Phase relation of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds annealed at different high-temperature and the magnetic property of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds

XIANG CHEN[†], YUNGUI CHEN^{*} and YONGBAI TANG

School of Materials Science and Engineering, Sichuan University, Chengdu 610 065, PR China

[†]Department of Physics and Electronic Information Engineering, Neijiang Teachers College, Neijiang 641 002, PR China

MS received 23 February 2011; revised 18 May 2011

Abstract. $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds are annealed at different high temperatures from 1323 to 1623 K. The powder X-ray diffraction patterns show that large amount of NaZn_{13} -type phase begins to be observed in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound after being annealed at 1423 K for 5 h. In the temperature range from 1423 to 1523 K, the α -Fe and LaFeSi phases rapidly decrease to form 1:13 phase. LaFeSi phase is rarely observed in the XRD pattern in the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound annealed at 1523 K (5 h). With annealing temperature increasing to 1573 K and 1673 K, La_5Si_3 phase is detected, and there is a certain amount of LaFeSi phase when the annealing temperature is 1673 K. The amount of impurity phases in the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound annealed by the two-stage annealing consisting of high temperature (>1523 K) and 1523 K is larger than that of the single stage annealing at 1523 K under the same time. According to the results of different high-temperature annealing, $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ ($0.1 \leq x \leq 0.8$) compounds are annealed at 1523 K (5 h). The main phase is NaZn_{13} -type phase, and the impurity phase is a small amount of α -Fe in $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds. With increase in Co content from $x = 0.1$ to 0.8, the Curie temperature T_C , goes up from 207 to 285 K. The introduction of Co element weakens the itinerant electron metamagnetic transition, and also results in the change of magnetic transition type from first to second order at about $x = 0.5$. The magnetic entropy change decreases from 19.94 to 4.57 J/kg K with increasing Co concentration at a low magnetic field of 0–2 T. But the magnetic hysteresis loss around T_C reduces remarkably from 26.2 J/kg for $x = 0.1$ to 0 J/kg for $x = 0.8$.

Keywords. $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound; high-temperature and short-time annealing; hysteresis; large magnetocaloric effect.

1. Introduction

Magnetic refrigeration has several advantages, such as energy efficiency and environmental safety, and is of interest as an alternative cooling technology (Pecharsky and Gschneidner 2006; Tishin 2007). Although the magnetic refrigeration is a quiet mature technology in ultra-low temperature field, it has not been achieved at room temperature. For the magnetic refrigerants of room temperature, magnetic refrigerants working with giant magnetocaloric effect (GMCE) and wide range of temperature covering room temperature is one of the crucial factors. First-order transition materials, such as $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$, $\text{MnFeP}_{1-x}\text{As}_x$, $\text{MnAs}_{1-x}\text{Sb}_x$, $\text{LaFe}_{13-x}\text{Si}_x$, have magnetoelastic coupling or magnetovolume coupling characteristic, they show giant magnetocaloric effect (GMCE) (Fujita *et al* 1999, 2003; Hu *et al* 2001, 2003; Hermann *et al* 2004; Wada and Tanabe 2001; Fujieda *et al* 2002; Mira *et al* 2003). Compared with other giant magnetocaloric effect compounds, $\text{LaFe}_{13-x}\text{Si}_x$ compounds have some advantages, such as the lower price

