VNU Journal of Science: Mathematics – Physics, Vol. 36, No. 3 (2020) 100-105

VNU Journal of Science: Mathematics - Physics

Journal homepage: https://js.vnu.edu.vn/MaP

Original Article

The Effect of Residual La on Crystal Structure and Magnetic Properties of $La_{1+\delta}Fe_{11.05}Si_{1.95}$ Compounds

Vuong Van Hiep[1], Do Thi Kim Anh[1,*], Ngac An Bang[1], Sai Cong Doanh[1], Nguyen Duy Thien[1], Huynh Dang Chinh[2], Pham Duc Hanh[3]

[1]*Faculty of Physics, VNU University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam*
[2]*Department of Inorganic Chemistry, Hanoi University of Technology, 1 Dai Co Viet, Hanoi, Vietnam*
[3]*Vietnam Institute for Building Science and Technology, 81 Tran Cung, Nghia Tan, Hanoi, Vietnam*

Received 16 June 2020
Revised 04 July 2020; Accepted 15 July 2020

Abstract: In this paper, we present the results of the study of the effect of residual La on crystal structure, magnetic properties of $La_{1+\delta}Fe_{11.05}Si_{1.95}$ (δ = 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 exihibit 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 attebtion 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 exihibit the cubic structure of $NaZn_{13}$ type with $1 \leq x \leq 2.6$; $Ce_2Ni_{17}Si_{13}$ 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

*Corresponding author.
Email address: kimanh72@gmail.com

https//doi.org/ 10.25073/2588-1124/vnumap.4556

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 α-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 $La_xFe_{11.05}Si_{1.95}$ compounds.

2. Experiment

The $La_{1+\delta}Fe_{11.05}Si_{1.95}$ (δ = 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 ^oC for 7 days. After removing from the incubator, the samples were immediately subjected into ice warter. The crystal structure of samples were studied by X-ray diffractometer with Cu-K_α radiation of wavelength λ = 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

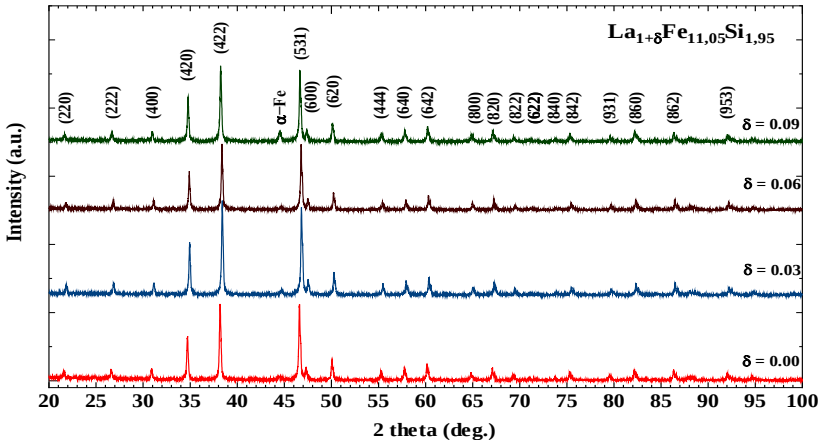

Figure 1. X-ray diffraction patterns of $La_{1+\delta}Fe_{11.05}Si_{1.95}$ compounds.

Figure 1 shows the XRD patterns of $La_{1+\delta}Fe_{11.05}Si_{1.95}$ (δ = 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 *Fm3c*. 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 α-Fe phase.

