VNU Journal of Science, Mathematics - Physics 25 (2009) 193-197

Synthesis and thermoelectric properties of La($Fe_{1-x}Si_x$)$_{13}$ compounds (x = 0.12, 0.14 and 0.15)

Do Thi Kim Anh[1,*], Makio Kurisu[2]

[1)]*Faculty of Physics, College of Science, VNU, 334 Nguyen Trai, Thanh Xuan, Ha Noi*
[2)]*Japan Advanced Institute of Science and Technology, School of Materials Science,*
Nomi, Ishikawa 923-1292, Japan

Received 2 October 2009

Abstract. The crystal structure and thermoelectric properties of La($Fe_{1-x}Si_x$)$_{13}$ compounds were investigated by means of X-ray powder diffraction and electrical resistivity, thermopower and thermal conductivity measurements. The single $NaZn_{13}$-type cubic structure phase is stabilized for the compounds with x = 0.12, 0.14 and 0.15. These magnetic phase transitions are also seen in the electrical resistivity, thermopower and thermal conductivity measurements. All compounds have the small values of thermopower and lattice conductivity. However, thermal conductivity is large.

Keywords: Thermoelectric, Itinerant-electron metamagnetic (IEM), keywords.

1. Introduction

The magnetic properties of LaT_{13} (T = Fe and Co) compounds of the $NaZn_{13}$-type cubic structure have been intensively studied. These compounds have the largest amount of transition metal in the crystalline formula unit among the rare-earth transition intermetallics [1,2]. The cubic $NaZn_{13}$-type structure is easily stabilized in the binary La-Co compound. For the La-Fe compound, this structure can be formed only in pseudo-binary La($Fe_{1-x}M_x$)$_{13}$ (M = Al, Si) compounds [3]. The magnetic state in La($Fe_{1-x}Al_x$)$_{13}$ compounds is ferromagnetic for $0.14 \le x < 0.38$, and antiferromagnetic for $0.08 \le x < 0.14$ [4]. La($Fe_{1-x}Si_x$)$_{13}$ compounds are ferromagnetic in the region $0.14 \le x < 0.38$. However, their Curie temperature T_C decreases with increasing Fe concentration, whereas the saturation magnetic moment increases [1]. For these La($Fe_{1-x}Si_x$)$_{13}$ compounds, it was reported that in the high Fe concentration region, an itinerant-electron metamagnetic (IEM) transition, i.e. a field-induced first-order paramagnetic-ferromagnetic transition, accompanied by a large negative lattice expansion, appeared just above the Curie temperature. It is interesting to mention that the pseudo-binary La($Fe_{1-x}M_x$)$_{13}$ compounds with M = Si and Al exhibit a giant magnetostriction effect, which is promising for applications [5].

Magnetic properties have been extensively investigated for La($Fe_{1-x}Si_x$)$_{13}$ compounds (x = 0.12, 0.14 and 0.15). In these compounds, an itinerant electron metamagnetic (IEM) transition near T_C has

---

[*] Corresponding author. Tel.: 84-904543849
E-mail: kimanh72@gmail.com

been demonstrated [6]. The IEM transition is closely related to the large positive curvature of the density of state (DOS) at the Fermi level in the compounds [7], therefore we can expect that the La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds possess a large thermopower (Seebeck coefficient). A small phonon thermal conductivity is also expected since the compounds have the NaZn$_{13}$ structure in which 112 atoms are accommodated in the unit cell. It is also interesting to examine the thermoelectric behavior near the Curie temperature in the compounds. In the present study, the thermopower, electrical resistivity and thermal conductivity of La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds have been investigated below room temperature.

2. Experimental

The La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds (x = 0.12, 0.14 and 0.15) have been prepared by arc-melting the appropriate amounts of high purity of La with 99.9%, Fe with 99.99% and Si with 99.999% in purified Ar atmosphere. The ingots were sealed into evacuated tubes and the heat treatment for homogenization was carried out at 1100 °C for 1 week.

The X-ray diffraction (XRD) patterns used to determine their crystal structure parameters were collected by Rigaku Rint-2000 with Cu K α. The thermopower, electrical resistivity and thermal conductivity were measured by using a Quantum Design PPMS in the temperature range from 5 K to 300 K.

