Large magnetocaloric effects in NaZn$_{13}$-type La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds and their hydrides composed of icosahedral clusters

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Abstract

The magnetocaloric effects (MCEs) in cubic NaZn$_{13}$-type La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds and their hydrides composed of icosahedral clusters have been investigated because these compounds exhibit the itinerant-electron metamagnetic (IEM) transition just above the Curie temperature $T_C$. The value of $T_C$ can be increased continuously up to about 336 K by hydrogen absorption into the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds. Therefore, the values of the isothermal magnetic entropy change $\Delta S_m$ and the indirectly estimated adiabatic temperature change $\Delta T_{ad}$ due to the IEM transition become $\sim 31 \text{ J/kg K}$ and $15.4 \text{ K}$, respectively, in the magnetic field change from 0 to 5 T at $T_C=287 \text{ K}$ for the La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$H$_{1.1}$ compound. The MCEs in the compounds having the IEM transition are much larger than those in the compounds exhibiting the second-order magnetic transition at $T_C$. The direct measurement of the adiabatic temperature change $\Delta T_{ad}$ has confirmed such a large value. Consequently, the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds and their hydrides having the IEM transition are promising as high performance magnetic refrigerants working in a wide temperature range covering room temperature in relatively low magnetic fields.

1. Introduction

La(Fe$_x$Si$_{1-x}$)$_{13}$ and La(Fe$_x$Al$_{1-x}$)$_{13}$ compounds crystallize in the cubic NaZn$_{13}$-type structure (space group Fm"{3}c) [1,2]. In this structure, La and Fe$_I$ atoms form a CsCl-type structure, and Fe$_I$ atoms are located at the center of icosahedral clusters. The icosahedral cluster is composed of 12 Fe$_{II}$ atoms, in other words, La, Fe$_I$ and Fe$_{II}$ atoms occupy 8a, 8b and 96i sites, respectively, in the space group of Fm"{3}c. The cubic NaZn$_{13}$-type structure is not formed in the La–Fe system, because the heat of mixing between La and Fe is positive [1]. Therefore, it is not so easy to obtain the cubic NaZn$_{13}$-type single phase of the La(Fe$_x$Si$_{1-x}$)$_{13}$ and La(Fe$_x$Al$_{1-x}$)$_{13}$ compounds in a relatively higher Fe concentration range. For the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds, the cubic NaZn$_{13}$-type structure has been reported in the concentration range $0.81 \leq x \leq 0.89$ [1].

The first-order magnetic transition materials are attractive for magnetic refrigerants, because they exhibit large magnetocaloric effects (MCEs) [3–7]. For example, at the first-order crystallographic transition temperature of 278 K, Gd$_5$(Si$_2$Ge$_2$) exhibits the isothermal entropy change $\Delta S_m=-18 \text{ J/kg K}$ and the adiabatic temperature change $\Delta T_{ad}=15.3 \text{ K}$ in the magnetic field change from 0 to 5 T ($\Delta H=5 \text{ T}$) [4]. These values are larger than those of Gd; $\Delta S_m=-9 \text{ J/kg K}$ and $\Delta T_{ad}=11.6 \text{ K}$ in $\Delta H=5 \text{ T}$ at the second-order magnetic transition temperature of 294 K [8]. Such large MCEs due to the first-order magnetic transition have been observed in Fe$_{50}$Rh$_{51}$ [5], ErCo$_2$ [6], and MnAs [7]. The MCEs of both $\Delta S_m$ and $\Delta T_{ad}$ in magnetic refrigerants should be evaluated, because a large $\Delta S_m$ does not always bring about a large value of $\Delta T_{ad}$ [9,10]. However, there are only a few data of $\Delta T_{ad}$ in contrast to various data of $\Delta S_m$ for materials having the first-order magnetic transition.

