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Excellent mechanical properties and age stability of hydrogenated $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ plates with extra Fe

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A B S T R A C T

Herein, hydrogenated $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ plates as thin as 0.4–0.6 mm with extra Fe were prepared, whereupon the microstructure, mechanical properties, age stability, and magnetocaloric effect (MCE) were systematically investigated. It was demonstrated that the introduction of extra α-Fe largely enhanced the mechanical properties. The bending strength was about 61 MPa for a single 0.6 mm-thick plate, while the compressive strength was as much as 352 MPa for the stacked plates. Meanwhile, the hydride plates showed considerable MCE around room temperature. The maximal entropy change was 14.2 J/kgK around its Curie temperature $T_C = \sim 298$ K and the effective refrigeration capacity was 284 J/kg under a magnetic field change of 0–5 T. Moreover, the hydride plates exhibited excellent age stability and good thermal conductivity. No age splitting occurred, even when the plates were held at room temperature for more than one year, owing to full hydrogenation. Finally, room-temperature thermal conductivity was as large as 9.5 $Wm^{-1}K^{-1}$. All of these results demonstrate that the hydride plates with extra Fe are desirable magnetic refrigerants, which is beneficial to increase the working efficiency in a device.

1. Introduction

In the past two decades, the discovery of giant magnetocaloric/barocaloric materials has greatly promoted the development of the solid-state cooling technique. The cubic $NaZn_{13}$-type (1:13) $La(Fe,Si)_{13}$-based materials, as potential magnetic refrigerants, have received intense attention owing to their large magnetocaloric effect (MCE) and low toxicity elements [1–8]. However, the Curie temperature (T_C) of the $La(Fe,Si)_{13}$ material without doping is far below room temperature [1,2]. It has been proven that the introduction of interstitial H atoms could increase the T_C significantly, while the MCE of the hydride remains at a high value [3,4]. Therefore, $La(Fe,Si)_{13}$ hydrides have been suggested as promising magnetic refrigeration materials around room temperature.

However, inevitable powdering occurs during hydrogenation for the $La(Fe,Si)_{13}$ hydrides owing to the intrinsic brittleness of the 1:13 phase and hydride cracking, which make the hydride only exist in powder form. Nevertheless, to use the materials in a device, to maximize the heat transfer efficiency and to meet the shape requirements for magnetic refrigerators, typically different shapes are required such as spheres or thin plates [9]. Several technologies have been adopted to machine the $La(Fe,Si)_{13}$-based materials, such as hot pressing [10,11], metal- or epoxy-bonding [9–12], electroless copper plating [13] and the sintering technique [14]. Katter et al. have reported a thermally-induced decomposition and recombination process to form the material into thin plates [15], and a satisfactory performance was achieved for the $La(Fe,Co,Si)_{13}$ undergoing a second-order transition. Shao et al. have fabricated off-stoichiometric $La(Fe,Co,Si)_{13}$ with extra Fe, where enhanced

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thermal conductivity and mechanical properties were observed at the expense of some reduction of the entropy change [8]. Lyubina et al. have proposed that introducing porosity can overcome the poor mechanical stability and cracking of the bulk alloys [6], but the introduced pores are found to be harmful to the thermal conductivity and the corrosion resistance of magnetocaloric materials under a heat-transfer medium. Meanwhile, the hot-pressing technique may be not suitable for La(Fe,Si)$_{13}$ hydrides because the dehydrogenation occurs at about 450 K [16], and the epoxy-bonded technique reduces the thermal conductivity owing to the inclusion of low thermal conductive epoxy [9,12].

Another serious problem is the age instability for the La(Fe,Si)$_{13}$ hydrides. Although it is possible to move the Curie point T_C to ~350 K by adjusting the H content, the hydrogen-unsaturated materials are unstable when they are used at temperatures close to their Curie temperature. The initial single magnetic transition gradually splits into hydrogen-rich and hydrogen-poor fractions with deteriorated magnetocaloric properties [17]. Therefore, it is necessary to find a new approach to overcome these drawbacks of fragility and age instability, which both seriously damage the performance of these materials in refrigerators, particularly for the first-order La(Fe,Si)$_{13}$H$_\delta$ hydrides.

