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Control of Working Temperature of Isothermal Magnetic Entropy Change in $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ by Hydrogen Absorption for Magnetic Refrigerants

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$La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ and their hydrides were investigated to obtain large magnetocaloric effects (MCEs) in a wide temperature range, including room temperature, for applications in magnetic refrigents. Since the magnetization change due to the itinerant-electron metamagentic (IEM) transition for $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ becomes larger with increasing z, the isothermal magnetic entropy change ΔS_m and the relative cooling power (*RCP*) are enhanced. In addition, the Curie temperatrue T_C of $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ is increased from 193 to 319 K by hydrogen absorption, with the IEM transition. The maximum value of $-\Delta S_m$, $-\Delta S_m^{max}$, in a magnetic field change of 2 T for $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}H_{1.1}$ is about 23 J/kg K at T_C = 288 K, which is larger than that of 19 J/kg K at T_C = 276 K for $La(Fe_{0.88}Si_{0.12})_{13}H_{1.0}$. The value of *RCP* = 179 J/kg of the former is also larger than 160 J/kg of the latter. It is concluded that the partial substitution of Nd improves MCEs in a wide temperautre range, including room temperature.

Keywords : itinerant-electron metamagnetic transition, Curie temperature, latent heat, relative cooling power, magnetic refrigeration

1. Introduction

A field-induced first-order transition from the paramagnetic to ferromagnetic state, that is, the itinerant-electron metamagnetic (IEM) transition has attracted much attention for applications in magnetic refrigerants [1-4]. $La(Fe_xSi_{1-x})_{13}$ compounds with a cubic $NaZn_{13}$-type structure exhibit the thermal-induced first-order transition at the Curie temperature T_C and the IEM transition just above T_C [5]. The IEM transition of $La(Fe_xSi_{1-x})_{13}$ is accompanied by large magnetocaloric effects (MCEs), which are characterized by the isothermal magnetic entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} [1, 2]. In addition, T_C of $La(Fe_xSi_{1-x})_{13}$ is increased from about 190 to about 330 K by hydrogen absorption, with keeping the IEM transition [6]. Hence, large MCEs due to the IEM transition are obtained in a wide range of temperature between 190 and 330 K by controlling the hydrogen content in hydrogenated $La(Fe_xSi_{1-x})_{13}H_y$ [2]. To improve magnetocaloric properties, the effects of partial substitutions in $La(Fe_xSi_{1-x})_{13}$ and their hydrides have been extensively investigated [7-16].

It has been reported that the La in $La(Fe_xSi_{1-x})_{13}$ can be partially replaced by other rare earth elements [7-10, 12, 16]. For example, T_C is decreased by the partial substitution of Ce for La in $La(Fe_xSi_{1-x})_{13}$, with keeping the IEM transition [7]. In addition, the ΔS_m and ΔT_{ad} are enhanced by the partial substitution of Ce. Such large MCEs due to the partial substitution of Ce are obtained after hydrogen absorption. Thus, large MCEs enhanced by the partial substitution of Ce are obtained in a wide temperature range, including room temperature. Similar behaviors are obtained by a partial substitution of Pr [8]. Hence, the partial substitution of other rare earth elements in $La(Fe_xSi_{1-x})_{13}$ and their hydrides is of particular interest to improve magnetocaloric properties for high-efficient magnetic refrigeration.

Recently, we have successfully synthesized a single phase of $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ in a range of $z \leq 0.2$ [17]. It was found that the partial substitution of Nd also enhances ΔS_m due to the IEM transition. Therefore, it is

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necessary to investigate the influence of Nd substitution on the IEM transition and the hydrogenation of $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ in order to obtain large MCEs in a wide temperature range, including room temperature. In this paper, the enhancement of ΔS_m for $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ is discussed in connection with the IEM transition. In addition, the hydrogen concentration dependence of T_C and ΔS_m for the $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ hydrides was investigated.

2. Experiments

$La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ compounds with z = 0.0, 0.1 and 0.2 were prepared by arc-melting in an argon gas atmosphere by using 99.9 mass% La and Fe, and 99.999 mass% Si. Subsequent heat-treatments were carried out in a vacuum quartz tube. The annealing temperature and duration were 1323 K and 10 days for z = 0.0, and 1373 K and 10 days for z = 0.1 and 0.2. All the compounds with the cubic $NaZn_{13}$-type structure were identified as a single phase without other phases by powder x-ray diffraction with Cu Kα radiation. Hydrogen absorption into $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ was conducted by annealing in the hydrogen gas atmosphere. The hydrogen content in $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}H_y$ was controlled by changing the annealing temperature and hydrogen gas pressure in ranges of 573-493 K and 0.03-01 MPa, respectively. Magnetization measurements were carried out with a SQUID magnetometer.

