Effect of Anomalous Crystal Structure of Iron Aluminides Fe₂Al₅ and Fe₄Al₁₃: Low Phonon Thermal Conductivity and Potentiality as Thermoelectric Materials^{*1}

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Iron Aluminide Fe₂Al₅ has a rigid framework of both fully occupied aluminum and iron sites and channels of partially occupied aluminum sites. On the other hand, Fe₄Al₁₃ possesses a large unit cell with 102 atoms. These complex and peculiar crystal structures bring a low phonon thermal conductivity. Here, we report the thermoelectric properties and discuss how the proposed chain structure and large unit cell can lead to a low phonon thermal conductivity. The calculated room-temperature phonon thermal conductivity by using the Wiedemann-Franz law is approximately 1.5 W/mK and 0.8 W/mK for Fe₂Al₅ and Fe₄Al₁₃, respectively. From the comparison with other Fe-Al alloys, which have neither plural partially occupied sites nor a large unit cell, we found that (1) the specific heat does not decrease at high temperature, i.e. aluminum atoms at partially occupied sites seem to be fixed rather than liquid behavior. (2) the speed of sound for Fe₂Al₅ and Fe₄Al₁₃ are almost identical among Fe-Al alloys, i.e. the average phonon group velocity of acoustic modes for Fe₂Al₅ and Fe₄Al₁₃ are not slower than that of Fe-Al alloys, (3) the electrical conductivities of Fe₂Al₅ and Fe₄Al₁₃ are lower than those of the other Fe-Al alloys. These results suggest that the low phonon thermal and electrical conductivities are brought by short relaxation times of both phonons and electrons due to chemical disorder such as the partially occupied sites. [doi:10.2320/matertrans.MF201607]

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1. Introduction

Thermoelectric materials have gained attention owing to the fact that they can contribute to the solution for the global energy demand through waste-heat recovery. In recent years, the potential of thermoelectric materials, dimensionless figure of merit ZT is getting over unity.¹⁾ ZT is defined as

$$ZT = \frac{S^2 \sigma}{\kappa_{el} + \kappa_{ph}} T, \quad (1)$$

where S , σ , κ_{el} , κ_{ph} , and T are the Seebeck coefficient, the electrical conductivity, the electron thermal conductivity, the phonon thermal conductivity and the temperature, respectively. σ is related to κ_{el} through the Wiedemann-Franz law

$$\kappa_{el} = L \sigma T, \quad (2)$$

where L is the Lorenz number, $L = 2.44 \times 10^{-8} \text{ V}^2/\text{K}^2$ for free electrons. κ_{ph} is given by

$$\kappa_{ph} = \frac{1}{3} C v^2 \tau, \quad (3)$$

where C , v , and τ are the phonon specific heat, the phonon group velocity, and the phonon relaxation time, respectively.

Unfortunately, a number of the existing high- ZT materials contain toxic and/or high-cost elements. For wide use of thermoelectric materials, it is necessary to use materials with low cost and nontoxicity as well as high- ZT values. Hence, in the present study, we have focused on iron-aluminum binary system as a candidate of environmentally friendly thermoelectric material.

According to Fe-Al phase diagram,²⁾ there are three stable phases, FeAl₂, Fe₂Al₅, and Fe₄Al₁₃, on Al-rich region, and all of them form complex crystal structures which contain some partially occupied sites.

FeAl₂ has a triclinic unit cell with two partially occupied sites and 19 atoms in total,³⁾ as shown in Fig. 1(a).⁴⁾ The density of states of this material shows that the Fermi level lies in a smooth peak of the density of states,³⁾ which accounts for low Seebeck coefficient.

The unit cell of Fe₂Al₅ with an orthorhombic structure consists of one iron site and three aluminum sites with different atomic occupancies, and it includes 15 atoms in total⁵⁾ as shown in Fig. 1(b).⁴⁾ The partially occupied sites are placed along c -axis and aluminum atoms are supposed to diffuse in a liquid-like manner along the channels.³⁾ This behavior is similar to superionic conductor such as Cu_{2-x}Se. The reduction in specific heat, which directly related to very low phonon thermal conductivity, is attributed to copper ion moving like liquid in Cu_{2-x}Se.⁶⁾ In the case of Fe₂Al₅, these properties will be dependent on the density of aluminum atoms in the channels. Besides, Fe₂Al₅ has a pseudogap near the Fermi level,³⁾ which is suitable for large Seebeck coefficient.