In the present work, we report good mechanical properties and age stability of hydrogenated $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_\delta$ plates as thin as 0.4–0.6 mm. The introduction of extra α-Fe largely increases the mechanical properties, while the magnetocaloric effect is exhibited at a considerable value around room temperature. The bending strength is about 61 MPa for a single 0.6 mm-thick plate, while the compressive strength reaches 352 MPa for the stacked plates. More importantly, the hydride plates exhibit good thermal conductivity, and excellent stability has been demonstrated owing to full hydrogenation.

2. Experimental details

The $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}$ ingot with extra Fe (one extra Fe atom was nominally added in the formula) was prepared by the conventional arc-melting technique. The ingots were then cut into thin plates with a thickness of about 0.4–0.6 mm and annealed at 1323 K for 8 weeks, followed by quenching in liquid nitrogen. Subsequently, hydrogenation was performed at 523 K in an H_2 atmosphere using a commercial P-C-T (pressure-composition-temperature) instrument. During the hydrogenation process, the gas pressure was gradually increased to 3 MPa in 0.15 MPa steps at a constant temperature of 523 K, where each step of pressure increase was held for 15 min, and the full pressure of 3 MPa was held for 5 h to ensure full hydrogenation. The hydrogen content was simultaneously determined by the P-C-T instrument using the ideal gas law $PV = nRT$, where P is the hydrogen pressure, V is the volume of the chamber, n is the mole number of H_2 in the chamber, R is the ideal gas constant (8.3145 J/mol K), and T is the temperature at which the compounds were annealed in H_2. The hydrogen content was determined from the difference in weight before and after hydrogenation. The microstructure was investigated by scanning electron microscopy (SEM), and the chemical composition, as determined by the energy-dispersive spectroscopy (EDS) in the SEM, was very close to the nominal composition. The test of compression strength was performed by compressing the four overlapped thin plates under ambient temperature using a universal material testing machine, while the bending strength was measured using the three-point bending test for a single plate with size of $15 \times 5 \times 0.6\ \mathrm{mm}^3$. Magnetic measurements were carried out using a superconducting quantum interference device (SQUID) vibrating sample magnetometer (Quantum Design). The thermal conductivity κ was measured using a thermal transport option equipped on a physical property measurement system (PPMS; Quantum Design).

3. Results and discussion

In the formula of the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}$ used herein, extra Fe was added as a binder, which is equivalent to 6.7 wt% nominally in weight. To analyze the microstructure and phase distributions in the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_\delta$ hydride plates with extra Fe, back-scattered SEM micrographs were taken, as shown in Fig. 1, wherein the colored areas indicate different phases. Accordingly, the grey, dark grey, and white areas in Fig. 1 correspond to the 1:13 structure, α-Fe, and 1:1:1 structure, respectively, based on EDS analysis. The phase equilibrium in La(Fe,Si)$_{13}$ materials have been investigated by several groups [7,18–20], where it was found that the resulting phase composition, i.e. the accompanying phase with 1:13 structure, crucially depends on the starting composition and annealing temperature. Basically, for the stoichiometric $LaFe_{1-x}Si_x$ materials ($1.1 \le x \le 3.0$), α-Fe is the main phase of the as-cast ingots, which coexists with the tetragonal Cu_2Sb-type 1:1:1 phase (space group $P4/nmm$) and a small amount of 1:13 phase (space group $Fm\bar{3}c$) [19,20]. After post-annealing, the 1:13 phase develops through the peritectic reaction: L_{La} (LaFeSi 1:1:1 phase) + α-Fe = La(Fe,Si)$_{13}$ [19]. However, for the starting materials with extra La, the accompanying phases tend to include La_5Si_3 [7]. For the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_\delta$ plates herein, possessing stoichiometric La and Ce but with extra Fe and undergoing annealing at 1323 K for 8 weeks and subsequent hydrogenation, the resulting plates included the 1:13 matrix phase, α-Fe and a small amount of the 1:1:1 phase of LaFeSi; while no La_5Si_3 phase was detected (Fig. 1).

To know the actual ratio of the 1:13 phase in the initial annealed alloy plate $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}$ and its corresponding hydride, we performed X-ray diffraction (XRD) measurements and Rietveld refinements, where the results are presented in Fig. 2. The Rietveld refinements indicate that the ratio of the 1:13 phase is about 86.6 and 84.5 wt%, and the lattice parameter a is ~11.4994(2) and 11.6065(1) Å for the initial plate $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}$ and its corresponding hydride $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_\delta$, respectively. We note that the lattice is enlarged upon hydrogenation while the content of the 1:13 phase exhibits a small decrease from 86.6 to 84.5 wt%. The 1:1:1 phase was not detected in the XRD measurements owing to its small amount.

