Effect of Ga Addition on Structure and Magnetic Properties of the $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Ga_x$ ($x = 0.1$, 0.2, 0.3) Alloys

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In the present work, the phase constitution and magnetic properties of the $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Ga_x$ (where $x = 0.1$, 0.2, 0.3) alloys, were investigated. It was revealed that increase of Ga content in the alloy composition causes the rise of lattice parameter of the La(Fe,Si)$_{13}$-type phase, which causes increase of the Curie temperature. However, the increase of Ga addition leads to decrease of magnetocaloric effect.

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1. Introduction

The magnetocaloric effect (MCE) is defined as a temperature change of magnetic material under the change of external magnetic field. It can be utilized in high efficiency and neutral for natural environment magnetic refrigerators, working in a vicinity of room temperature. MCE is studied by the measurements of adiabatic temperature changes $\Delta T_{\rm ad}$ or isothermal magnetic entropy changes $\Delta S_{\rm M}$ [1]. MCE is observed in all magnetic materials but these with the highest MCE are called the magnetocaloric materials (MCM). The most frequently studied MCM are pure Gd [2] and $Gd_5Ge_2Si_2$ alloy discovered in 1997 by Pecharsky and Gscheidner Jr. [3]. In Gd-based alloy giant magnetocaloric effect [3] is an effect of transition from ferro- to paramagnetic state accompanied by structural transition in a vicinity of the Curie point. Since 1997 investigations of magnetocaloric effect and magnetocaloric materials have been carried out intensively. These almost two decades of research have resulted in discovery of MCE in crystalline ($Gd_5Ge_2Si_2$ [3], MnAs [4], RE_2Fe_{17} [5]) and amorphous materials (Fe-based [6], Co-based [7] or Gd-based [8]). The La(Fe,Si)$_{13}$-type alloys based on cubic $NaZn_{13}$-type structure represent very attractive and relative cheap group of MCM. In these type of alloys, large magnetic entropy changes $\Delta S_{\rm M}$ in vicinity of room temperature were observed [9]. Excellent magnetocaloric properties are caused by metamagnetic transition and negative lattice expansion in this type of alloys [10]. The Curie temperature and magnetic entropy changes strongly depend on modification of chemical composition of the La(Fe,Si)$_{13}$-type alloys [8, 11–13]. Cubic structure is formed by long time annealing at 1323 K, which causes the change of microstructure from dendritic to fully homogenized [14]. In our previous studies [13], the influence of Si substitution by Ga on the increase of lattice parameter and the Curie temperature were investigated. However, in the present paper, our studies were expanded to larger amount of gallium addition and its influence on structure and magnetocaloric properties of the $LaFe_{11.14}Co_{0.66}Si_{1.1-x}Ga_x$ (where $x = 0.1$, 0.2, 0.3) alloys.

2. Sample preparation and experimental details

$LaFe_{11.14}Co_{0.66}Si_{1.2-x}Ga_x$ (where $x = 0.1$, 0.2, 0.3) alloys were prepared by arc-melting of high purity elements under the low pressure of Ar. In order to compensate lanthanum losses during arc-melting, 5 wt% excess of La was used. During arc-melting, the pure titanium was used as an O_2 getter. The ingot samples were remelted several times to achieve complete fusion and homogeneous composition. Subsequently samples were annealed in quartz tubes under the Ar atmosphere at 1323 K for 15 days. X-ray diffraction (XRD) data were collected using Bruker D8 Advance diffractometer with Cu K_α radiation equipped with LynxEye detector. X-ray diffractometry was supported by the Rietveld analysis using PowderCell 2.4 package [15]. The Curie temperature and magnetocaloric properties investigations were carried out using LakeShore 7400 rev A VSM vibrating sample magnetometer equipped with 2 T magnet over the temperature range of 180–390 K.

3. Results and discussion

The XRD patterns measured for the alloys of $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Ga_x$ are shown in Fig. 1. In all samples α-Fe and La(Fe,Si)$_{13}$-type phases were recognized. In case of samples with $x = 0.2$ and 0.3, additional low intensity peaks were present. They might be attributed to La-rich phase as was suggested in other work [16]. However, single peaks corresponding to this phase cannot clearly prove its presence. Peaks corresponding to the dominant La(Fe,Si)$_{13}$-type phase (Fig. 1) were described by the Miller indexes appropriate for specific crystallographic planes.

