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Effect of Ca on the microstructure and magnetocaloric effects in the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds

H. Zhang[a,b,*], Y. Long[a], Q. Cao[b,c], M. Zou[b,c], K.A. Gschneidner Jr.[b,c], V.K. Pecharsky[b,c]

[a] School of Materials Science and Engineering, University of Science and Technology of Beijing, Beijing 100083, PR China
[b] The Ames Laboratory U.S. Department of Energy, Iowa State University, Ames, IA 50011-3020, USA
[c] Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011-2300, USA

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ABSTRACT

The effect of Ca on the microstructure and magnetocaloric effects has been investigated in the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ ($x = 0$, 0.1, 0.2 and 0.3) compounds. The introduction of Ca leads to the appearance of minor α-Fe and Ca-rich phases, which affects the actual compositions of the main phases for the Ca containing samples. With increasing the Ca concentration, the Curie temperature T_C increases from 183 to 208 K, and the maximum magnetic entropy changes $|\Delta S|$ at the respective T_C with a magnetic field change from 0 to 5 T are 21.3, 19.5, 16.9, and 11.2 J/kg K for $x = 0$, 0.1, 0.2, and 0.3, respectively. The nature of the magnetic transition changes from first-order to second-order with an increase in Ca concentration, which leads to a reduction of the hysteresis and a decrease of the magnetic entropy change. However, the relative cooling power for $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds remains comparable with or even larger than that of other magnetocaloric materials over a wide temperature range. The higher T_C and the smaller hysteresis in comparison with those of the parent compound suggest that the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds could be suitable candidates for magnetic refrigerants in the corresponding temperature range.

1. Introduction

Magnetic refrigeration has attracted considerable attention due to its various advantages in comparison with conventional vapor compression refrigeration, such as high efficiency, energy saving and reduced environmental concerns. For high performance magnetic refrigeration, materials with large magnetocaloric effect (MCE) have been extensively investigated [1–3]. It has been reported that $NaZn_{13}$-type $La(Fe_xSi_{1-x})_{13}$ compounds with $0.86 \leq x \leq 0.90$ show a large magnetic entropy change in the vicinity of their Curie temperatures, T_C, because of the itinerant electron metamagnetic (IEM) transition [4–7]. However, the Curie temperatures of these compounds are usually much lower than the room temperature, and therefore many studies have been carried out to enhance the T_C. It has been demonstrated that the Curie temperature of these compounds can be tuned to room temperature by substituting Co for Fe or by introducing the interstitial elements H, C and B into the lattice [8–13].

On the other hand, materials with a first-order transition often exhibit large thermal and magnetic hystereses, which may lower the efficiency of magnetic refrigeration [3,14–16]. Recent investigations revealed that partial substitutions of Ce, Pr or Nd for La in the $La(Fe_xSi_{1-x})_{13}$ compounds can give rise to a remarkable enhancement of MCE [17–19]. However, these alloying agents also increase the magnetic hysteresis and lower the Curie temperature [20]. Consequently, it is important to enhance T_C and to depress the thermal and magnetic hystereses in the magnetic refrigeration materials. Here, the effect of introducing Ca on the microstructure, hysteresis and magnetic entropy change of $LaFe_{11.5}Si_{1.5}$ has been studied in detail. This composition was chosen because the parent compound exhibits a large magnetic entropy change due to the first-order IEM transition.

2. Experimental

$La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ ($x = 0$, 0.1, 0.2 and 0.3) compounds were prepared in a purified Ar atmosphere by arc-melting of the stoichiometric mixtures of components weighed with the accuracy of 0.0001 g. The weight of each sample was 10–13 g. The La used was prepared by the Materials Preparation Center [21] of the Ames Laboratory and was 99.8+ at.% pure with respect to all other elements in the periodic table. The Fe, Si and Ca were purchased from commercial vendors and were 99.9 or better wt.% pure. Considering the volatility of Ca, ~50 wt.% excess Ca was added to compensate for the evaporation losses during the melting. Because of the reactivity of Ca the weighing and handling was carried out in an argon filled glove box. The Ca and

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* Corresponding author at: School of Materials Science and Engineering, University of Science and Technology of Beijing, Beijing 100083, PR China. Tel.: +86 10 62334807; fax: +86 10 82649485.
E-mail address: zhanghuxt@gmail.com (H. Zhang).