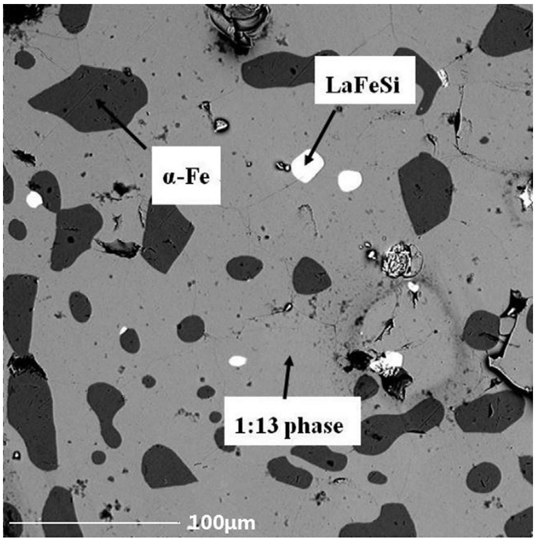

Fig. 1. SEM backscattered electron image for $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_\delta$ hydride plate.

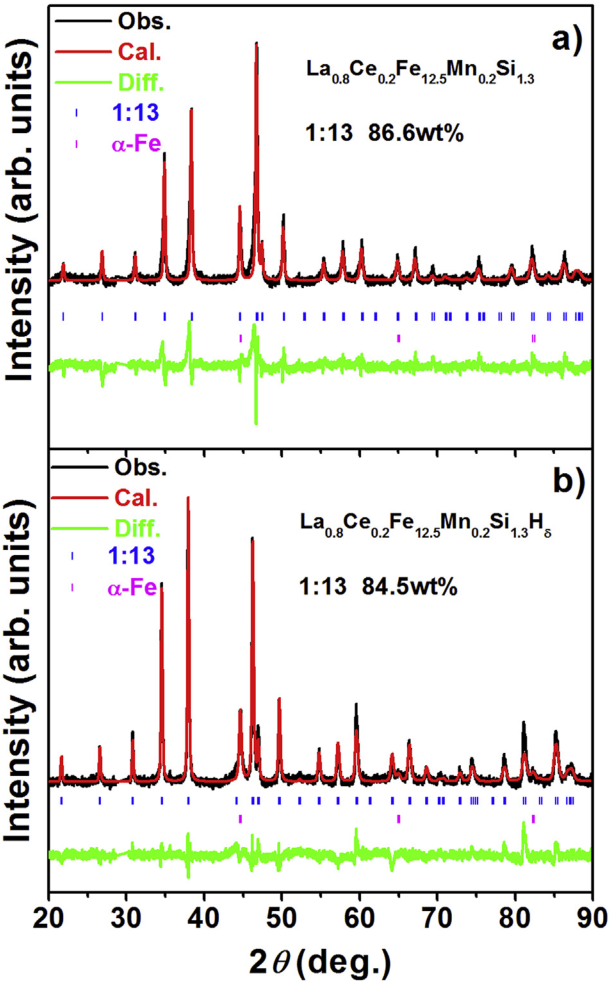

Fig. 2. Rietveld refinement of the XRD patterns for (a) $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}$ and (b) $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$. The vertical marks denote the Bragg peak positions for the 1:13 and α-Fe phases. The difference between the observed and calculated patterns is shown at the bottom (green line). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

