Effects of Pr substitution on the hydrogenating process and magnetocaloric properties of $La_{1-x}Pr_xFe_{11.4}Si_{1.6}H_y$ hydrides*

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In this paper, we study the effects of Pr substitution on the hydrogenating process and magnetocaloric properties of $La_{1-x}Pr_xFe_{11.4}Si_{1.6}H_y$ hydrides. The powder x-ray diffraction patterns of the $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ and its hydrides show that each of the alloys is crystallized into the single phase of cubic $NaZn_{13}$-type structure. There are hydrogen-absorbing plateaus under 0.4938 MPa and 0.4882 MPa in the absorbing curves for the $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}$ and $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$ compounds. The releasing processes lag behind the absorbing process, which is obviously different from the coincidence between absorbing and releasing curves of the $LaFe_{11.4}Si_{1.6}$ compound. The remnant hydrogen content for $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$ is significantly more than that for $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}$ after hydrogen desorption, indicating that more substitutions of Pr for La are beneficial to retaining more hydrogen atoms in the alloys. The values of maximum magnetic entropy change are 14.91 J/kg·K and 17.995 J/kg·K for $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}H_{0.13}$ and $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}H_{0.87}$, respectively.

Keywords: $La(Fe,Si)_{13}$ compounds, hydrogenating process, magnetocaloric effect, magnetic refrigeration materials

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1. Introduction

Magnetic materials showing large magnetocaloric effects (MCEs) have been extensively investigated due to their potential applications as magnetic refrigerants.[1–11] The compounds $LaFe_{13-x}Si_x$ each with a cubic $NaZn_{13}$-type structure are one of the most attractive compounds because of their considerably large MCEs, low cost, easy preparation and toxin-free property, and have been intensively studied in the past decades.[12] The large MCEs in $LaFe_{13-x}Si_x$ result from the itinerant-electron metamagnetic (IEM) transition in the vicinity of the first-order phase transition temperature. However, with the great MCEs, a concomitant hysteresis loss occurs inevitably because of the nature of the first-order phase transition. The large hysteresis losses make magnetic entropy less efficient.[13] Many efforts have been made to increase MCE and to reduce or even eliminate the hysteretic loss for the $LaFe_{13-x}Si_x$ compounds by the addition of substitutional or interstitial atoms. The substitution of Co for Fe in $LaFe_{13-x}Si_x$ compound can lead to an obvious reduction in the hysteresis loss and an increase in Curie temperature, but result in a decrease in magnetic entropy change caused by turning the magnetic transition from first-order to second-order.[14] Partial replacement of Pr[15] or Nd[16] can increase MCE, but lead also to an increase in hysteresis loss in the IEM transition process, which has the same effect as the effect caused by a decrease in Si. In addition, the adding of interstitial N,[17] B[18] or C[19,20] atoms into $LaFe_{13-x}Si_x$ can also increase the T_C and depress the hysteresis. However, the extent of the increase in T_C is limited to about 50 K with less than 0.5 interstitial atom concentration and leads to an obvious decrease in MCE. Moreover, the $NaZn_{13}$-type phase is difficult to form with increasing the interstitial atom content. In contrast, interstitial hydrogen addition leads to an increase in Curie temperature rapidly, and preserving a large magnetic entropy change as well as maintaining the first-order transition.[21–26]

In this paper, the influences of Pr substitution on the MCE and especially on the hydrogenating process in $La_{1-x}Pr_xFe_{11.4}Si_{1.6}H_y$ ($x = 0$, 0.2, 0.4) compounds are discussed from the viewpoint of magnetic refrigerants.