It has been reported that the ground state of the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds is the ferromagnetic state in the concentration range $0.81 \leq x \leq 0.89$ [1]. Recently, we have prepared the cubic NaZn$_{13}$-type structure single phase of the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds in a relatively higher Fe concentration range, and observed the itinerant-electron
metamagnetic (IEM) transition, that is, the field-induced first-order magnetic transition from the paramagnetic (P) to the ferromagnetic (F) state in the concentration range 0.86 ≤ x ≤ 0.90 [11–14]. Fundamental properties of the IEM transition for the La(Fe_xSi_{1-x})_{13} compounds have been discussed by taking spin fluctuations into consideration [11,13]. From the magnetization and heat capacity measurements, it has been estimated that both ΔS_m and ΔT_ad for the La(Fe_xSi_{1-x})_{13} compounds are very large just above T_C because of the IEM transition [14–17]. Additionally, T_y of the La(Fe_{0.88}Si_{0.12})_{13} compound can be increased up to 336 K by hydrogen absorption without any crystal structure changes [14,18,19]. Therefore, the large values of both ΔS_m and ΔT_ad have been realized in a wide temperature range covering room temperature by controlling y in the La(Fe_xSi_{1-x})_{13}H_y compounds [14,16,17].

Recently, the magnetic phase diagram of the La(Fe_xSi_{1-x})_{13} compounds has been established [13]. The IEM transition properties of the La(Fe_xSi_{1-x})_{13} compounds are sensitive to x, and hence the magnetic transition at T_C changes from the first-order to the second-order. Therefore, the investigations of MCEs for the La(Fe_xSi_{1-x})_{13} compounds in various Fe concentrations are meaningful for practical uses to magnetic refrigerants. In the present study, the Fe concentration dependence of MCEs in the La(Fe_xSi_{1-x})_{13} compounds have been investigated. We compare the difference in the data between the first-order and the second-order magnetic transition. In addition, the direct measurement of the adiabatic temperature change, ΔT_ad, has been carried out. Finally, the MCEs in the La(Fe_xSi_{1-x})_{13}H_y compounds are discussed in comparison with those of other candidates reported as magnetic refrigerants.

2. Experiments

La(Fe_{0.88}Si_{0.12})_{13} compounds with nominal composition of x = 0.84, 0.86, 0.88, and 0.90 were prepared by arc-melting in an argon gas atmosphere. The heat treatment was carried out in a vacuum quartz tube at 1323 K for 10 days. The X-ray powder diffractions identified that, all the specimens are in a NaZn_{13}-type single phase. The hydrogen absorption in the La(Fe_xSi_{1-x})_{13} compounds was carried out by annealing under a hydrogen gas atmosphere. The control of the hydrogen concentration y in the La(Fe_xSi_{1-x})_{13}H_y compounds was made by changing both the hydrogen gas pressure and the annealing temperature. The hydrogen concentration was determined by both gas chromatograph and gas fusion analyses. The magnetization was measured with a superconducting quantum interference device magnetometer and the specific heat measurements were carried out by a relaxation method. For the direct measurement of the adiabatic temperature change, ΔT_ad, the sample was placed in the holder made of quartz and glass fibers. The temperature change of the specimen was measured with an alumina-based resistance thermometer. The mass of the thermometer was negligibly smaller than that of the sample. To reduce the heat leak through the lead wires, very thin manganin alloy wires were used as the electrical wire.

3. Results and discussion

Fig. 1 shows the variation of magnetization as functions of magnetic field and temperature around the Curie temperature T_C for the La(Fe_{0.90}Si_{0.10})_{13} compound. In this figure, the solid and dotted lines stand for the magnetization curves in the constant temperature and the thermomagnetization curves in the constant magnetic field, respectively. Since the present compound exhibits the IEM transition [14], the magnetic field dependence of the magnetization exhibits an S-shape behavior, accompanied by a significant magnetization change as indicated by the solid lines above T_C = 184 K. The magnitude of the magnetization change due to the IEM transition is about 1.6μ_B at 185 K. The IEM transition field determined from the inflection point of the magnetization curve increases linearly with temperature at a rate of 0.25 T/K. The large magnetization change due to the IEM transition is observed even at the temperature higher than T_C by about 20 K. These behaviors are very similar to those of the La(Fe_{0.88}Si_{0.12})_{13} compound [11,12]. On the other hand, the thermomagnetization curves in the constant magnetic field presented by the dashed lines exhibit a remarkable magnetization change at T_C. From X-ray diffraction measurements, a discontinuous volume change has been confirmed around T_C without any changes in the crystal structure [11,12]. The Mössbauer spectra indicate the ferromagnetic (F) state with the sextet just below T_C, which is changed to the paramagnetic (P) state with the doublet just above T_C. Additionally, the coexistence of

