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Influence of Al and Ga on Formation of the $La(Fe,Si)_{13}$-Type Phase in the $LaFe_{11.14}Co_{0.66}Si_{1.2-x}M_x$ (where $x = 0.1, 0.2, 0.3$; M=Al, Ga) Alloys

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In the present work the influence of Al and Ga on formation of $La(Fe,Si)_{13}$-type phase in magnetocaloric $LaFe_{11.14}Co_{0.66}Si_{1.2-x}M_x$ (where $x = 0.1, 0.2, 0.3$; M = Al, Ga) alloys subjected to annealing at 1323 K for 15 days was studied using the Mössbauer spectroscopy. For annealed samples, two crystalline phases were recognized: the dominant paramagnetic $La(Fe,Si)_{13}$-type phase, and minor fraction of ferromagnetic α-Fe(Co,Si). It was revealed that Al improved formation of 1:13 phase in contrast to Ga, which caused reduction of the ability of formation of the expected phase.

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1. Introduction

Conventional refrigeration technique is based on gas transformation of freon compounds, which are known to have negative influence on ozone layer. A more environment friendly and efficient cooling method is the magnetocaloric effect (MCE). This effect is described as a cooling or heating of a magnetic material in the external magnetic field. Idea of application of MCE in household appliances led to studies of soft magnetic materials. These investigations resulted in formulation of several experimental requirements for ideal magnetocaloric materials (MCMs). The most important of these rules are: large values of magnetic entropy change ΔS_M and adiabatic temperature change ΔT_{ad} [1]. Well known, natural magnetocaloric material is Gd, for which magnetic entropy change reaches 10.2 J/(kg K) under the change of external magnetic field up to 5 T [2]. More intensive studies of MCE have started since 1997 after discovery of the giant magnetocaloric effect (GMCE) at the vicinity of ambient temperature in $Gd_5Ge_2Si_2$ by Pecharsky and Gschneidner Jr. Magnetic entropy change of this alloy reaches 18.6 J/(kg K) under $\mu_0 \Delta H = 5$ T at the Curie temperature of 276 K [3]. High content of Gd, the high purity of constituent elements needed as well as inert atmosphere required during melting [4], generate high costs of processing of this type of alloys. Parallel to $Gd_5Ge_2Si_2$ alloy other MCMs were studied i.e. crystalline (MnAs [5], Ni–(Mn,Cu)–Ga [6]) and amorphous materials (Fe-based [7, 8], Co-based [9] or Gd-based [10]).

In the Fe-based group of MCMs, $La(Fe,Si)_{13}$-type alloys belong to the lowest cost group of magnetocaloric materials. Microstructure of these alloys in the as-cast state is dendritic, but long time annealing at 1323 K leads to formation of cubic $La(Fe,Si)_{13}$-type phase and homogeneity of microstructure [11]. This type of alloys reveals relatively high ΔS_M, which reaches even 31 J/(kg K) at the T_C of 185 K. The Curie temperature and the value of MCE are strongly dependent on the chemical composition and processing techniques [12, 13]. Such promising magnetocaloric properties are related to the magnetic phase transition in the crystalline pseudobinary $La(Fe,Si)_{13}$ cubic phase (1:13) [12]. Recent studies of this type of alloys are concentrated on the influence of alloying addition such as Ce, Co, and B on the formation of the $La(Fe,Si)_{13}$-type phase [14, 15]. In the present work influence of Al and Ga on the formation of the 1:13 phase in $LaFe_{11.14}Co_{0.66}Si_{1-x}M_x$ (where $x = 0.1$, 0.2, 0.3; M = Al, Ga) alloys was studied.

2. Sample preparation and experimental details

Two series of samples were obtained by arc-melting of high purity elements under inert gas atmosphere (Ar). Master alloys of the $LaFe_{11.14}Co_{0.66}Si_{1.2-x}M_x$ (where $x = 0.1$, 0.2, 0.3; M = Al, Ga) were prepared for stoichiometric composition corresponding to the formation $La(Fe,Si)_{13}$-type phase. In order to compensate loses of La during arc-melting, 5 wt% excess of La was used. Specimens were sealed in quartz tubes under low pressure of the Ar gas and subsequently annealed at 1323 K for 15 days. The Mössbauer spectra were measured at room temperature using Polon Mössbauer spectrometer with a ^{57}Co:Rh source of the activity of 50 mCi in transmission geometry and subsequently analyzed using WinNormos for Igor software [16]. The Mössbauer study was performed above the Curie temperature of the $La(Fe,Si)_{13}$-type phase. The Mössbauer spectra were analyzed using thin absorber approximation.

