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

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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

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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.

3. Results and discussion

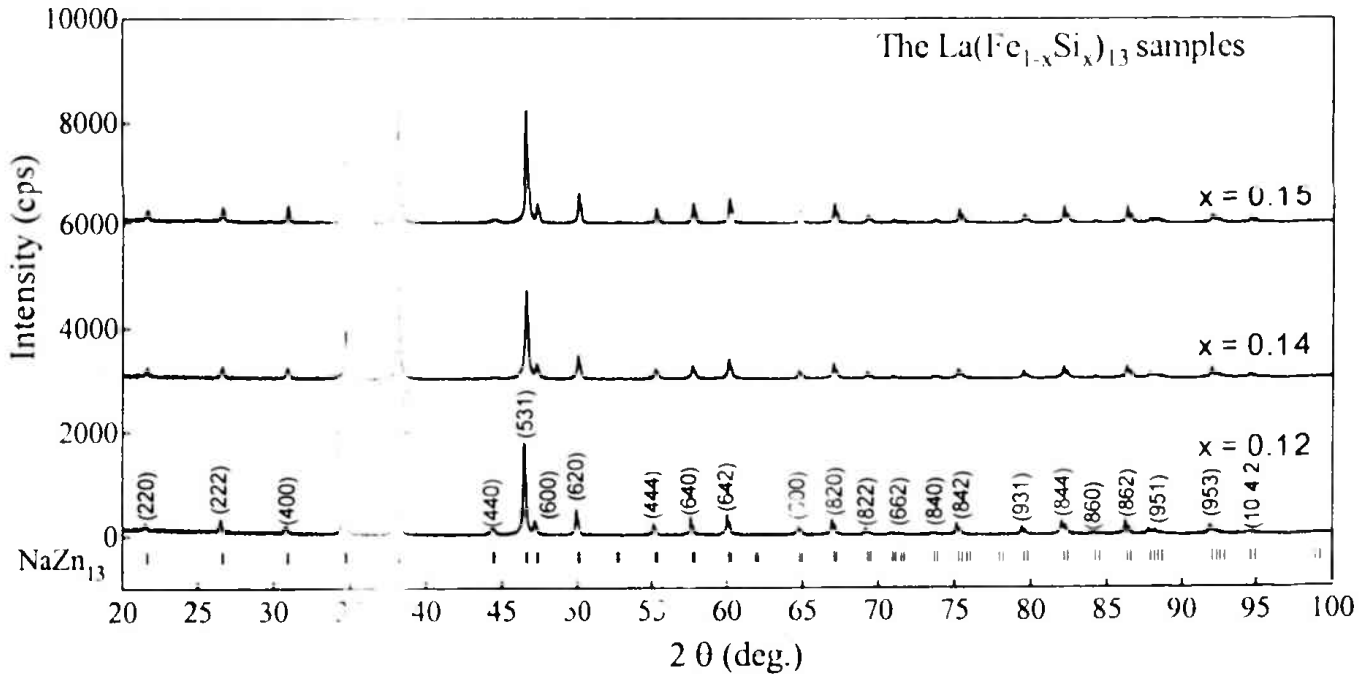

Fig. 1. The X-ray diffraction patterns of $La(Fe_{1-x}Si_x)_{13}$ compounds.

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)	α (μV/K)	ρ (μΩ cm)	κ (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 (ρ) 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.

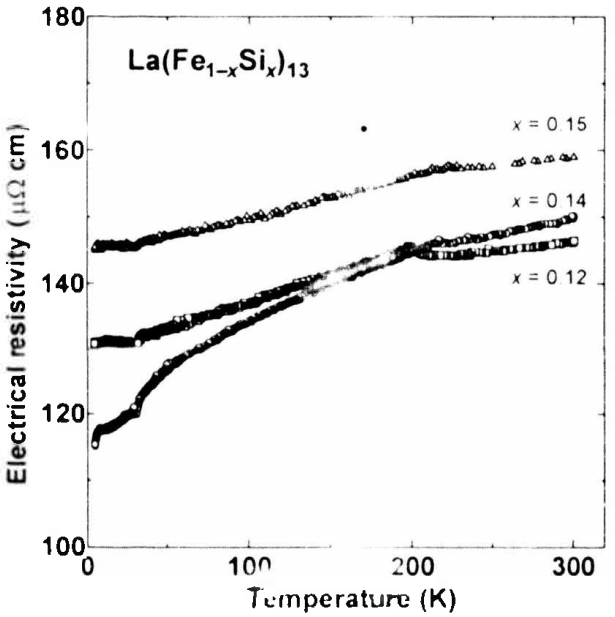

Fig. 2. Temperature dependence of the electrical resistivity of $La(Fe_{1-x}Si_x)_{13}$ compounds.