of starting material. Despite the fact that $\text{LaFe}_{13-x}\text{Si}_x$ compounds' Curie temperatures are around 200 K (Hu *et al* 2001, 2003; Fujieda *et al* 2002; Liu *et al* 2004; Mandal *et al* 2005; Zhu *et al* 2005; Balli *et al* 2007; Zou *et al* 2007), it can be said that they cannot directly be used as the magnetic refrigerant working at room temperature. This problem can be solved by partly substituting Fe by Co in $\text{LaFe}_{13-x}\text{Si}_x$ compounds, which is a simple and effective method to adjust T_C to $\text{La}(\text{Fe},\text{Si})_{13}$ compound at room temperature. It was reported that the T_C of $\text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1}$, $\text{LaFe}_{11}\text{Co}_{0.8}\text{Si}_{1.2}$, and $\text{La}(\text{Fe}_{0.94}\text{Co}_{0.06})_{11.4}\text{Si}_{1.6}$ are 274 K, 290 K and 280 K, respectively. The maximum magnetic entropy change of these compounds is 20.3 J/kg K, 13.5 J/kg K and 11.6 J/kg K under a magnetic field of 0–5 T, 0–7 T and 0–5 T, respectively (Hu *et al* 2002; Liu and Altounian 2003; Shen *et al* 2007). From the angle of phase transition, the NaZn_{13} -type structure (hereinafter 1:13 phase) in $\text{LaFe}_{13-x}\text{Si}_x$ compounds is hard to be obtained directly from common solidification process due to the intrinsic incompleteness of a peritectic reaction: $\gamma\text{-Fe} + \text{L} \rightarrow \text{La}(\text{Fe},\text{Si})_{13}(\tau_{1a})$, which often results in the mixed phases of $\alpha\text{-Fe} + \text{La}(\text{Fe},\text{Si})_{13}(\tau_{1a}) + \text{LaFeSi}(\tau_4)$ (Raghavan 2001). As-cast sample of $\text{LaFe}_{13-x}\text{Si}_x$ almost has no 1:13 phase in low Si ratio. Although there are melt-spun

*Author for correspondence (ygchen60@yahoo.com.cn)

or rapid quenching/short-time annealing to prepare 1:13 phase, most of the researchers used the arc-melting/long time annealing and quenching in medium. Long time annealing obviously wastes a large amount of time and energy and limits the application of this material in room temperature magnetic refrigeration. Therefore, it is very important to analyse the formation of 1:13 phase in this compound and improve the preparation process of $\text{La}(\text{Fe},\text{Si})_{13}$ compounds.

In this paper, we have studied the effect of different high-temperature and short-time annealing from 1323 K for 5 hours (hereinafter h) to 1673 K (0.5 h) on the phase relation of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds. According to optimum annealing temperature, $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ ($0.1 \leq x \leq 0.8$) compounds were annealed at 1523 K (5 h). The phase relation, Curie temperature, hysteresis of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds are investigated. Because magnetic field of 0–5 T is difficult to reach for magnetic refrigerator of AMR-type with permanent magnets, magnetocaloric effects of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds were studied under a magnetic field of 0–2 T.

2. Experimental

Approximately 10 g of polycrystalline $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.75$ and 0.8) buttons were fabricated by conventional arc melting in a high purity argon atmosphere using high purity (La: 99.4 wt.%, Fe: 99.9 wt.%,

Si: 99.9999 wt.% and Co: 99.9 wt.%) elements, the compounds were re-melted five times to achieve a homogeneous composition. The as-cast compounds were annealed in a molybdenum wire furnace of 3×10^{-3} Pa vacuum, followed by furnace cooling down to room temperature. The phase purity and crystal structures were determined by powder X-ray diffraction (XRD) using Cu (K_α) radiation (Dandong DX-2600). Magnetic measurements were performed using a vibrating-sample magnetometer (VSM, Lakeshore 7410). The Curie temperatures (T_C) were determined from the maxima of dM/dT of the M – T curves and were measured in an applied magnetic field of $H = 0.02$ T. The magnetic entropy changes $\Delta S_M(T, H)$ were calculated from isothermal magnetization curves (M – H curves) in the vicinity of the Curie temperature using the thermodynamic Maxwell relation (Hashimoto *et al* 1981).

3. Results and discussion

Figure 1 shows the XRD patterns of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound after being annealed at 1223 K (5 h), 1373 K (5 h), 1423 K (5 h), 1473 K (5 h), 1523 K (5 h), 1573 K (4 h), 1623 K (2 h) and 1673 K (0.5 h), and the as-cast, respectively. By analysing and indexing the X-ray diffraction patterns of samples, one can find that the as-cast $\text{LaFe}_{11.6}\text{Si}_{1.4}$ alloy mainly consists of α -Fe and LaFeSi phases, and a small amount of 1:13 phase is observed in as-cast compound. XRD pattern of the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound annealed at 1223 K (5 h) is

Figure 1. XRD patterns of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds after being annealed at different high temperatures.