As shown in Fig. 1(c),⁴⁾ Fe₄Al₁₃ has a monoclinic unit cell with four partially occupied sites and 102 atoms in total, which is known as an approximant of decagonal quasicrystals.⁷⁾ The unit cell volume of Fe₄Al₁₃ is seven times larger than that of Fe₂Al₅. The small Brillouin zone due to the large unit cell volume leads to the intensified Umklapp process of the phonon-phonon scattering and increases scattering rate of phonon at zone boundaries. These characteristics can lead to low phonon thermal conductivity.

We mainly report thermoelectric properties of Fe₂Al₅ and Fe₄Al₁₃, and also compare them with those of other Fe-Al compounds.

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Fig. 1 Crystal structures of (a) FeAl_2 ,³⁾ (b) Fe_2Al_5 ,⁵⁾ and (c) $\text{Fe}_4\text{Al}_{13}$.⁷⁾ The crystal structures are illustrated using the computer program VESTA.⁴⁾

2. Experimental Details

We synthesized four kinds of iron-aluminide, FeAl , FeAl_2 , Fe_2Al_5 and $\text{Fe}_4\text{Al}_{13}$ with nominal compositions of Fe_4Al_x ($x = 4.0, 7.1, 7.4, 7.6, 8.0, 8.4, 8.7, 9.0, 9.4, 9.7, 10.0, 10.2, 10.3, 10.6, 11.0, 11.8$). Iron powders (99.9%, Kojundo Chemical Lab. Co., Ltd.) and aluminum shots (99.99%, Kojundo Chemical Lab. Co., Ltd.) were arc-melted under an argon atmosphere. The ingots were melted 2–4 times for homogenization. All of the ingots were crushed into powders with particle sizes below $100\ \mu\text{m}$, and then they were set in a 10 mm-diameter carbon die for spark plasma sintering (SPS) (SPS-515S, Sumitomo Coal Mining Co., Ltd.). The temperature of specimens was increased from ambient temperature to 1223 K for 30 min with a uniaxial pressure of 56 MPa under an argon atmosphere. After SPS treatment, the specimens were cooled to ambient temperature under argon atmosphere.

The characterization of the samples was performed by powder X-ray diffraction (XRD) measurements with $\text{Cu K}\alpha$ radiation (Smartlab, Rigaku Co.). Samples were also analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) (JSM-6010LA, JEOL) in order to identify impurity phases. We also determined lattice parameter with standard silicon sample (NIST, 640d) by using RIETAN-FP,⁸⁾ a Rietveld analysis software. The electrical conductivity and the Seebeck coefficient were measured in a helium atmosphere at temperatures between 373 K and 973 K by the four-probe method and the steady-state temperature gradient method, respectively (ZEM-1, Advance-Riko, Inc.). The thermal conductivity was obtained by the geometric density, which is determined using the dimensions and mass of the samples, specific heat, and thermal diffusivity which are measured from 373 K to 973 K by using the laser flash method (TC-7000, Advance-Riko, Inc.). The transverse and longitudinal speed of sound were measured by the ultrasonic pulse echo method (Echometer 1061, Karl Deutsch Prüf- und Messgerätebau GmbH & Co. KG).

3. Results and Discussion

3.1 Structure characterization

Table 1 lists the results of the sample synthesis. The mass losses during arc-melting were less than 2%. The relative densities of the sintered samples were over 95%.

Figure 2 shows the experimental powder XRD patterns for Fe_4Al_x ($x = 8.7\text{--}10.3$) together with the simulated pattern for Fe_2Al_5 . The obtained XRD patterns of Fe_4Al_x ($x = 9.4\text{--}10.2$) are identified with the calculated patterns of the Fe_2Al_5 phase. The patterns for $\text{Fe}_4\text{Al}_{8.7}$ and $\text{Fe}_4\text{Al}_{9.0}$ contain impurity peaks around $2\theta = \sim 41^\circ$ as indicated with arrows in Fig. 2, which do not conform with those of neighboring phase, FeAl_2 . On the other hand, the impurity peaks of $\text{Fe}_4\text{Al}_{10.3}$ conform with those of $\text{Fe}_4\text{Al}_{13}$. We attempted to identify the impurities of $\text{Fe}_4\text{Al}_{9.0}$ and $\text{Fe}_4\text{Al}_{8.7}$ by using SEM and EDX, finding the aluminum contents can vary by 1%. These results, however, could not explain the impurity peaks. Assuming that the lattice parameter increased by 4%, the impurity peaks around $2\theta = \sim 41^\circ$ could be identified with the peaks of FeAl_2 . However, it seems unlikely that such large lattice expansion happened in the present synthesis procedure. This fact indicates $\text{Fe}_4\text{Al}_{8.7}$ and $\text{Fe}_4\text{Al}_{9.0}$ do not contain FeAl_2 .