3. Results and discussion

Detailed XRD studies supported by the Rietveld analysis for all annealed samples were described in our previous studies [17, 18]. They revealed coexistence of two main crystalline phases: the dominant $La(Fe,Si)_{13}$-type

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and minority α-Fe(Co,Si) phase. XRD investigations also revealed an increase of lattice parameter with increase of Al or Ga in alloy composition. Volume fraction of La(Fe,Si)$_{13}$-type phase doped with Al increased with increasing content of this element in the alloy. In contrast to the effect of Al, the increase of Ga addition caused a decrease of volume content of La(Fe,Si)$_{13}$-type phase and an increase of the α-Fe(Co,Si) phase. The Fe atoms in La(Fe,Si)$_{13}$-type phase occupy two nonequivalent crystallographic positions: 8b (I) and 96i (II) in the unit cell of La(Fe,Si)$_{13}$-type phase. Fe-I atoms are located at the corners of cubic unit cell (8b), and Fe-II atoms occupy 96i positions around Fe-I. Relative intensities of lines corresponding to 8b and 96i positions were assumed as 1:12, respectively [19]. Furthermore, Fe-atoms occupying 96i positions are replaced by Si, Al, Co, or Ga atoms, which leads to local structural disorder in La(Fe,Si)$_{13}$-type unit cell. As a result of this effect distributions of hyperfine parameters such as: the isomeric shift IS, quadrupole splitting QS and magnetic hyperfine field B_{hf} appear [20]. Therefore, broadening of the Mössbauer line corresponding to La(Fe,Si)$_{13}$-type phase is expected. Due to a higher filling of 96i positions by Fe atoms in the unit cell of the La(Fe,Si)$_{13}$-type phase one should expect a greater probability of occupancy of this positions by substitution atoms [21]. The Mössbauer spectra measured with the best fits for all the samples doped with Al are shown in Fig. 1.

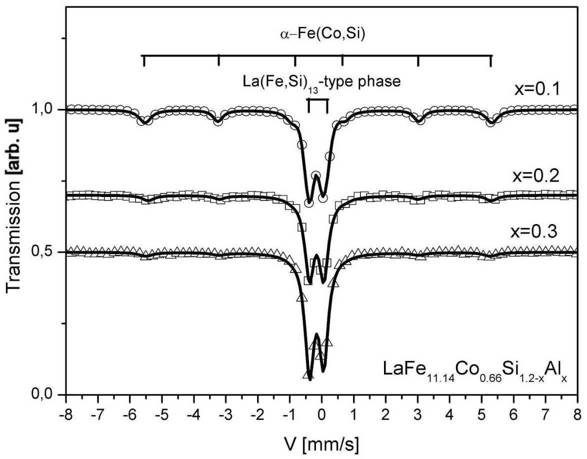

Fig. 1. Mössbauer spectra collected for $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Al_x$ (where x=0.1, 0.2, 0.3) alloys.

In the Mössbauer spectrum collected for the $LaFe_{11.14}Co_{0.66}Si_{1.1}Al_{0.1}$ alloy two components were identified. A sextet, typical for ferromagnetic ordering with hyperfine field B_{hf} of about 33 T confirms the presence of α-Fe(Co,Si) phase in the alloy. The second component — a doublet was attributed to the La(Fe,Si)$_{13}$-type phase, which has paramagnetic state at room temperature. The increase of Al content at the expense of Si atoms, led to a change in the Mössbauer spectrum. In the case of spectrum collected for $LaFe_{11.14}Co_{0.66}Si_{1.0}Al_{0.2}$ the analysis confirmed the presence of component lines that were attributed to the ferromagnetic α-Fe(Co,Si) and paramagnetic La(Fe,Si)$_{13}$-type phases. Furthermore, lower intensity of sextet line corresponding to the α-Fe(Co,Si) phase confirms reduction of its content in the volume of the sample. The analysis of the Mössbauer spectrum collected for sample with the highest Al content, revealed similar results as in earlier cases, where the occurrence of two phases ferromagnetic α-Fe(Co,Si) and paramagnetic La(Fe,Si)$_{13}$-type phase was shown. The hyperfine parameters determined corresponding to particular component lines that fit the experimental spectra were collected in Table I for all the investigated samples.

TABLE I

Hyperfine parameters of Mössbauer spectra components determined for all the investigated samples doped with Al.

Al content x	Phase	B_{hf} [T]	IS [mm/s]	QS [mm/s]	Vol. content [wt.%]
0.1	La(Fe,Si)$_{13}$-type	–	−0.06 ±0.01	0.45 ±0.01	76
	$\alpha-$Fe(Co,Si)	33.25 ±0.01	−0.11 ±0.01	0.04 ±0.01	24
0.2	La(Fe,Si)$_{13}$-type	–	−0.08 ±0.01	0.45 ±0.01	88
	α-Fe(Co,Si)	33.18 ±0.03	−0.08 ±0.01	0.04 ±0.01	12
0.3	La(Fe,Si)$_{13}$-type	–	−0.06 ±0.01	0.45 ±0.01	93
	α-Fe(Co,Si)	33.13 ±0.06	−0.11 ±0.01	−0.03 ±0.01	7

A decrease of the intensity of the sextet corresponding to α-Fe(Co,Si) with the increase of Al content, confirms conclusion that Al addition improves formation of the La(Fe,Si)$_{13}$-type phase. The Mössbauer studies revealed paramagnetic state of the La(Fe,Si)$_{13}$-type phase at room temperature for all the investigated specimens, which shows that the Curie temperature of this phase is lower than room temperature. Detailed Curie temperature investigations were described in our previous works [17, 18].