2. Results and discussion

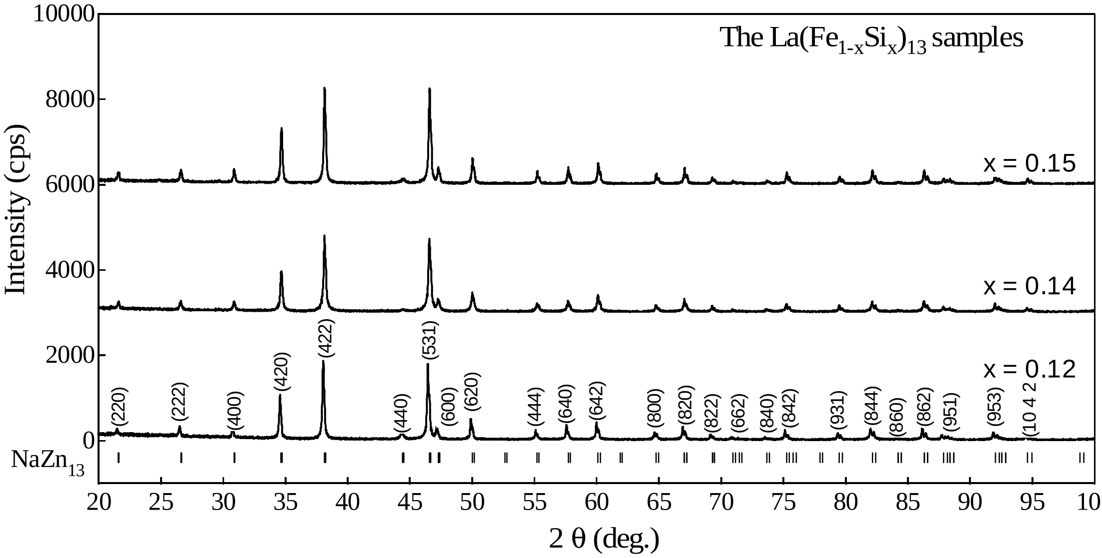

Fig.1. The X-ray diffraction patterns of La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds.

Fig. 1 shows the XRD patterns of the La(Fe$_{1-x}$Si$_x$)$_{13}$ (x = 0.12, 0.14 and 0.15) compounds. X-ray diffraction confirms that the solid solution of La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds crystallizes in the cubic NaZn$_{13}$ - type structure with space group Fm$\bar{3}$c. The lattice parameters of the compounds are listed in Table 1.

Table 1. The thermoelectric properties of La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds and other thermoelectric materials at room temperature

Compound	a (Å)	T_C (K)	a (µV/K)	r (µΩ cm)	k (W/K m)	ZT
x = 0.12	11.4513	200	-5.5	146.4	7.44	0.00083
x = 0.14	11.5487	220	-5.6	150.0	7.51	0.00084
x = 0.15	11.4471	232	-5.6	159.0	6.80	0.00087
Bi_2Te_3 [8]	-	-	220	1000	1.4	1.0
Fe_3Se_4 [9]	-	-	-5.0	700	1.4	0.00077
$FeCr_2Se_4$ [9]	-	-	128	10000	1.3	0.0378

The temperature dependence of the electrical resistivity (r) in the La(Fe$_{1-x}$Si$_x$)$_{13}$ (x = 0.12, 0.14 and 0.15) samples is shown in Fig. 2. Normal metallic behaviour is seen all the compounds. The electrical resistivity decreases rapidly below the magnetic transition in La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds due to the freezing of spin disorder contribution to electrical resistivity. It is also noted that the electrical resistivity increases with increasing Si concentration. The room temperature electrical resistivity decreases from 159 µΩ·cm for x = 0.15 down to 146.4 µΩ·cm for x = 0.12.

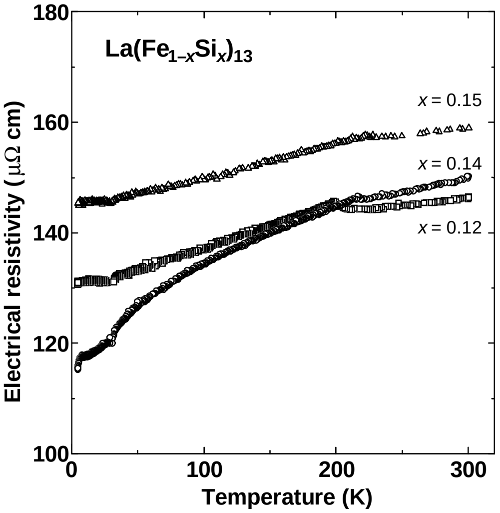

Fig. 2. Temperature dependence of the electrical resistivity of La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds.

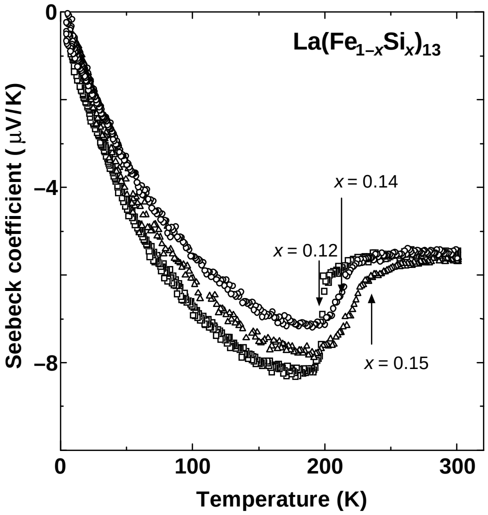

Fig. 3. Temperature dependence of the thermopower of La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds.