For all peaks corresponding to the La(Fe,Si)$_{13}$-type phase, small shift to lower angles with increase of Ga content was observed. This suggests change of lattice

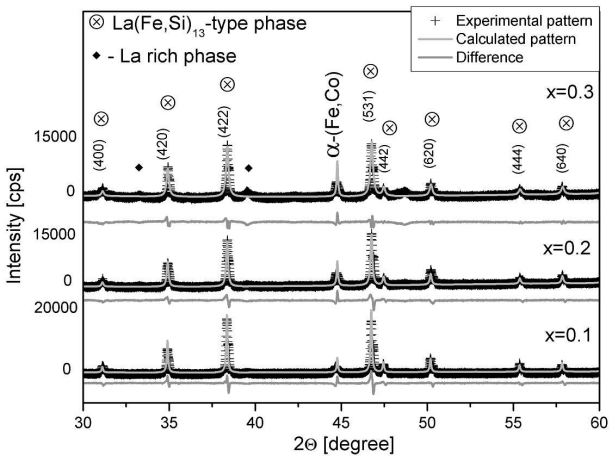

Fig. 1. X-ray diffraction pattern measured for all investigated samples.

parameter of this phase. The Rietveld analysis allowed to simulate the unit cell of the $La(Fe,Si)_{13}$-type phase and theoretical X-ray pattern and to compare it with experimental data. Additionally, lattice parameters and volume fractions of constituent phases were determined. All results of the Rietveld analysis were collected in Table I. It was shown that the lattice parameter of the $La(Fe,Si)_{13}$-type phase increases slightly with increasing Ga content. In the unit cell of the $La(Fe,Si)_{13}$-type phase the La atoms occupy 8a positions, while Fe atoms are located in two nonequivalent crystallographic positions: 8b (Fe(I)) and 96i (Fe(II)). It was shown in [17] that additional atoms such like Si, Al, and Co replace iron in the positions 96i. Furthermore, our previous studies [13] showed that Ga atoms added to $La(Fe,Si)_{13}$-type alloys occupy 96i positions. Moreover, the XRD investigations have shown the increase of volume fraction of α-Fe with increase of Ga content in the alloy. Deng et al. [18] have shown that small Ga addition caused improvement in formation of $La(Fe,Si)_{13}$-type phase formation and decrease of α-Fe content. Further increase of Ga addition caused increase of the α-Fe phase volume fraction.

TABLE I

Results of the Rietveld analysis carried out for all samples.

Recognized phases	Alloy $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Ga_x$					
	$x = 0.1$		$x = 0.2$		$x = 0.3$	
	Lattice const. a [Å]	Volume fraction [vol.%]	Lattice const. a [Å]	Volume fraction [vol.%]	Lattice const. a [Å]	Volume fraction [vol.%]
$La(Fe,Si)_{13}$-type	11.4802	92	11.4832	88	11.4866	86
α-Fe	2.86	8	2.86	12	2.86	14

As was previously stated, the XRD studies supported by the Rietveld analysis have shown an increase of lattice parameter with increase of Ga content in chemical composition of the alloy. According to [9] and our previous observations [11, 13, 19], one can assume that the changes of unit cell parameter have strong influence on the values of the Curie temperature. In order to determine the Curie point for the investigated alloys, temperature dependences of magnetization $M(T)$ were measured. The normalized $M(T)/M_{\max}$ are presented in Fig. 2. Calculations of first derivative $\mathrm{d}M/\mathrm{d}T$ revealed characteristic minimum, which corresponds to the Curie temperatures, $T_C = 271$, 275, and 285 K, respectively for $x = 0.1$, 0.2 and 0.3 alloys. The results confirm that the T_C of the $La(Fe,Si)_{13}$-type phase increases with increase of its lattice parameter of the $La(Fe,Si)_{13}$-type phase.

