showed an adiabatic temperature change (ΔT_{ad}) higher than 1 K for a temperature range of 40 K with a maximum value of 1.57 K for an applied magnetic field of 1.75 T. As the duration of the hydrogenation step of the HDSH process decreased to

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2 h, ΔT_{ad} was larger than 1 K for a temperature range of 24 K. However the maximum value of ΔT_{ad} at 328 K was 2.2 K, which is 37.5 % larger than the maximum value for a hydrogenation period of 4 h.

Keywords: La(Fe,Si)₁₃H_y magnetic refrigerants, magnetocaloric materials, HDSH, hydrogenation

1. Introduction

The magnetocaloric effect (MCE) is the thermal response of certain materials when subjected to a changing magnetic field. It has been investigated since the early 19th century [1] and the pioneering work of Giauque and MacDougall [2] on the use of adiabatic magnetization to cool below 1 K was awarded Nobel Prize in Chemistry in 1949. Magnetic refrigeration at room temperature was firstly demonstrated with gadolinium (Gd) as the magnetocaloric material, where a no-load temperature span of 47 K was achieved with approximately 157 g of Gd and a magnetic field of 7 T [3].

Magnetic refrigeration has a great potential for high thermodynamic cycle efficiency due to the reversible nature of the MCE [3, 4, 5]. The discovery of the giant MCE in Gd₅Si₂Ge₂ by Pecharsky and Gschneidner [6] prompted the research for other first-order phase transition (FOPT) materials with similar characteristics [7].

A more recent group of materials with promising properties is the La-based alloys, LaFe_{13-x}Si_x, which crystallise in the NaZn₁₃-type phase structure for values of x between 1.05 and 2.5 [8, 9]. Usually materials based on this phase are produced by a conventional melting, casting and annealing. The latter is necessary in order to achieve nearly 100 % of the desired phase and it is a long-term homogenization step, which may take up seven days in high temperature heat treatments [10]. Faster routes have been proposed, e.g. melt-spinning, for which a nearly monophasic microstructure has been stabilised after a 2 h high-temperature heat treatment [11]. Other routes based on powder metallurgy have been suggested [12, 13].

25 $\text{LaFe}_{13-x}\text{Si}_x$ compounds have Curie temperatures, T_C , between 180 and
230 K, for increasing amounts of Si [14]. Therefore, to use this material for
magnetic cooling around room temperature, the T_C must be increased. One
possible method to increase the T_C of this material is by expanding the lattice
parameter, e.g. inserting interstitial atoms such as H or C [15, 16]. The hydro-
30 genation step is commonly performed in the powder form [17]. Nevertheless,
after the hydrogenation process, where the hydrogen is inserted interstitially
into the NaZn_{13} -type structure, some difficulties may be pointed out. Firstly,
the resulting powder cannot be heat treated in order to shape it, since the hy-
drogen stability in the microstructure goes only up to around 500 K [16]. If one
35 try to sinter under H_2 atmosphere, at around 1023 K LaH_2 starts to stabilize,
destroying the desired phase. Hence, without being able to shape it, its appli-
cation is now limited since in many cases a functional part with well-defined
geometry is demanded [18].

In this work, the recently reported [19] Hydrogen-Decreepitation-Sintering-
40 Hydrogenation (HDSH) process was used to produce bulk parts of $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_y$,
varying the H content in order to cover a broader range of working tempera-
tures. Samples from the same ingot were also produced by the conventional
process and the resulting samples from both processes were then compared.

2. Experimental Procedure

45 Bulk parts of $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_y$ were produced by HDSH, as described in pre-
vious work [19]. The process is divided in 3 basic steps:

- 1 The process uses a La-Fe-Si ingot as raw material, which is hydrogen-
decreepitated into small pieces, at 423 K during 1 hour.
- 2 The material is then milled, pressed into 1 mm thick pellets and sintered
50 at 1423 K, for 6 h under argon atmosphere. During the heating step of
the sintering, the hydrogen that was inserted in the material during HD
is desorbed due to the high temperatures.

3 In the cooling step after the sintering, the temperature is reduced to 773 K and the hydrogenation step is, thus, performed during two different time spans: 2 and 4 h; under pure H₂ atmosphere at pressures above 1 atm. In this step the interconnected pores are the free path for hydrogen, so it may reach the whole sample volume. Subsequently, the samples are slowly cooled to room-temperature in the furnace.

