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Fine control of Curie temperature of magnetocaloric alloys La(Fe,Co,Si)$_{13}$ using electrolytic hydriding

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Abstract

This work demonstrates precision control of hydrogen content in La(Fe,Co,Si)$_{13}$H$_{\delta}$ for the development of environmentally friendly magnetocaloric-based cooling technologies, using an electrolytic hydriding technique. We show the Curie temperature, a critical parameter which directly governs the temperature window of effective cooling, can be varied easily and reproducibly in 1 K steps within the range 274 K to 402 K. Importantly, both partially (up to 10%) and fully hydrided compositions retain favorable entropy change values comparable to that of the base composition. Crucially, we show in these second-order phase transition compounds, partial hydriding is stable and not susceptible against phase separation.

Keywords

Magnetocaloric effect, intermetallics, electrolytic hydriding, synchrotron radiation

Magnetocaloric cooling has attracted much attention due to potential to be more energy efficient and environment-friendly than conventional gas compression [1-3]. Refrigeration and cooling account for a considerable energy consumption meaning new cooling technologies are urgent and crucial for a low carbon future.

Two vital considerations towards the implementation of magnetocaloric effect (MCE) technologies are the design of the solid refrigerant and the choice of the constituent MCE-material. The magnetic materials that offer large isothermal entropy changes (ΔS) and adiabatic temperature changes (ΔT_{ad}) in response to magnetic fields of the order of 1 T, have a sharp first-order character to the magnetic phase transition, and operate effectively over a narrow temperature range (approximately 5 – 10 K, above their respective Curie temperatures, T_C) [4-8]. To function over the required temperature range using an active magnetic regenerator cooling cycle, a "cascade" set of materials with individually controlled T_C offset from each other by only 1-2 K increments are required [8,9].

A promising attribute of La(Fe,Si)$_{13}$, in addition to large ΔS and ΔT_{ad} due to the field-induced paramagnetic (PM) to ferromagnetic (FM) transition [8,10], is the tuneability of T_C and therefore the possibilities of T_C-cascaded sets. Previous work has shown that the T_C can be controlled monotonically by substitution on to the Si/Fe sites (*e.g.* with Co or Mn) [11-14], or by absorption of interstitial hydrogen atoms [15-19]. Although the amount of hydrogen absorbed offers the *theoretical* potential of targeted T_C control, only full hydrogenation is practicable for such first-order (large volume change, sharp magnetic phase transition) compositions due to phase-separate effect where two separate spatial regions with distinctly differing T_Cs are formed when the material is thermally cycled through the magnetic transition or when it sits close to T_C for several days. The origin of this instability is the lattice expansion in the FM state, prompting hydrogen atoms to diffuse from the PM into FM regions of the material that transform first [20]. Partial hydrogenation therefore results in undesirable heterogeneous changes to the samples' properties within very short time scales [21,22].

In the conventional hydrogenation process, molecular hydrogen must first dissociate requiring high temperatures and pressures. In contrast, electrolytic hydriding involves electrochemical processes and directly produces *atomic* hydrogen at the material surface, which then diffuses into the material at room temperature (RT). The technique is inexpensive, expedient, controllable and safe [23].

La(Fe,Si)$_{13}$ with Co substitutionally doped on to the Fe sites (with T_C control of the order of 2 K) [11,12,24] produces a second order broad transition at high Co concentration with impaired ΔS and ΔT_{ad} performance compared to the base material [11,12], and more accurate targeting of T_C near RT is difficult due to very reliable variations in Co content of the order of 1% required. This is similarly the case for Mn doping followed by full hydrogenation (a first-order transition) [17,25-27]. However, a significant advantage in having a broad transition is that it offers a greater effective operation temperature range per composition, relaxing the stringency on the step size of T_C in a cascaded set to perhaps 3 K. Nevertheless, accurate and reliable targeting of any compound's T_C is a strong advantage for future scale-up of MCE refrigerant production. To our knowledge, apart from a single patent application [28], there have been no literature reports of *partial* hydriding as a method of fine T_C control in cobalt-doped or other second-order transition compositions of La(Fe,Si)$_{13}$.