3. Results and Discussion

The lattice constant is decreased by the partial substitution of Nd [16, 17], because the ionic radius of Nd is smaller than that of La due to the lanthanide contraction. By applying hydrostatic pressure, T_C of $La(Fe_{0.88}Si_{0.12})_{13}$ is decreased significantly, whereas the change of M_s is not so remarkable [18]. In connection with such a magneto-volume effect, T_c of $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ decreases with increasing z. Figure 1 shows the magnetization curves of $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ with T_C = 193 K and $La(Fe_{0.88}Si_{0.12})_{13}$ with T_C = 195 K at T_C + 1 K and T_C + 10 K. The increasing and decreasing magnetic field processes are indicated by the arrows. The magnetization curve of $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ at T_C + 1 K exhibits a large magnetization change with a clear hysteresis because of the itinerant-electron metamagnetic (IEM) transition. Its magnitude is larger than that at T_C + 1 K for $La(Fe_{0.88}Si_{0.12})_{13}$. Therefore, the magnetization change due to the IEM transition is increased by the partial substitution of Nd. The critical field B_c of the IEM transition for $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ and $La(Fe_{0.88}Si_{0.12})_{13}$ increases with increasing temperature. The value of B_c for $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ at T_C + 10 K is almost the same as that for $La(Fe_{0.88}Si_{0.12})_{13}$, and as a result, their temperature dependence of B_c is very similar.

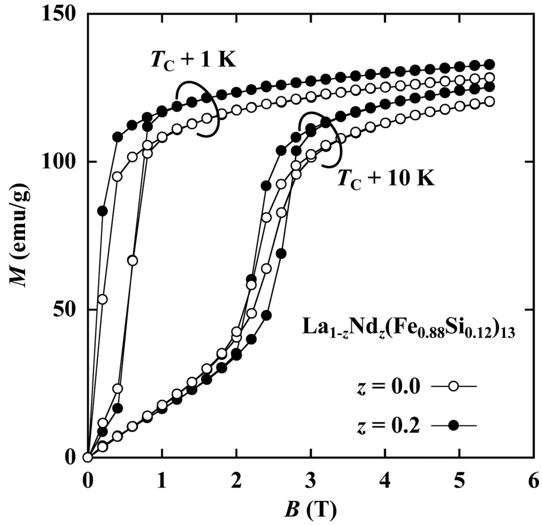

Fig. 1. Magnetization curves of $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ at the Curie temperature T_C + 1 K and T_C + 10 K. The values of T_C for z = 0.2 and 0.0 are 193 and 195 K, respectively.

It has been pointed out that the large isothermal magnetic entropy change ΔS_m due to the IEM transition is dominated by the entropy change ΔS_l due to the latent heat for the first-order phase transition [19]. According to the Clausius-Clapeyron equation, -ΔS_l is obtainable by the following expression:

$$-\Delta S_l = \Delta M \frac{dB_c}{dT}, \quad (1)$$

where ΔM is the magnetization change at the IEM transition and B_c is the critical field of the IEM transition. In many cases, on the other hand, ΔS_m is obtained from the magnetization M at various temperatures T and in various magnetic fields B by the following Maxwell relation:

$$\Delta S_m = \int_0^B \left(\frac{\partial M}{\partial T}\right)_B dB. \quad (2)$$

Figure 2(a) shows the Nd concentration dependence of ΔM and dB_c/dT. In addition, Nd concentration dependence of -ΔS_l and -ΔS_m^{max} calculated from Eqs. (1) and (2), respectively, is presented in Fig. 2(b). The values of ΔS_m obtained from Eq. (2) for the first-order magnetic phase transition materials are often overestimated. Hence, the validity of Eq. (2) for the first-order phase transition materials has been examined. A complicated modified