In order to compare and evaluate the HDSH process, La(Fe,Si)₁₃H_y powder was prepared by the conventional method, which is divided in 3 basic steps:

- 1** Cylindrical parts of the same ingot used to produce the HDSH parts, were cut by electro-erosion.
- 2** The parts were homogenized during 20 h at 1423 K under a 90 kPa Ar atmosphere.
- 3** The parts were then milled into powder (<100 μm) and a hydrogenation step was carried out, for 2 h at 773 K under pure H₂ atmosphere at pressures above 1 atm.

The phase constitution of the samples was determined via means of powder X-ray diffraction (XRD) on a Phillips X'Pert Plus Diffractometer with Cu K_α radiation. The quantitative phase analyses and the crystal structure parameters were analysed by the Rietveld method, refining the XRD patterns by GSAS code [20]. The hydrogen content and thermal stability were analysed and calculated by thermo-gravimetric (TG) analysis on a Netzsch simultaneous thermal analyser (STA), model 449 F3 Jupiter.

The MCE was quantified via the adiabatic temperature change, ΔT_{ad} , measured in different synthesised samples using a home-built ΔT_{ad} -ometer device [21]. In this device the sample is rapidly subjected to an applied magnetic field change from 0 to 1.75 T, starting from a stabilised sample temperature between 258 K and 348 K.

80 **3. Results**

In order to study the influence of the hydrogenation step on the amount of $\text{La}(\text{Fe,Si})_{13}$ and on the lattice parameter a in the HDSH samples, XRD diffraction patterns were refined for both the samples before and after the hydrogenation processes as can be seen in Fig. 1(a). The amount of α -Fe increases with
 85 the hydrogenation time, from 0.97 wt.% for the as-sintered sample to 2.92 wt.% and 6.13 wt.% for 2 h and 4 h of hydrogenation step, respectively, as shown in Fig. 1(b). The increase of α -Fe content could be related to formation of La oxide or LaH_2 , which even in amounts undetectable by XRD, could lead to significant precipitation of α -Fe, as the structure $\text{La}(\text{Fe,Si})_{13}$ is mostly Fe.

90 The lattice parameter a after the hydrogenation was increased from 11.48 Å to 11.59 Å, for both 2 h and 4 h of hydrogenation, which in the XRD data may be seen as a shift of the XRD pattern to lower angles, as shown in Fig. 1(b). These results are summarized in Table 1.

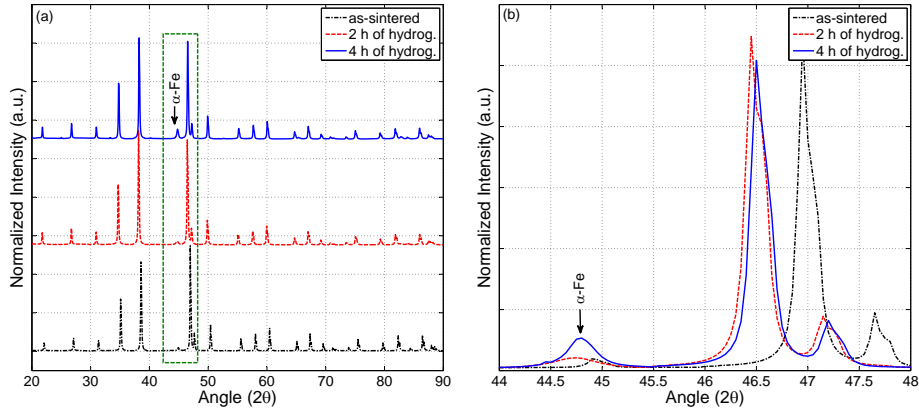


Figure 1: Colors are available in online version. (a) Rietveld pattern for the XRD data of samples prepared by HDSH before hydrogenation (as-sintered), after 2 h (red line) and 4 h (blue line) of hydrogenation. (b) A zoom in the green dashed box from Fig.1(a) showing the shift on the pattern due to hydrogenation and the α -Fe peaks.

95 Thermal analyses of the hydrogenated samples were performed to understand the thermal stability of the interstitial hydrogen as a function of the tem-

perature. Fig. 2 summarizes the thermo-gravimetric analyses performed in the samples produced by HDSH compared to those produced by the conventional method. The thermal analyses shows two different H desorption ranges for the samples produced by HDSH, which may be related to a gradient of hydrogen, since these parts were hydrogenised in the bulk form. Also, as shown in Fig. 2, the gradient increases with the duration of the hydrogenation. Furthermore, these results indicate that the amount of interstitial H is higher for the parts produced by HDSH.