Here we show fine T_C control across large temperature ranges (such as that required for domestic refrigeration) using room-temperature electrolytic hydriding of post-synthesised La(Fe,Co,Si)$_{13}$. We are able to achieve a consistent, partially hydrided compound in which the MCE performance is not compromised - and the hydrogen distribution, and therefore magnetic properties, remain stable over time.

Four compositions of La(Fe,Co,Si)$_{13}$ were investigated to represent a range of Co doping. They were designated A, B, C and D, with systematic variations in Co contents and consequently T_Cs, in the range 272 K to 294 K. The compositions were measured by energy dispersive X-ray spectroscopy, and are shown in the supplementary information (SI).

Electrolytic hydriding experiments were carried out to partially and fully hydride the samples, and to assess the impact on the T_C. Partial and full hydriding of the compounds (A and B) was performed under potentiostatic control in a conventional 3-electrode cell set-up where a Pt wire was used as the counter electrode, and Ag/AgCl/3 M KCl was used as the reference electrode against which the potential values are reported. The samples were held at fixed potentials in NaOH for various periods of time. NaOH is used as the electrolyte since the corrosion rates of La(Fe,Co,Si)$_{13}$ alloys in alkaline solutions are relatively low [23]. Two types of working electrode were used: i) for hydriding times up to and including 1200 s, a single La(Fe,Co,Si)$_{13}$ plate was used as the working electrode. A typical exposure area was 0.5 cm^2; ii) for hydriding times greater than 1200 s, a stainless steel gauze container with at least five sample plates was the working electrode. The second type was used to ensure sample stability over long hydriding time. Argon purging was carried out throughout the tests to avoid oxygen reduction during the hydriding process. All electrochemical tests were carried out using Ivium CompactStat at RT.

In order to resolve the small difference in lattice parameters of the partially hydrided materials, synchrotron-based X-ray powder diffraction of powdered samples was carried out with the multi-analysing crystal detectors on Beamline I11 at Diamond Light Source, UK (see details in the SI) [29]. Rietveld refinement, as implemented in the TOPAS program suite, was used to determine the lattice parameters of the matrix. Hydrogen contents of the partially hydrided samples were estimated through the extracted lattice constants, in conjunction with literature data which demonstrates the relationship between content and lattice constant to be highly consistent for a large variety of La(Fe,Si)$_{13}$-based compositions (see details in the SI) [29-35]. For accurate determination of the hydrogen content of the fully hydrided sample, Horiba EMGA-830 oxygen-nitrogen-hydrogen elemental gas analyser was used for a direct (albeit destructive) measure of composition.

Magnetisation, M, measurements were conducted using a Quantum Design Physical Properties Measurement System in vibrating sample magnetometry mode allowing applied fields, H, up to 9 T and a temperature range 2 – 400 K. All measurements were conducted on small (< 1 mm) pieces of material with varying size. $M(T)$ measurements were performed in 10 mT and 1 T. T_Cs were determined from the $M(T)$ curves in 10 mT. Due to the relatively broad nature of the transition, T_C is given to 1 K. Magnetic entropy curves were calculated from $M(H)$ isotherms by the standard method of evaluating the Maxwell relation using numerical integration for 1 to 0 T change.