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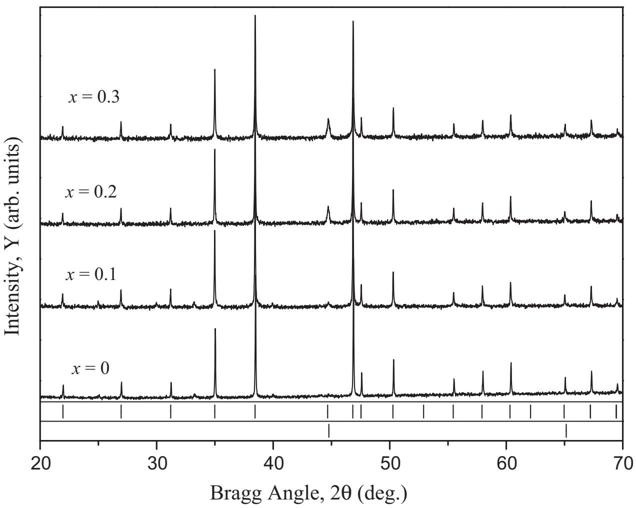

Fig. 1. The X-ray diffraction (XRD) patterns of $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds with $x = 0$, 0.1, 0.2, and 0.3. The Bragg peak positions for the $La(Fe, Si)_{13}$ (1:13) and α-Fe phases are shown respectively from top to bottom below the XRD patterns.

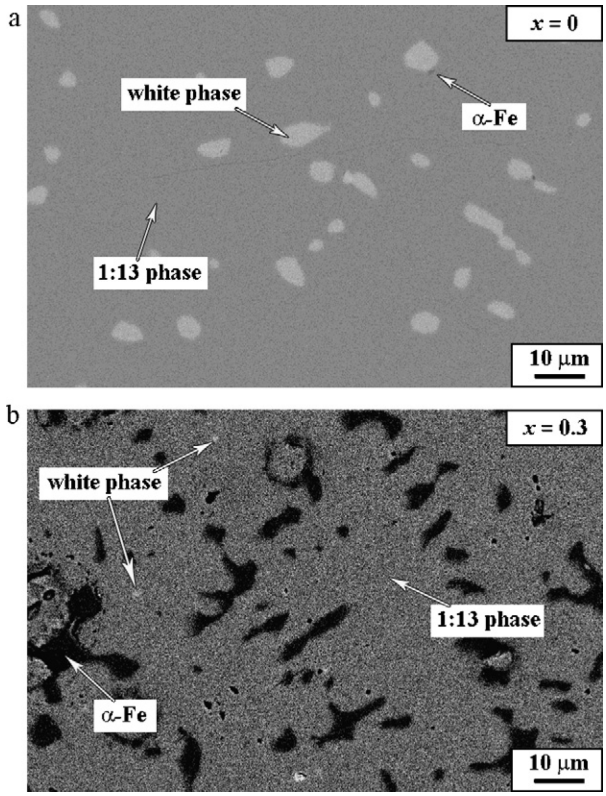

Fig. 2. SEM microstructure of $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds with $x = 0$ and 0.3.

other components were quickly transferred to the arc-melter to keep the exposure time of the Ca to air to a minimum. The ingots were re-melted several times with the button being turned over after each melting to achieve compositional homogeneity. The weight losses after the arc melting were less than 1 wt.%, and hence, the compositions of the compounds were accepted as weighed. To obtain a single phase sample with the $NaZn_{13}$-type structure, the compounds were heat treated in quartz tubes backfilled with helium at 1373 K for 2 weeks.

Powder X-ray diffraction (XRD) patterns were obtained on a PANalytical X'Pert PRO diffractometer using monochromatic Cu $K\alpha_1$ radiation. The phases present and the crystal lattice parameter of the matrix phase were determined by the Rietveld refinement method using LHPM-Rietica [22]. Microstructures were investigated by scanning electron microscopy (SEM) using a JEOL-6060 (20 kV) microscope. The magnetic measurements were carried out in a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-XL from Quantum Design Inc.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns of the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ ($x = 0$, 0.1, 0.2 and 0.3) samples measured at room temperature. They revealed that the samples are nearly single phase with the cubic $NaZn_{13}$-type (1:13) structure, except for the presence of minor amounts of the α-Fe phase and a "white" phase which was identified to be LaFeSi. The amount of α-Fe increases from 0 to 8.8, 11.6, and 13.8 vol.% while the amount of the white phase decreases from 2.1 to 1, 0.8 and 0.3 vol.% for $x = 0$, 0.1, 0.2 and 0.3, respectively (Table 1). The lattice parameters, calculated using the Rietveld refinement, decrease slightly from 11.4703 to 11.4693, 11.4693 and 11.4666 Å with increasing Ca content from 0 to 0.3, respectively (Table 1). These results show that the introduction of Ca leads to a reduction in the amount of the impurity LaFeSi phase and a lattice contraction.