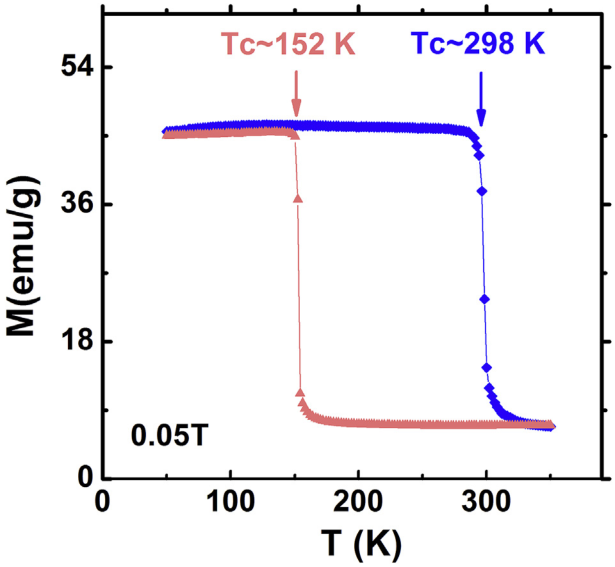

Fig. 3. Comparison of the temperature-dependent magnetization measured under a 0.05 T magnetic field for the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ plates before (pink curve) and after (blue curve) hydrogenation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The hydrogen content as determined during hydrogen absorption using the P-C-T instrument is about 0.185 wt% in the hydride plate $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ with extra Fe, which is equivalent to $\delta \simeq 1.8$ in the formula $La_{0.8}Ce_{0.2}Fe_{11.5}Mn_{0.2}Si_{1.3}H_{\delta}$ of the stoichiometric 1:13 structure if the coexisting amount (15.5 wt%) of the α-Fe phase was taken into consideration (Note that the α-Fe phase does not absorb hydrogen). Previous literature results [17,21] have demonstrated that the hydrogen content has actually reached saturation as $\delta > 1.6$ in the formula $La(Fe,Si)_{13}H_{\delta}$. Accordingly, the hydrogen content in the present 1:13 phase of $La_{0.8}Ce_{0.2}Fe_{11.5}Mn_{0.2}Si_{1.3}H_{\delta}$ ($\delta \simeq 1.8$) should be considered as a saturated state.

Fig. 3 shows the temperature-dependent magnetization (M-T curves) measured under a 0.05 T magnetic field for the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ plates before and after hydrogenation. One can find that the Curie temperature T_C of the hydride plates is located exactly at room temperature (298 K). For this purpose, the composition of $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}$ with a T_C around 150 K was first designed. For $La(Fe,Si)_{13}$ without doping, ferromagnetic (FM) coupling is completely dominated by Fe—Fe interactions because La is a non-magnetic atom. When the Fe—Fe distance is shorter than 2.45 Å, antiferromagnetic coupling prevails; but FM coupling appears and becomes stronger when the Fe—Fe bond length is equal to 2.45 Å or larger [22]. Typically, the FM coupling between R—Fe (where R: Ce, Pr, Nd) is enhanced along the sequence of Ce, Pr, Nd. It has been demonstrated that the replacement of La by Ce can lead to contraction of the lattice owing to the lanthanide contraction law, while T_C decreases. The rate of decrease of T_C is about 85.9 K/Ce atom for Ce-doped $La_{1-x}Ce_xFe_{11.5}Si_{1.5}$, which is similar to that of $La(Fe,Si)_{13}$ [2]. This result confirms that the Fe—Fe interaction dominates the value of T_C, while the contribution from FM coupling between Ce—Fe is negligibly weak. Moreover, it was found that the introduction of Mn lowers the T_C more rapidly. The replacement of Fe by 1 at% Mn can lead to a linear decrease of T_C by 20 K in $La(Fe_{1-x}Mn_x)_{11.7}Si_{1.3}$, and nonlinear reduction of the saturated magnetization M_S by about 0.6 μ_B, because Mn atoms carry a magnetic moment antiparallel to that of Fe [23]. In addition, it has been found that the incorporation of Mn can enhance the age stability of $LaFe_{13-x-y}Mn_ySi_xH_z$ hydrides and avoid phase decomposition [21]. Considering all of these results, we designed and successfully fabricated $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}$ alloys with a T_C at 152 K by introducing 20 at% Ce to replace La, 1.7 at% Mn to replace Fe, and 6.7 wt% extra Fe as a binder nominally. Through full hydrogenation, a desirable room-temperature T_C (298 K) was realized in the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ hydride plates. One can notice that the value of magnetization above T_C is abnormally large (Fig. 3), which originates from the considerable amount of α-Fe phase (Figs. 1 and 2) owing to the introduction of extra Fe.

Furthermore, one can find that the magnetic transition remains sharp after the hydrogenation (Fig. 3). This result indicates that the excess Fe does not affect the hydrogenation process, which can be related to the dispersed distribution of α-Fe in the 1:13 matrix (Fig. 1). Such a sharp magnetic transition in the hydride plates suggests that the magnetocaloric effect should remain large.