2. Experiment

Samples with nominal compositions of $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0$, 0.2, 0.4) were first prepared by arc-melting an appropriate quantity of the starting materials of La (99.5% in

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purity), Pr (99.5% in purity), Fe (99.9% in purity), and Si (99.99% in purity) under high purity argon atmosphere. The obtained ingots were subsequently annealed at 1393 K for 4 weeks, and then quenched in liquid nitrogen. The interstitial hydrogen atoms were introduced into the $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0$, 0.2, 0.4) compounds by gas–solid phase reaction using commercial *P–C–T* (pressure–composition–temperature) equipment. The hydrogen absorptions were carried out by annealing $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0$, 0.2, 0.4) compounds at 373 K in a chamber with different hydrogen pressures. The amounts of hydrogen content in $La_{1-x}Pr_xFe_{11.4}Si_{1.6}H_y$ ($x = 0$, 0.2, 0.4) were determined by 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. Powder x-ray diffraction (XRD) measurement was performed by using Cu Kα radiation to identify the phase purity and crystal structure at room temperature. Magnetization measurements were performed on a vibrating sample magnetometer (VSM).

3. Results and discussion

Figure 1 shows the powder x-ray diffraction (XRD) patterns of compound $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$ and its hydride, which identify that the prepared $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0$, 0.2, 0.4) compounds and their hydrides are of single phase, each crystallizes into a cubic $NaZn_{13}$-type structure. The interstitial H atoms, which occupy the 24d sites,[27] lead to the lattice expansion rather than changing the crystal structure. The lattice parameter determined by using the Rietveld refinement method is found to increase with increasing hydrogen content.

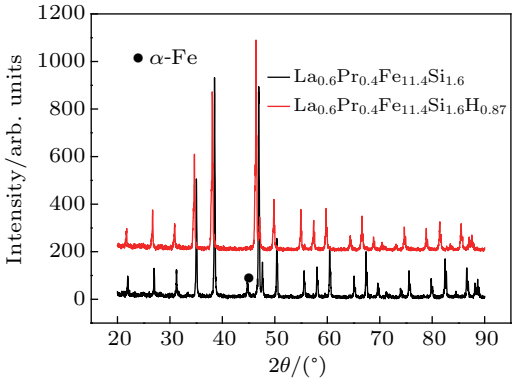


Fig. 1. (color online) XRD patterns of the $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$ and its hydride.

Figure 2 shows the *P–C–T* relationships for $La_{1-x}Pr_xFe_{11.4}Si_{1.6}H_y$ ($x = 0$, 0.2, 0.4) at 373 K. For the $LaFe_{11.4}Si_{1.6}$ compound, the absorbing curve and releasing curve are basically coincident. This indicates that the residual hydrogen atoms are nearly all released. By contrast, there are hydrogen-absorbing plateaus under 0.4938 MPa and 0.4882 MPa in the absorbing curves for the $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}$ and $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$ compounds, and the releasing processes lag behind the absorbing process. The amounts of remnant hydrogen content are about 0.01737 wt% ($\sim$ 0.13 H per formula unit) for $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}$ and about 0.10679 wt% ($\sim$ 0.87 H per formula unit) for $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$, respectively. It means that the substitution of Pr for La is in favor of preserving hydrogen in the $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ compounds. In addition, the hydrogen absorbing plateau pressures for $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}$ and $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$ compounds are about the same at 373 K. This could mean that further increasing the Pr content has little effect on the pressure of hydrogen absorption platform. The remnant hydrogen content for $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$ is significantly higher than that for $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}$ after hydrogen desorption, indicating that more substitutions of Pr for La are beneficial to retaining more hydrogen atoms in the alloys.

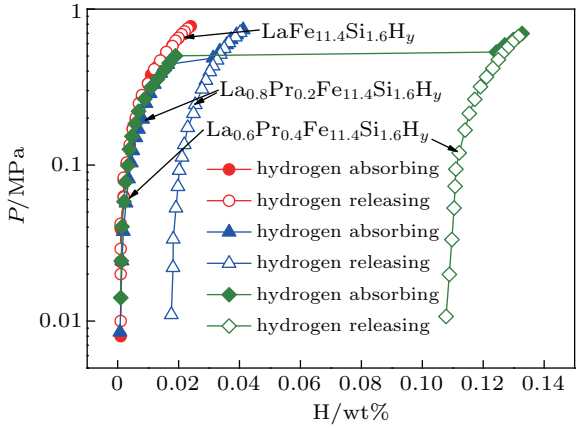


Fig. 2. (color online) Hydrogen pressure-dependent hydrogen content values (wt%) for $La_{1-x}Pr_xFe_{11.4}Si_{1.6}H_y$ ($x = 0$, 0.2, 0.4) measured at 373 K in absorbing and releasing processes.