In order to get a better insight on the microstructure of these compounds, a scanning electron microscopy (SEM) investigation was carried out, and the results for $LaFe_{11.5}Si_{1.5}$ and $La_{0.7}Ca_{0.3}Fe_{11.5}Si_{1.5}$ are shown for comparison in Fig. 2. The phase concentrations for the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ ($x = 0$, 0.1, 0.2 and 0.3) samples are listed in Table 1. With the introduction of Ca atoms, the amounts of α-Fe increased while the amounts of both the white phase and 1:13 phase decreased. It is found that essentially no Ca (~0.2 at.%) was found in the $NaZn_{13}$-type main phase based on the energy dispersive spectrometer (EDS) measurements for all of the studied samples. On the other hand, the white phase in the parent compound was detected to be tetragonal LaFeSi (1:1:1) phase, whereas ~15 at.% Ca was found in the 1:1:1 phase for the Ca containing compounds. This fact demonstrates clearly that Ca atoms do not substitute La atoms in the 1:13 phase as expected. On the contrary, Ca atoms enter into the 1:1:1 impurity phase in the compounds. Moreover, only a few grains of the 1:1:1 phase were observed in the Ca containing compounds. It must be pointed out that the weight loss was calculated to be about ~1.5 wt.% if all of the Ca atoms evaporate during the melting, but the observed weight loss was less than 1 wt.%. Therefore, most of the Ca atoms (about two-thirds) evaporated during the preparation.

The compositions of the $NaZn_{13}$-type main phase, determined by the EDS results, are shown in Table 1. In comparison with the parent compound, the actual compositions for all the Ca containing samples are different from the intended nominal compositions. This is caused by the following two reasons: (1) because of the loss of Ca, the decrease of La content leads to an increase of the (Fe, Si) concentrations in the main phase; (2) the presence of the α-

Table 1
The lattice parameter *a*, the concentrations of the three phases, and the actual compositions in the $NaZn_{13}$-type main phase for the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds with $x = 0$, 0.1, 0.2, and 0.3.

x	Lattice parameter (Å)	α-Fe (vol. %)	1:1:1 phase (vol. %)	1:13 phase (vol. %)	Actual composition of the matrix
0	11.4703(8)	0	2.1(3)	97.9(3)	$LaFe_{11.51}Si_{1.51}$
0.1	11.4693(2)	8.8(4)	1.0(1)	90.2(4)	$LaFe_{10.94}Si_{1.52}$
0.2	11.4693(2)	11.6(1)	0.8(2)	87.6(2)	$LaFe_{10.86}Si_{1.62}$
0.3	11.4666(2)	13.8(9)	0.3(1)	85.9(8)	$LaFe_{10.82}Si_{1.82}$

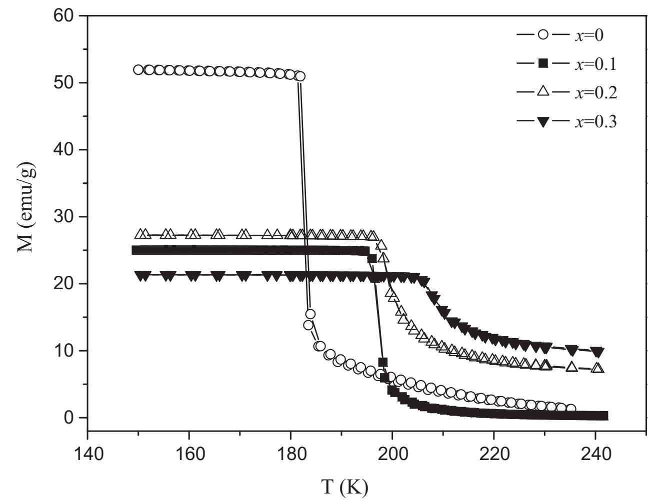

Fig. 3. Temperature dependencies of the magnetization of $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds with $x = 0$, 0.1, 0.2, and 0.3 measured in a magnetic field of 0.05 T.

