Optimization of La(Fe,Co)$_{13-x}$Si$_x$ based compounds for magnetic refrigeration

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Abstract

The effect of Co on the magnetic, structural and magnetocaloric properties of the LaFe$_{11.7-x}$Co$_x$Si$_{1.3}$ ($x = 0$, 0.3, 0.4, 0.5, 0.6) and LaFe$_{11.2-x}$Co$_{0.7+x}$Si$_{1.1}$ ($x = 0$, 0.1, 0.2) compounds was investigated by x-ray diffraction and magnetic measurements. For LaFe$_{11.7-x}$Co$_x$Si$_{1.3}$ series, the Curie temperature T_C increases with increasing Co content. By varying x up to 0.6, the T_C of LaFe$_{11.7-x}$Co$_x$Si$_{1.3}$ alloys increases from 190 to 265 K and the peak of the isothermal entropy change $-\Delta S_{max}$ decreases from 28 to 15 J kg^{-1} K^{-1} under 5 T. Meanwhile, with Co concentration increasing from 0 to 0.2 in LaFe$_{11.2-x}$Co$_{0.7+x}$Si$_{1.1}$ formula, T_C passes from 270 to 294 K and $-\Delta S_{max}$ decreases from 16.5 to 13.5 J kg^{-1} K^{-1} under 5 T. Besides, for magnetic refrigeration systems using the Ericsson cycle, the entropy change must remain constant over the refrigeration range. So, we selected some alloys based on LaFe$_{11.7-x}$Co$_x$Si$_{1.3}$ ($x = 0.4$, 0.5, 0.6) and LaFe$_{11.2-x}$Co$_{0.7+x}$Si$_{1.1}$ ($x = 0.1$ and 0.2) compounds in order to form a composite material working in the 240–300 K temperature range. The optimal mass ratios of the constituents versus magnetic field were calculated. The obtained entropy change of the composite remains approximately constant within the temperature range 240–300 K.

1. Introduction

Based on the magnetocaloric effect (MCE), magnetic refrigeration is an emerging technology that has a potentially smaller environmental impact and higher energy efficiency than traditional cooling. The MCE is defined as the heating or cooling of magnetic materials due to the application or removal of a magnetic field. So, the compression and relaxation of fluids in traditional refrigerators are replaced by the magnetization and demagnetization of magnetocaloric materials in magnetic systems. Therefore, magnetic cooling technology presents many advantages such as high efficiency, small volume and ecological cleanliness. Recently, much interest has been focused on magnetocaloric studies, aiming to identify a

potential magnetic refrigerant. The first-order magnetic transition materials are attractive for magnetic refrigerants, because they exhibit a large MCE. In 1997, a giant MCE was discovered in $Gd_5Si_2Ge_2$ which is due to a simultaneous magnetic and crystallographic first-order transition [1]. In this compound, the isothermal entropy change is found to be about twice as high as that obtained in gadolinium. Since the discovery of the giant magnetocaloric effect in $Gd_5Si_2Ge_2$, some materials with a giant magnetocaloric effect, such as $MnFeP_{0.45}As_{0.55}$ [2], $MnAs_{1-x}Sb_x$ [3] and $La(Fe_xSi_{1-x})_{13}$ [4], have been reported. Besides, effort is needed to develop new materials with interesting MCE or to improve and optimize the magnetocaloric properties of the existing compounds.

