Enhancements of Magnetocaloric Effects in La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$ and Its Hydride by Partial Substitution of Ce for La

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Magnetocaloric effects due to the itinerant-electron metamagnetic transition for La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$ compounds promising as refrigerants are enhanced by a partial substitution of Ce for La. The values of the isothermal magnetic entropy change $\Delta S_m$ and the adiabatic temperature change $\Delta T_{ad}$ for La$_{1-x}$Ce$_x$(Fe$_{0.90}$Si$_{0.10}$)$_{13}$ compound with $z = 0.1$ are $-32.1$ kJ/kg K and 12.8 K, respectively, just above the Curie temperature in the magnetic field change from 0 to 4 T. Such large magnetocaloric effects can also be obtained in the vicinity of room temperature by hydrogen absorption. Annealing at 1373 K for 20 days makes it possible to substitute up to $z = 0.2$.

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1. Introduction

La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds with the cubic NaZn$_{13}$-type structure (space group $Fm\overline{3}c$) exhibit the thermal-induced first-order magnetic transition between the paramagnetic (P) and ferromagnetic (F) states at the Curie temperature $T_C$ in the concentration range $0.86 \leq x \leq 0.90$. In the P state just above $T_C$, the field-induced first-order magnetic transition from the P to F state, that is, the itinerant-electron metamagnetic (IEM) transition takes place without any crystallographic structural change.

Recently, it has been reported that the IEM transition for the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds causes large magnetocaloric effects (MCEs) such as the large values of the isothermal magnetic entropy change $\Delta S_m$ and the adiabatic temperature change $\Delta T_{ad}$. Furthermore, $T_C$ for La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds has been increased up to room temperature by hydrogen absorption, and hence large MCEs due to the IEM transition have been obtained in a wide temperature range covering room temperature by controlling the hydrogen concentration $y$ in La(Fe$_x$Si$_{1-x}$)$_{13}$H$_y$ compounds.

By changing the magnetic field from 0 to 2 T at room temperature, the La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$H$_1$ compound exhibits $\Delta S_m = -28.1$ kJ/kg K. In comparison with the data of the candidates for magnetic refrigerants, this value is larger than the $\Delta S_m = -14.1$ kJ/kg K of Gd$_3$Si$_2$Ge$_2$ alloy, comparable to the $\Delta S_m = -31.1$ kJ/kg K of MnAs compound. Therefore, $\Delta T_{ad} = 7.3$ K of the La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$H$_1$ compound is comparable to the $\Delta T_{ad} = 7.1$ K of Gd$_3$Si$_2$Ge$_2$ alloy, larger than the $\Delta T_{ad} = 4.7$ K of MnAs compound.

It is well known that the bed of active magnetic regenerator refrigerator is necessary to have low thermal conductivity along the heat transfer flow, while excellent heat exchange between the bed and the heat transfer fluid should be performed. Therefore, the bed is composed porously by fine particles of magnetic refrigerants having excellent thermal transport properties. Thermal conductivity of La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$H$_{1.1}$ compound is superior to that of Gd$_3$Si$_2$Ge$_2$ alloy and MnAs compound in the vicinity of room temperature. Therefore, the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds and their hydrides are of particular interest as the magnetic refrigerants working in a wide temperature range covering room temperature. The MCEs in the La(Fe$_{0.90}$Si$_{1.1}$)$_{13}$ compounds become larger with increasing concentration $x$. However, the formation of La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds with $x > 0.90$ is difficult because of the immiscibility of La and Fe. The largest values of $\Delta S_m$ and $\Delta T_{ad}$ for the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds have been reported in the concentration $x = 0.90$. Recently, the cubic NaZn$_{13}$-type phase has been confirmed in the La$_{1-x}$Ce$_x$(Fe$_{0.90}$Si$_{0.10}$)$_{20}$ compounds with $0.0 \leq x \leq 1.0$, and the concentration dependences of $T_C$ and saturation magnetization have been discussed. However, no IEM transition has been confirmed in these compounds. What is important in the development of magnetic refrigerants is to investigate of MCEs in the La$_{1-x}$Ce$_x$(Fe$_{0.90}$Si$_{1-x}$)$_{13}$ compounds with $0.86 \leq x \leq 0.90$, because the IEM behavior is restricted within this concentration range.

In the present study, the MCEs caused by the IEM transition in La$_{1-x}$Ce$_x$(Fe$_{0.90}$Si$_{12}$)$_{13}$ compounds and their hydrides have been investigated in order to enhance the MCEs.

2. Experiments

La$_{1-x}$Ce$_x$(Fe$_{0.90}$Si$_{10}$)$_{13}$ compounds were arc-melted by using 99.9 mass% pure La, Ce and Fe and 99.999 mass% pure Si in an argon gas atmosphere. The subsequent heat-treatments were carried out in a vacuum quartz tube. The annealing temperature and duration were 1323 K and 10 days for the compound with $z = 0.0$, 1373 K and 14 days for the compound with $z = 0.1$ and 1373 K and 20 days for the compound with $z = 0.2$ and 0.3, respectively. The crystal structure and the lattice constant were determined by x-ray diffraction measurements with Cu Kα radiation. The hydrogen absorption was carried out by annealing at 373 K under hydrogen gas atmosphere of 5 MPa. The magnetization was measured with a SQUID magnetometer and the heat capacity measurements in magnetic field were carried out by a relaxation method. By using the Maxwell relationship, the isothermal magnetic entropy change $\Delta S_m$ was estimated from the magnetization data measured in the vicinity of the Curie temperature at intervals of 2 K and the magnetic field step of 0.2 T from 0 to 5.4 T. The adiabatic temperature
change $\Delta T_{ad}$ was evaluated from the magnetic and heat capacity data in the magnetic field. Details of the calculation method have been reported in elsewhere.\(^5\)