Fig. 3 shows the temperature dependence of the thermopower (a) in the La(Fe$_{1-x}$Si$_x$)$_{13}$ (x = 0.12, 0.14 and 0.15) compounds. All the compounds have negative thermopower, indicating the n-type nature of these materials. At room temperature, the thermopower of all the compounds is a = - 5.5 µV/K. A growth of the peak is found below T_C. The difference in the value between the ferromagnetic and paramagnetic states is 27 % and 18% for x = 0.12 and 0.14, respectively.

Finally, the thermal conductivity (k) of La(Fe$_{1-x}$Si$_x$)$_{13}$ (x = 0.12, 0.14 and 0.15) compounds is shown in Fig. 4. For general, the thermal conductivity of a material can be described as: $k(T) = k_{el}(T) + k_{ph}(T)$, where k_{el} and k_{ph} are the electronic conductivity and the lattice thermal conductivity, respectively. The lattice thermal conductivity value, k_{ph}, can be estimated by subtracting the electronic contribution k_{el} from the total thermal conductivity k, where k_{el} is related with the electrical resistivity according to the Wiedemann–Franz law $k_{el} = L_0T/r$, where L_0 is the Lorenz number 2.45×10^{-8} WΩK^{-2}. The value of k of all the compounds is large (see Table 1). The k_{ph} contribution to k is 30 % (inset of Fig. 4). Only a small increase is found in its value at T_C.

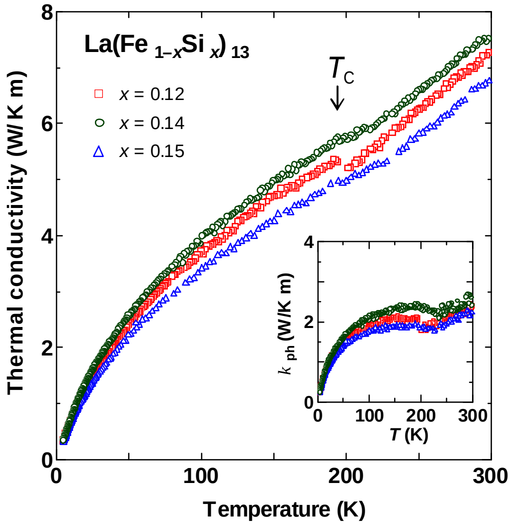

Fig. 4. Temperature dependence of the thermal conductivity of La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds.

The thermoelectric properties of La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds at room temperature are listed in Table 1, together with the data of other typical thermoelectric materials. Our compounds have relatively larger thermal conductivity than the references. Furthermore, the value of thermopower and electric resistivity are smaller than those of other thermoelectric materials. The figure of merit (ZT), which is defined by $ZT = a^2T/rk$, is found to be very small (see Table 1).

4. Conclusion

The structural and thermoelectric properties have been investigated in La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds. The following conclusion can be drawn from this study:

- The La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds have a cubic NaZn$_{13}$– type crystal structure.
- The thermoelectric properties of La(Fe$_{1-x}$Si$_x$)$_{13}$ compounds have been investigated below 300 K. The values of thermopower and lattice conductivity are small. Thermal conductivity is large. The dimensionless figure of merit (ZT) is very small.

Acknowledgments. This work was supported by the Vietnam National University (VNU) research program under the grant No. QT-09-15.

References

[1] P.I. Kripyakevich, O.S. Zarechnyuk, E.I. Gladyshevsky, O.I. Bodak, *Z. Anorg. Chem.* 358 (1968) 90.

[2] T.T.M. Palstra, J.A. Mydosh, G.J. Nieuwenhuys, A.M. Van der Kraan, K.H.J. Buschow, *J. Magn. Magn. Mater.* 36 (1983) 290.

[3] T.T.M. Palstra, G.J. Nieuwenhuys, J.A. Mydosh, K.H.J. Buschow, *J. Appl. Phys.* 55 (1984) 2367

[4] T.T.M. Palstra, G.J. Nieuwenhuys, J.A. Mydosh, K.H.J. Buschow, *Phys. Rev.* B 31 (1985) 4622

[5] A. Fujita, K. Fukamichi, *IEEE Trans. Magn.* 35 (1999) 1796.

[6] A. Fujita Y. Akamatsu, K. Fukamichi, *J. Appl. Phys.* 84 (1999) 4756.

[7] M. Cyrot, M. Lavagna, *J. Appl. Phys.* 50 (1979) 2333.

[8] J. P. Fleurial, *Proc. SCT – 93* (1993) Lecture 3.

[9] G. Jeffrey Snyder, T. Caillat, J. P. Fleurial, *Mat. Res. Soc. Proc.* 545 (1999) 339.