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Simultaneous enhancements of Curie temperature and magnetocaloric effects in the $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds

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ABSTRACT

The effects of introducing Ce and C atoms on the Curie temperature (T_C), the magnetic entropy change (ΔS_M) and the hysteresis loss have been investigated in the $NaZn_{13}$-type $LaFe_{11.5}Si_{1.5}$ compound. Partial replacement of La with Ce leads to a decrease in T_C and an increase in ΔS_M; however, the introduction of interstitial C atoms can adjust T_C to high temperature. The itinerant-electron metamagnetic transition is weakened after carbonization, which results in a reduction of both the hysteresis loss and magnetocaloric effect (MCE). The maximum value of ΔS_M for $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.2}$ is found to be -28 J/kg K at $T_C=207$ K with an effective refrigeration capacity of 420 J/kg for a field change from 0 to 5 T. Our study reveals that the enhancements of both T_C and MCEs can be achieved simultaneously in the $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds by adjusting the concentrations of Ce and C atoms appropriately.

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 magnetic entropy change (ΔS_M) and/or adiabatic temperature change (ΔT_{ad}). Recently magnetocaloric materials with first-order phase transition, such as $Gd_5(Si_xGe_{1-x})_4$, $LaFe_{13-x}Si_x$, MnAs, $MnFe(P_{1-x}As_x)$, Heusler alloys, etc., have attracted much attention due to their giant MCEs and ΔT_{ad} [4–8]. Among these materials, the cubic $NaZn_{13}$-type $LaFe_{13-x}Si_x$-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 $LaFe_{13-x}Si_x$ compounds. It was found that partial replacement of La with Ce, Pr, and Nd in the $LaFe_{13-x}Si_x$ compounds can enhance MCE remarkably but also lead to a reduction of the Curie temperature (T_C) and an increase of hysteresis 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 hysteresis loss is also depressed strongly due to the weakening of the IEM transition. However, the improvement of both T_C and hysteresis 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 $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds.

2. Experimental details

The samples of $La_{1-x}Ce_xFe_{11.5}Si_{1.5}$ ($x=0$, 0.1, and 0.2) and $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_y$ ($y=0.2$, 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 $K\alpha$ 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 $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds at room temperature. The refinement

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reveals that all the compounds crystallize in a single phase with cubic $NaZn_{13}$-type structure except the sample of $y=0.4$, in which a minor α-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 $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ 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 $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.4}$ exhibit an obvious thermal hysteresis, indicating the presence of a thermal-induced first-order magnetic transition around T_C. 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 $LaFe_{11.5}Si_{1.5}$ to 6 K for $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}$, suggesting that the partial substitution of Ce for La enhances the first-order IEM transition around T_C. 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 T_C for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ is defined as the minimum in each dM/dTT curve and the values are given in Table 1. It is revealed that the partial substitution of Ce for La lowers T_C, while the introduction of interstitial C atoms enhances T_C. Fig. 2(b) presents T_C as a function of the lattice parameter for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$. It is well known that the Curie temperature is mainly determined by the Fe–Fe, R–Fe, and R–R interactions in the Fe-rich rare-earth (R) iron compounds. Generally, the Fe–Fe exchange is the strongest, while the R–R 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 shorter 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 $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.4}$. Therefore, the change in T_C for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ mainly results from the contraction or expansion of lattice volume caused by the substitution of Ce atoms and the insertion of C atoms.