Table 1 shows T_C, lattice parameters, a, and hydrogen contents of the pre-hydrided samples (A0, B0, with respective compositions $La_{1.06}Fe_{10.85}Co_{0.88}Si_{1.21}$ and $La_{1.13}Fe_{10.75}Co_{0.99}Si_{1.13}$), partially-hydrided samples (A1-A6, B1) and one fully-hydrided sample (A7). The table clearly shows that T_C can be finely and highly controlled by adjusting the NaOH concentration, the applied cathodic potential and the hydriding time during the electrolytic hydriding process. T_C is found to vary from that of the non-hydrided sample with systematic 1 K steps – achieved by partial hydriding. The fine-tuning has been demonstrated over a temperature range of 11 K and is expected to be extendable over a larger range towards a maximum increase in T_C corresponding to the fully hydrided sample (in the case of composition A, the maximum increase is 128 K, A7). Fine-tuning of T_C is also applicable for other similar compositions, as demonstrated by samples B0 and B1: compared with pre-hydrided sample B0, T_C of B1 has increased by 6 K. The hydrogen contents for hydrided samples indicate that the changes in H required to produce 1 K steps are on the order of 0.005 to 0.01 per formula unit (note that this value is at the limit of resolution of determination).

Table 1 Concentration of NaOH, applied potential (*E*) and hydriding time of electrolytic hydriding of the A and B samples, with measured T_C, lattice parameter, *a*, of the 1:13 phase determined from synchrotron-based X-ray powder diffraction patterns, and H (for A1-A6 and B1) estimated using a linear best fitting of several reported values of a and H-content for $La(Fe,Si)_{13}$ compounds in the literature (see Figure S2 in the SI). H-content for A7 was measured by a gas combustion analyser.

Sample	NaOH [M]	*E* [V]	time [s]	T_C [K]	*a* [Å]	$H_{est.}$ [per f.u.]
A0	N/A	N/A	N/A	274	11.48610(3)	0
A1	3	-1.35	450	280	11.49038(7)	0.096±0.002
A2	0.5	-1.3	600	281	11.49066(7)	0.103±0.002
A3	0.5	-1.3	750	281	11.49070(9)	0.103±0.003
A4	0.5	-1.3	1200	282	11.49094(12)	0.109±0.003
A5	3	-1.35	930	285	11.49269(11)	0.148±0.003
A6	3	-1.3	1200	285	11.49441(13)	0.187±0.004
A7	3	-1.4	10800	402	11.63108(2)	1.708 ± 0.127
B0	N/A	N/A	N/A	294	11.49284(4)	0
B1	3	-1.3	1200	300	11.50712(3)	0.321±0.002

Figure 1 shows the relationship between T_C and *a*, for our experimental results (Figure 1(a)) and reported literature values for a number of varied compositions (Figure 1(b) and (c)) [30-34,36]. Figure 1(a), as expected, reveals a close to linear correlation between T_C and *a*, similar for both compositions A and B – specifically, the extent of increase in *a* caused by the introduction of interstitial hydrogen atoms strongly impacts the rise of T_C.

The studies of $La(Fe,Si)_{13}$-based compositions within the literature which report *a*, H content and T_C as a function of hydrogen content reveal some interesting features regarding the general trends of the family (Figure 1(b) and (c)). Across the compositions (given in the legend) there are similarities in the change of T_C with change of *a* in response to increasing H content, *i.e.* the slope. In particular, there is a reasonable agreement between the

$LaFe_{11.57}Si_{1.43}$ and $LaFe_{11.5}Si_{1.5}$ of Refs. [30-33] as should be expected since these are close in composition, and in addition Li *et al*. observed remarkable consistency in the slope as the Si content in the formula unit increases to 2.0 and 2.4 [36]. Indeed, these latter two compositions have a second-order phase transition, as do the samples A and B in this study. However, as Figure 1(b) and (c) also include other compositions that undergo sharp, first-order transitions the implication is that the change of T_C with H content (although not the absolute value) is insensitive to the order of the magnetic transition (or in other words to the strength of the magnetovolume coupling). We note that since hydrogenation as a technique is advantageous in that it raises T_C without significantly degrading the MCE properties of the compound [15], it is predominantly used for first-order compositions with large MCE which after *full* hydrogenation retain their large MCE at temperatures close to RT. Therefore, there are few reports on hydrogenated second-order compositions for further comparison. With regard to the samples in this study, sample A in particular demonstrates a remarkably similar trend to the three $LaFe_{13-x}Si_x$ (x = 1.5, 2.0, and 2.4) compositions of Ref. [36], even though the compositions are significantly different. For comparison, increasing T_C by Co doping, as shown by Lyubina *et al*. in $LaFe_{11.8-x}Co_xSi_{1.2}$, shows a very different trend to that from hydrogenation (Figure 1(c)) [32]. It should also be noted that the magnetic state of the samples at RT (the temperature at which measurements to obtain the lattice constants were performed) will determine the lattice constants obtained: those whose T_C is above RT are measured in the larger lattice constant FM state creating a step change in the baseline lattice constant close to 300 K in first-order transition compounds (as reported previously [33] and apparent in Figure 1(b); see further details and discussion of the impact on second-order transition materials in the SI).