Although it is expected that longer hydrogenation times should lead to a lower H gradient [22], the different hydrogen contents might be related to the α -Fe precipitation. When α -Fe precipitates, the ratio α -Fe/Si changes, hence changing the hydrogen saturation locally, which could lead to a greater gradient. Other relevant hydrogenation methods are found in the literature [13, 22], which might hydrogenate the sintered samples more efficiently.

Fig. 3 shows the ΔT_{ad} of the different samples with T_C around room temperature. it should be noted that the demagnetization factor, N_D , is different for each sample due to the differences in the shape between each sample. The N_D for the samples from the conventional process, HDSH with 2 h and 4 h of hydrogenation are 0.27, 0.32 and 0.49, respectively [23]. The temperature at which ΔT_{ad} is maximum, T_{peak} , was found to be around 329 K for the samples produced by the conventional process and by HDSH with 2 h of hydrogenation, while T_{peak} was 328 K for the sample produced by HDSH with 4 h of hydrogenation. The sample obtained by the conventional process and tested

Table 1: Relative phase amount and lattice parameter a , obtained by Rietveld refinement, of the samples produced by HDSH before the hydrogenation step (as-sintered), after 2 h and after 4 h of hydrogenation. The as-sintered sample measurements were taken before hydrogenation.

Description	a	$\text{La(Fe,Si)}_{13}\text{H}_y$	α -Fe	LaFeSi
As-Sintered	11.48 Å	99.03 wt.%	0.97 wt.%	0.00 wt.%
HDSH (2 h)	11.59 Å	97.08 wt.%	2.92 wt.%	0.00 wt.%
HDSH (4 h)	11.59 Å	93.58 wt.%	6.13 wt.%	0.34 wt.%

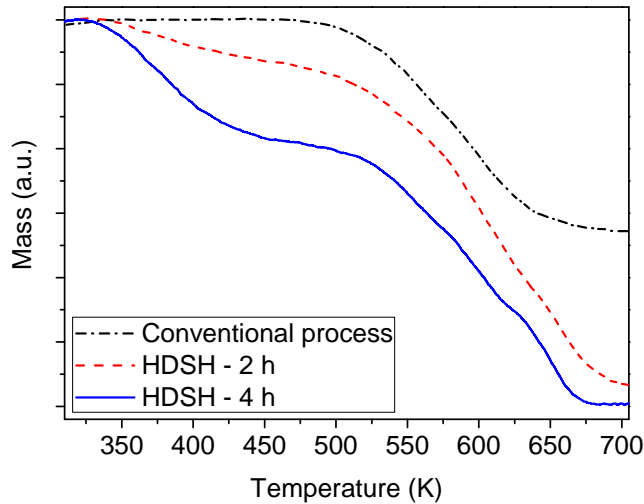


Figure 2: Colors are available in online version. Thermo-gravimetric analyses comparing the H desorption dependence on the temperature for the samples produced by the conventional method (black line) and HDSH with 2 h (red line) and 4 h (blue line) of hydrogenation.

in powder form still resulted in a larger ΔT_{ad} , with a maximum value of 2.64
 120 K. The maximum values of the ΔT_{ad} for the bulk parts produced by HDSH
 process with 2 h and 4 h of hydrogenation were 2.07 K and 1.57 K, respectively.
 However, the parts produced by HDSH exhibited peaks that were broader than
 those produced by the conventional process. It is important to point out that
 the part hydrogenised for 4 h had a ΔT_{ad} larger than 1 K for a temperature
 125 range of 40 K. These range differences can be also related to the H gradients
 which are observed in Fig. 2. The results are summarized in Table 2. Consider-
 ing the broader MCE observed in the samples produced by HDSH, this process
 may be advantageous in the production of bulk materials for magnetic cooling
 devices, since fabrication of graded FOPT magnetocaloric materials is still in
 130 development.

It should be noted that the measured MCE is influenced by the N_D of the
 samples, which reduces the resulting internal magnetic field. Therefore, the
 three curves should exhibit larger values of ΔT_{ad} . In this way, the samples
 produced by HDSH process should have maximum values of ΔT_{ad} closer to

135 that of the sample produced by the conventional process. Simple calculations
 based on the scaling relationship $\Delta T_{ad} \sim H^{2/3}$ show that the difference between
 the maximum value of ΔT_{ad} is significantly larger only for the sample produced
 by HDSH with 4 h of hydrogenation, as its N_D is 0.49.

