Original Article

The Effect of Residual La on Crystal Structure and Magnetic Properties of La$_{1+\delta}$Fe$_{11.05}$Si$_{1.95}$ Compounds

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Abstract: In this paper, we present the results of the study of the effect of residual La on crystal structure, magnetic properties of La$_{1+\delta}$Fe$_{11.05}$Si$_{1.95}$ ($\delta =$ 0.00; 0.03; 0.06 and 0.09) compounds. The analysis of X-ray diffractions showed that when the La content increases to 9%, the structure still remains cubic in a typical NaZn$_{13}$ arrangement with unchanged lattice constant (about 0.5%). All compounds exhibit ferromagnetic–paramagnetic phase transitions. The Curie temperature $T_C$ increases slightly from 235 to 245 K.

Keywords: NaZn$_{13}$-type cubic structure, Magnetocaloric materials.

1. Introduction

Potential materials applicable in magnetic cooling due to low cost, simple fabrication technology and large magneto-caloric effect (MCE) such as Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ [1], MnAs, MnFe(P$_{1-x}$As$_x$) [2], Heusler alloys Ni-Mn-Ga [3], perovskite ABO$_3$ [4], ... have attracted the attention of many research groups in the world. The LaFe$_{13-x}$Si$_x$ compounds with NaZn$_{13}$ type cubic structure is the one of these materials.

Recently, a number of studies on structure, and magnetic properties of NaZn$_{13}$-type compounds have been published [5-10]. After crystallization, the LaFe$_{13-x}$Si$_x$ compounds exhibit the cubic structure of NaZn$_{13}$ type with $1 \leq x \leq 2.6$; Ce$_5$Ni$_{17}$Si$_{13}$ tetrahedra structure with $3.2 \leq x \leq 5$; and both above types for $2.6 \leq x \leq 3.2$ [11]. The Fe: Si ratio affects not only the crystal structure but also the...
Curie temperature $T_C$ and MCE of LaFe$_{13-x}$Si$_x$ compounds. Most studies have found that when Si concentration increases, the Curie temperature increases and the MCE decreases [12]. The giant thermal effect (GMCE) in LaFe$_{13-x}$Si$_x$ compound is derived from the first order phase transition (FOPT) was found only with Si content $x \leq 1.6$ while the nature of phase transition is the second order with $x > 1.6$ [12-14]. The magnetic and MCE properties of LaFe$_{13-x}$Si$_x$ compounds are also affected by Fe replacement with other elements such as Mn and Co. The presence of Mn and Co plays different roles in changing magnetic and thermal properties. The value of $T_C$ decreased and MCE changed insignificantly when Fe was replaced by Mn [15]. On the other hand, when Fe was replaced by Co, the $T_C$ value increased and MCE significantly reduced [16]. The replacement of La by other rare earth elements such as Pr, Nd, Ce, Er resulted that the Curie temperature decreased but the MCE increased slightly [17-19]. During the sample preparation process, a small amount of La usually evaporates due to its low melting point. Therefore, in order to stabilize the structure, and reduce the formation of $\alpha$-Fe phase, a small surplus of La is added to compensate for the evaporated portion of La.

In this report, we present the effect of residual La on the structure and magnetic properties of the La$_{1+\delta}$Fe$_{11.05}$Si$_{1.95}$ compounds.

2. Experiment

The La$_{1+\delta}$Fe$_{11.05}$Si$_{1.95}$ ($\delta = 0.00; 0.03; 0.06$ and $0.09$) compounds were prepared from the precursor materials consisting of purified metallic elements (La, R 99.9%; Fe 99.99%; Si 99.999%) by using arc-melting method in argon atmosphere with pressure $P = 10^{-5}$ Torr. The weight of La is compensated by 2% surplus due to the volatile nature of the melting process. After being melted, all samples were heated by inserting into a quartz tube, vacuumed at $10^{-5}$ Torr and then sealed. The samples were incubated at $1100$ °C for 7 days. After removing from the incubator, the samples were immediately subjected into ice water. The crystal structure of samples were studied by X-ray diffractometer with Cu-K$_\alpha$ radiation of wavelength $\lambda = 1.54056$ Å at room temperature. Magnetic properties were measured by SQUID system in temperature range from 4 to 300 K and a magnetic field of 70 kOe.

3. Results and Discussion

Figure 1. X-ray diffraction patterns of La$_{1+\delta}$Fe$_{11.05}$Si$_{1.95}$ compounds.
Figure 1 shows the XRD patterns of La$_{1+\delta}$Fe$_{11.05}$Si$_{1.95}$ ($\delta = 0.00; 0.03; 0.06$ and $0.09$) at room temperature. As seen, the all diffraction peaks of all samples completely coincide with the peaks of NaZn$_{13}$ structure. This means that the samples are crystallized in a cubic space group $Fm\overline{3}c$. However, the compounds with residual La of $9\%$ content have not only the main phase 1:13 but also a small amount of the secondary $\alpha$-Fe phase.