In Li *et al*. [36], the decreasing shift in T_C and a between zero and fully hydrided as the Si content increases is explained by the smaller lattice of the non-hydrided sample, meaning that less hydrogen is able to enter the lattice (although the corresponding H contents are not given). Consistent with this, due to Co increasing the lattice volume, we see a large lattice increase when composition A is fully hydrided. The change is comparative with the largest changes reported in the literature, indicating that it has a high hydrogen capacity, confirmed by the measured value of 1.71 per formula unit.

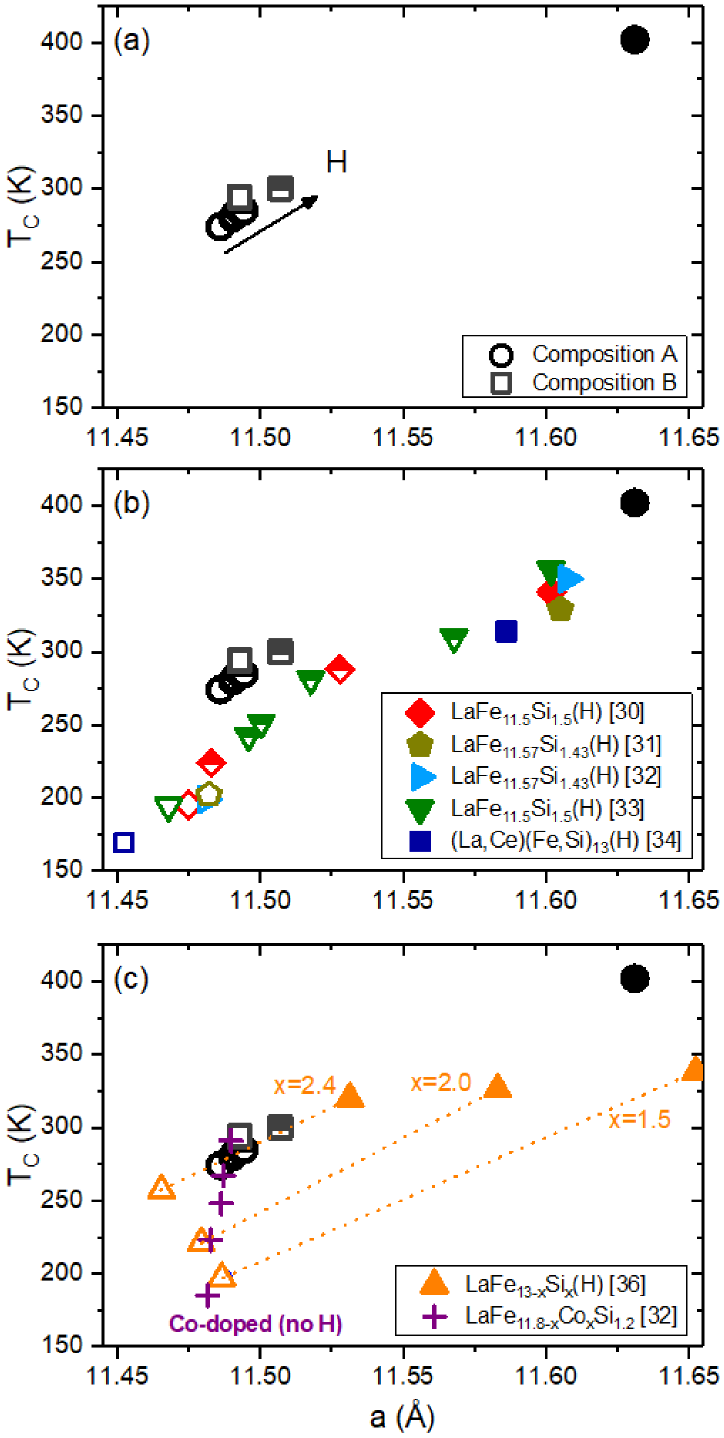

Figure 1 (a) T_C dependence on lattice constants (1:13 phase) for the samples (listed in Table 1) in response to various extents of hydriding, and (b) and (c) the same data with various La(Fe,Si)$_{13}$-based samples reported in other studies included [30-34,36]. For each material, the non-hydrided base, partially and fully hydrided compounds are designated by open, partially filled and closed symbols, respectively. Increased *a* or T_C for one composition reflects increased content of H. The three different compositions of LaFe$_{13-x}$Si$_x$ from Li's work are linked by a dotted line for clarity and labelled [36]. The exception to all the aforementioned is the "LaFe$_{11.8-x}$Co$_x$Si$_{1.2}$/Co-doped (no H)" sample set [32], in which there is no hydrogen and whose increase of *a* and T_C is caused by increased Co content.

Figure 2(a) shows the magnetisation as a function of temperature for all samples, showing no significant change in the shape of the transition as the hydrogen content is increased: specifically, there is no broadening of the transition, which would indicate non-uniform distribution of H atoms throughout the material [23]. Note that no samples show magnetic hysteresis, reflected in the $M(H)$ data (examples for two samples are shown in the SI, Figure S3), as we expect for second-order or continuous phase transitions. Figure 2(b) shows that hydrogen incorporation does *not* degrade ΔS_m, even up to the fully hydrided sample A7, as similarly reported in first-order compositions [15,17]. Although T_C can be increased by increasing Co content, ΔS_m decreases, contrary to hydriding [24] (Figure 2(c) for samples A-D). Consequently, the method of hydriding a lower Co content and low T_C composition (*e.g.* at the colder end of the required temperature range) represents an effective way to both retain desirable ΔS properties and achieve the desired T_C.

