

# The Influence of Alloy Admixture on Structure and Properties of $\text{La}(\text{Fe}, \text{Co}, \text{Si})_{13}$ -Type Phase

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In the present study, the influence of Al and Ga admixture on the lattice parameters and the Curie point  $T_C$  of the  $\text{La}(\text{Fe}, \text{Co}, \text{Si})_{13}$  compound was discussed. The measurements were carried out on ribbon samples of  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.2}$ ,  $\text{LaFe}_{11.0}\text{Co}_{0.8}(\text{Si}_{0.4}\text{Al}_{0.6})_{1.2}$  and  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.1}\text{Ga}_{0.1}$  alloys. The samples were subjected to annealing in the inert gas atmosphere at 1323 K for 24 h. The change of lattice parameters  $a$  with admixture of Al and Ga was determined from the X-ray diffraction analysis. Furthermore, changes of the Curie point with the alloy composition were observed.

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## 1. Introduction

Negative impact of the freon compounds on the natural environment was well recognized in the scientific literature. Harmless to the atmosphere devices using magnetocaloric effect are an intriguing alternative to the refrigerators using gas conversion processes [1, 2]. In such equipments the component containing material revealing magnetocaloric effect at specific temperature range plays the most important role. Among materials revealing magnetocaloric effect, those which except the second order transition from ferro- to paramagnetic state, experiencing the presence of structural rearrangement around  $T_C$  are of the great interest. Presence of both first- and second order phase transitions significantly improve the entropy change around  $T_C$  [3, 4]. The well known material that can be used in the refrigerant working around room temperature is  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  compound discovered in 1997 by Gschneidner and Pecharsky [5]. For this composition, the entropy change  $|\Delta S_M|$  measured around  $T_C$  of  $\approx 276$  K reaches  $18.5 \text{ J} (\text{kg K})^{-1}$  at the alteration of external magnetic field  $\mu\Delta H = 5$  T. However, large volume fraction of Gd and rigorous processing conditions do not allow to use this compound for commercial applications.

An interesting alternative much cheaper than the Gd containing alloys of promising magnetic properties are the  $\text{La}(\text{Fe}_{1-x}, \text{Si}_x)_{13}$ -type alloys. These materials are also intensively studied due to the possibility of tailoring their Curie temperature by appropriate doping. For this system, ferro- to paramagnetic phase transition around  $T_C$  is accompanied by the rearrangement of the lattice param-

eter of cubic  $\text{NaZn}_{13}$ -type structure (space group  $Fm\bar{3}c$ ) [6, 7]. The La atoms occupy  $8a$  sites in the unit cell of these phase, while two nonequivalent positions  $8b$  and  $96i$  are filled by Fe atoms [8]. All the admixture atoms (Co, Al, Si and Ga) statistically replace Fe positions in the  $96i$  sites [9, 10]. Model of the unit cell with indicated two nonequivalent Fe positions in the unit cell of the  $\text{NaZn}_{13}$ -type phase is shown in Fig. 1.

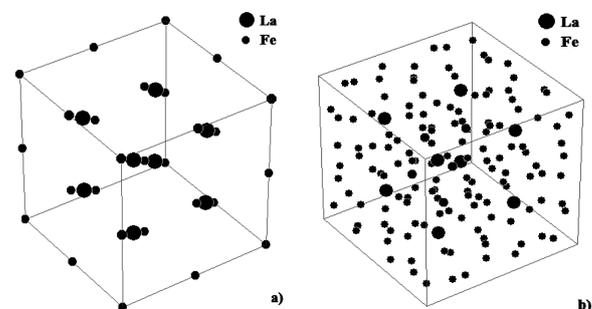


Fig. 1. Unit cell of the  $\text{LaFe}_{13}$ -type phase derived by PowderCell 2.4. software: (a) La atoms in  $8a$  and Fe in  $8b$  positions; (b) La atoms in  $8a$  and Fe in  $96i$  occupations.