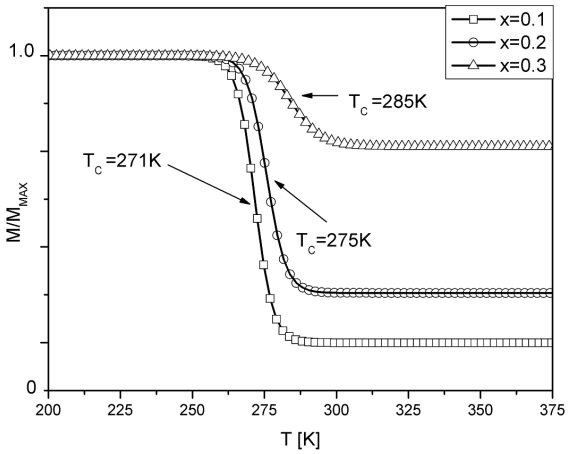

Fig. 2. Temperature dependences of magnetization measured for all investigated samples.

Continuous changes of magnetization around T_C suggest occurrence of the second order phase transition from ferro- to paramagnetic state for all investigated samples. Moreover, $M(T)$ studies confirmed increase of α-Fe content in the sample volume with increasing Ga content, which is expressed by different magnitudes of magnetization measured above 300 K (Fig. 2). In order to determine magnetic entropy changes ΔS_M, the magnetic field dependences of magnetization in wide range of temperature were measured. Based on these curves and using thermodynamic Maxwell relation [20] the magnetic entropy changes were calculated

$$\Delta S_M(T,H) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H \mathrm{d}H, \tag{1}$$

where T — temperature, $M(T,H)$ — magnetization, H — external magnetic field.

This relation was implemented into Mathematica 7.0 software based on algorithm proposed in [21]:

$$\Delta S_M\left(\frac{T_i+T_{i+1}}{2}\right) \approx \frac{1}{T_{i+1}-T_i}\left[\int_0^{B_{\max}} M(T_{i+1},B)\mathrm{d}B - \int_0^{B_{\max}} M(T_i,B)\mathrm{d}B\right], \tag{2}$$

where T_{i+1} and T_i are consecutive temperatures for which magnetization is measured.

The computed values of isothermal magnetic entropy changes $|\Delta S_{\mathrm{M}}|$ versus temperature for two maxima of the external magnetic field were shown in Fig. 3.

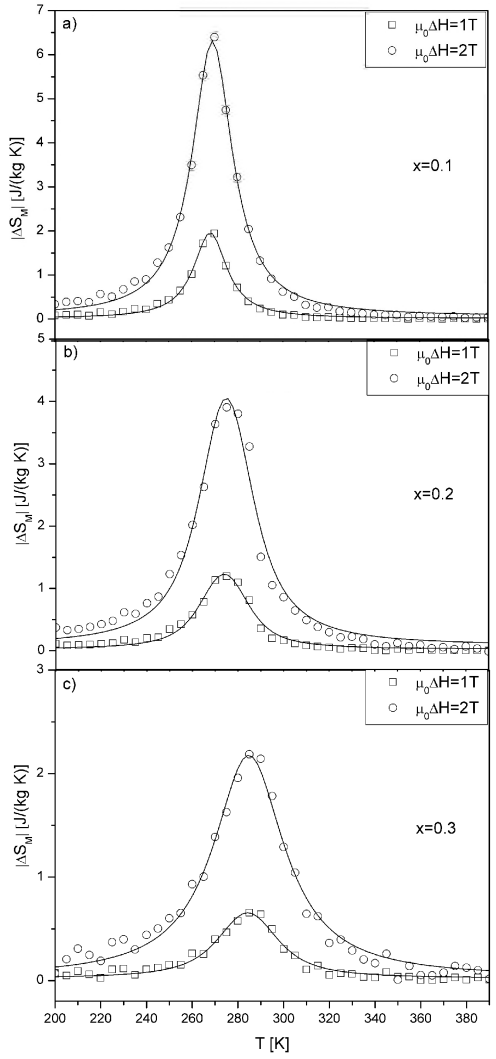

Fig. 3. The temperature dependences of magnetic entropy changes ΔS_{M} calculated for different changes of external magnetic field $\mu_0\Delta H$ for the $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Ga_x$ (where $x = 0.1$, 0.2, 0.3).