The $La(Fe_xSi_{1-x})_{13}$ compounds, when stabilized in the cubic $NaZn_{13}$-type structure with $0.81 \leqslant x \leqslant 0.9$, have a ferromagnetic ground state [5]. In the paramagnetic state near the Curie temperature, these compounds exhibit an itinerant-electron metamagnetic transition (IEM), i.e. a field-induced first-order magnetic transition. This transition causes a large magnetocaloric effect in $La(Fe_xSi_{1-x})_{13}$ close to 200 K. Aiming to change T_C, many papers have reported on the influence of some transition-metal and rare-earth element substitutions for Fe and La, respectively, in various $La(Fe_xSi_{1-x})_{13}$ based alloys [6–11]. Besides, the effects of interstitial C and H atoms on the magnetic properties and magnetocaloric effect have also been studied [4, 12]. In order to increase the Curie temperature toward room temperature, Fujita *et al* [4] reported that hydrogen insertion into the $La(Fe_xSi_{1-x})_{13}$ lattice considerably increases T_C without affecting the magnetocaloric effect much. On the other hand, the chemical instability of hydrides remains a serious problem for practical application. $LaFe_{11.7}Si_{1.3}$ presents a giant magnetocaloric effect close to 190 K ($\sim$28 J kg^{-1} K^{-1} under 5 T), but on account of its low Curie temperature it cannot be used as a refrigerant near room temperature. So, in this paper we first report the effect of Co content on the structure, magnetism and magnetocaloric effect of $LaFe_{11.7-x}Co_xSi_{1.3}$ compounds. Then some $LaFe_{11.7-x}Co_xSi_{1.3}$ based compounds ($x = 0.4$, 0.5 and 0.6) were combined with $LaFe_{11.2-x}Co_{0.7+x}Si_{1.1}$ ($x = 0.1$ and 0.2) in order to form a composite material working in the 240–300 K temperature range.

2. Experimental details

Alloys with the nominal compositions $LaFe_{11.7-x}Co_xSi_{1.3}$ ($x = 0$, 0.3, 0.4, 0.5 and 0.6) and $LaFe_{11.2-x}Co_{0.7+x}Si_{1.1}$ ($x = 0$, 0.1 and 0.2) were prepared by the arc melting technique in a purified argon atmosphere. The samples were melted several times to ensure homogeneity. A heat treatment was performed at 1050 °C for 15 days after the samples had been sealed in an evacuated quartz tube. X-ray diffraction analysis was carried out on a Siemens D5000 x-ray powder diffractometer with Co Kα radiation. Magnetic measurements were realized using the BS2 magnetometer developed at the Néel Institute, Grenoble.

3. Results and discussion

The x-rays diffraction (XRD) results indicate that all the samples $LaFe_{11.7-x}Co_xSi_{1.3}$ ($x = 0$, 0.3, 0.4, 0.5 and 0.6) and $LaFe_{11.2-x}Co_{0.7+x}Si_{1.1}$ ($x = 0$, 0.1 and 0.2) are single phase with the cubic $NaZn_{13}$ structure with a small amount of α-Fe as a second phase. The presence of this second phase may be due to the fact that the heat treatment is not long enough to obtain the pure cubic $NaZn_{13}$-type structure phase. However, as will be shown hereafter, the presence of α-Fe does not affect the influence of cobalt on the magnetic and magnetocaloric properties. No obvious shift of XRD patterns was observed due to Co substitution, indicating that the lattice parameters remain relatively unchanged, as shown in table 1. The temperature dependence of the magnetization for $LaFe_{11.7-x}Co_xSi_{1.3}$ compounds in a magnetic field of 0.1 T is given

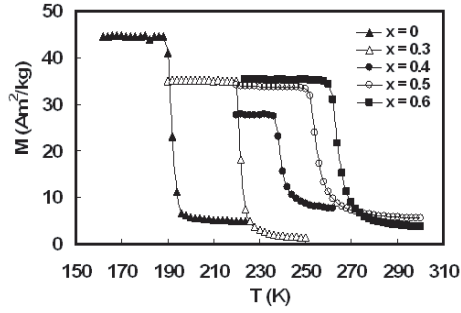**Figure 1.** Temperature dependence of magnetization for $LaFe_{11.7-x}Co_xSi_{1.3}$ alloys with $x = 0$, 0.3, 0.4, 0.5 and 0.6 measured in an applied field of 0.1 T.

Table 1. Lattice parameters, Curie temperature, maximum entropy change, density and relative cooling power of the compounds that were studied.