Fe impurity phase indicates that the Si atoms substitute for the Fe in the 1:13 phase, and this results in the reduction of the lattice constants.

Fig. 3 shows the temperature dependencies of the magnetization for the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ ($x = 0$, 0.1, 0.2 and 0.3) compounds measured in a low magnetic field of 0.05 T. The Curie temperatures were defined as the minimum in dM/dT value and are listed in Table 2. As seen, the T_Cs are ~183 K, ~198 K, ~200 K and ~208 K, respectively, increasing continuously with the increase in Ca concentration. As is well known, the Curie temperatures of the rare-earth (R) transition–metal (T) compounds are determined by the T–T, R–T, and R–R interactions. In general, the Curie temperature of $LaFe_{13-x}Si_x$ is mainly determined by the Fe–Fe interaction because of the nonmagnetic character of La [23,24]. According to previous work [25,26], replacing Fe with Si in $LaFe_{13-x}Si_x$ can strengthen the hybridization of the Si *s* orbital and the Fe *d* orbital, which leads to an increase of T_C. Therefore, the increase of T_C with increasing Ca in $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds can be attributed to the variation of Fe and Si concentrations in the main phase [27–29]. In addition, because of the presence of the minor α-Fe phase, the magnetization of $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds above T_C with $x = 0.2$ and 0.3 is larger than that of the parent compound.

Fig. 4(a)–(d) show the magnetization isotherms of the four $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ samples measured both on increasing and decreasing field over a wide temperature range with different temperature steps. The hysteresis is defined as the enclosed area between the ascending and descending curves of magnetization and the maximum values of the hysteresis for the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ samples are listed in Table 2. An obvious magnetic hysteresis during the increase and decrease of field can be observed in the parent compound, which indicates the first-order nature of the magnetic transition. However, the maximum values of the hysteresis decrease from 11.8 to 2, 0, and 0 with increasing Ca concentration. It is clear that the magnetic transition changes from