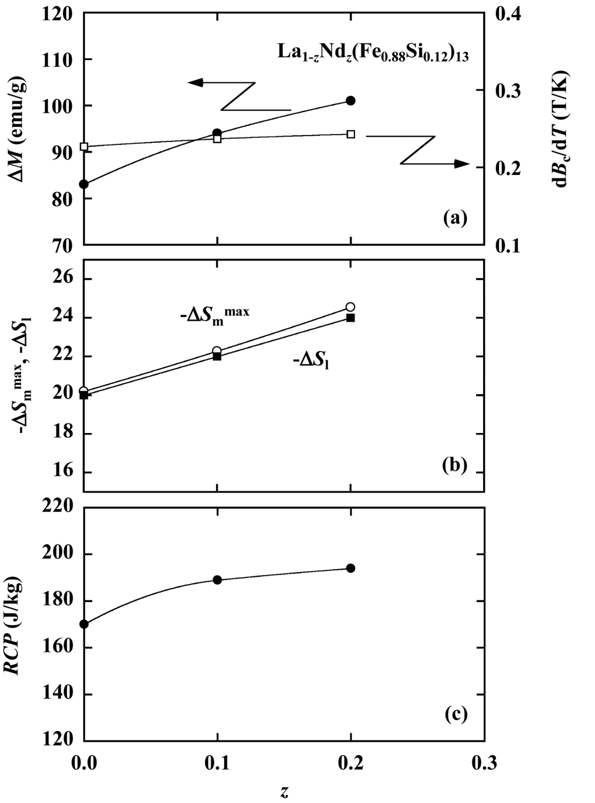

Fig. 2. Nd concentration dependence of (a) the magnetization change ΔM due to the IEM transition and the temperature derivative of critical field dB_c/dT, (b) the maximum value of the isothermal magnetic entropy change, $-\Delta S_m^{max}$ in the magnetic field change ΔB from 0 to 2 T and (c) the relative cooling power *RCP*.

Maxwell relation (two-phase model) has been proposed [20]. However, the present values of $-\Delta S_m^{max}$ obtained from Eq. (2) are almost the same as values of $-\Delta S_l$ obtained from Eq. (1) as seen on Fig. 2(b). Therefore, in the present paper, we discuss ΔS_m by using the results obtained from Eq. (2).

As reported previously [17], the value of $-\Delta S_m^{max}$ increases with increasing z. The temperature dependence of B_c has been discussed by using the spin-fluctuation theory based on the Landau-type expression of magnetic free energy [21]. It has been pointed out that dB_c/dT is proportional to the thermal growth rate of spin fluctuations [21]. The Nd concentration dependence of dB_c/dT is small, implying that the thermal growth rate of spin fluctuations is hardly affected by the partial substitution of Nd. On the other hand, ΔM increases with increasing z. As a result, $-\Delta S_l$ increases with increasing z. It should be noted that the increase of $-\Delta S_l$ is almost the same as that of the $-\Delta S_m^{max}$. Accordingly, the increase of $-\Delta S_m^{max}$ for $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ can be attributed to the increase of ΔM.

Relative cooling power (*RCP*) is also important for magnetic refrigerants, because it is measures the heat that can be transferred from the cold to the hot sink [22]. The value of *RCP* is defined as

$$RCP = -\Delta S_m^{max} \times \delta T, \quad (3)$$

where δT is the full-width at half maximum of ΔS_m^{max}. The Nd concentration dependence of *RCP* calculated from Eq. (3) in ΔB = 2 T is indicated in Fig. 2(c). The value of *RCP* also increases with increasing z. It has been pointed out that ΔS_m^{max} and δT of $La(Fe_xSi_{1-x})_{13}$ can be approximated by $\Delta M \times dB_c/dT$ and $(dB_c/dT) \times \Delta B$, respectively [23]. Thus, *RCP* is related to ΔM by the following equation.

$$RCP = -\Delta B \times \Delta M. \quad (4)$$

This expression indicates that the increase of *RCP* for $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ is also mainly attributable to the increase of ΔM.

The Nd concentration dependence of the saturation magnetization M_s at 4.2 K is presented in Fig. 3. By the least-square method, the magnetic moment per Nd atom is estimated to be about 3.3 μ_B. This value is very close to that of a free Nd^{3+} ion, indicating a ferromagnetic coupling with the Fe moment. The vertical axis indicates the difference from M_s of z = 0.0. The curve is slightly convex downward, and the value of M_s increases with increasing z. To discuss the influence of Nd partial substitution on ΔM, the values of ΔM are also plotted in Fig. 3. The Nd concentration dependence of ΔM is much stronger than that of M_s. The result shows that the increase of ΔM for $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ is not explained by only the contribution of the Nd magnetic moment. It is considered that

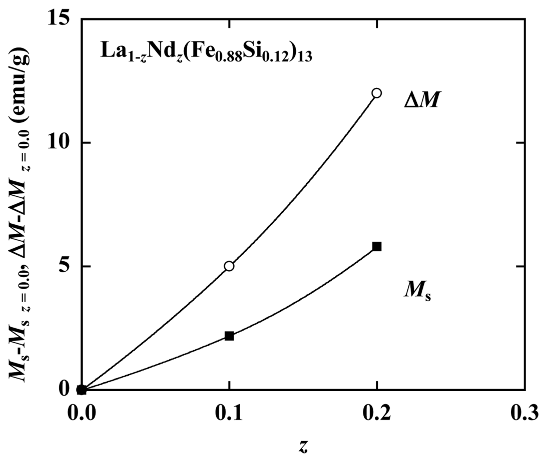

Fig. 3. Comparison between the saturation magnetization M_s at 4.2 K and the magnetization change ΔM due to the IEM transition for $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$. In a shorthand notation, the vertical axis indicates the difference from data of z = 0.0.