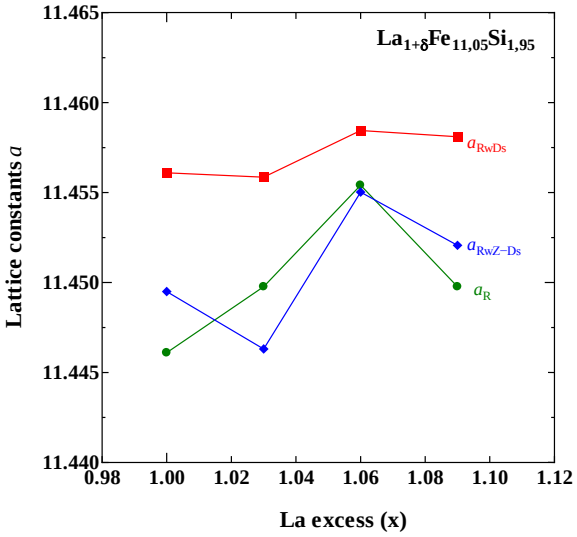

Figure2. Dependence of the lattice constant on La in $La_{1+\delta}Fe_{11.05}Si_{1.95}$ compounds.

To study the effect of diffraction angle θ 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 ($a_{RwZ\text{-}Ds}$). These lattice constants are investigated by a function $a(x)$ of diffraction angle θ through the expression: $x = \cos^2\theta/\sin\theta + \cos^2\theta/\theta$. The calculation results show that when the diffraction angle θ increases, the function x decreases, the value of the lattice constants increases linearly with the increase of the function x. For all three components δ = 0.03; 0.06 and 0.09: corresponding to large θ angle ($1 < x < 4$), the lattice constants are almost similar, real crystal lattice constant a_R and lattice constant derived from eliminating errors $a_{RwZ\text{-}Ds}$ have no change when the angle θ 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 $a_{RwZ\text{-}Ds}$ with small θ angle ($5 < x < 6$). The lowest deviation is found in the compound with δ = 0.06. Thus, with large angle θ of lattice constant values, a_R, $a_{RwZ\text{-}Ds}$ and a_{RwDs} are almost unchanged (Figure 2).

Table 1: Crystal lattice constant, T_C phase transition temperature and M_S saturation of $La_{1+\delta}Fe_{11.05}Si_{1.95}$ compounds.

δ	$a = b = c$ (Å)	T_C (K)	M_S (μ_B/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 δ = 1.03 and 1.09 is almost unchanged, however this value increase by 0.5% for compound with δ = 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 δ = 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.

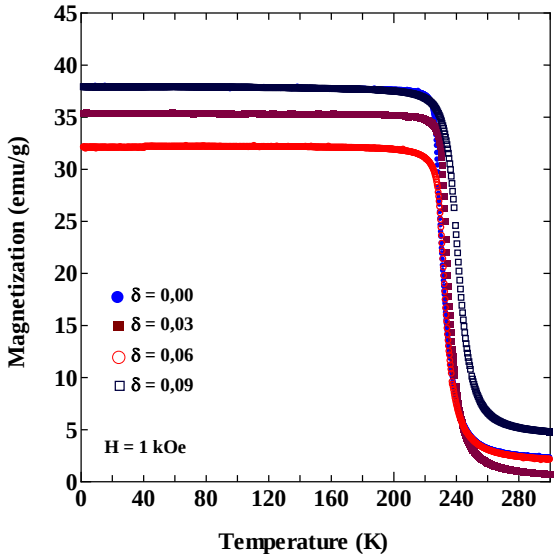

Figure3. Dependence of magnetization on temperature in compounds $La_{1+\delta}Fe_{11.05}Si_{1.95}$ (δ = 0.00; 0.03; 0.06 and 0.09) at H = 1 kOe magnetic field.

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 α-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 $n_{Fe\text{-}Fe}$ of transition metal Fe is given by the formula:

$$n_{\mathrm{Fe-Fe}} = \frac{T_{\mathrm{Fe}}}{C_{\mathrm{Fe}}} \quad (1)$$

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

$$C_{\mathrm{Fe}} = \frac{4N_{\mathrm{Fe}}S^*(S^*+1)\mu_B^2}{3k_{\mathrm{B}}} \quad (2)$$

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 $n_{Fe\text{-}Fe}$ molecular field coefficient increases that leads to the increase of Curie temperature T_C.