Depending on the alloy composition, the  $|\Delta S_M|$  may reach up to  $30 \text{ J}/(\text{kg K})$  and the Curie point may vary from 195 K to 330 K [11–13]. Processing of base alloy by arc-melting of high purity constituent elements results in loss of elements (especially La) by evaporation, therefore an excess of La in the base alloy composition is used for compensation [14, 15]. Some attempts to modify the alloy composition by admixture of Al or Ga were carried out in [16, 17] and led to the change of the Curie temper-

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ature. Microstructure of these type of alloys is dendritic in as-cast state and after annealing is fully homogenized [18, 19]. In these papers [18, 19] the dependence of microstructure and magnetocaloric effect on annealing time of the  $\text{LaFe}_{11.0}\text{Co}_{0.8}(\text{Si}_{0.4}\text{Al}_{0.6})_{1.2}$  alloy obtained by different techniques, were studied. In the present work, the effect of Al and Ga admixture on the lattice parameter changes and  $T_C$  of the  $\text{La}(\text{Fe}, \text{Co}, \text{Si})_{13}$  compound were investigated.

## 2. Samples preparation and experimental methods

The ingot samples of  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.2}$ ,  $\text{LaFe}_{11.0}\text{Co}_{0.8}(\text{Si}_{0.4}\text{Al}_{0.6})_{1.2}$  and  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.1}\text{Ga}_{0.1}$  alloys were obtained by argon arc-melting of high purity constituent elements. The base alloys were prepared for stoichiometric composition corresponding to crystallization of single  $\text{La}(\text{Fe}, \text{Si})_{13}$  phase. Excess of 15 wt% of La was used for compensation of losses occurring during arc-melting. From the ingot samples, the ribbons were melt-spun under an Ar atmosphere with the linear wheel speed of  $\approx 35$  m/s. Subsequently, samples were sealed-off in quartz tubes under protective atmosphere and annealed at 1323 K for 24 h. X-ray diffraction patterns were measured using Bruker D8 Advance diffractometer with  $\text{Cu } K_\alpha$  radiation. The fitting of the experimental XRD data was performed using PowderCell 2.4 [20] software, that allowed to adjust the unit cell parameters for each alloy composition. Magnetic measurements were carried out using Magnetic Property Measuring System model MPMS-XL-5 (Quantum Design) equipped with 5 T superconducting magnet.

## 3. Results and discussion

The X-ray diffraction patterns measured for ribbon samples of all investigated alloy compositions are shown in Fig. 2. For all three alloys, the phase analysis revealed presence of two crystalline phases. The dominant  $\text{NaZn}_{13}$ -type cubic phase (space group  $Fm\bar{3}c$ ) reaches 90 vol.%, 86 vol.%, and 85 vol.%, respectively for  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.2}$ ,  $\text{LaFe}_{11.0}\text{Co}_{0.8}(\text{Si}_{0.4}\text{Al}_{0.6})_{1.2}$  and  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.1}\text{Ga}_{0.1}$  alloys. Calculated lattice constant  $a$  for the  $\text{NaZn}_{13}$ -type phase reaches 11.4979 Å for the  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.2}$ , 11.5049 Å for the  $\text{LaFe}_{11.0}\text{Co}_{0.8}(\text{Si}_{0.4}\text{Al}_{0.6})_{1.2}$  and 11.5138 Å for the  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.1}\text{Ga}_{0.1}$  alloy. The remaining crystalline phase for each alloy is the  $\alpha$ -Fe, for which the lattice constant  $a = 2.86$  Å stays constant for all alloy compositions.

The temperature dependences of magnetization measured at constant heating rate for all annealed ribbon samples are shown in Fig. 3. This allows to assess values of the Curie temperatures for particular alloy. For the  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.2}$  ribbon, the  $T_C$  value reaches 285 K, while doping by Al and Ga results in the increase of  $T_C$  to 295 K for the  $\text{LaFe}_{11.0}\text{Co}_{0.8}(\text{Si}_{0.4}\text{Al}_{0.6})_{1.2}$  and 320 K

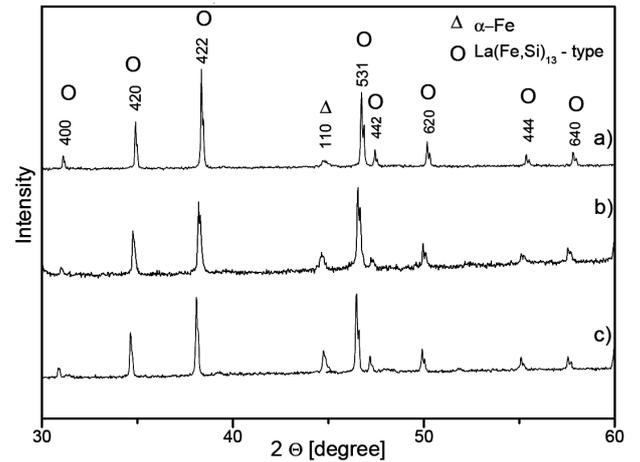


Fig. 2. X-ray diffraction patterns measured for annealed ribbon samples of the  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.2}$  alloy (a),  $\text{LaFe}_{11.0}\text{Co}_{0.8}(\text{Si}_{0.4}\text{Al}_{0.6})_{1.2}$  (b), and  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.1}\text{Ga}_{0.1}$  (c).