Fig. 4 displays the isothermal magnetization curves cycling in magnetic fields up to 5 T, and the entropy change calculated using the Maxwell relation for the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ hydride plates before and after hydrogenation. The considerable magnetic hysteresis in $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}$ without interstitial hydrogen present indicates the first-order nature of the field-induced itinerant electron metamagnetic transition [1]. The maximal magnetic hysteresis before hydrogenation, ~14.0 J/kg, occurs at

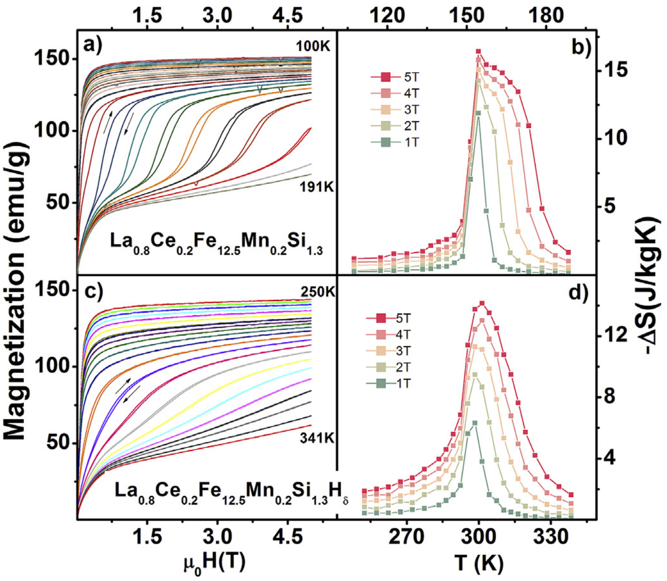

Fig. 4. (a,c) Isothermal magnetization curves and (b,d) entropy change under different magnetic fields for the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ plates (a,b) before and (c,d) after hydrogenation.

156 K, which reduces to 3.8 J/kg (297 K) after the hydrogenation. This result indicates that the hydrogenation affects the metamagnetic transition process. The origin of this can be related to the change of grain boundaries and internal strain, along with the possible change of band structure when considering that the lattice has been significantly enlarged during the hydrogenation [24]. For a magnetic field change of 0–5 T, the maximal entropy change $|\Delta S|$ is about 16.4 J/kgK at 154 K for the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}$ without hydrogen. This $|\Delta S|$ value is smaller than that of the alloy with the counterpart composition $LaFe_{11.7}Si_{1.3}$ [2]. Besides the dilution effect from the extra Fe, the main reason for the smaller $|\Delta S|$ can be ascribed to the declined saturated magnetization owing to the introduced Mn atoms carrying a magnetic moment antiparallel to that of Fe. Consequently, the $|\Delta S|$ of $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ should be also smaller than that of the counterpart composition $LaFe_{11.7}Si_{1.3}H_{\delta}$ after a full hydrogenation [3], whose $|\Delta S|$ usually appears higher than room temperature by 30–40 K. After the full hydrogenation, the plates show a satisfactory age stability. The maximal $|\Delta S|$ is observed at 301 K, whose value is 9.5 and 14.1 J/kgK for the magnetic field change of 0–2 and 0–5 T, respectively. When comparing $|\Delta S|$ with that previously reported for the measurements performed around room temperature, the present $|\Delta S|$ (9.5 J/kgK, 301 K) under 0–2 T is about 20–35% higher than that reported for $LaFe_{11.0}Co_{0.8}Si_{1.2}$ ribbons (7 J/kgK, 283 K) [25], $LaFe_{10.7}Co_{0.8}Si_{1.2}$ (7 J/kgK, 280 K) [26], $La_{0.8}Pr_{0.2}Fe_{10.7}Co_{0.8}Si_{1.2}$ (7.2 J/kg K, 275 K) [27], and also the recently reported $LaFe_{12.1}Co_{0.8}Si_{1.2}$ (7.9 J/kg K, 278 K) [8], where a similar amount of excessive Fe was added but Co instead of H was introduced to raise the T_C. Although the addition of either Co or H can shift the T_C to higher temperature, the introduction of H atoms can maintain the first-order nature of the transition and hence the large MCE is maintained [3,4]. In contrast, the introduction of Co weakens the first-order transition and makes it gradually becoming a second-order transition nature, and hence causes a reduction of MCE [2,28]. The reason can be attributed to the significant differences in local atomic environment and exchange interaction caused by the introduction of Co or interstitial H atoms.