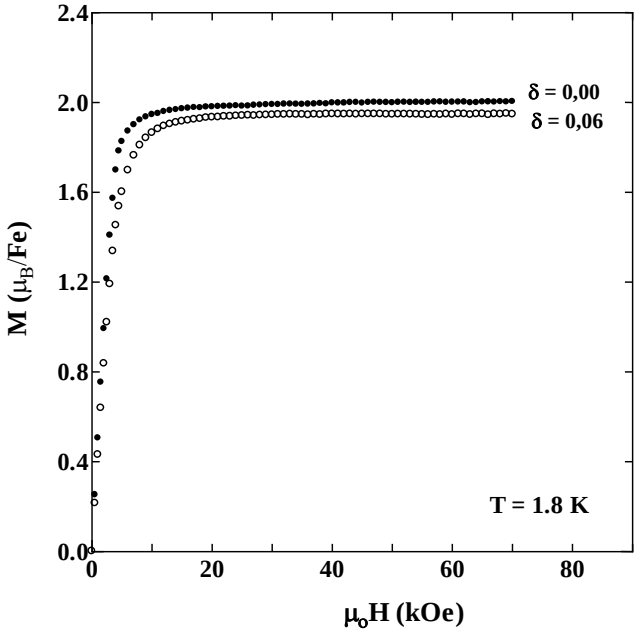

Figure 4. The magnetization isotherms for the $La_{1+\delta}Fe_{11.05}Si_{1.95}$ compounds (δ = 0.00 and 0.06) at T = 1.8 K.

Figure 4a displays the magnetization isotherms for the $La_{1+\delta}Fe_{11.05}Si_{1.95}$ compounds (δ = 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 μ_B/f.u.

4. Conclusion

Successfully fabricated La $La_{1+\delta}Fe_{11.05}Si_{1.95}$ (δ = 0.00; 0.03; 0.06 and 0.09). After being annealed, the samples existedt the phase with cubic structure of $NaZn_{13}$ (1:13) of *Fm3c* space group and a small fraction of α-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.

Acknowledgments

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02 -2017.326.

References

[1] V.K. Pecharsky, K.A. Gschneidner, Tunable magnetic regenerator alloys with a giant magnetocaloric effect for magnetic refrigeration from ~20 to ~290 K, Appl. Phys. Lett. 70 (1997) 3299 -3303. https://doi.org/10.1063/1.119206.

[2] O. Tegus, E. Bruck, K. H. J. Buschow, and F. R. de Boer, Transition-metal-based magnetic refrigerants for room-temperature applications, Nature (London) 415 (2002) 150-156. https:// doi.org/10.1038/415150a.

[3] J. Marcos, A. Planes, L. Mañosa, F. Casanova, X. Batlle, A. Labarta, and B. Martínez, Magnetic field induced entropy change and magnetoelasticity in Ni-Mn-Ga alloys, Phys. Rev. B 66 (2002) 224413. https://doi.org/10.1103/PhysRevB.66.224413.

[4] Z. B. Guo, Y. W. Du, J. S. Zhu, H. Huang, W. P. Ding, and D. Feng, Large Magnetic Entropy Change in Perovskite-Type Manganese Oxides, Phys. Rev. Lett. 78 (1997) 1142-1145. https://doi.org/10.1103/PhysRevLett.78.1142.

[5] A. Fujita, K. Fukamichi, J.T. Wang, Y. Kawazoe, Large magnetovolume effects and band structure of itinerant-electron metamagnetic compounds, Phys. Rev. B 68 (2003) 104431. https://doi.org/10.1103/PhysRevB.68.104431.

[6] J. Lyubina, K. Nenkov, L. Schultz, O. Gutfleisch, Multiple Metamagnetic Transitions in the Magnetic Refrigerant Phys. Rev. Lett. 101 (2008) 177203. https://doi.org/10.1103/PhysRevLett.101.177203.

[7] A.K. Pathak, B.R. Gautam, I. Dubenko, M. Khan, S. Stadler, and N. Ali, Phase transitions and magnetoresistance in Heusler alloys J. Appl. Phys. 103, 07F315 (2008). https://doi.org/10.1063/1.2828599.