almost same as that of the as-cast compound. This indicates that 1223 K (5 h) as annealing temperature is too low to form the 1:13 phase, or the speed of 1:13 phase is very low. Thus the 1:13 phase can be obtained only when the as-cast $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds are annealed at higher temperature. It is well known that higher the temperature is, the faster the speed of diffusion of atoms is during the reaction of high temperature and solid phase diffusion. By comparing the XRD patterns of the compounds annealed at 1323 K, 1373 K and 1423 K, respectively the amount of 1:13 phase in the compound annealed at 1423 K is obviously much more than that of other two compounds annealed at 1323 K (5 h) and 1373 K (5 h). It indicates that 1423 K is one of the critical temperatures for forming 1:13 phase. The speed of phase transforming to form 1:13 phase is slow when annealing is lower than 1423 K. With the increase of temperature from 1423 K to 1523 K, the LaFeSi phase in the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds reduces in turn. When the annealing temperature reaches 1523 K, the LaFeSi phase is rarely observed in the XRD pattern. Although the $\alpha\text{-Fe}$ always existed in the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds, the amount is very small at 1523 K. So, 1523 K is the second critical temperature for obtaining the 1:13 phase by high-temperature and short-time annealing. The XRD patterns have no diffraction peaks of LaFeSi phase in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds after being annealed at 1523 K. For further observing the effect of annealing temperature on the phase relation, the as-cast $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds were annealed at 1543 K (5 h), 1573 K (4 h), 1623 K (2 h) and 1673 K (0.5 h), respectively. When the annealing temperature increased to 1573 K and 1673 K, there is a new phase crystallized as La_5Si_3 phase whose main diffraction peak is

at $2\theta = 31.5^\circ$, and more amount of La_5Si_3 phase appears with higher annealing temperature. The LaFeSi phase appears in the XRD pattern of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds annealed at 1673 K (0.5 h) again. In addition, despite the fact that there is no diffraction peaks of LaFeSi phase in the sample after being annealed at 1543 K (5 h), the amount of $\alpha\text{-Fe}$ is more than that after being annealed at 1523 K (5 h). Thus, the most amount of 1:13 phase is obtained after being annealed at 1523 K in the temperature range from 1323 K to 1673 K under the same annealing time.

Figure 2 is the XRD pattern of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds annealed at 1523 K (5 h) and different two-stage processes, they are 1523 K (5 h) + 1623 K (1.5 h), 1523 K (5 h) + 1673 K (0.5 h), 1673 K (0.5 h) + 1523 K (4 h), 1623 K (1 h) + 1523 K (4 h) and 1573 K (1 h) + 1523 K (4 h), respectively. The result shows that the annealing processes of 1523 K (5 h) + 1623 K (1.5 h) and 1523 K (5 h) + 1673 K (0.5 h) bring forth the La_5Si_3 phase, and even there is a certain amount of LaFeSi phase in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds annealed at 1523 K (5 h) + 1673 K (0.5 h), which is not observed in the XRD patterns of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds annealed at 1523 K (5 h). For obtaining more 1:13 phase in the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound at the same time, the other two-stage processes consisting of high temperature annealing (higher than 1523 K) and 1523 K annealing were carried out based on the higher temperature which can provide the more diffused driving force of phase transition. But there are La_5Si_3 phase and a small amount of LaFeSi phase in the XRD patterns of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound annealed at 1673 K (0.5 h) + 1523 K (5 h). In addition, the peaks of La_5Si_3 phase in the XRD patterns of $\text{LaFe}_{11.6}\text{Si}_{1.4}$

Figure 2. XRD patterns of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds annealed by different two-stage processes.

Figure 3. XRD patterns of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds ($0.1 \leq x \leq 0.8$).

Figure 4. Details of XRD pattern around peaks (420) and (422) of NaZn_{13} -type phase for samples.

compound annealed at 1623 K (1 h) + 1523 K (4 h), and 1573 K (1 h) + 1523 K (4 h) almost are not observed, but the intensity ratio of α -Fe peaks are higher than that in the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound annealed at 1523 K (5 h). The

amount of impurity phases in the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound annealed by the two-stage annealing consisting of high temperature (higher than 1523 K) and 1523 K is larger than that of the single stage annealing at 1523 K at the same time.