Compounds	a (Å)	T_C (K) ± 1 K	$\mu_0 H$ (T)	$-\Delta S_{max}$ (J kg^{-1} K^{-1})	ρ (g cm^{-3})	RCP(S) (J kg^{-1})
$LaFe_{11.7}Si_{1.3}$	11.4673	190	2/5	26.2/28	7.3041	157/564
$LaFe_{11.4}Co_{0.3}Si_{1.3}$	11.4690	223	2/5	20/24	7.3090	200/480
$LaFe_{11.3}Co_{0.4}Si_{1.3}$	11.4736	240	2/5	12.3/18.4	7.3029	148/405
$LaFe_{11.2}Co_{0.5}Si_{1.3}$	11.4752	253	2/5	9.2/15.5	7.3026	147/418
$LaFe_{11.1}Co_{0.6}Si_{1.3}$	11.4780	265	2/5	8.7/15	7.2999	148/420
$LaFe_{11.2}Co_{0.7}Si_{1.1}$	11.4763	270	2/5	9.4/16.5	7.3547	133/430
$LaFe_{11.1}Co_{0.8}Si_{1.1}$	11.4781	282	2/5	8/15	7.3540	160/360
$LaFe_{11}Co_{0.9}Si_{1.1}$	11.4773	294	2/5	7.4/13.5	7.3582	163/350

in figure 1. The ordering temperature of each compound was determined from these curves when (dM/dT) reached the peak point. One can observe that the Curie temperature increases almost linearly with the cobalt content at a rate of about 15 K/Co%. So, by changing the Co concentration x from 0 to 0.6, T_C passes from 190 to 265 K. The significant improvement in T_C is attributed to the strong Co–Fe exchange interaction. The Curie temperature of our master alloy $LaFe_{11.7}Si_{1.3}$ (190 K) is slightly higher than that reported in references [4] and [13], where T_C is 184 and 188 K, respectively. This is probably due to the presence of the α-Fe phase and, accordingly, the existence of higher Si content in the $NaZn_{13}$-type structure. Besides, a very sharp change in magnetization was observed for low Co content. However, by increasing the Co, one can observe that magnetization evolves more gradually around the Curie temperature, which would imply a reduction in thermal hysteresis.

The MCE is characterized by the isothermal entropy change ΔS and by the adiabatic temperature change ΔT_{ad} upon magnetic field variation, both quantities being a function of the initial temperature T and of the magnetic field variation. In this paper, the magnetocaloric effect was evaluated from the calculated isothermal entropy change, ΔS, in the vicinity of the ordering temperature, according to the Maxwell relation given by:

$$\Delta S(T, 0 \to H) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_{H'} dH'. \tag{1}$$

From magnetization measurements performed at constant temperature as a function of magnetic field H, the Maxwell relation can be approximated by the following expression:

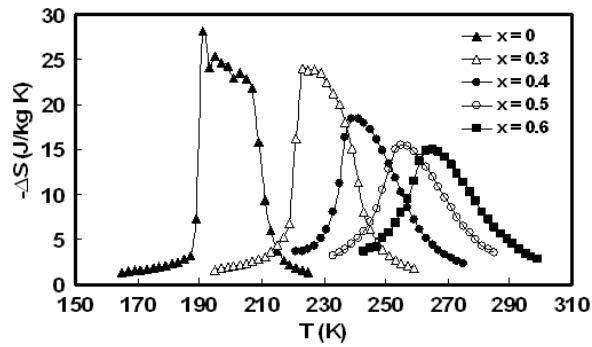$$\Delta S = \sum_i \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \Delta H_i \tag{2}$$

Figure 2. Temperature dependence of the entropy change of LaFe$_{11.7-x}$Co$_x$Si$_{1.3}$ upon an external field change of 5 T for $x = 0$, 0.3, 0.4, 0.5 and 0.6.
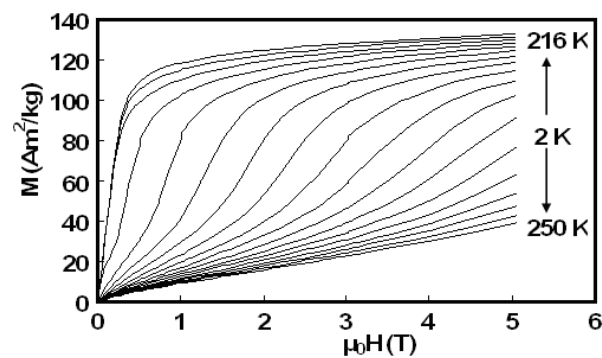

Figure 3. Magnetization isotherms of LaFe$_{11.4}$Co$_{0.3}$Si$_{1.3}$ between 216 and 250 K. The step is 2 K.