[8] M.X. Zhang, J. Liu, C. He, A.R. Yan, Novel microstructure and large magnetocaloric effect in $La_2Fe_{11}Si_2$ magnetic refrigerant Mater. Lett. 134 (2014) 87-90. https://doi.org/10.1016/j.matlet.2014.07.060.

[9] J.J. Ipus, J.M. Borrego, L.M. Moreno-Ramírez, J.S. Blázquez, V. Franco, A. Conde, Grinding and particle size selection as a procedure to enhance the magnetocaloric response of $La(Fe,Si)_{13}$ bulk samplesIntermetallics 84 (2017) 30-34. https://doi.org/10.1016/j.intermet.2016.12.022.

[10] Van Hiep Vuong, Kim Anh Do Thi, Duy Thien Nguyen, Quang Hoa Nguyen, Nam Nhat Hoang, Physica B 532 (2018) 115-118. https://doi.org/10.1016/j.physb.2017.07.014.

[11] M.K. Han, G.J. Miller, An Application of the "Coloring Problem": Structure−Composition−Bonding Relationships in the Magnetocaloric Materials $LaFe_{13-x}Si_x$, Inorg. Chem. 47 (2008) 515-528.https://doi.org/10.1021/ic701311b.

[12] O. Gutfleisch, A. Yan, K.H. Müller, Large magnetocaloric effect in melt-spun, J. Appl. Phys. 97 (2005) 10M305. https://doi.org/10.1063/1.1847871.

[13] A. Fujita, S. Fujieda, K. Fukamichi, H. Mitamura, T. Goto, Itinerant-electron metamagnetic transition and large magnetovolume effects in compounds Phys. Rev. B 65 (2001) 014410. https://doi.org/10.1103/PhysRevB.65.014410.

[14] S. Fujieda, A. Fujita, K. Fukamichi, Large magnetocaloric effect in itinerant-electron metamagnetic compounds, Appl. Phys. Lett. 81 (2002) 1276. https://doi.org/10.1063/1.1498148.

[15] F. Wang, Y.F. Chen, G.J. Wang, B.G. Shen, The effect of Mn substitution in $LaFe_{11.7}Si_{1.3}$ compound on the magnetic properties and magnetic entropy changes, J. Phys. D: Appl. Phys. 36 (2003) 301-206. https://doi.org/10.1088/0022-3727/36/1/301.

[16] F.X. Hu, J. Gao, X.L. Qian, M. Ilyn, A.M. Tishin, J.R. Sun, B.G. Shen, Magnetocaloric effect in itinerant electron metamagnetic systems, J. Appl. Phys. 97 (2005) 10M303-305. https://doi.org/10.1063/1.1847071.

[17] D.T.K. Anh, N.P. Thuy, N.H. Duc, T.T. Nhien, N.V. Nong, Magnetism and magnetocaloric effect in $La_{1-y}Nd_y(Fe_{0.88}Si_{0.12})_{13}$ compounds, J. Magn. Magn. Mater. 262 (2003) 427-431.https://doi.org/10.1016/S0304-8853(03)00073-8.

[18] Do Thi Kim Anh, Vuong Van Hiep, Makio Kurisu, Dinh Van Chau and Hoang Nam Nhat, Effect of Cerium Doping on Crystal Structure and Magnetic Properties of $La_{1-y}Ce_yFe_{11.44}Si_{1.56}$ Compounds, Mat. Trans. 56(9) (2015) 1335-1338. https://doi.org/10.2320/matertrans.MA201518.

[19] Vuong Van Hiep, Nguyen Khac Thuan, Do Thi Kim Anh, and Hoang Nam Nhat, Crystal Structure and Magnetic Properties of $La_{0.8}R_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ (R = Sm and Tb) Compounds, Mat. Trans. 59(7) (2018) 1068-1070. https://doi.org/10.2320/matertrans.MD201716.