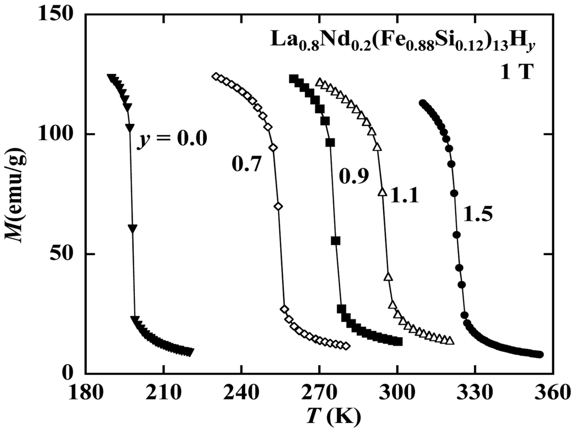

Fig. 4. Thermomagnetization curves in the heating process under a magnetic field of 1 T for $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}H_y$.

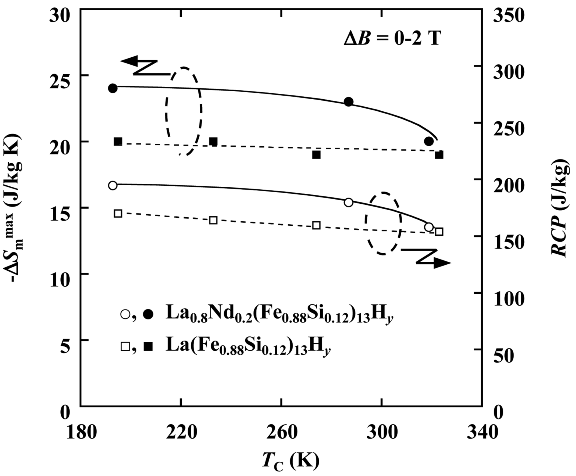

Fig. 5. Relationships among the Curie temperature T_C, the maximum value of the isothermal magnetic entropy change $-\Delta S_m^{max}$ and the relative cooling power *RCP* in the magnetic field change ΔB from 0 to 2 T for the $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}H_y$, together with those for the $La(Fe_{0.88}Si_{0.12})_{13}H_y$.

the Fe magnetic moment also contributes to the increase of ΔM and the enhancements of ΔS_m and *RCP* for $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$.

Figure 4 shows thermomagnetization curves in the heating process under a magnetic field of 1 T for $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}H_y$. With increasing *y*, T_C of $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}H_y$ increases up to 319 K. The thermomagnetization curve after hydrogen absorption also indicates a significant magnetization change because of the thermal-induced first-order transition at T_C, although the magnetization change at T_C reduces with increasing *y*. Thus, the maintenance of the IEM transition for $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}H_y$ is analogous to that of $La(Fe_{0.88}Si_{0.12})_{13}H_y$ [2].

The relationship among T_C, $-\Delta S_m^{max}$ and *RCP* in $\Delta B = 2$ T for $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}H_y$ is shown in Fig. 5, together with that of $La(Fe_{0.88}Si_{0.12})_{13}H_y$. The magnitudes of $-\Delta S_m^{max}$ and the *RCP* for the both systems slightly decrease with increasing T_C. Note that the values of $-\Delta S_m^{max}$ and *RCP* for $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}H_y$ are larger than those for $La(Fe_{0.88}Si_{0.12})_{13}H_y$ in a wide temperature range. In other words, large MCEs are enhanced by the partial substitutions of Nd, which remains after hydrogen absorption. Consequently, the partial substitution of Nd and hydrogenation are effective for improving MCEs for high-performance magnetic refrigerants in a wide temperature range, including room temperature.

4. Conclusion

$La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ and their hydrides were investigated to obtain high-performance magnetic refrigerants in a wide temperature range, including at room temperature. The magnetization change ΔM due to the itinerant-electron metamagnetic (IEM) transition for $La_{1-z}Nd_z(Fe_{0.88}Si_{0.12})_{13}$ increases with increasing *z*, though the temperature dependence of the critical field of the IEM transition is hardly affected. Accordingly the maximum value of the isothermal magnetic entropy change $-\Delta S_m^{max}$ and the relative cooling power (*RCP*) are enhanced by the partial substitution of Nd. In addition, the Curie temperatrue T_C of $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ is increased from 193 to 319 K by hydrogen absorption, with the IEM transition. As a result, $La_{0.8}Nd_{0.2}(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds exhibit larger values of $-\Delta S_m^{max}$ and *RCP* around room temperature in comparison with $La(Fe_{0.88}Si_{0.12})_{13}H_y$ compounds. Therefore, it is concluded that the partial substitutions of Nd improves MCEs in a wide temperature range, including at room temperature.

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