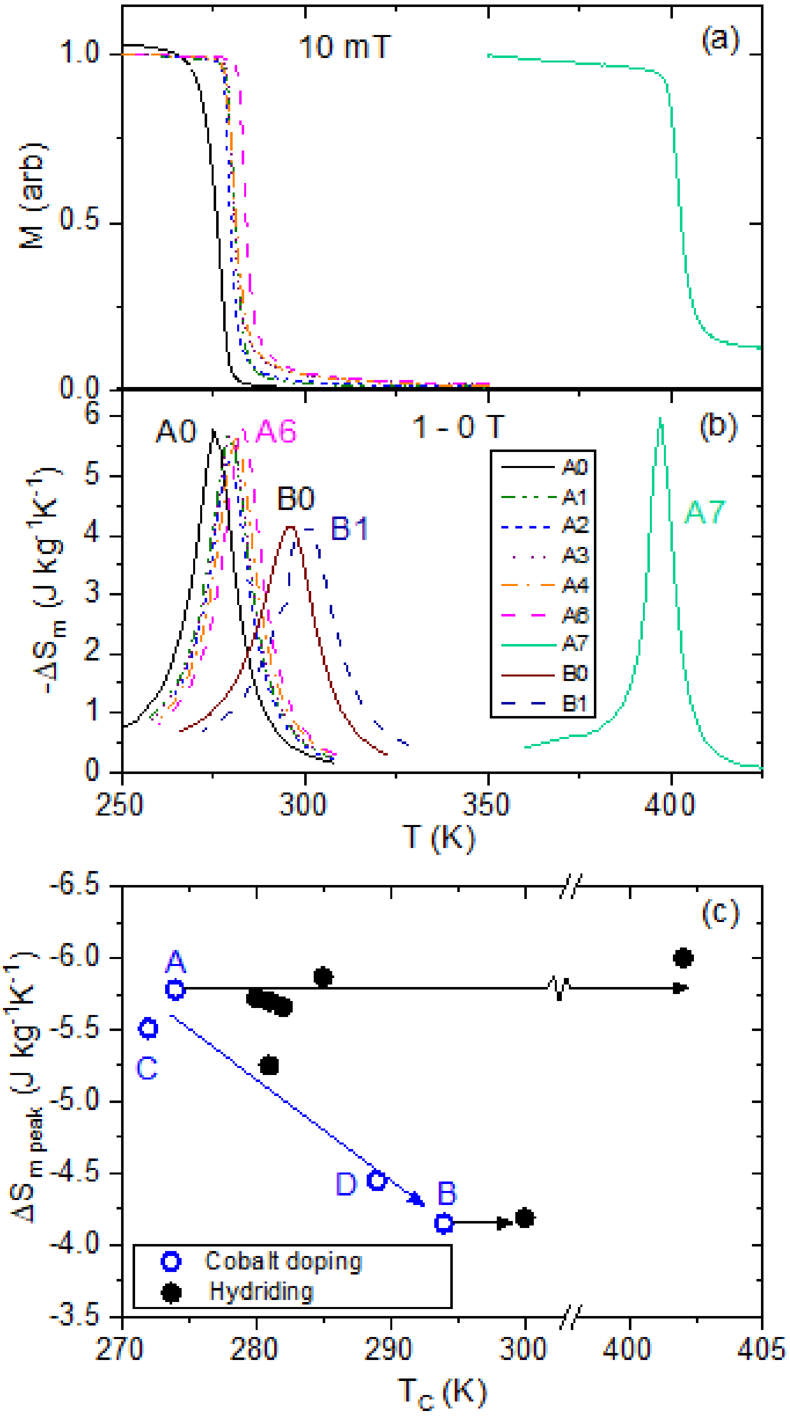

Figure 2 (a) $M(T)$ of composition A with T rate 1 K min^{-1}, normalised to the saturation magnetisation in 10 mT field, and (b) $\Delta S_m(T)$ within 1 T of the two La(Fe,Co,Si)$_{13}$ compositions, without and with partial/full hydriding, showing the fine T_C control afforded and that the entropy change is not significantly altered. (c) The peak entropy change as a function of T_C for the cobalt-doped samples A, B, C and D (non-hydrided, compositions shown in Table S1 in the SI) and the partially/fully hydrided versions of both samples A and B as shown in (b). Increasing hydrogen content for samples A and B are shown by the black arrows, and increasing Co content is represented by the blue arrow.

Figure 3 confirms the stability of the partially hydrided material prepared here. As previously detailed, an important issue for partially hydrided samples is the stability of the phase (against phase segregation) where the hydrogen diffusion in non-fully hydrogenated samples leads to a splitting into two T_C volumes - a significant detriment to its cooling properties. However, in a second-order material, as studied here, the volume change at the transition is greatly reduced and, vitally, coexistence of two magnetic phases (i.e., two separate distinct volumes) does not occur, therefore we hypothesize that the driving force for redistribution of hydrogen will be absent or at least strongly reduced. In Figure 3 the $M(T)$ properties of sample (A6) have been measured after two months at $T = T_C + 10$ K, then 24 h and 48 h at T_C (= 285 K), timescales over which significant hydrogen distribution instability is present in first-order compositions [20], and then finally after repeated fast cycling (15 cycles) across the transition. As shown from the $M(H)$ derivative, only one transition is observed and this is unchanged after all 4 protocols, demonstrating that the properties of partially hydrided samples are stable, behaviour we expect to be general for materials with second-order transitions.

