Simultaneous enhancements of Curie temperature and magnetocaloric effects in the $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}\text{C}_y$ compounds

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1. Introduction

In the recent years, many studies have been carried out on the magnetic refrigeration based on magnetocaloric effect (MCE) due to its high energy efficiency and friendly environment in comparison with the conventional vapor compression refrigeration [1–3]. In response to a magnetic field change, the magnitude of MCE can be characterized as isothermal magnetocaloric entropy change ($\Delta S_{\text{MCE}}$) and/or adiabatic temperature change ($\Delta T_{\text{MCE}}$). Recently magnetocaloric materials with first-order phase transition, such as $\text{Gd}_x\text{Si}_y\text{Ge}_z\text{As}_w$, $\text{LaFe}_{13-x}\text{Si}_x\text{MnAs}$, $\text{MnFe}_x\text{P}_{1-x}\text{As}_y$, Heusler alloys, etc., have attracted much attention due to their giant MCEs and hysteretic loss [4–8]. Among these materials, the cubic NaZn$_{13}$-type $\text{LaFe}_{13-x}\text{Si}_x$-based compounds ($x \leq 1.6$), exhibiting itinerant-electron metamagnetic (IEM) transition, have been suggested as potential candidates for magnetic refrigeration applications [9–11]. So far, many efforts have been devoted to the research on the improvement of MCE by substitutional or interstitial addition in the $\text{LaFe}_{13-x}\text{Si}_x$ compounds. It was found that partial replacement of La with Ce, Pr, and Nd in the $\text{LaFe}_{13-x}\text{Si}_x$ compounds can enhance MCE remarkably but also lead to a reduction of the Curie temperature ($T_C$) and an increase of hysteretic loss [12,13], which may lower the efficiency of magnetic refrigeration. On the other hand, it has been demonstrated that the $T_C$ can be tuned even to room temperature by substituting Co for Fe or by introducing the interstitial elements H, C, and B into the lattice [9,10,14–17]. Meanwhile, the hysteretic loss is also depressed strongly due to the weakening of the IEM transition. However, the improvement of both $T_C$ and hysteretic loss usually accompanies the reduction of MCEs in the magnetocaloric materials with first-order phase transition. Consequently, from a practical point of view, it is important to enhance $T_C$ and to depress thermal and magnetic hysteresis while retaining large MCEs in the magnetic refrigeration materials. In the present paper, we report on the magnetic and magnetocaloric properties in the $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}\text{C}_y$ compounds.

2. Experimental details

The samples of $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ ($x=0, 0.1$, and 0.2) and $\text{La}_{0.8}\text{Ce}_0.2\text{Fe}_{11.5}\text{Si}_{1.5}\text{C}_y$ ($y=0.2, 0.4$) were prepared in a purified Ar atmosphere by arc-melting of the stoichiometric amounts of high purity (> 99.9 wt%) constituent elements on a water cooled copper hearth. The obtained ingots were wrapped in molybdenum foils, sealed in a high-vacuum quartz tube, annealed at 1373 K for a month, and then quenched into liquid nitrogen. Powder x-ray diffraction (XRD) patterns were obtained using Cu Kα radiation to identify the phase structure and the crystal lattice parameters. The magnetic properties were carried out by employing a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-7 from Quantum Design Inc.

3. Results and discussion

Fig. 1 shows the powder x-ray diffraction patterns of $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}\text{C}_y$ compounds at room temperature. The refinement...
reveals that all the compounds crystallize in a single phase with cubic NaZn13-type structure except the sample of y = 0.4, in which a minor z-Fe phase (≈5 wt%) was detected. The lattice parameter a determined using the Rietveld refinement is listed in Table 1. It can be seen that the substitution of Ce for La can cause a contraction of the lattice, while the introduction of C atoms leads to a volume expansion, indicating that C atoms dissolve into the interstitial sites. These results are in a good agreement with the previously published reports [12,13,16–19].

Fig. 2(a) shows the temperature dependence of magnetization for the La1-xCeFe11.5Si1.5 compounds measured in the heating and cooling processes under a low magnetic field of 0.01 T. It is found that all the compounds except La0.8Ce0.2Fe11.5Si1.5 exhibit an obvious thermal hysteresis, indicating the presence of a thermal-induced first-order magnetic transition around TC. The thermal hysteresis is estimated from the temperature difference between magnetic transitions during the cooling and heating cycles. The substitution of Ce leads to an increase of thermal hysteresis from 2 K for LaFe11.5Si1.5 to 6 K for La0.8Ce0.2Fe11.5Si1.5, suggesting that the partial substitution of Ce for La enhances the first-order IEM transition around TC. On the other hand, a small thermal hysteresis or no thermal hysteresis is observed for the C-inserted compounds, and this implies that the introduction of C atoms can weaken the thermal induced first-order magnetic transition. The TC for La1-xCeFe11.5Si1.5C y is determined using the Rietveld refinement is listed in Table 1. It is revealed that the partial substitution of Ce for La lowers TC, while the introduction of interstitial C atoms enhances TC. Fig. 2(b) presents TC as a function of the lattice parameter a for La1-xCeFe11.5Si1.5C y compounds.