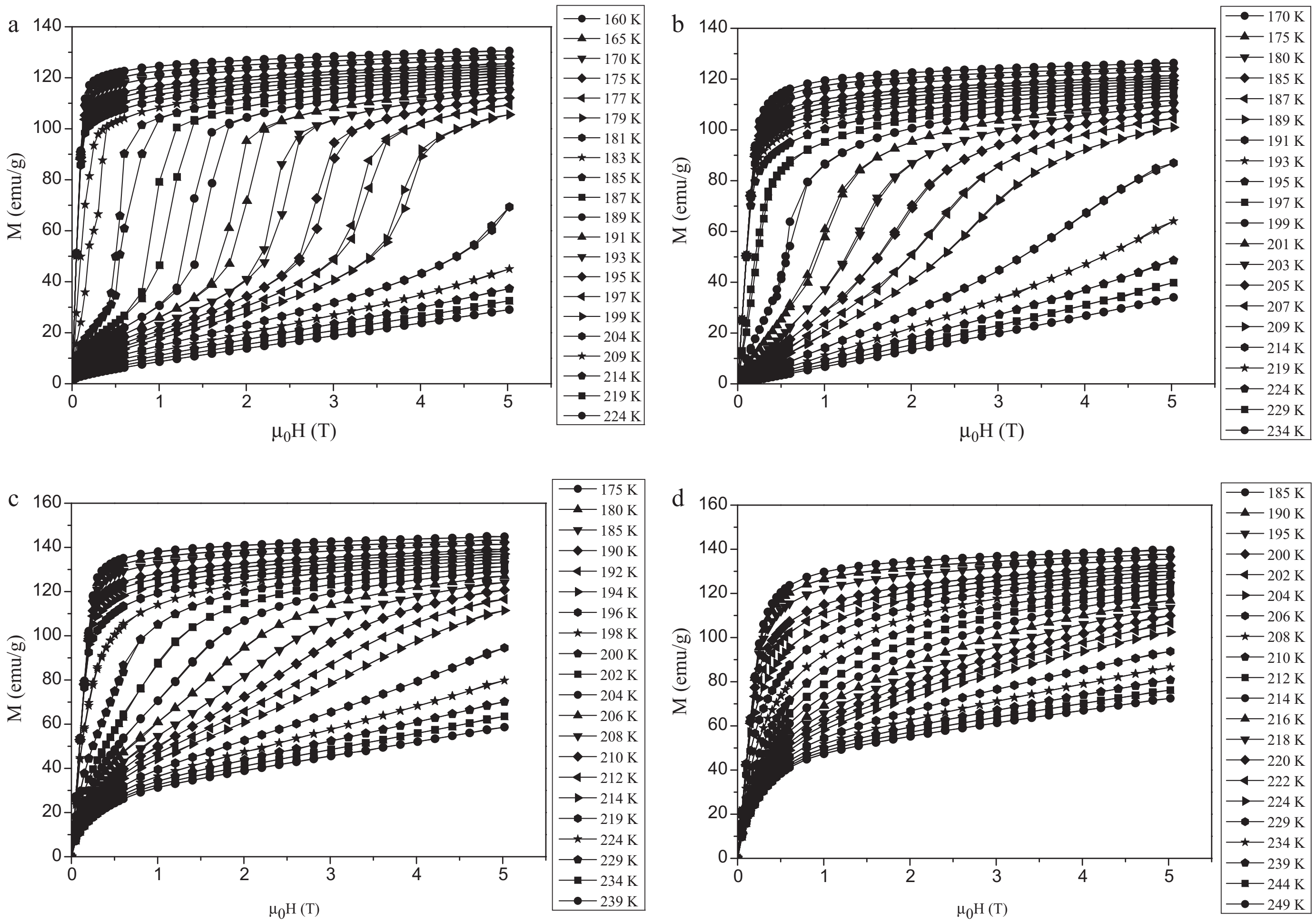

Fig. 4. Magnetization isotherms of $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds with $x =$ (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3. The temperature was changed in steps of 2 K in the vicinity of T_C, and it was in 5 K steps for temperature further away from T_C.

Table 2
The comparison of the main parameters of the magnetocaloric effects for the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds with $x = 0$, 0.1, 0.2, and 0.3.

x	T_C (K)	$\|\Delta S\|$ (0–2 T) (J/kg K)	$\|\Delta S\|$ (0–5 T) (J/kg K)	Hysteresis (J/kg)	RCP (0–5 T) (J/kg)
0	183	18.4	21.3	11.8	469
0.1	198	15.4	19.5	2	390
0.2	200	12.4	16.9	0	456
0.3	208	6.8	11.2	0	325

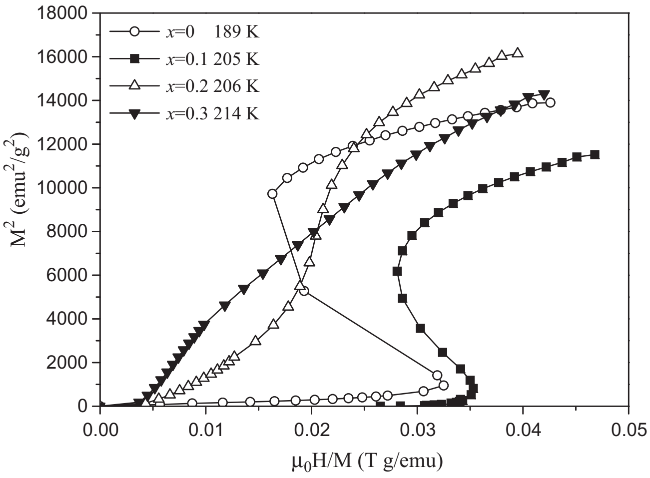

Fig. 5. Arrott plots of $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds with $x = 0$, 0.1, 0.2, and 0.3 constructed from $M(H)$ data collected at 6 K above T_C.

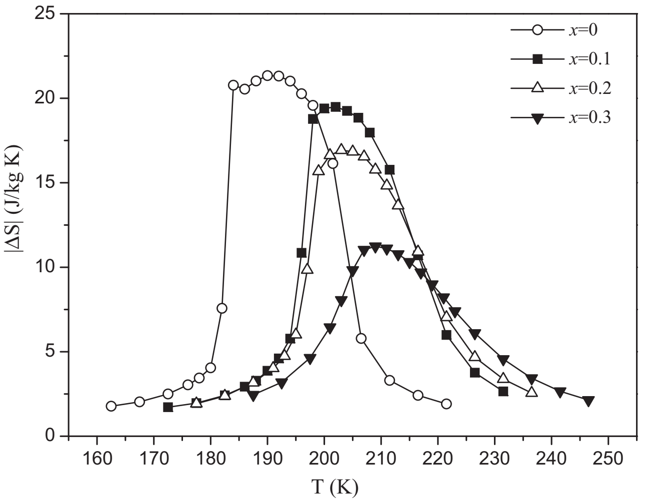

Fig. 6. Temperature dependence of the magnetic entropy change for $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds with $x = 0$, 0.1, 0.2, and 0.3 for a magnetic field change from 0 to 5 T.