Martin *et al.*[28] suggested that the absorbing of hydrogen can be divided into five steps: (i) physisorption of hydrogen molecules; (ii) dissociation of hydrogen molecules and chemisorption; (iii) surface penetration of hydrogen atoms; (iv) diffusion of hydrogen atoms through the hydride layer; (v) hydride formation at the metal/hydride interface. The H atoms are absorbed in the form of solid solution when contacting with the surface of alloy. Further increasing the hydrogen pressure until the hydrogen absorbing platform appears, the H atoms will be absorbed by the unit cell of the alloy to generate the hydride. That is to say, solid solution phase changes into hydride phase in the platform area, while the solid solubility of hydrogen remains unchanged. What is more, the inserting of H atoms into the compound makes the lattice expand, which introduces the micro cracks. The tiny cracks cause new surfaces, and further promote the hydrogenation reaction. The process of hydrogen absorption finishes until all compounds form the hydrides. Wang *et al.*,[29] considered the diffusion process as the dominant process in the gas–solid reaction. It is observed that hydrogen absorbing platforms are shown in

the curves of the $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}$ and $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$ compounds. It means that the substitution of Pr for La can reduce the pressure of the hydrogen absorbing platform at the same absorption temperature. The substitution of Pr for La makes a larger interstitial site and lattice contraction due to the smaller radius of Pr than that of La. This may lead to the easier insertion of H atoms into the compound and the lower pressure hydrogen absorbing plateaus.

Figures 3(a) and 3(b) show the hydrogen absorbing kinetic curves for the $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}$ and $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$ compounds, obtained at starting hydrogen pressures of 0.4882 MPa and 0.4938 MPa at 373 K, respectively. Each inset shows the dependence of hydrogen pressure on time accordingly. It is found that the velocity of hydrogen absorbing is slow in the starting process, which is the reaction process of the hydrogen with the surface oxides, and then reaches a maximum with time going by. Finally, the hydrogen absorption rate approaches to zero when the hydrogen absorption reaches a saturated state. It can also be seen that the hydrogen absorption rate of $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$ at 373 K is higher than that of $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}$ at 373 K, which provides additional data for the Pr-enhanced hydrogen diffusion rate. It indicates that the substitution of Pr for La is beneficial to the absorption of hydrogen.