The Mössbauer spectra measured with the best fits for all samples doped with Ga are shown in Fig. 2. For these samples, similarly to specimens doped with Al, two components of the Mössbauer spectra were identified as sextet and doublet lines. The sextet, with hyperfine field B_{hf} of 33 T, was recognized as a component which corresponds to the α-Fe(Co,Si) phase. The doublet was attributed to the La(Fe,Si)$_{13}$-type phase, which at room temperature has a paramagnetic state for all the contents of Ga addition. Quite different effect was observed with the change of volume content of constituent phases.

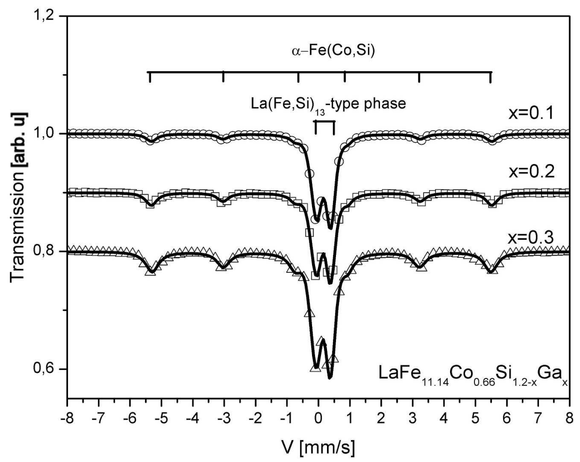

Fig. 2. Mössbauer spectra collected for $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Ga_x$ (where x = 0.1, 0.2, 0.3) alloys.

The increase of Ga addition in alloy composition led to a decrease of volume fraction of the expected $La(Fe,Si)_{13}$-type phase. An increase of intensity of the sextet line corresponding to α-Fe(Co,Si) with the increase of Ga content, may be caused by hampering of formation of $La(Fe,Si)_{13}$-type phase. Formation of $La(Fe,Si)_{13}$-type phase is realized by diffusion of constituent atoms in the solid state during annealing. Ga atom has larger ionic radius and mass than Si, so its movement forced by diffusion is slower. It causes a retardation of formation of $La(Fe,Si)_{13}$-type phase, which undergoes a peritectic transformation. Similar effect was studied by Chen et al., who investigated the influence of Co, Ce, and B on the formation of $La(Fe,Si)_{13}$-type phase [14, 15]. Results of analysis of the Mössbauer spectra for samples doped with Ga are collected in Table II for all the investigated samples.

TABLE II

Hyperfine parameters of Mössbauer spectra components determined for all the investigated samples doped with Ga.

Ga content x	Phase	$B_{\rm hf}$ [T]	IS [mm/s]	QS [mm/s]	Vol. content [wt.%]
0.1	$La(Fe,Si)_{13}$-type	–	−0.06 ±0.01	0.45 ±0.01	85
	α-Fe(Co,Si)	33.23 ±0.01	−0.11 ±0.01	0.03 ±0.01	15
0.2	$La(Fe,Si)_{13}$-type	–	−0.08 ±0.01	0.45 ±0.01	74
	α-Fe(Co,Si)	33.23 ±0.02	−0.08 ±0.01	0.03 ±0.01	26
0.3	$La(Fe,Si)_{13}$ -type	–	−0.06 ±0.01	0.46 ±0.01	68
	α-Fe(Co,Si)	33.14 ±0.06	−0.11 ±0.01	−0.03 ±0.01	32

In the paper [22] the authors observed a decrease of α-Fe content after addition of Ga, but with no significant change. This observation is in contrast with the present results. Probably these differences are strongly dependent on the chemical composition.

4. Conclusions

It was shown that the Al and Ga additions to the $LaFe_{11.14}Co_{0.66}Si_{1.2}$-based alloy cause changes in the Mössbauer spectra. The Mössbauer studies confirmed that Al addition improves formation and stabilization of 1:13 phase. In the case of Ga addition, the Mössbauer studies revealed a decrease of ability to formation of 1:13 phase and the increase of α-Fe(Co,Si) phase content. Furthemore, the Mössbauer investigations allowed to determine magnetic state of $La(Fe,Si)_{13}$-type phase, which is paramagnetic at room temperature in all the measured samples.

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