where M_{i+1} and M_i are the magnetization values measured in a field H at temperatures T_{i+1} and T_i, respectively. The accuracy of ΔS calculated using this technique is about 3–10% [14]. The entropy change ΔS as a function of temperature determined from the isothermal magnetization curves using equation (2) for the LaFe$_{11.7-x}$Co$_x$Si$_{1.3}$ compounds when the magnetic field changes from 0 to 5 T is plotted in figure 2. The isothermal entropy change is a maximum near the Curie temperature. For the parent LaFe$_{11.7}$Si$_{1.3}$ compound, this maximum reaches about 28 J kg^{-1} K^{-1} at 191 K. This value is in fair agreement with that of LaFe$_{11.7}$Si$_{1.3}$ reported in references [4] and [13], where the largest values of ΔS are 30 and 29 J kg^{-1} K^{-1} under 5 T, respectively. The maximum values of entropy change for all the samples close to their Curie temperature are 28 (191 K), 24 (223 K), 18.4 (240 K), 15.5 (255 K) and 15 J kg^{-1} K^{-1} (265 K) for $x = 0$, 0.3, 0.4, 0.5 and 0.6 respectively. The large magnetocaloric effect observed for low Co content is essentially attributed to the considerable variation in the magnetization near the Curie temperature (figure 1) because of the itinerant-electron metamagnetic (IEM) transition. The IEM transition is the field-induced first-order transition from the paramagnetic state to the ferromagnetic state (figure 3), which is related to the change in the band structure of 3d electrons by applying a magnetic field [4]. As shown in figure 2, the isothermal entropy change is reduced by about 50% with increasing Co concentration x from 0 to 0.6. This can be explained by the fact that the replacement of Fe by Co weakens the field-induced magnetic transition near the Curie temperature, as shown by the Arrott plots given in figure 4. Besides, the increase in Co content can completely eliminate the
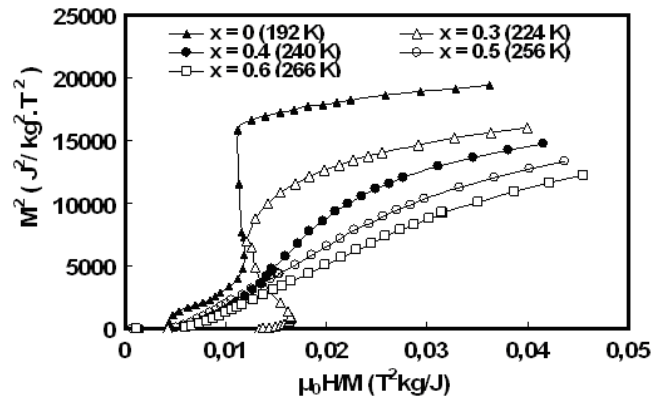
Figure 4. Arrott plots close to the transition temperature for LaFe$_{11.7-x}$Co$_x$Si$_{1.3}$ with $x = 0$, 0.3, 0.4, 0.5 and 0.6.
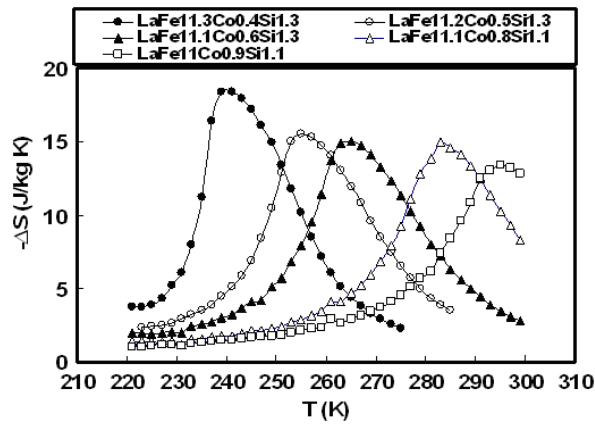

Figure 5. Temperature dependence of the entropy change of LaFe$_{11.7-x}$Co$_x$Si$_{1.3}$ ($x = 0.4$, 0.5, 0.6) and LaFe$_{11.2-x}$Co$_{0.7+x}$Si$_{1.1}$ ($x = 0.1$ and 0.2) based compounds upon an external field change of 5 T.