![Fig. 1. Variation of magnetization as functions of magnetic field and temperature around the Curie temperature T_C for the La(Fe_{0.90}Si_{0.10})_{13} compound. The solid and dotted lines stand for the magnetization curves in the constant temperature and the thermomagnetization curves in the constant magnetic field, respectively.](image-url)
the F and P spectra due to the supercooling phenomenon has been confirmed just at \( T_C \) [13]. All these behaviors mean that a thermal-induced first-order magnetic transition between the F and P states takes place at \( T_C \). The magnitude of the magnetization change due to the thermal-induced first-order magnetic transition is about 1.6\( \mu_B \) in 0.2 T, almost the same value as that of the IEM transition just above \( T_C \). Since the IEM transition field increases with temperature, \( T_C \) becomes larger with increasing applying magnetic field at a rate of 4 K/T. A discontinuous large magnetization change is observed around \( T_C \) even in 5 T, because the IEM transition for the compound with \( x = 0.90 \) is clear even in a relatively higher temperature range.

According to the theoretical considerations, the onset of the IEM transition means that the free energy as a function of magnetization \( M \) has two minima in the P state with \( M = 0 \) and in the F state with \( M \) equals to the spontaneous magnetization \( M_S \), and these two states are separated by the energy barrier [20,21]. When the minimum in the F state is lower than that in the P state at 0 K, the ground state is in the F state. However, the minimum in the F state becomes shallower with increasing temperature, because the magnetic free energy in the itinerant-electron magnets is renormalized by spin fluctuations at finite temperatures [21]. When the minimum in the F state is eliminated by the renormalization effect, the thermal-induced first-order magnetic transition between the F and P states takes place at \( T_C \). By applying magnetic field in the P state, both the minimum in the F state and the maximum value of the energy barrier become lower because of the Zeeman energy, inducing the IEM transition [21].

The double-minimum structure of the magnetic free energy is closely associated with the special 3d band structure, which exhibits a sharp peak of the density of states just below the Fermi level [20,21]. Therefore, the metamagnetic properties are changed by changing \( x \) in the La(Fe\(_{1-x}\)Si\(_x\))\(_{13}\) compounds. Fig. 2 depicts the thermomagnetization curves around \( T_C \) for the compound with \( x = 0.84 \) in various magnetic fields. All the thermomagnetization curves expect for the magnetic field of 0.2 T were measured in the heating process. The value of \( T_C \) increases with decreasing \( x \) in the La(Fe\(_{1-x}\)Si\(_x\))\(_{13}\) compounds [1,11], and hence \( T_C \) for the compound with \( x = 0.84 \) reaches 2.33 K. It has been reported that \( x = 0.84 \) is very close to the concentration of the tricritical point, where the magnetic transition at \( T_C \) changes from the first-order to the second-order and the IEM transition disappears [13]. For both the heating and cooling processes in the magnetic filed of 0.2 T, the magnetization change around \( T_C \) is very clear, resulting in no clear hysteresis. Therefore, the magnetization for the compound with \( x = 0.84 \) at \( T_C \) is of the second-order, accompanied by no IEM transition.

From \( M \) as functions of temperature \( T \) and magnetic field \( H \), the magnetic entropy change, \( \Delta S_m \), is given by the following equation associated with the Maxwell relationship:

\[
\Delta S_m = \int_{0}^{H} \frac{\partial M}{\partial T} \, dH,
\]

Fig. 3(a) and (b) shows the temperature dependence of \( \Delta S_m \) obtained from Eq. (1) for the compounds with \( x = 0.84, 0.86, 0.88, \) and 0.90 in the magnetic field changes (a) from 0 to 2 T (\( \Delta H = 2 \) T) and (b) from 0 to 5 T (\( \Delta H = 5 \) T), respectively. The magnetization for the compound with \( x = 0.84 \) exhibits a gradual change around \( T_C \) due to the second-order magnetic transition, and hence \( \Delta S_m \) indicates a negative broad peak around \( T_C \). The negative maximum value of \( \Delta S_m \) in \( \Delta H = 2 \) and 5 T for the compound with \( x = 0.84 \) are \(-2\) and \(-9\) J/kg, respectively. The value of \( T_C \) decreases with increasing \( x \) in the La(Fe\(_{1-x}\)Si\(_x\))\(_{13}\) compounds, and the negative peak of \( \Delta S_m \) appears at a lower temperature range. Furthermore, with increasing \( x \), the magnetic transition at \( T_C \) changes from the second-order to the first-order. Therefore, \( \partial M/\partial T \) around \( T_C \) becomes larger with increasing \( x \). As a result, a negative peak of \( \Delta S_m \) around \( T_C \) becomes larger and shaper with increasing \( x \). For the compound with \( x = 0.90 \), the negative maximum value of \( \Delta S_m \) reaches about \(-30\) J/kg at \( T_C = 184 \) K in \( \Delta H = 5 \) T. It should be noted that such a large \( \Delta S_m \) is obtained even in relatively low magnetic fields for the compound with \( x = 0.90 \). Since the IEM transition for the compound with \( x = 0.90 \) is very sharp, the large magnetization change due to the IEM transition takes place in relatively low magnetic fields just above \( T_C \). Therefore, the negative maximum
value of $\Delta S_m$ in $\Delta H = 2$ T for the compound with $x = 0.90$ is about $-28$ J/kg K, being about 93% of that in $\Delta H = 5$ T.