Figure 5. Temperature dependent magnetization measured under 0.02 T on heating and cooling processes of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds ($0.1 \leq x \leq 0.8$).

According to the above result, the $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds were annealed at 1523 K (5 h) with $x = 0.1, 0.3, 0.5, 0.7, 0.75$ and 0.8 , respectively. Figure 3 shows the X-ray diffraction (XRD) patterns collected at room temperature. One can find that the samples consist of the main cubic 1:13 phase and a small amount of impurity phase of α -Fe. For $0.1 \leq x \leq 0.75$, the main diffraction peaks of 1:13 phase have obvious shift to high angle with increased content of Co, as shown in figure 4. This is a signature of lattice contraction. It attributes to the radius of Co ($1.67 \text{ \AA}$) which is smaller than that of Fe ($1.72 \text{ \AA}$). The values of lattice decrease from $11.4838(9)$ to $11.4685(6) \text{ \AA}$, with $x = 0.1$ and 0.75 , respectively. However, the lattice parameter increases substantially to about $11.4954(2) \text{ \AA}$ for $x = 0.8$. It indicates that the T_C of $\text{LaFe}_{10.8}\text{Co}_{0.8}\text{Si}_{1.4}$ compound is above experimental environment temperature, and it presents the ferromagnetic state, in which the lattice constant is larger than that of the paramagnetic state. But for $0.1 \leq x \leq 0.75$,

Figure 6. Curie temperature dependent the change of Co content of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds.

the compounds are in a paramagnetic state at room temperature, the lattice constants have large negative expansions phenomenon when the $\text{La}(\text{Fe},\text{Si})_{13}$ compounds occur, the change of magnetic state from ferromagnetic to paramagnetic near T_C .

The Curie temperature is mainly determined by the exchange interactions between the magnetic atoms. In $\text{La}(\text{Fe},\text{Si})_{13}$ compounds, La and Si are nonmagnetic, the Curie temperature is determined only by the Fe-Fe interactions. For $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds, both Fe and Co are magnetic atoms, the Curie temperature is determined by the Fe-Fe, Fe-Co and Co-Co interactions. The T_C is 1297 K of the LaCo_{13} ferromagnetic compound, which is much higher than that of $\text{La}(\text{Fe},\text{Si})_{13}$ compounds (Huang *et al* 1998). It indicates that Co-Co interactions are much stronger than those of the Fe-Fe ones in 1:13 phase. In addition, the Fe-Co interaction is much stronger than that of the Fe-Fe one. Figure 5 displays the temperature dependent magnetization measured under 0.02 T in heating processes for $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds. T_C is defined as the maximum of dM/dT . From table 1, one can find that T_C increases

Table 1. Crystal cell parameters, phase transition temperatures, maximum magnetic entropy changes, $\Delta S_{\max}(T, H)$, thermal hysteresis of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds ($x = 0.1, 0.3, 0.5, 0.7, 0.75$ and 0.8).

x	a ($\text{\AA}$)	T_C	$ \Delta S_{\max} $ (J/kg K)	Magnetic hysteresis (J/kg)
0.1	11.4838(9)	207	19.94	26.24
0.3	11.4743(6)	226	12.46	4.25
0.5	11.4740(1)	250	8.10	2.08
0.7	11.4700(3)	276	5.23	No
0.75	11.4685(6)	281	5.20	No
0.8	11.4954(2)	285	4.57	No

from 207 to 285 K along with the increase of Co content from $x = 0.1$ to 0.8. The increase of T_C in the Co-substituted compound of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ mainly comes from the Fe–Co and Co–Co interactions, which are much stronger than those of the Fe–Fe ones in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound. The T_C and Co contents almost show linear relation, as shown in figure 6. Properly replacing Fe with Co can adjust T_C to around room

temperature, which is essential for the application of room temperature magnetic refrigeration.