Refrigerant capacity (RC) is another measure characterizing magnetic refrigerants, which can be evaluated by integrating the area under the ΔS curve from $T1$ to $T2$; noting $RC = \int_{T1}^{T2} \Delta S dT$, where $T2-T1$ denotes the half-maximum width [29]. For the plates herein before and after the hydrogenation, the calculated RC is 341 and 284 J/kg, and the effective RC_{effe} after deducting the maximal hysteresis loss is 327 and 280 J/kg under 5 T, respectively. We note that the RC_{effe} still remains relatively large for the hydride plates.

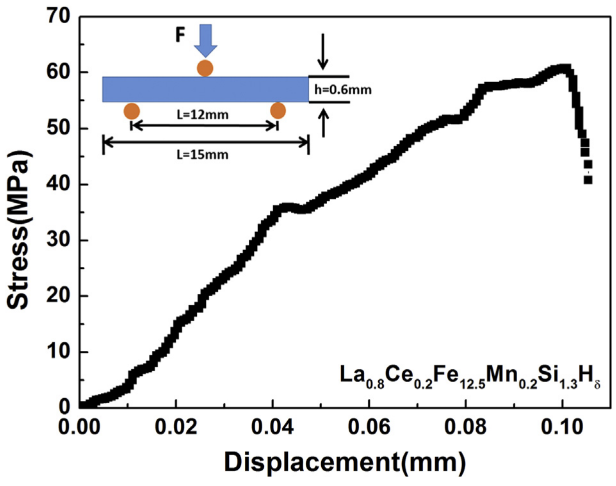

Fig. 5. Bending strength of a single plate of 0.6 mm thickness measured by the three-point bending method for $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ hydrides. (Inset) Schematic of the three-point bending test.

Moreover, the mechanical properties and thermal conductivity of the present hydride plates were both studied. The bending strength was about 61 MPa for a single 0.6 mm-thick plate, as measured by the three-point bending method and shown in Fig. 5, which is nearly the same as that of the $LaFe_{13.9}Si_{1.4}H_{1.8}$ plate with 1.2 mm-thick measured using the same method [30]. Meanwhile, the compressive strength reaches 352 MPa for the overlapped plates (Fig. 6), which is 2–3 times higher than that of metal-bonded $LaFe_{11.65}Si_{1.35}/Cu$ (105.6 MPa) [31], $LaFe_{11.6}Si_{1.4}H_y/Sn$ (170 MPa) [10] and epoxy-bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ (162 Mpa) [12], but lower than that of the recently reported $LaFe_{12.1}Co_{0.8}Si_{1.2}$ (1057 MPa) with similar excess Fe, where Co instead of H was added to raise the T_C [8]. The good mechanical property is a consequence of introducing

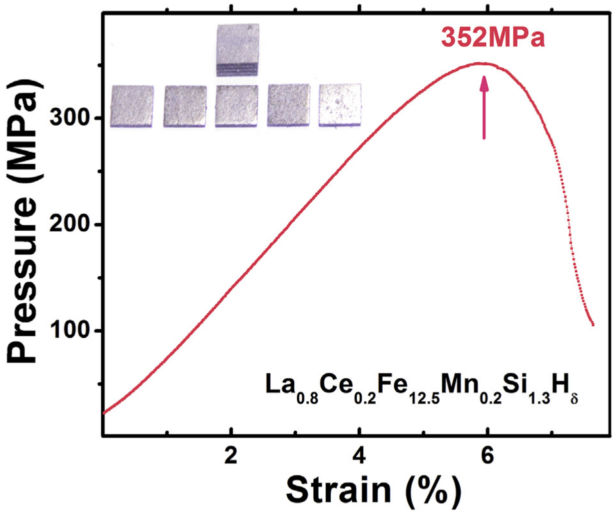

Fig. 6. Compressive pressure as a function of strain for the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ hydride plates of 0.4 mm thickness. (Inset) Photographs of the plates. Four plates were overlapped for the measurements, as shown on the top.