Fig. 4(a) and (b) shows the temperature dependence of the total entropy $S$ for the compounds with (a) $x = 0.90$ and (b) 0.84 in various magnetic fields. The presented $S$–$T$ diagram was calculated from the specific heat and magnetization data. For the compound with $x = 0.90$, $S$ exhibits a significant jump in the magnetic field of 0 T. Its position increases with the magnetic field and agrees with $T_C$ in Fig. 1. Therefore, it is clear that discontinuous change of $S$ is attributed to the latent heat of the thermal-induced first-order magnetic transition between the P and the F states. The latent heat of the magnetic transition between the P and the F states becomes smaller as the Fe concentration comes close to the critical concentration of the IEM transition. Therefore, $S$ for the compound with $x = 0.84$ varies linearly around $T_C$. The value of $\Delta T_{ad}(T)$ is given by using the following relation

$$\Delta T_{ad}(T)_{\Delta H} = [T(S)_{H} - T(S)_{0}]S. \quad (2)$$

Fig. 5(a) and (b) shows the temperature dependence of the adiabatic temperature change, $\Delta T_{ad}$, evaluated indirectly from the $S$–$T$ diagram by using Eq. (2) for the compounds with $x = 0.84, 0.86, 0.88, \text{ and } 0.90$ in (a) $\Delta H = 2$ T and (b) 5 T. For the compound with $x = 0.90$, $\Delta T_{ad}$ exhibits a peak around $T_C$, and the maximum value of $\Delta T_{ad}$ in $\Delta H = 2$ T is about 8.1 K. The value of $\Delta T_{ad}$ in $\Delta H = 5$ T goes up to about 12.1 K, because $T_C$ increases with the magnetic field. With decreasing $x$ in the La(Fe$_{x}$Si$_{1-x}$)$_{13}$ compounds, the peak of $\Delta T_{ad}$ shifts toward a higher temperature range as a result of increase of $T_C$. Furthermore, the latent heat of the magnetic transition becomes smaller, and hence $S$ varies linearly around $T_C$ of the second-order. Therefore, the peak of $\Delta T_{ad}$ becomes broader and its maximum value becomes smaller with decreasing $x$ in the La(Fe$_{x}$Si$_{1-x}$)$_{13}$ compounds. As a result, the La(Fe$_{0.86}$Si$_{0.14}$)$_{13}$ compound having the second-order magnetic transition at $T_C$ indicates $\Delta T_{ad} = 2.1$ and 4.3 K in $\Delta H = 2$ and 5 T, respectively. Accordingly, both $\Delta S_m$ and $\Delta T_{ad}$ are enhanced by increasing $x$ for the La(Fe$_{x}$Si$_{1-x}$)$_{13}$ compounds, and hence the largest MCEs are observed for the compound with $x = 0.90$. From these results, it is concluded that such large MCEs are attributed to the IEM transition.

