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 $\Delta T_{ad}$ or isothermal magnetic entropy changes $\Delta S_M$ [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 magneto caloric materials (MCM). In these type of alloys, large magnetic structure represent very attractive and relatively cheap group of MCM. In these type of alloys, large magnetic entropy changes $\Delta S_M$ 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 $K_\alpha$ 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 180-300 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 $\alpha$-Fe and La(Fe,Si)$_{13}$-type phases were recognized. In case of samples with $x = 0.2$ and 0.3, additional peaks corresponding to this phase were present. 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...
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.

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 $M(T)/M_{\text{max}}$ are presented in Fig. 2. Calculations of first derivative $dM/dT$ 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.

TABLE I

<table>
<thead>
<tr>
<th>Recognized phases</th>
<th>$x = 0.1$</th>
<th>$x = 0.2$</th>
<th>$x = 0.3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(Fe,Si)$_{13}$-type</td>
<td>$T = 11.4802$</td>
<td>92</td>
<td>La(Fe,Si)$_{13}$-type</td>
</tr>
<tr>
<td>α-Fe</td>
<td>2.86</td>
<td>8</td>
<td>2.86</td>
</tr>
</tbody>
</table>

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

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 $\Delta S_M$, 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

$$\Delta S_M(T, H) = \int_0^\mu \frac{\partial M(T, H)}{\partial T} dH,$$

(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]:

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

(2)

where $T_{i+1}$ and $T_i$ are consecutive temperatures for which magnetization is measured.
The computed values of isothermal magnetic entropy changes $|\Delta S_M|$ versus temperature for two maxima of the external magnetic field were shown in Fig. 3.

Characteristics maxima of $|\Delta S_M|$ 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 $|\Delta S_M|$ reach 6.40, 3.91, and 2.19 J/(kg K), respectively for $x = 0.1, 0.2, 0.3$. 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 $|\Delta S_M|$. 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 $|\Delta S_M|$ [23]. However increase of $\alpha$-Fe phase volume fraction with Ga content has also effect in decrease of $|\Delta S_M|$. $|\Delta S_M|$ 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]:

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

(3)

where RCP — cooling power, $\Delta S_{M \text{max}}$ — maximum of magnetic entropy change, $\delta T_{\text{FWHM}}$ — a full width at half maximum of temperature dependence of magnetic entropy change.

The calculated values of maximum magnetic entropy change $|\Delta S_M|$ and cooling power (RCP) are collected in Table II. The $|\Delta S_M|$ 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 ($\delta T_{\text{FWHM}}$) of temperature dependence of magnetic entropy change increases with increase of Ga content. The $\delta T_{\text{FWHM}}$ parameter describes work range of alloy.

![Fig. 3. The temperature dependences of magnetic entropy changes $\Delta S_M$ 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 $x = 0.1, 0.2, 0.3$).](image-url)

**Table II**

| Ga content $x$ | $\mu_0\Delta H$ [T] | $|\Delta S_{M \text{max}}|$ [J/(kg K)$^{-1}$] | $\delta T_{\text{FWHM}}$ [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)$_{11.3}$-type phase with a minority of $\alpha$-Fe. The lattice parameter of the La(Fe, Si)$_{11.3}$-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 $\alpha$-Fe phase volume fraction with Ga content has also effect in decrease of $|\Delta S_M|$. Moreover, increase of Ga addition resulted in the increase of working range of investigated alloys.
References