To study the effect of diffraction angle $\theta$ on lattice constant in La$_{1+\delta}$Fe$_{11.05}$Si$_{1.95}$ compound system, we analyzed the real lattice constant ($a_R$), the lattice constant calculated by using the best fitting function ($a_{RwDs}$) and lattice constant derived from eliminating the error ($a_{RwZ-Ds}$). These lattice constants are investigated by a function $a(x)$ of diffraction angle $\theta$ through the expression:

$$ x = \cos^2\theta(\sin\theta + \cos^2\theta) $$

The calculation results show that when the diffraction angle $\theta$ increases, the function $x$ decreases, the value of the lattice constants increases linearly with the increase of the function $x$. For all three components $\delta = 0.03; 0.06$ and $0.09$: corresponding to large $\theta$ angle ($1 < x < 4$), the lattice constants are almost similar, real crystal lattice constant $a_R$ and lattice constant derived from eliminating errors $a_{RwZ-Ds}$ have no change when the angle $\theta$ changes. Only the value of the lattice constant calculated according to the best fitting $a_{RwDs}$ function has a strong change compared to $a_R$ and $a_{RwZ-Ds}$ with small $\theta$ angle ($5 < x < 6$). The lowest deviation is found in the compound with $\delta = 0.06$. Thus, with large angle $\theta$ of lattice constant values, $a_R$, $a_{RwZ-Ds}$ and $a_{RwDs}$ are almost unchanged (Figure 2).

| $\delta$  | $a = b = c$ (Å)   | $T_C$ (K)  | $M_S$ ($\mu_0$/f.u) |
|-----------|-------------------|------------|----------------------|
| 0.00      | 11.446 ± 0.001    | 235 ± 1    | 2.01 ± 0.01          |
| 0.03      | 11.449 ± 0.001    | 237 ± 2    | -                    |
| 0.06      | 11.455 ± 0.001    | 236 ± 2    | 1.95 ± 0.01          |
| 0.09      | 11.449 ± 0.001    | 245 ± 1    | -                    |
The lattice constant of compounds $La_{1+\delta}Fe_{11.05}Si_{1.95}$ is recorded in Table 1. The effect of La concentration on the lattice constant in Figure 2 show that the lattice constant of compounds with $\delta = 1.03$ and 1.09 is almost unchanged, however this value increase by 0.5% for compound with $\delta = 1.06$. Thus, La deficiency concentration does not significantly affect the lattice constant of the studied compounds.

The magnetic properties of the $La_{1+\delta}Fe_{11.05}Si_{1.95}$ compounds were determined through measurements of $M(T)$. Figure 3 shows the dependence of magnetization on the temperature for the compounds $La_{1+\delta}Fe_{11.05}Si_{1.95}$ with $\delta = 0.00; 0.03; 0.06$ and 0.09 at the magnetic field $H = 1$ kOe. The results showed that all compounds exist phase transition from ferromagnetic state to paramagnetic state at $T_C$.

The $T_C$ Curie temperatures of compounds recorded in Table 1 show that the magnitude of $T_C$ is almost unchanged when the added amount of La is less than 9%. However, when the residual La is 9%, the $T_C$ temperature rises 10 K, and the presence of small amounts of $\alpha$-Fe phase (as indicated in the results of X-ray diffraction measurements) raises the paramagnetic background higher than that of other compounds.

The change of $T_C$ transition temperature due to increased residual La by 9% can be explained by molecular field model. Because La is a rare-earth type, the coefficient of molecular field $n_{Fe-Fe}$ of transition metal Fe is given by the formula:

$$n_{Fe-Fe} = \frac{T_{Fe}}{c_{Fe}}$$  \hspace{1cm} (1)

Where $c_{Fe}$ is the Curie constant of Fe calculated by:

$$c_{Fe} = \frac{4N_{Fe}S^2(S+1)\mu_B^2}{3k_B}$$  \hspace{1cm} (2)
Where $T_{Fe}$ is the temperature of the transition metal Fe and here $T_{Fe} = T_C$, $k_B$ is Boltzmann's constant, $N_{Fe}$ is the number of Fe atoms per mole. The effective magnetic moment of Fe in the paramagnetic state is defined as $2[S*(S* + 1)]^{1/2} = 3.5 \mu_B$. When the concentration of La increases to a certain extent, the disorder of the compound increases, the distance of Fe-Fe interaction increases, the $n_{Fe-Fe}$ molecular field coefficient increases that leads to the increase of Curie temperature $T_C$.

![Figure 4](image-url)  

Figure 4. The magnetization isotherms for the La$_{1+\delta}$Fe$_{11.05}$Si$_{1.95}$ compounds ($\delta = 0.00$ and 0.06) at $T = 1.8$ K.

Figure 4a displays the magnetization isotherms for the La$_{1+\delta}$Fe$_{11.05}$Si$_{1.95}$ compounds ($\delta = 0.00$ and 0.06) at $T = 1.8$ K. Note that both samples have the saturation magnetization values at $\mu_0 H = 10$ kOe and this value changes about 3% that is quite close to the magnetic moment of Fe to $2.2 \mu_B$/f.u.

### 4. Conclusion

Successfully fabricated La$_{1+\delta}$Fe$_{11.05}$Si$_{1.95}$ ($\delta = 0.00; 0.03; 0.06$ and 0.09). After being annealed, the samples existed the phase with cubic structure of NaZn$_{13}$ (1:13) of Fm$\overline{3}$c space group and a small fraction of $\alpha$-Fe phase. When the amount of La residual increases to $9\%$, the compound still exists structure 1:13 and the lattice constant is not significantly changed (about $0.5\%$), whereas the Curie temperature $T_C$ slightly increases from 235 K to 245 K. Therefore, this alloy can be a candidate for magnetic refrigerant at the corresponding temperature range.

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