In order to confirm such large MCEs, we have carried out the direct measurement of $\Delta T_{ad}$. Fig. 6 shows the time dependence of the temperature change for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound. The specimen was moved quickly into the magnetic field of 2 T at the time indicated by the arrow, and then the adiabatic change of $\Delta H = 2$ T was realized. The spike at the arrow would be caused by an electromagnetic
induction. By neglecting such a spike, an increase in the specimen temperature is observed adiabatically by changing the magnetic field. That is, the specimen temperature is quickly increased and saturated within about one second by the adiabatic change of the magnetic field. The directly measured adiabatic temperature change $\Delta T_{ad}$ becomes larger as the temperature comes close to $T_C$. The temperature dependence of $\Delta T_{ad}$ together with that of $\Delta T_{ad}$ in $\Delta H = 2$ T for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound is given in Fig. 7. The value of $\Delta T_{ad}$ indicates the peak around $T_C$. The temperature dependence of $\Delta T_{ad}$ virtually corresponds to that of $\Delta T_{ad}$. In addition, the large maximum value of $\Delta T_{ad}$ is very large of about 5.2 K just above $T_C$, comparable with that of $\Delta T_{ad}$ just above $T_C$. Accordingly, the large adiabatic temperature change due to the IEM transition for the La(Fe$_{x}$Si$_{1-x}$)$_{13}$ compounds has been confirmed by both the direct and indirect measurements. Therefore, it is revealed that the La(Fe$_{x}$Si$_{1-x}$)$_{13}$ compounds exhibit excellent magnetic refrigerant properties in relatively low magnetic fields.

Recently, we have demonstrated that $T_C$ for the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds can be increased continuously up to about 336 K by hydrogen absorption [14,18,19]. For the cubic NaZn$_{13}$-type La(Fe$_x$Al$_{1-x}$)$_{13}$N$_y$ compounds, the neutron diffraction measurements confirmed that nitrogen atoms occupy the 24d sites [22]. The 24d sites are surrounded by four icosahedral clusters and two La atoms, namely, the 24d sites occupy the face-centered cubic lattice of FeI atoms. Therefore, the icosahedral cluster size defined by the distance between the FeI atom at the center of cluster

Fig. 5. Temperature dependence of the adiabatic temperature change $\Delta T_{ad}$ evaluated indirectly from the magnetization and heat capacity measurements for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compounds with $x = 0.84, 0.86, 0.88$ and 0.90 in the magnetic field changes. (a) From 0 to 2 T ($\Delta H = 2$ T), (b) from 0 to 5 T ($\Delta H = 5$ T).

Fig. 6. Time dependence of the temperature change for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound. The specimen was moved quickly into the magnetic field of 2 T at the time indicated by the arrow.

Fig. 7. Temperature dependence of the directly measured adiabatic temperature change $\Delta T_{ad}$ for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ compound in the magnetic field change from 0 to 2 T ($\Delta H = 2$ T), together with that of the adiabatic temperature change $\Delta T_{ad}$ evaluated indirectly from the magnetization and heat capacity measurements.
and the FeII atom at the vertices is hardly changed by the absorbed nitrogen, whereas the distance between the neighboring icosahedral clusters significantly increases, resulting in the increase of the lattice constant [22]. The X-ray diffraction data of the present La(Fe0.9xSi1.2x)13 compounds after hydrogen absorption are very similar to the results mentioned above [18,19,23]. In addition, the hydrogen absorption behavior of the La(Fe,Al1-x)13H y compounds [24] are in analogy with the present data. Therefore, almost all hydrogen atoms would occupy the 24d sites in the La(Fe0.9xSi1.2x)13H y compounds. The thermomagnetization curves are given in Fig. 8 for the La(Fe0.9xSi0.10)13H y compound in various magnetic fields. All the thermomagnetization curves represent the heating process, except for the curve in 0.2 T. By applying magnetic field of 0.2 T, a discontinuous magnetization change is observed around T C, accompanied by a small hysteresis of about 1 K. Therefore, the thermal-induced first-order magnetic transition is maintained at T C. The magnetization change at T C for the La(Fe0.90Si0.10)13H1.1 compound is almost the same as that of the La(Fe0.90Si0.10)13 compound (see Fig. 1). Furthermore, since the IEM transition also takes place after hydrogen absorption, T C for the La(Fe0.9xSi0.10)13H1.1 compound exhibits the large magnetic field dependence, keeping the large magnetization change at T C.

The large MCEs due to the IEM transition for the La(Fe0.9xSi1.2x)13 compounds are obtained in relatively low magnetic fields just above T C. Namely, the control of T C for the La(Fe0.9xSi1.2x)13 compounds is necessary to extend the working temperature range in relatively low magnetic fields. From Figs. 3 and 5, T C increases and the MCEs become smaller with decreasing x in the La(Fe0.9xSi1.2x)13 compounds, because the magnetic transition at T C changes from the first-order to the second-order. However, T C for the La(Fe0.9xSi1.2x)13 compounds increases up to room temperature, keeping the IEM transition with the first-order magnetic transition. Therefore, large values of ΔS m and ΔT ad are expected for the La(Fe0.90Si0.10)13H1.1 compound.