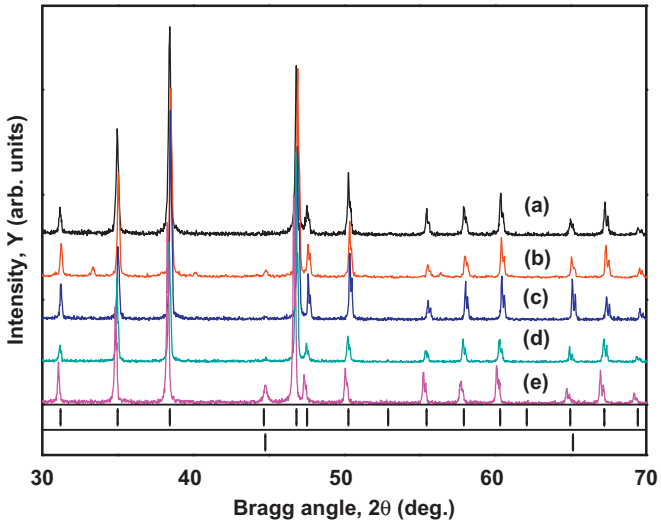

Fig. 1. Observed (dots) and calculated intensities (line drawn through the data points) of the fully refined powder diffraction patterns of (a) $LaFe_{11.5}Si_{1.5}$, (b) $La_{0.9}Ce_{0.1}Fe_{11.5}Si_{1.5}$, (c) $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}$, (d) $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.2}$, and (e) $La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.4}$. The Bragg peak positions for the La(Fe, Si)$_{13}$ (1:13) and α-Fe phases are shown from top to bottom below the XRD patterns.

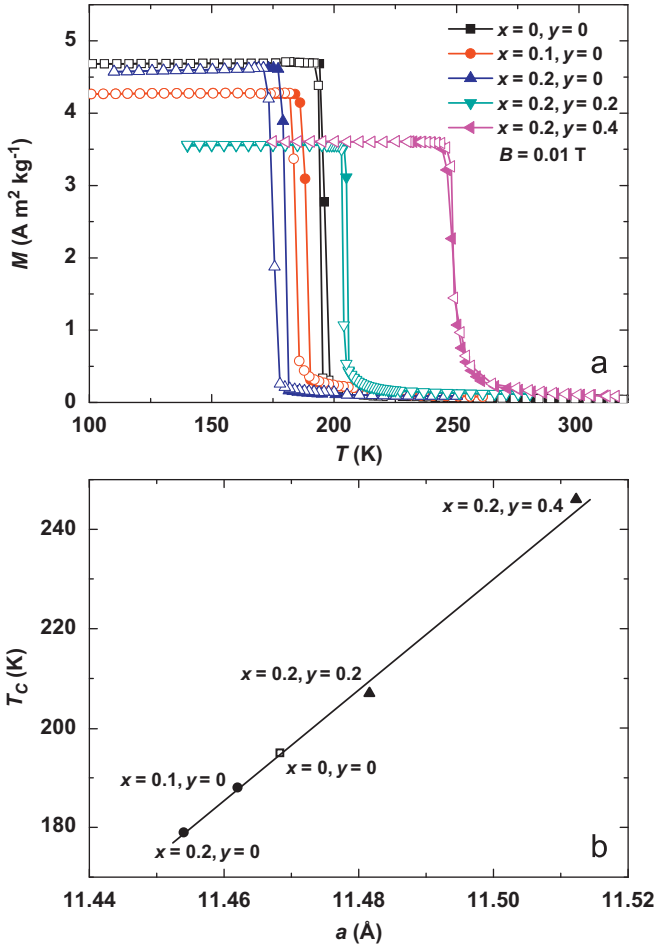

Fig. 2. (a) Temperature dependence of the magnetization measured during heating (filled symbols) and cooling (open symbols) cycles under a magnetic field of 0.01 T, and (b) Curie temperature T_C as a function of lattice parameter a for $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds.

Table 1
Lattice parameter a, Curie temperature T_C, magnetic entropy change $|\Delta S_M|$, effective refrigerant capacity RC_{eff}, and effective relative cooling power RCP_{eff} for the $La_{1-x}Ce_xFe_{11.5}Si_{1.5}C_y$ compounds.

Compounds	a (Å)	T_C (K)	$\|\Delta S_M\|$ (0–2 T) (J/kg K)	$\|\Delta S_M\|$ (0–5 T) (J/kg K)	Hysteresis loss (J/kg)	RC_{eff} (0–5 T) (J/kg)	RCP_{eff} (0–5 T) (J/kg)
$LaFe_{11.5}Si_{1.5}$	11.4683(5)	195	19.7	23.7	22	385	438
$La_{0.9}Ce_{0.1}Fe_{11.5}Si_{1.5}$	11.4619(8)	188	22.7	26.6	99	379	430
$La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}$	11.4539(4)	179	26.7	30.4	158	244	310
$La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.2}$	11.4816(7)	207	24.6	28.0	30	420	494
$La_{0.8}Ce_{0.2}Fe_{11.5}Si_{1.5}C_{0.4}$	11.5123(1)	246	7.6	13.5	0	330	426