Characteristic maxima of $|\Delta S_{\mathrm{M}}|$ in vicinity of the Curie temperature were observed for all studied samples. For the change of external magnetic field up to $\mu_0\Delta H = 2$ T the magnetic entropy changes $|\Delta S_{\mathrm{M}}|$ reach 6.40, 3.91, and 2.19 J/(kg K), respectively for $x = 0.1$, 0.2 and 0.3 alloys. These values are about twice lower than those determined for $LaFe_{11.2}Co_{0.7}Si_{1.1}$ alloy reaching 13 J/(kg K) [17, 22]. Moreover, the increase of Ga addition in alloy chemical composition causes the decrease of $|\Delta S_{\mathrm{M}}|$. Similar effect was shown by Shen et al. [12] and in our previous studies concerning Al addition to this group of alloys [23]. It is expected that both Ga and Al additions cause weakening of itinerant electron metamagnetic transition, that is responsible for decrease of $|\Delta S_{\mathrm{M}}|$ [23]. However increase of α-Fe phase volume fraction with Ga content has also effect in decrease of $|\Delta S_{\mathrm{M}}|$. $|\Delta S_{\mathrm{M}}|$ vs. T curves have symmetrical shapes, that suggests occurrence of second order phase transition from ferro- to paramagnetic state in all investigated samples. Based on temperature dependences of magnetic entropy change, the relative cooling power (RCP) was calculated using relation [24]:

$$\mathrm{RCP} = -\Delta S_{\mathrm{M\,max}} \times \delta T_{\mathrm{FWHM}}, \tag{3}$$

where RCP — cooling power, ΔS_{Mmax} — maximum of magnetic entropy change, δT_{FWHM} — a full width at half maximum of temperature dependence of magnetic entropy change.

The calculated values of maximum magnetic entropy change $|\Delta S_{\mathrm{M}}|$ and cooling power (RCP) are collected in Table II. The $|\Delta S_{\mathrm{M}}|$ and RCP values decrease with increase of Ga content in the alloy composition. The highest RCP value was obtained for $LaFe_{11.14}Co_{0.66}Si_{1.1}Ga_{0.1}$ alloy and was much lower than this calculated for the $LaFe_{11.2}Co_{0.7}Si_{1.1-x}Ga_x$ (where $x = 0.03$, 0.05) alloys [18]. However, full width at half maximum (δT_{FWHM}) of temperature dependence of magnetic entropy change increases with increase of Ga content. The δT_{FWHM} parameter describes work range of alloy.

TABLE II

Values of magnetic entropy change $|\Delta S_{\mathrm{M}}|$, δT_{FWHM} and cooling power RCP for $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Ga_x$ (where $x = 0.1$, 0.2, 0.3).

Ga content x	$\mu_0\Delta H$ [T]	$\lvert\Delta S_{\mathrm{Mmax}}\rvert$ [J(kg K)$^{-1}$]	δT_{FWHM} [K]	RCP [J/kg]
0.1	1	1.94	16	31
	2	6.40	22	141
0.2	1	1.20	26	31
	2	3.91	29	113
0.3	1	0.66	32	21
	2	2.19	38	83

4. Conclusions

In the present work influence of Ga addition to the $LaFe_{11.14}Co_{0.66}Si_{1.2}$ base alloy on its structural and magnetocaloric properties was investigated. The phase structure for all investigated samples consists of major crystalline fcc La(Fe,Si)$_{13}$-type phase with a minority of α-Fe. The lattice parameter of the La(Fe,Si)$_{13}$-type phase and the Curie temperature increased with increase of Ga content in alloy composition. Moreover, increase of Ga addition causes decrease of the magnetic entropy change and cooling power. Decrease of these parameters is the result of weakening of itinerant electron metamagnetic phase transition from ferro- to paramagnetic state. However, increase of α-Fe phase volume fraction with Ga content has also effect in decrease of $|\Delta S_{\mathrm{M}}|$. Moreover, increase of Ga addition resulted in the increase of working range of investigated alloys.

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