Fig. 9(a) and (b), respectively, shows the temperature dependence of ΔS m for the La(Fe0.90Si0.10)13H1.1 compound in (a) ΔH = 2 T and (b) 5 T, together with those of Gd5(Si2Ge2) [4] and MnAs [7] reported as candidates for magnetic refrigerants having the first-order transition. For the La(Fe0.90Si0.10)13H1.1 compound, the negative maximum values of ΔS m due to the IEM transition at 287 K become -28 and -31 J/kg K in ΔH = 2 and 5 T, respectively, which are larger than those of Gd5(Si2Ge2) and almost the same as those of MnAs. Fig. 10(a) and (b), respectively, shows the temperature dependence of ΔT ad for the La(Fe0.90Si0.10)13H1.1 compound in (a) ΔH = 2 T and (b) 5 T, together with those of Gd5(Si2Ge2) [4] and MnAs [7]. The maximum values of ΔT ad for the La(Fe0.90Si0.10)13H1.1 compound at 287 K are 7.1 and 15.4 K in ΔH = 2 and 5 T, respectively, which are almost the same as those of Gd5(Si2Ge2) and larger than those of MnAs. It should be pointed out that the values of ΔS m and ΔT ad for the La(Fe0.90Si0.10)13H1.1 compound are almost the same as that of the La(Fe0.90Si0.10)13 compound. Similar results have

![Fig. 8. Thermomagnetization curves of the La(Fe0.90Si0.10)13H1.1 compound in various magnetic fields. The curves in the magnetic field of 0.2 T are the heating and cooling processes as given by the arrows.](image)

![Fig. 9. Temperature dependence of the isothermal magnetic entropy change ΔS m for the La(Fe0.90Si0.10)13H1.1 compound, together with that of Gd5(Si2Ge2) [4] and MnAs [7] in the magnetic field changes. (a) From 0 to 2 T (ΔH = 2 T), (b) from 0 to 5 T (ΔH = 5 T).](image)
have confirmed that the thermal conductivity in the working surroundings is necessary. Therefore, thermal conductivity rapidly transfers from magnetic refrigerants to the surroundings.

4. Conclusion

For the La(Fe$_{1-x}$Si$_{1-x}$)$_{13}$ compounds consisting of icosahedral clusters, the magnetic transition at the Curie temperature $T_C$ changes from the first-order to the second-order with decreasing $x$ in the concentration range $0.84 \leq x \leq 0.90$. In the compounds having the first-order magnetic transition, the IEM transition takes place above $T_C$. By using such characteristic compounds, the MCEs for magnetic refrigerants have been investigated. For the La(Fe$_{0.90}$Si$_{10.10}$)$_{13}$ compound, the values of the isothermal magnetic entropy change, $\Delta S_m$, and the indirectly evaluated adiabatic temperature change, $\Delta T_{ad}$, are $-30$ J/kg K and 12.1 K at $T_C = 184$ K in the magnetic field change from 0 to 5 T ($\Delta H = 5$ T), respectively. Such large MCEs are closely correlated with the IEM transition. The value of $T_C$ increases and the MCEs become smaller with decreasing $x$. As a result, La(Fe$_{0.84}$Si$_{0.16}$)$_{13}$ compound exhibits $\Delta S_m = -9$ J/kg around the second-order magnetic transition of $T_C = 233$ K in $\Delta H = 5$ T, accompanied by no IEM transition. However, it should be pointed out that $T_C$ can be increased continuously up to about 336 K, keeping the IEM transition, by hydrogen absorption into the La(Fe$_{2}$Si$_{1-x}$)$_{13}$ compounds. As a consequence, the values of $\Delta S_m$ and $\Delta T_{ad}$ for the La(Fe$_{0.84}$Si$_{0.16}$)$_{13}$H$_{1.0}$ compounds due to the IEM transition are $-31$ J/kg K and 15.4 K, respectively, at $T_C = 287$ K in $\Delta H = 5$ T. Consequently, the present results lead us to the conclusion that La(Fe$_{2}$Si$_{1-x}$)$_{13}$ compounds and their hydrides having the IEM transition are promising as high performance magnetic refrigerants working in a wide temperature range covering room temperature in relatively low magnetic fields.

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