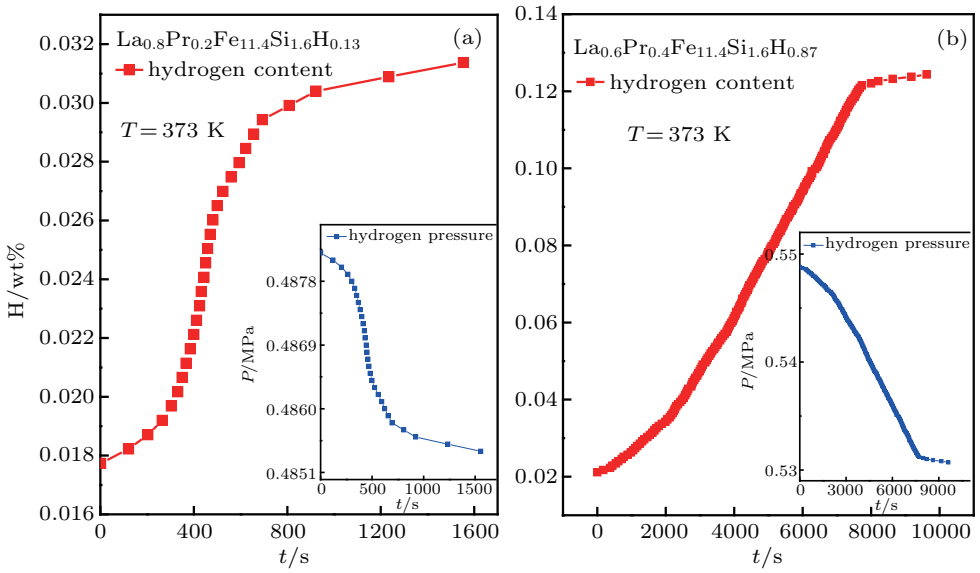


Fig. 3. (color online) Time-dependent hydrogen content values (in unit wt%) measured at (a) $P = 0.4938$ MPa and $T = 373$ K for $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}$, (b) $P = 0.4882$ MPa and $T = 373$ K for $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}$. The insets each show the time-dependent hydrogen and pressure-dependent time accordingly.

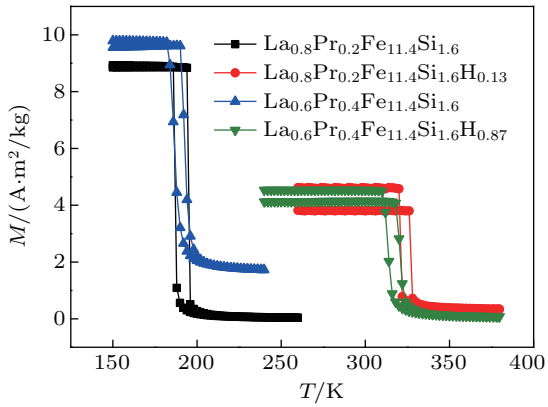


Fig. 4. (color online) Temperature-dependent magnetizations measured under a field of 0.01 T for $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0.2, 0.4$) compounds and their hydrides.

Figure 4 shows the temperature-dependent magnetizations measured in the heating and the cooling processes in a magnetic field of 0.01 T for $La_{1-x}Pr_xFe_{11.4}Si_{1.6}H_y$ ($x = 0.2$, 0.4) compounds. Each of the compounds presents a ferromagnetic state. Each of the samples has a magnetic transition from ferromagnetic (FM) state to the paramagnetic (PM) state. The Cure temperature T_C can be defined as the temperature at which the value of first derivative of the magnetization in the heating process is largest.[30] For the $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}H_y$ compound, the T_C increases from 196 K for $y = 0$ to 324 K for $y = 0.13$. For the $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}H_y$ compound, the T_C increases from 192 K for $y = 0$ to 320 K for $y = 0.87$. The introduction of H atoms into the $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0.2$, 0.4) compounds causes their lattices to expand. On the other hand, the substitution of Pr for La can lead to the lattice shrinking due to the smaller radius of Pr atom. But the interstitial H atom plays a major role in affecting the lattice expansion, compared with the case of the substitution of Pr for La. The effect of interstitial H atoms on T_C is two-fold. First, the hydrogen atom narrows the 3d energy band due to the lattice expansion that diminishes the overlap of the Fe 3d electron wave functions. Therefore, the Fe–Fe interaction is enhanced and the T_C grows. Second, it causes a hybridization between the H and Fe electron orbits, which produces an opposite effect on T_C. The rise of T_C with interstitial H atom content increasing reveals that the effect of lattice expansion plays a dominant role,

while, the hybridization between Fe and interstitial H atoms plays a minor role.[31,32]

Figure 5 shows the magnetization isotherms of $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0.2$, 0.4) and their hydrides, measured under ascending and descending fields around T_C. A remarkable IEM transition from paramagnetic (PM) to ferromagnetic (FM) states and an obvious magnetic hysteresis loop above T_C are observed in each of $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0.2$, 0.4) compounds and their hydrides, indicating a characteristic of the first-order magnetic transition.[33] The concentration of the itinerant electrons is enhanced by partially substituting Pr,[34] which is favorable for achieving large $-\Delta S_M$. In addition, the hydrogen absorption leads to a prominent reduction in hysteresis, which can be interpreted by the renormalization effect of spin fluctuations.