for  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.1}\text{Ga}_{0.1}$  alloy. Variations of magnetization  $M$  vs. temperature  $T$  are a reflection of the phase constitutions of samples. For those containing large fraction of  $\alpha$ -Fe the magnetization does not drop significantly above the  $T_C$  corresponding to the  $\text{La}(\text{Fe}, \text{Co}, \text{Si})_{13}$  phase.

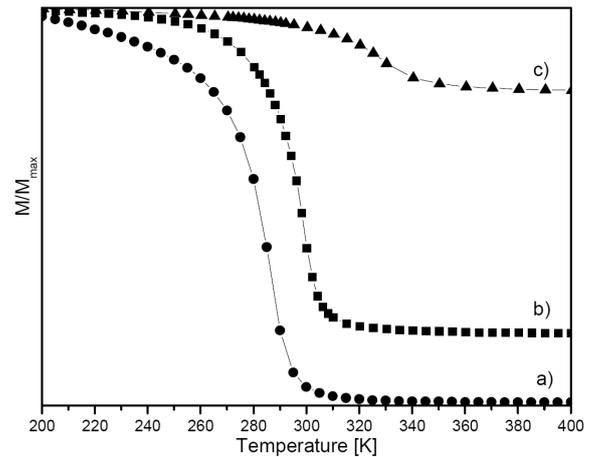


Fig. 3. Magnetization  $M/M_{\max}$  vs. temperature  $T$  dependences measured for: (a)  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.2}$ , (b)  $\text{LaFe}_{11.0}\text{Co}_{0.8}(\text{Si}_{0.4}\text{Al}_{0.6})_{1.2}$  and (c)  $\text{LaFe}_{11.0}\text{Co}_{0.8}\text{Si}_{1.1}\text{Ga}_{0.1}$  alloys at low external magnetic field of 0.01 T.

The lattice constant  $a$  and Curie temperature  $T_C$  determined for particular alloy samples are collected in Table for comparison. The doping by Al and Ga that substitute the Fe atoms in 96i positions results in change of the lattice constant due to the variation of atomic radius of the doping element, that has also an effect in the change of the Curie temperature.

TABLE

Volume fraction of the NaZn<sub>13</sub>-type phase, lattice constant  $a$  and the Curie temperature  $T_C$  determined for investigated alloys.

Alloy composition	Volume fraction of the NaZn <sub>13</sub> -type phase in the alloy [vol.%]	$a$ [Å]	$T_C$ [K]
LaFe <sub>11.0</sub> Co <sub>0.8</sub> Si <sub>1.2</sub>	90	11.4979	285
LaFe <sub>11.0</sub> Co <sub>0.8</sub> (Si <sub>0.4</sub> Al <sub>0.6</sub> ) <sub>1.2</sub>	86	11.5049	295
LaFe <sub>11.0</sub> Co <sub>0.8</sub> Si <sub>1.1</sub> Ga <sub>0.1</sub>	85	11.5138	320

#### 4. Conclusions

It was shown in the present work that the admixture of Al and Ga atoms into the LaFe<sub>11.0</sub>Co<sub>0.8</sub>Si<sub>1.2</sub>-based alloy plays detrimental role in a formation of the NaZn<sub>13</sub>-type phase, where large fraction of parasitic  $\alpha$ -Fe phase is also formed. This suggests that in order to get better performance of the alloys, longer time of annealing should be applied. However, the admixture of these elements results in the small increase of the lattice constant. This has also effect in the increase of  $T_C$  of the La(Fe, Co, Si)<sub>13</sub> phase from 285 K for the LaFe<sub>11.0</sub>Co<sub>0.8</sub>Si<sub>1.2</sub> alloy to 320 K for the LaFe<sub>11.0</sub>Co<sub>0.8</sub>Si<sub>1.1</sub>Ga<sub>0.1</sub> alloy.

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