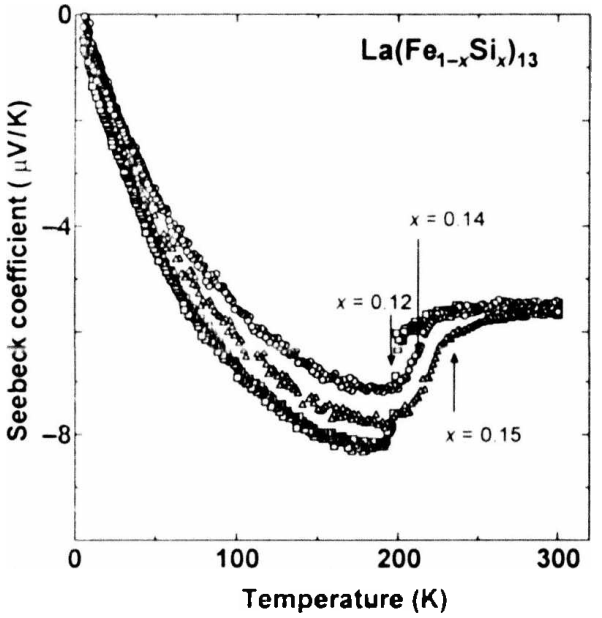

Fig. 3. Temperature dependence of the thermopower of $La(Fe_{1-x}Si_x)_{13}$ compounds.

Fig. 3 shows the temperature dependence of the thermopower (α) 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 α = - 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 (κ) 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: $\kappa(T) = \kappa_{el}(T) + \kappa_{ph}(T)$, where κ_{el} and κ_{ph} are the electronic conductivity and the lattice thermal conductivity,

respectively. The lattice thermal conductivity value, κ_{ph}, can be estimated by subtracting the electronic contribution κ_{el} from the total thermal conductivity κ, where κ_{el} is related with the electrical resistivity according to the Wiedemann–Franz law $\kappa_{el} = L_0 T/\rho$, where L_0 is the Lorenz number 2.45×10^{-8} $W\Omega K^{-2}$. The value of κ of all the compounds is large (see Table 1). The κ_{ph} contribution to κ is 30 % (inset of Fig. 4). Only a small increase is found in its value at T_C.

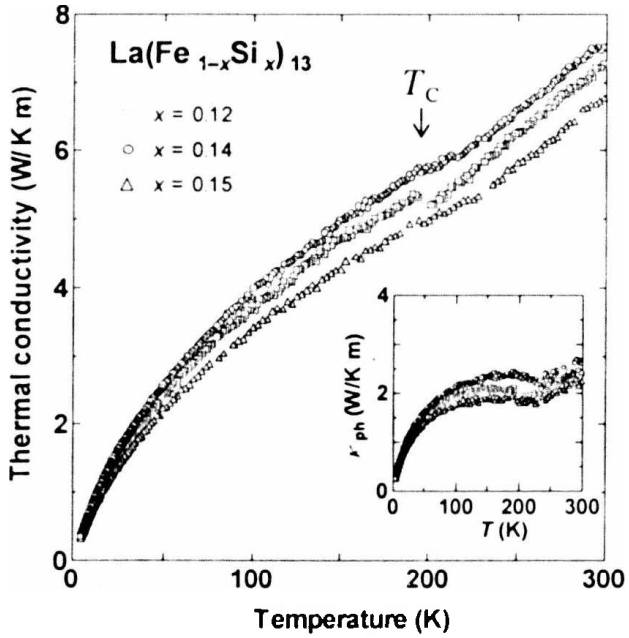

Fig. 4. Temperature dependence of the thermal conductivity of $La(Fe_{1-x}Si_x)_{13}$ compounds.

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 $ZT = \alpha^2 T/\rho\kappa$, 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.

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