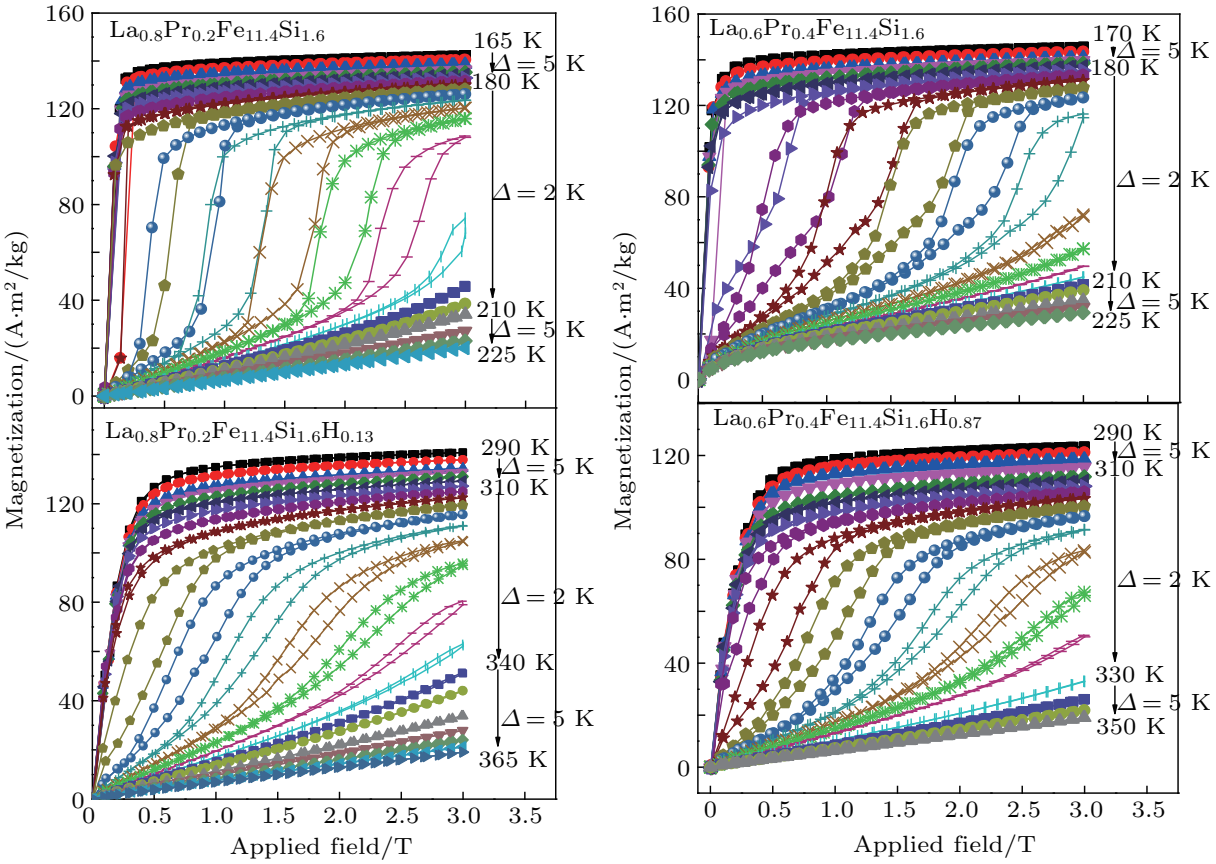


Fig. 5. (color online) Magnetization isotherms of $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0.2$, 0.4) compounds and their hydrides, measured in the vicinity of the T_C with magnetic field increasing and decreasing.