A relationship has been identified between the reduction of the MCE and the
 140 phase content fraction as well. Firstly, due to α -Fe precipitation, some distri-
 bution on x and y of $\text{LaFe}_{11.3-x}\text{Si}_{1.7+x}\text{H}_y$ may be found, instead of one singular
 value. For the 2 h hydrogenation HDSH sample, the total amount of α -Fe was
 2.92 wt.%, while for the 4 h hydrogenation HDSH sample the α -Fe amount was
 6.13 wt.%. The difference of α -Fe content, not only decreases the MCE due to
 145 the lower global amount of $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_y$, but it may also create preferential
 pathways for the magnetic flux through the α -Fe impurity grains rather than
 through the surrounding $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_y$ matrix, because of the higher magnetic
 susceptibility of the former. A simple 2D magnetostatic model was set up to
 analyse the effect of the magnetic susceptibility. In the model a magnetic field
 150 is applied to rectangular sample with the susceptibility of $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_y$, and
 the average internal field is calculated. Then areas equivalent to 2.92 and 6.13
 wt.% of α -Fe were substituted as randomly positioned fine grains in the matrix
 of $\text{La}(\text{Fe},\text{Si})_{13}\text{H}_y$, equivalent to the samples produced by HDSH with 2 and 4 h
 of hydrogenation, respectively. In both situations the average internal field in
 155 the matrix around the α -Fe grains was observed to be within 1% of the value
 for the pure sample. Thus, the effect of the α -Fe impurities on the internal

Table 2: Summary of the ΔT_{ad} measurements. In this case, ΔT_{ad}^{Max} is the maximum value
 of ΔT_{ad} at T_{peak} .

Sample	N_D	T_{peak}	ΔT_{ad}^{Max}	Range of $\Delta T_{ad} \geq 1 \text{ K}$
Conventional	0.27	329 K	2.64 K	18 K
HDSH (2 h)	0.32	329 K	2.07 K	24 K
HDSH (4 h)	0.49	328 K	1.57 K	40 K

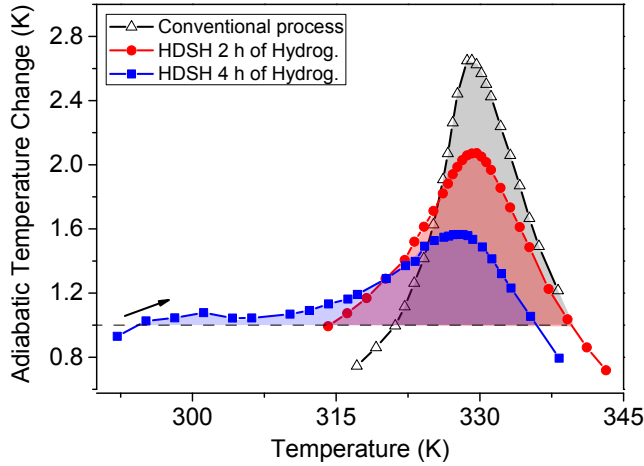


Figure 3: Colors are available in online version. Adiabatic temperature changes, measured during heating and magnetization, for the $\text{La}(\text{Fe,Si})_{13}\text{H}_y$ samples produced by the conventional process (black line), HDSH with 2 h (red line) and 4 h (blue line) of hydrogenation.

magnetic field is negligible.

4. Conclusions

In this paper, a comparison between the hydrogenation process of $\text{La}(\text{Fe,Si})_{13}\text{H}_y$ compound in: i) powder and ii) sintered porous samples was carried out, from
 160 which the following conclusions could be withdrawn. Firstly, XRD patterns have shown an increasing intensity of α -Fe after the hydrogenation, in the case of samples prepared by HDSH. Thermal analysis revealed a gradient of H desorption ranges in the samples produced by HDSH. This gradient was also identified
 165 in the ΔT_{ad} measurements, where the sample produced by HDSH with 4 h of hydrogenation showed a ΔT_{ad} larger than 1 K in a range of 40 K. The maximum ΔT_{ad} of the samples produced by the conventional process, HDSH with 2 h and 4 h of hydrogenation were 2.64, 2.07 and 1.57, respectively. 2D modelling showed that the effect of α -Fe on the surrounding magnetocaloric material is
 170 negligible.

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