first-order to second-order by the introduction of Ca, leading to the reduction of the hysteresis. As noted earlier, a small hysteresis is favorable for magnetic refrigeration applications.

The Arrott plots for the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ ($x = 0$, 0.1, 0.2 and 0.3) samples just above the respective T_C are displayed in Fig. 5. The negative slopes for the $x = 0$ and 0.1 and the inflection point for the $x = 0.2$ compounds in the Arrott plots indicate the occurrence of a first-order field-induced IEM transition. However, neither a negative slope nor an inflection point is found for $x = 0.3$ compound, suggesting that this compound exhibits a second-order magnetic transition.

The magnetic entropy change, ΔS, was calculated from the isothermal magnetization data by using the Maxwell thermodynamic relation $\Delta S(T, H) = \int_0^H (\partial M/\partial T)_H dH$. The accuracy of the calculated ΔS using this technique is 3–10% [30]. Fig. 6 displays the temperature dependence of the isothermal magnetic entropy changes $|\Delta S|$ for these samples for a magnetic field change from 0 to 5 T. Table 2 lists the maximum values of $|\Delta S|$ for magnetic field changes from 0 to 2 T and 0 to 5 T. It is noted that the magnetic entropy change obviously decreases from 21.3 for the parent compound to 11.2 J/kg K for $x = 0.3$ with a magnetic field change of 0–5 T. The low values of $|\Delta S|$ are mainly due to the fact that introduction of Ca gradually changes the first-order nature of the magnetic transition to second-order by affecting the actual compositions of the 1:13 phase, i.e. transforms these materials from a giant to a conventional magnetocaloric compound.

Relative cooling power (RCP), which is another useful parameter to quantify the magnetocaloric properties, was calculated from the following expression:

$$RCP = -\Delta S_m^{\max} \times \delta T_{FWHM}^{s} \quad (1)$$

where δT_{FWHM}^{S} is the full width at half maximum of ΔS–T curve [1,31].

It is found that values of RCP are reduced by the introduction of Ca (Table 2), but still remain comparable with or larger than those of some magnetetocaloric materials, such as $LaFe_{10.2}Si_{2.8}$ (455 J/kg at 195 K) [32], $Tb_5(Si_3Ge)$ (344 J/kg at 209.6 K) [33], $MnAs_{0.6}Sb_{0.4}$ (308 J/kg at 210 K) [34], and $Mn_{1.95}Cr_{0.05}Sb$ (147 J/kg at 198 K) [35]. It is noted that δT_{FWHM}^{S} expands from 22 K to 29 K, indicating that the working temperature range of $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds becomes broader with the amount of Ca increasing in these compounds.

4. Conclusions

The influence of Ca on the microstructure and magnetocaloric effects for $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ ($x = 0$, 0.1, 0.2 and 0.3) compounds has been investigated. Scanning electron microscopy analysis shows that Ca atoms do not substitute La atoms in the 1:13 phase as expected. On the contrary, Ca atoms enter into the 1:1:1 impurity phase in the compounds, which leads to a difference between the actual compositions and the intended nominal compositions. With increasing the Ca concentration, the Curie temperature increases while the lattice parameter a decreases due to the variation of Fe and Si concentrations in the main phase. The magnetic transition changes from first-order to second-order with an increase in Ca concentration, resulting in a reduction of the MCE and the hysteresis. The maximum values of $|\Delta S|$ for $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds decrease from 21.3 to 11.2 J/kg K for a field change of 0–5 T, but the relative cooling power of $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ remains comparable with other magnetocaloric materials and working temperature range becomes wider by the introduction of Ca. Consequently, in comparison with that of the parent compound, the smaller hystereses make the $La_{1-x}Ca_xFe_{11.5}Si_{1.5}$ compounds with $x > 0.1$ candidates for magnetic refrigerants at ∼200 K.

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