The values of isothermal magnetic entropy change $(-\Delta S)$ of $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0.2$, 0.4) and their hydrides can be calculated from the collected magnetization data by using the Maxwell relationship.[35] Figure 6 shows the temperature-dependent magnetic entropy changes for $La_{1-x}Pr_xFe_{11.4}Si_{1.6}H_y$ ($x = 0.2$, 0.4) hydrides under magnetic field change of 0 T–3 T. The values of maximum magnetic entropy change are 14.91 J/kg·K and 17.995 J/kg·K for $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}H_{0.13}$ and $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}H_{0.87}$ for a field change 0 T–3 T, respectively. Previous studies show that the introduction of interstitial hydrogen atoms can weaken the IEM transition and result in a small decrease in $-\Delta S$.[32] Thus, the larger value of magnetic entropy change of $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}H_{0.87}$ than the value of $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}H_{0.13}$ indicates that the increase of the content of Pr can eliminate the adverse effects from hydrogen absorption.

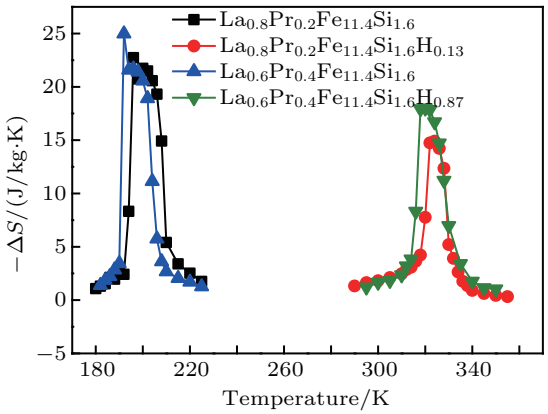


Fig. 6. (color online) Temperature-dependent isothermal magnetic entropy changes under the field changes of 0–3 T for $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0.2$, 0.4) compounds and their hydrides.

The values of the refrigerant capacity (RC) of $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0.2$, 0.4) and their hydrides are calculated using the approach by Fujii and Sun,[36] according to

the following equation:

$$\mathrm{RC} = \int_{T_2}^{T_1} |\Delta S_{\mathrm{M}}| \, \mathrm{d}T, \tag{1}$$

where T_1 and T_2 are the temperatures corresponding to both sides of the half maximum value of the $-\Delta S_{\mathrm{M}}$ peak, respectively. The maximum values of RC are found to be 318 J/kg and 324 J/kg for $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}H_{0.13}$ and $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}H_{0.87}$ under a magnetic field change from 0 T to 3 T, respectively.

4. Conclusions

In this work, the effects of Pr substitution on the hydrogenating process and magnetocaloric properties of $La_{1-x}Pr_xFe_{11.4}Si_{1.6}H_y$ ($x = 0.2,\ 0.4$) hydrides are studied. Each of the samples crystallizes into a cubic $NaZn_{13}$-type structure. It is worth noting that partial replacement of Pr for La leads to hydrogen-absorbing plateaus and an obvious lag of the releasing processes behind the absorbing processes. Moreover, the increasing of the content of Pr can eliminate the adverse effects of small decreasing in $-\Delta S$ because of hydrogen absorption. The T_{C} can increase to the room temperature by introducing H atoms. The values of maximum magnetic entropy change are 14.91 J/kg·K and 17.995 J/kg·K for $La_{0.8}Pr_{0.2}Fe_{11.4}Si_{1.6}H_{0.13}$ and $La_{0.6}Pr_{0.4}Fe_{11.4}Si_{1.6}H_{0.87}$, respectively. The $La_{1-x}Pr_xFe_{11.4}Si_{1.6}$ ($x = 0,\ 0.2,\ 0.4$) hydrides are a promising candidate for being used as magnetic refrigerants near room temperature.

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