Fig. 1. Observed (dots) and calculated intensities (line drawn through the data points) of the fully refined powder diffraction patterns of (a) LaFe11.5Si1.5, (b) La0.9Ce0.1Fe11.5Si1.5, (c) La0.8Ce0.2Fe11.5Si1.5, (d) La0.8Ce0.2Fe11.5Si1.5C0.2, and (e) La0.8Ce0.2Fe11.5Si1.5C0.4. The Bragg peak positions for the La(Fe, Si)13 (1:13) compounds measured in the heating (filled symbols) and cooling (open symbols) cycles under a magnetic field B = 0.01 T. It is well known that the Curie temperature is mainly determined by the Fe–Fe interaction, and the Fe–Fe interaction is the weakest. According to the results of Givord and Lemaire [20] and Li and Morrish [21], the Fe–Fe interaction increases monotonically with the Fe–Fe distance when the latter is smaller than 2.55 Å. For all the studied compounds, the Fe–Fe distances vary with the lattice volume and are smaller than 2.55 Å, i.e. the maximum Fe–Fe distance is ≈2.52 Å in La0.8Ce0.2Fe11.5Si1.5C0.4. Therefore, the change in TC for La1-xCeFe11.5Si1.5C y mainly results from the contraction or expansion of lattice volume caused by the substitution of Ce atoms and the insertion of C atoms.

Table 1

| Compounds           | a (Å)   | TC (K)  | |ΔSA| (0–2 T) (J/kg K) | |ΔSA| (0–5 T) (J/kg K) | Hysteresis loss (J/kg) | RC_{eff} (0–5 T) (J/kg) | RCP_{eff} (0–5 T) (J/kg) |
|---------------------|--------|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| LaFe11.5Si1.5       | 11.4683(5) | 195    | 19.7 | 23.7   | 22   | 385   | 438   |
| La0.9Ce0.1Fe11.5Si1.5 | 11.4619(8) | 188    | 22.7 | 26.6   | 99   | 379   | 430   |
| La0.8Ce0.2Fe11.5Si1.5 | 11.4530(4) | 179    | 26.7 | 30.4   | 158  | 244   | 310   |
| La0.8Ce0.2Fe11.5Si1.5C0.2 | 11.4816(7) | 207    | 24.6 | 28.0   | 30   | 420   | 494   |
| La0.8Ce0.2Fe11.5Si1.5C0.4 | 11.5123(1) | 246    | 7.6  | 13.5   | 0    | 330   | 426   |

Fig. 2. (a) Temperature dependence of the magnetization measured during heating (filled symbols) and cooling (open symbols) cycles under a magnetic field of 0.01 T, and (b) Curie temperature TC as a function of lattice parameter a for La1-xCeFe11.5Si1.5C y compounds.
Besides, it is interesting to note that $T_C$ increases linearly with lattice parameter $a$ at a rate of $\sim 1132$ K/Å for all the studied samples, no matter how the phase volume is modified. This observation is consistent with the previous study [22].

Fig. 3(a), (b), and (c) shows the magnetization isotherms around $T_C$ for $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}$, $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.2}$, and $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.4}$, respectively. The hysteresis loss is defined as the enclosed area between the ascending and descending magnetization curves and the maximum values around $T_C$ atoms. Furthermore, Fig. 3(c) shows that almost no hysteresis loss decreases significantly with the introduction of C atoms. However, it is clearly seen from Fig. 3(b) that the magnetic hysteresis loss decreases significantly with the introduction of C atoms. Therefore, the introduction of C atoms in $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ is favorable to the practical applications of magnetic refrigeration.

The $\Delta S_M$ of $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ is calculated from the isothermal magnetization data using the Maxwell relation $\Delta S(T,H) = \frac{\partial}{\partial T} (\frac{\partial M}{\partial T})_H dH$. Fig. 4(a) and (b) shows the temperature dependence of the $\Delta S_M$ for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ under magnetic field changes of 0–2 T and 0–5 T, respectively, and the maximum values of $\Delta S_M$ are summarized in Table 1. It should be noted that these compounds with the first-order magnetic transition exhibit extra spike-shaped peaks, which are fictitious as discussed in previous reports and are not considered here [23,24]. It is observed that the $\Delta S_M$ increases with the substitution of Ce for La because of the strengthening of IEM transition. However, the introduction of C atoms would suppress the IEM transition and weaken the nature of first-order magnetic transition, giving rise to a reduction of $\Delta S_M$. It is worthwhile to note that the $\Delta S_M$ of $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.2}$ still attains $-28$ J/kg K at $T_C=207$ K for a field change of 0–5 T, which is larger than that of the Ce- and C-free parent compound, although the $\Delta S_M$ decreases slightly by introducing interstitial C atoms.

Up to now, two approaches are often chosen to evaluate the amount of heat transferred in one thermodynamic cycle and the suitability of magnetic materials for practical applications. One is refrigerant capacity (RC) given by $RC = \int_{T_1}^{T_2} |\Delta S| dT$, where $T_1$ and $T_2$ are the temperatures corresponding to both sides of the half-maximum value of $|\Delta S|$ peak [25]. Another is relative cooling power (RCP) suggested by Gschneidner and Pecharsky [26], and it

![Fig. 3. Magnetization isotherms around $T_C$ for (a) $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}$, (b) $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.2}$, and (c) $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.4}$ compounds.](image1)

![Fig. 4. Temperature dependence of the isothermal magnetic entropy changes $\Delta S_M$ for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds under magnetic field changes of 0–2 T and 0–5 T.](image2)
loss. On the other hand, the introduction of C atoms can drive TC relatively high.

Conclusions

appropriately.

pounds by adjusting the concentrations of Ce and C atoms decrease in TC, and RCP

strengthened, resulting in an enhancement of RC.

determine that Ce and C atoms properly. The present study suggests that the La1-xCeFe11.5Si1.5C compounds may be promising candidates as high-performance magnetic refrigerants for practical applications in corresponding temperature range.

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References