3. Results and Discussion

The La$_{1-x}$Ce$_x$(Fe$_{0.90}$Si$_{0.10})_{13}$ compounds with $z = 0.0$, 0.1 and 0.2 were found to be in a single phase with the cubic NaZn$_{13}$-type structure by x-ray diffraction measurements. Figure 1 shows the temperature dependence of the isothermal magnetic entropy change $\Delta S_m$ in the magnetic field change $\Delta B$ from 0 to 4 T ($\Delta B = 4$ T) for La$_{1-x}$Ce$_x$(Fe$_{0.90}$Si$_{0.10})_{13}$ compounds with $z = 0.0$, 0.1 and 0.2.

Fig. 1 Temperature dependence of the isothermal magnetic entropy change $\Delta S_m$ in the magnetic field change $\Delta B$ from 0 to 4 T ($\Delta B = 4$ T) for La$_{1-x}$Ce$_x$(Fe$_{0.90}$Si$_{0.10})_{13}$ compounds with $z = 0.0$, 0.1 and 0.2.

From these results, it is concluded that the increase of $\Delta S_m$ caused by a partial substitution of Ce originates from the increase of the latent heat. Compared with $\Delta S_m$ for the compound with $z = 0.0$, the large $\Delta S_m$ can be obtained in relatively low magnetic fields for the compound with $z = 0.2$.

Magnetic refrigerants are claimed to have not only a large $\Delta S_m$ but also a large adiabatic temperature change $\Delta T_{ad}$. A large $\Delta S_m$ is not always accompanied by a large $\Delta T_{ad}$ and therefore, $\Delta T_{ad}$ for magnetic refrigerators should be evaluated. Figure 3 shows the temperature dependence of $\Delta T_{ad}$ for La$_{0.9}$Ce$_{0.1}$(Fe$_{0.90}$Si$_{0.10})_{13}$ compounds in $\Delta B = 4$ T, together with that for La(Fe$_{0.90}$Si$_{0.10})_{13}$ compound. The maximum value of $\Delta T_{ad}$ for the former is 12.8 K, which is larger than $\Delta T_{ad} = 11.7$ K for the latter. Accordingly, the MCEs in the La(Fe$_{0.90}$Si$_{0.10})_{13}$ compound are enhanced by a partial substitution of Ce for La.

When the IEM transition takes place above $T_C$, a significant volume dependence of $T_C$ has been expected.
from the theoretical studies.\textsuperscript{25,26} By applying hydrostatic pressure, La(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\) compounds with \(x = 0.86\) and 0.88 indeed exhibit the significant decrease of \(T_C\).\textsuperscript{27} From x-ray measurements, the lattice constants for La\(_{1-z}\)-Ce\(_z\)(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\) compounds with \(z = 0.0, 0.1\) and 0.2 are 1.1474, 1.1468 and 1.1463 nm, respectively. Apparently, the decrease of \(T_C\) for La\(_{1-z}\)-Ce\(_z\)(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\) compounds as shown in Fig. 1 is accompanied by the decrease of lattice constant. Since the volume of the La(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\) compounds has been increased by hydrogen absorption,\textsuperscript{31,122} the MCEs for the hydrogenated La\(_{0.9}\)Ce\(_{0.1}\)(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\)\(_{1.6}\) compounds should be investigated to extend a working temperature range toward a higher temperature range. Figure 4 illustrates the temperature dependence of \(\Delta S_m\) for the La\(_{0.9}\)Ce\(_{0.1}\)(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\)\(_{1.6}\) compound in \(\Delta B = 2\) and 4 T. The magnitude of \(\Delta S_m\) in \(\Delta B = 2\) and 4 T for the La\(_{0.9}\)Ce\(_{0.1}\)(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\)\(_{1.6}\) compound with \(T_C = 334\) K is \(-30\) and \(-32\) J/kg K, respectively. These values are almost the same as those of the La\(_{0.9}\)Ce\(_{0.1}\)(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\) compound as seen from Figs. 1 and 2. Consequently, the working temperature range of the La\(_{1-z}\)-Ce\(_z\)(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\) compounds can be extended up to around room temperature by hydrogen absorption without appreciable decrease of the MCEs.

### 4. Conclusion

The cubic NaZn\(_{13}\)-type single phase has been confirmed in the La\(_{1-z}\)-Ce\(_z\)(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\) compounds with \(z \leq 0.2\). Since the latent heat of the itinerant-electron metamagnetic transition becomes larger with increasing concentration \(z\), the isothermal magnetic entropy change \(\Delta S_m\) increases. Additionally, the adiabatic temperature change \(\Delta T_{ad}\) is also enhanced by a partial substitution of Ce for La. The values of \(\Delta S_m\) and \(\Delta T_{ad}\) of the compound with \(z = 0.1\) are \(-32\) J/kg K and 12.8 K, respectively, in the magnetic field change from 0 to 4 T just above the Curie temperature \(T_C = 179\) K. Furthermore, similar large value of \(\Delta S_m\) is obtained in the vicinity of room temperature after hydrogen absorption. Accordingly, the magnetocaloric effects are enhanced by a partial substitution of Ce for La, and La\(_{1-z}\)-Ce\(_z\)(Fe\(_{0.90}\)Si\(_{0.10}\))\(_{13}\) compounds and their hydrides are promising candidates for magnetic refrigerants working in a wide temperature range covering room temperature in relatively low magnetic fields.

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