The isothermal magnetization curves measured at different temperatures in the vicinity of T_C under a field of 0–2 T are shown in figure 7 (a–f) for $x = 0.1, 0.3, 0.5, 0.7, 0.75$ and 0.8, respectively. The measurements were performed in field increasing process. In order to check whether the isothermal

Figure 7. Magnetization isotherms of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds measured under field of 0–2 T.

magnetization process involves magnetic hysteresis, one of $M-H$ curves was measured during up and down field near T_C . One can find that the $M-H$ curves below T_C exhibit a characteristic ferromagnetic behaviour for all samples. With increasing temperature above T_C , there is a field-induced itinerant-electron metamagnetic (IEM) transition from the paramagnetic state to the ferromagnetic state for $x = 0.1$ and 0.3 , characterized by a sharp change in the magnetization, and the transition disappears in the samples with higher Co content. T_C increases with increase in Co concentration due to the strong exchange interactions of Fe-Co and Co-Co bonds. But M vs H plots show decrease in magnetization value upon increasing Co concentration. This is probably a consequence of the magnetic moment of Co atom ($1.72 \mu_B$) being smaller than that of Fe atom ($2.22 \mu_B$), and the total magnetic moment will decrease with increasing Co concentration in $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds. Soft magnetic materials have low remanence and coercivity, the high magnetic permeability, and the easy magnetized and demagnetized etc characters. There is no remanence and coercivity at zero field for magnetic refrigerants materials with the first or second order magnetic phase transition. But the magnetic hysteresis has great influence on the cooling efficiency or capacity during the magnetic refrigeration cycle (Basso *et al* 2006; Sasso *et al* 2006). The magnetic hysteresis loss is defined as the enclosed area between the ascending and descending branches of magnetization curve. To some extent, the value of magnetic hysteresis is responsible for the first-order magnetic transition intensity. For $\text{LaFe}_{11.5}\text{Co}_{0.1}\text{Si}_{1.4}$ compound, a large magnetic hysteresis occurs, the value is 26.24 J/kg at 205 K [see figure 7(a)]. When the value of Co content reaches $x = 0.5$, the magnetic hysteresis reduces to 2.01 J/kg at 250 K [see figure 7(c)], the magnetic hysteresis is zero up to $x = 0.7$. It indicates that the field-induced first-order transition from paramagnetic to ferromagnetic state is notably weakened upon introducing Co. Figure 8 shows the compared Arrott plots for the samples. One can find that negative slope still remains for $x = 0.3$ as $x = 0.1$, but the value of negative slope becomes small for $x = 0.3$. The Arrott plots are almost in line for $x \geq 0.5$ at T_C . According to the $I-S$ model, negative slopes in Arrott plots curve often indicate a first order transition and the linear relation in Arrott plot above T_C implies that a second-order magnetic transition occurs. Thus there exists changes of magnetic transition type from first-order to second-order in $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds, the transition point being about $x = 0.5$.

Magnetic entropy change, $\Delta S_M(T, H)$ was calculated by using Maxwell relation based on the magnetization data. Figure 9 shows the $\Delta S_M(T, H)$ as functions of temperature and magnetic field for $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds. It is found that the maximum magnetic entropy change decreases with Co content. The compound of $\text{LaFe}_{11.5}\text{Co}_{0.1}\text{Si}_{1.4}$ has a maximum magnetic entropy change of 19.94 J/kg K near its T_C under a magnetic field of 2 T . While for the compound with $x = 0.8$, the maximum magnetic entropy change is only about 4.57 J/kg K . This difference in $\Delta S_M(T, H)$ is related to the different nature of the magnetic phase transi-

Figure 8. Arrott plots of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds.

Figure 9. Magnetic entropy change, $\Delta S_M(T, H)$ as functions of temperature of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ compounds ($x = 0.1, 0.3, 0.5, 0.7, 0.75$ and 0.8).

tion in the compounds. In addition, one can find that $\Delta S_M(T, H)$ peak gradually broadens to higher temperature with increasing magnetic field for $x = 0.1$ and 0.3 , especially $x = 0.1$, which is a result of the field-induced IEM transition from paramagnetic to ferromagnetic state at temperatures above T_C . But for the compound of $x \leq 0.5$, the $\Delta S_M(T, H)$ peak broadens symmetrically, which indicates a second-order phase transition. In other angles, the symmetrical $\Delta S_M(T, H)$ peak also shows the magnetic phase transition completely reversing in field and temperature. Thus,

the maximum of $\text{LaFe}_{10.8}\text{Co}_{0.8}\text{Si}_{1.4}$ is only 4.57 J/kg K under a field change of 0–2 T, but no magnetic hysteresis loss appears. It has a completely reversible MCE.