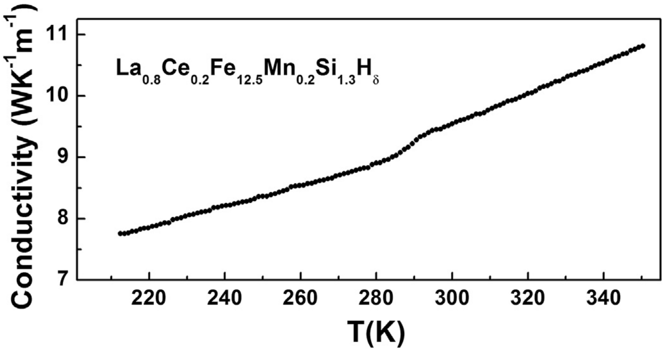

Fig. 7. Temperature dependence of the thermal conductivity κ measured in zero magnetic field for a $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ plate of 0.4 mm thickness.

the excessive α-Fe phase, and thus hindering fissures and cracks under compression and bending.

As shown in Fig. 7, the thermal conductivity was measured for the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ hydride plates at zero magnetic field using the thermal transport option equipped on the PPMS. The value of the thermal conductivity κ varies from 8.2 to 11.4 $Wm^{-1}K^{-1}$ in the temperature range from 210 K to 350 K. At 300 K, $\kappa \simeq 9.5$ $Wm^{-1}K^{-1}$ for the present $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ plate, which is rather competitive compared to other materials, noting $\kappa \simeq 9.5$ $Wm^{-1}K^{-1}$ (300 K) for the traditional refrigerant Gd [32], 9.0 $Wm^{-1}K^{-1}$ (300 K) for $La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$ [32], 5.0 $Wm^{-1}K^{-1}$ (300 K) for silver epoxy-bonded $La(Fe,Mn,Si)_{13}H_y$ hydrides [33], and 8.0 $Wm^{-1}K^{-1}$ (300 K) for $LaFe_{12.1}Co_{0.8}Si_{1.2}$ [8] where the same amount of extra-Fe was added as binder but Co instead of H was introduced to raise the T_C. The good thermal conductivity for the present hydride plate is rather beneficial to increase heat transfer, and thus refrigeration efficiency, in a device.

Generally, the behavior of phonons and electrons determines the thermal conductivity κ, whose value is expressed as

$$\kappa = \kappa_e + \kappa_{ph}, \tag{1}$$

where κ_e and κ_{ph} correspond to the electron and phonon thermal conductivity, respectively. Further, the contribution of κ_e can be calculated by the following expression according to the Wiedemann-Franz law:

$$\kappa_e = L_0 T/\rho, \tag{2}$$

where L_0 is the Lorentz number (2.443×10^{-8} $W\Omega/K^2$), and ρ is the electrical resistivity [8]. As the consequence of extra Fe doping, the electrical resistivity decreases, which brings about a small increase in the electron thermal conductivities. From Eq. (2), κ_e can be roughly evaluated to be $\kappa_e \simeq 5.2$ $Wm^{-1}K^{-1}$ by using $\rho = 1.4 \times 10^{-6}$ Ωm (taking the maximal value around transition point ($T_C = 274$ K) for $LaFe_{11.2}Co_{0.7}Si_{1.1}$ as a reference [34]). This κ_e value is about 55% of the thermal conductivity κ around room temperature for the plates herein, indicating that more than half may be contributed by electrical conductivity, and the rest by phonons. This phenomenon is very similar to $LaFe_{13.2}Co_{0.8}Si_{1.2}$, which contains more excessive Fe and shows enhanced thermal conductivity κ [8]. Careful analysis indicates that, in this alloy, the phonon contribution plays a dominant role, which exceeds that from the electrons. The origin was discussed, and the coexistence of a large amount of second-phase α-Fe was considered to play a key role. Previous studies using first principle calculations have revealed that the phonon contribution to the thermal conductivity for $Si_{1-x}Ge_x$ alloys increases quickly with dilutedly doping by Ge, which was considered to be owing to the altered phonon scattering caused by mass disorder [35]. In the present alloy plates, a considerable amount of second-phase α-Fe coexists with the 1:13 phase (Figs. 1 and 2), which may lead to a certain degree of mass disorder and hence improve the thermal conductivity. However, the thermal conductivity of the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ plate (9.5 $Wm^{-1}K^{-1}$, 300 K) is still much lower than that of pure Fe (80 $Wm^{-1}K^{-1}$) at room temperature because of the low connectivity of the α-Fe phase in the matrix of the 1:13 phase (Fig. 1).