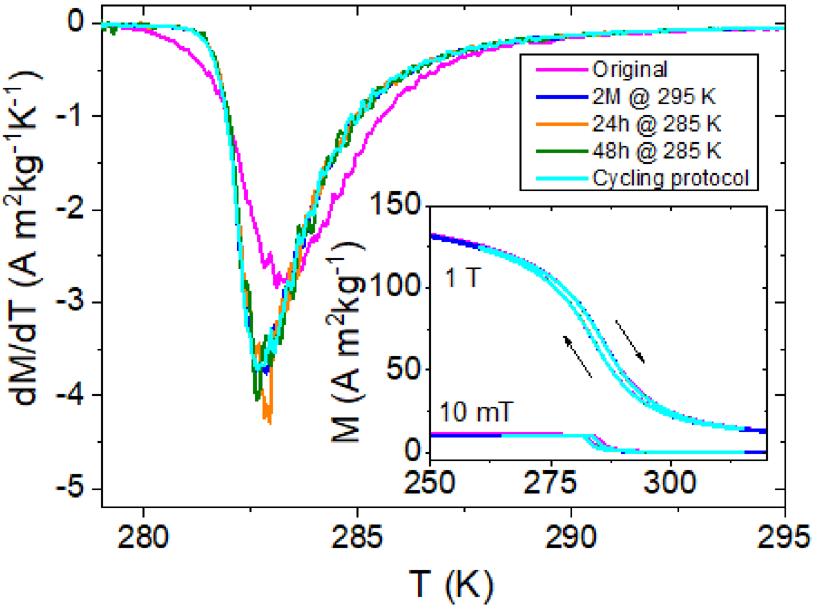

Figure 3 The derivative of *M*(*T*) on cooling in 10 mT (inset: *M*(*T*) in 1 T and 10 mT on both cooling and heating, indicated by the arrows) for partially hydrided sample A6 showing that there is no splitting of the transition after several protocols, given in the legend. In the cycling protocol, the sample was driven in *T* between 280 K and 290 K, across the transition, for 15 cycles at 10 K/min.

In summary, we have shown that electrolytic hydriding of second-order phase transition $La(Fe,Co,Si)_{13}$ compounds is a highly controllable technique which can allow targeting and fine-tuning of the effective working temperature of the magnetic refrigeration cooling cycle, close to room temperature, with 1 K accuracy. This sensitivity has been demonstrated up to 11 K above the T_C of the non-hydrided compound. The magnitude of the entropy change associated with the magnetic transition shows no significant decrease with added hydrogen and raised T_C. This work demonstrates that the technique would permit coverage of the full 40 K T_C span required (~273 to 313 K) for a working refrigerant with stepped-T_C cascaded sets of material, derived from one base-composition. Such a set would also have a significantly larger MCE (by more than 30% for the highest partially hydrided sample measured) for increased temperature working plates compared with the equivalent compounds prepared by increasing Co content [37]. Electrolytic hydriding is inexpensive, safe and rapid, which, added to the requirement of only one base composition, makes the application of this technique in the construction of an efficient magnetocaloric effect (MCE)-based device promising. Finally, the partial hydrogen contents (up to around 10% of full saturation) required for this exquisite control in La(Fe,Co,Si)$_{13}$ compounds are shown to be stable over time and with respect to magnetic cycling, a behaviour we associate with the second order nature of the transition. Further analysis of a wider compositional range of materials with variation in hydrogen should be carried out to establish whether this is a general feature of materials exhibiting a second order transition.

Appendix A. Supplementary data

Supplementary data to this article can be found online at xxxx.

Acknowledgments

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