4. Conclusions

The phase relation of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compound annealed at different high temperature from 1323 K (5 h) to 1673 K (0.5 h) shows that 1423 K and 1523 K are critical temperature to obtain the 1:13 phase. Large amount of 1:13 phase begins to appear in the matrix phases in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds annealed at 1423 K (5 h). The LaFeSi phase is rarely observed in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ compounds annealed at 1523 K (5 h). The main phase is 1:13 phase and the impurity phase is α -Fe in $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ ($0.1 \leq x \leq 0.8$) compounds annealed at 1523 K (5 h). With the increase of Co content, the T_C shows linear increase, and there exists a change of transition type from first to second order, which leads to a sharper decrease of $\Delta S_M(T, H)$ and the magnetic hysteresis loss. The maximum entropy change, $\Delta S_M(T, H)$ decreases from 19.94 to 4.57 J/kg K under magnetic field change of 0–2 T, and the magnetic hysteresis decreases from 26.24 to 0 J/kg as Co content increases from 0.1 to 0.8. By Arrott plot and the isothermal magnetization curves, the critical point of x for changing transition type from first-order to second-order was found to be about $x = 0.5$.

Acknowledgements

The present work was supported by the Key Project of National Natural Science Foundation of China (grant number 50731007) and the National High Technology Research and Development Program of China (grant number 2007AA03Z440).

References

- Balli M, Fruchart D, Gignoux D, Rosca M and Miraglia S 2007 *J. Magn. Magn. Mater.* **313** 43
- Basso Vittorio, Sasso Carlo Paolo, Bertotti Giorgio and LoBue Martino 2006 *Int. J. Refrig.* **29** 1358
- Fujieda S, Fujita A and Fukamichi K 2002 *Appl. Phys. Lett.* **81** 1276
- Fujita A, Akamatsu Y and Fukamichi K 1999 *J. Appl. Phys.* **85** 4756
- Fujita A, Fujieda S, Hasegawa Y and Fukamichi K 2003 *Phys. Rev.* **B67** 104416
- Hashimoto T, Numasawa T, Shino M and Okada T 1981 *J. Cryog.* **21** 647
- Hermann R P, Tegus O, Bruck E, Buschow K H J, de Boer F R, Long G J and Grandjean F 2004 *Phys. Rev.* **B70** 214425
- Huang M Q, Wallace W E and McHenry M E 1998 *J. Appl. Phys.* **83** 6471
- Hu F X, Shen B G, Sun J R, Cheng Z H, Rao G H and Zhang X X 2001 *Appl. Phys. Lett.* **78** 3675
- Hu F X, Shen B-G, Sun J-R, Wang G-J and Cheng Z-H 2002 *Appl. Phys. Lett.* **80** 826
- Hu F X *et al* 2003 *J. Appl. Phys.* **93** 5503
- Liu X B and Altounian Z 2003 *J. Magn. Magn. Mater.* **264** 209
- Liu X B, Altounian Z and Tu G H 2004 *J. Phys. Condens. Matter* **16** 8043
- Mandal K, Gutfleisch O, Yan A, Handstein A and Muller K-H 2005 *J. Magn. Magn. Mater.* **290** 673
- Mira J *et al* 2003 *Phys. Rev. Lett.* **90** 097203
- Pecharsky Vitalij K and Gschneidner Jr Karl A 2006 *Int. J. Refrig.* **29** 1239
- Raghavan V 2001 *J. Phase Equilib.* **22** 158
- Sasso Carlo P, Basso Vittorio, LoBue Martino and Bertotti Giorgio 2006 *Physica* **B372** 9
- Shen J, Li Y-X, Gao B, Sun J-R and Shen B-G 2007 *J. Magn. Magn. Mater.* **310** 2823
- Tishin A M 2007 *J. Magn. Magn. Mater.* **316** 351
- Wada H and Tanabe Y 2001 *Appl. Phys. Lett.* **79** 3302
- Zhu Yaomin, Xie Kun, Song Xiaoping, Sun Zhanbo and Lv Weipeng 2005 *J. Alloys Compd.* **392** 20
- Zou J D, Shen B G and Sun J R 2007 *J. Phys. Condens. Matter.* **19** 196220