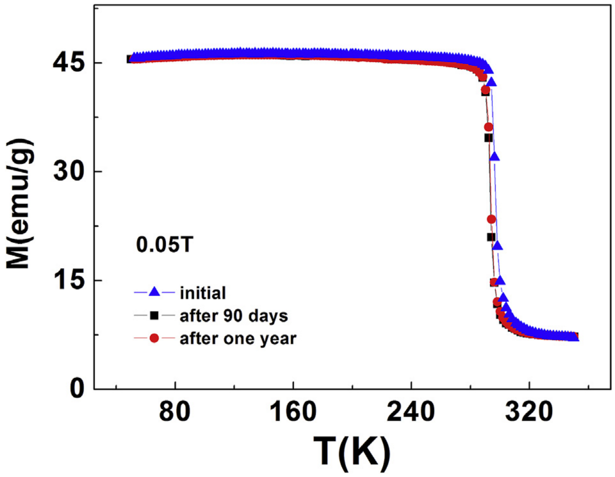

Fig. 8. Temperature dependent magnetization measured under a 0.05 T magnetic field for the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ hydride plates measured after initial preparation, after 90 days, and after one year when held at room temperature.

We also examined the stability of the $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ hydride plates. For the hydrogen-unsaturated $La(Fe,Si)_{13}H_{\delta}$ hydride, an unusual instability typically occurs. If the hydride is held within a few K around its initial T_C, an initial single magnetic transition gradually splits into two transitions separated by a temperature gap as wide as ~20 K. This is called “age splitting” [17]. Such unusual instability seriously damages the performance of materials in a refrigeration device. Our investigations demonstrate excellent stability for the present $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_{\delta}$ hydride plates. Fig. 8 shows the comparison of the temperature dependent magnetization (M-T curves) of the initially-prepared plates, after 90 days, and after one year held at room temperature. After the first 90 days held at room temperature, the sharpness of the transition remains the same and no age splitting occurs, though the T_C shifts to lower temperatures. After prolonging the hold time to one year, no further shift of T_C occurs and the M-T curve remains unchanged if to compare with the data measured after 90 days. Such excellent stability can be ascribed to the formation of a stable hydride with H atoms occupying the 24*d* interstitial site in the $NaZn_{13}$-type structure. The introduction of interstitial H atoms expands the lattice, where all the Fe—Fe bonds become elongated, and the distances around the H atom become the most expanded, resulting in the large shift of T_C to the higher temperature [24]. For the initially-prepared plate, some redistribution of the H atoms may occur, leading to the slight shift of the T_C within the first 90 days when held at room temperature. Once the site occupancies of the H atoms become stable, the H atoms no longer move, the T_C becomes stable, and the thin plates show an excellent stability.

4. Conclusions

The present work provides a simple and effective method to obtain good mechanical properties and age stability for the

$La(Fe,Si)_{13}H_δ$ hydrides. By introducing excessive Fe and by adjusting chemical composition, hydrogenated $La_{0.8}Ce_{0.2}Fe_{12.5}Mn_{0.2}Si_{1.3}H_δ$ plates as thin as 0.4–0.6 mm with good mechanical properties and excellent stability are successfully prepared. The bending strength is about 61 MPa for a single 0.6 mm-thick plate, while the compressive strength can be as much as 352 MPa for the stacked plates. Meanwhile, the hydride plates exhibit considerable MCE around room temperature because the introduction of H can maintain the first-order transition. The maximal entropy change $|ΔS|$ (9.5 J/kgK) under 0–2 T around room temperature can be 20–35% higher than that previously reported for $LaFe_{11.0}Co_{0.8}Si_{1.2}$ ribbons, $LaFe_{10.7}Co_{0.8}Si_{1.2}$, $La_{0.8}Pr_{0.2}Fe_{10.7}Co_{0.8}Si_{1.2}$, and the recently reported $LaFe_{12.1}Co_{0.8}Si_{1.2}$ where a similar amount of excess Fe was added but Co instead of H was introduced to raise the T_C. Moreover, the hydride plates exhibit excellent age stability and good thermal conductivity, which is very beneficial to increase heat transfer and thus efficiency. All of these results suggest that the hydride plates with extra Fe can be ideal magnetic refrigerants working around room temperature in a device.

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