IEM transition and, accordingly, the magnetic transition becomes of second order, as reported in [10].

Ilyn *et al* [13] showed that the compound LaFe$_{11.2}$Co$_{0.7}$Si$_{1.1}$ exhibits a large MCE value in the vicinity of the first-order magnetostructural phase transition at 274 K, and that the isothermal magnetic entropy change induced by a magnetic field of 5 T reached in this material is 20.3 J kg^{-1} K^{-1}. The directly measured normalized adiabatic temperature change was 2.2 K T^{-1}. The Curie temperatures of LaFe$_{11.1}$Co$_{0.8}$Si$_{1.1}$ and LaFe$_{11}$Co$_{0.9}$Si$_{1.1}$ compounds with larger amounts of cobalt are still closer to room temperature, i.e. 282 and 294 K, respectively. The obtained $-\Delta S$ in both alloys close to their transition temperature are, respectively, 15 and 13.5 J kg^{-1} K^{-1} under 5 T. Thus, with all these compounds, one can cover a large temperature range with a relatively large magnetocaloric effect, as shown in figure 5. As will be developed hereafter, the compounds given in figure 5 are combined in order to form a composite material working in the 240–300 K temperature range. The lattice parameter, Curie temperature, $-\Delta S_{max}$, density ρ (g cm^{-3}) and the relative cooling power (RCP) of the presently studied compounds are listed in table 1.
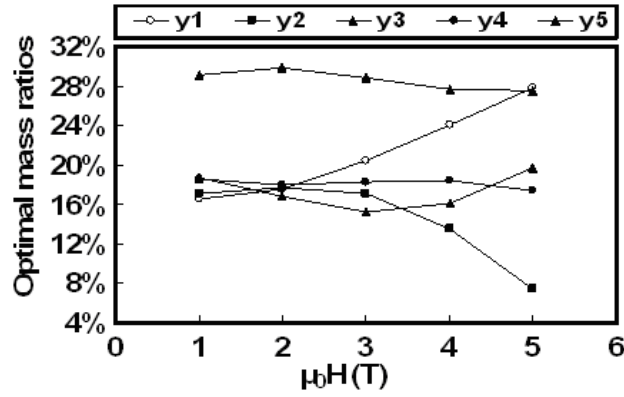
Figure 6. Influence of magnetic field change on optimal mass ratio y_i of LaFe$_{11.3}$Co$_{0.4}$Si$_{1.3}$ (y_1), LaFe$_{11.2}$Co$_{0.5}$Si$_{1.3}$ (y_2), LaFe$_{11.1}$Co$_{0.6}$Si$_{1.3}$ (y_3), LaFe$_{11.1}$Co$_{0.8}$Si$_{1.1}$ (y_4) and LaFe$_{11}$Co$_{0.9}$Si$_{1.1}$ (y_5) constituent materials.

For an ideal magnetic Ericsson refrigeration cycle, the isothermal entropy change as a function of temperature must be as constant as possible in the desired temperature range of refrigeration. In addition, the magnetocaloric effect cannot be achieved by a single material, and the active magnetic regenerative refrigerator (AMRR) cycle [15] needs relatively large temperature span. Therefore, these conditions can be realized by using a series of magnetocaloric compounds in order to form a composite refrigerant working in the temperature range limited by their Curie temperatures. So, in this paper we propose the materials given in figure 5 as constituent materials for refrigeration over the temperature range 240–300 K. Based on the isothermal entropy change of individual compounds, we have used a numerical method [16] to calculate the optimum mass ratios y_i of LaFe$_{11.3}$Co$_{0.4}$Si$_{1.3}$ (y_1), LaFe$_{11.2}$Co$_{0.5}$Si$_{1.3}$ (y_2), LaFe$_{11.1}$Co$_{0.6}$Si$_{1.3}$ (y_3), LaFe$_{11.1}$Co$_{0.8}$Si$_{1.1}$ (y_4) and LaFe$_{11}$Co$_{0.9}$Si$_{1.1}$ (y_5) refrigerant materials and then the resulting entropy change ΔS_{Com} of the composite. In general, for a refrigerant composed of n magnetic compounds in $y_1, y_2 \ldots y_n$ proportions having different Curie temperatures $T_C^1, T_C^2 \ldots T_C^n$ conveniently positioned in the required temperature range, the entropy change is given by:

$$\Delta S_{\text{Com}} = \sum_{i=1}^{n} y_i \Delta S_i. \tag{3}$$

For an ideal composite refrigerant, ΔS_{Com} must be constant, and the above equation becomes:

$$\sum_{j=1}^{n} y_j \left[\Delta S_j(T_c^{i+1}) - \Delta S_j(T_c^{i}) \right] = 0, \qquad \text{for } i = 1, 2 \ldots n - 1. \tag{4}$$

By combining this equation and the fact that $\sum_{j=1}^{n} y_j = 1$, one obtains the mass ratios $y_1, y_2 \ldots y_n$. Here ΔS_j is the entropy change of the jth magnetic material. Figure 6 shows the evolution of the optimal mass ratios (y_1, y_2, y_3, y_4 and y_5) as a function of applied magnetic field changes. One observes that the proportions vary with the applied field. As a consequence, the composition of the appropriate composite refrigerant depends on the value of magnetic field at which the device is to operate. The resulting ΔS_{Com} versus temperature and magnetic field is given in figure 7; the entropy change of the composite remains approximately constant within the temperature range 240–300 K. Note that the performance of the composite can be improved by increasing the number of constituents.
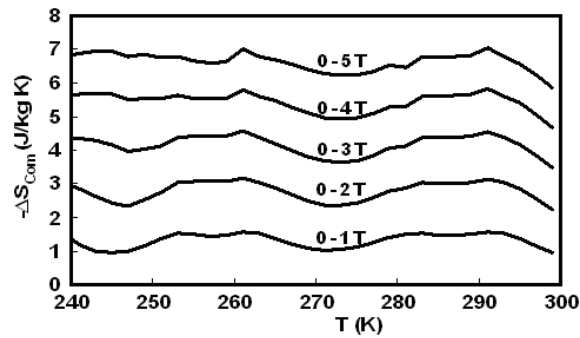
Figure 7. Temperature dependence of the isothermal entropy change for a composite material $LaFe_{11.3}Co_{0.4}Si_{1.3}/LaFe_{11.2}Co_{0.5}Si_{1.3}/LaFe_{11.1}Co_{0.6}Si_{1.3}/LaFe_{11.1}Co_{0.8}Si_{1.1}/LaFe_{11}Co_{0.9}Si_{1.1}/$ under different magnetic fields.

4. Conclusion

The magnetic and magnetocaloric properties of $LaFe_{11.7-x}Co_xSi_{1.3}$ alloys with $x = 0, 0.3, 0.4,$ 0.5 and 0.6 and $LaFe_{11.2-x}Co_{0.7+x}Si_{1.1}$ ($x = 0, 0.1, 0.2$) were investigated. The substitution of Co for Fe atoms in $LaFe_{11.7}Si_{1.3}$ formula leads to a linear increase in the Curie temperature from 190 to 265 K for x varying from 0 to 0.6. This increase is accompanied by a decrease in the isothermal entropy change. Under 5 T, the maximum entropy change decreases from 28 to 15 J kg^{-1} K^{-1} when the Co content x increases from 0 to 0.6. This reduction in the magnetocaloric properties is essentially due to the fact that the presence of Co in $LaFe_{11.7}Si_{1.3}$ weakens the itinerant-electron metamagnetic transition. Besides, we have combined the $LaFe_{11.3}Co_{0.4}Si_{1.3}$, $LaFe_{11.2}Co_{0.5}Si_{1.3}$, $LaFe_{11.1}Co_{0.6}Si_{1.3}$, $LaFe_{11.1}Co_{0.8}Si_{1.1}$ and $LaFe_{11}Co_{0.9}Si_{1.1}$ compounds in order to form a composite refrigerant working in the 240–300 K temperature range. The calculated optimal mass ratios depend on the external magnetic field, and the isothermal entropy change of the composite remains approximately constant within the temperature range 240–300 K. The results indicate that these materials can be good candidates for magnetic systems using the Ericsson cycle.

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