We determined lattice parameter of Fe_4Al_x ($x = 8.4\text{--}10.2$). Figure 3 shows the lattice parameter of a -, b -, and c -axes, and unit cell volume. The parameters a , c , and V increase and b decreases with increasing the aluminum content except for $\text{Fe}_4\text{Al}_{8.4}$, suggesting that $\text{Fe}_4\text{Al}_{8.4}$ contains the secondary phase.

Taking above variations of lattice parameters into account, $\text{Fe}_4\text{Al}_{8.7}$ and $\text{Fe}_4\text{Al}_{9.0}$ seems to consist of Fe_2Al_5 though XRD patterns of them show impurity peaks, and we classified the samples into five categories shown as Table 1. Comparing the experimental range of Fe_2Al_5 with phase diagram ($x_{\text{Al}} = 0.70\text{--}0.73$), the nominal mole fraction of aluminum is lower than phase diagram by 1.5%, due to weight loss during arc-melting.

Table 1 Mole fraction for Fe_4Al_x ($x = 7.1, 7.4, 7.6, 8.0, 8.4, 8.7, 9.0, 9.4, 9.7, 10.0, 10.2, 10.3, 10.6, 11.0, 11.8$).

Phase	Nominal composition	Mole fraction of Al (%)
FeAl_2	$\text{Fe}_4\text{Al}_{7.1}$	63.96
$\text{FeAl}_2 + \text{Fe}_2\text{Al}_5$	$\text{Fe}_4\text{Al}_{7.4}$	64.91
	$\text{Fe}_4\text{Al}_{7.6}$	65.52
	$\text{Fe}_4\text{Al}_{8.0}$	66.67
	$\text{Fe}_4\text{Al}_{8.4}$	67.74
Fe_2Al_5	$\text{Fe}_4\text{Al}_{8.7}$	68.50
	$\text{Fe}_4\text{Al}_{9.0}$	69.23
	$\text{Fe}_4\text{Al}_{9.4}$	70.15
	$\text{Fe}_4\text{Al}_{9.7}$	70.80
	$\text{Fe}_4\text{Al}_{10.0}$	71.43
	$\text{Fe}_4\text{Al}_{10.2}$	71.83
$\text{Fe}_2\text{Al}_5 + \text{Fe}_4\text{Al}_{13}$	$\text{Fe}_4\text{Al}_{10.3}$	72.03
	$\text{Fe}_4\text{Al}_{10.6}$	72.60
	$\text{Fe}_4\text{Al}_{11.0}$	73.33
$\text{Fe}_4\text{Al}_{13}$	$\text{Fe}_4\text{Al}_{11.8}$	74.68

Fig. 2 Experimental and calculated X-ray diffraction patterns. Arrows indicate the peaks of secondary phases.

Fig. 3 Lattice parameters of (a) a , (b) b , (c) c , and (d) unit cell volume, V , of Fe_4Al_x ($x = 8.4, 8.7, 9.0, 9.4, 9.7, 10.0, 10.2$). The literature data are given in the reference.⁵⁾ Fig. 4 Specific heat, C , of Fe_4Al_x ($x = 9.0, 9.4, 9.7, 10.0, 10.2$) as a function of temperature. R is the gas constant. $3R$ is the specific heat of solids in Dulong-Petit's law, calculated from $C = 3RN/M$, where N is the number of atoms per unit cell, and M is the molar mass. Fig. 5 Thermal conductivity and phonon thermal conductivity of Fe_4Al_x ($x = 9.0, 9.4, 9.7, 10.0, 10.2, 11.8$) as a function of temperature. Fig. 6 Seebeck coefficient of Fe_4Al_x ($x = 9.0, 9.4, 10.0, 11.8$) as a function of temperature.

3.2 Thermoelectric properties

We measured the specific heat, the thermal conductivity, the phonon thermal conductivity, the Seebeck coefficient and ZT of the single phase samples, Fe_4Al_x ($x = 9.0, 9.4, 9.7, 10.0, 10.2, 11.8$) (Fig. 4–7).

In the case of the samples consist of Fe_2Al_5 , thermoelectric properties have little dependence on aluminum contents. The specific heat increases with the rise in temperature contrary to our expectation that aluminum atoms diffuse in a liquid-like

Fig. 7 ZT of Fe_4Al_x ($x = 9.0, 9.4, 10.0, 11.8$) as a function of temperature.

Fig. 8 Phonon thermal conductivity vs number of atoms per unit cell.

manner along the channels and inhibit thermal transport. The room-temperature phonon thermal conductivity of Fe_2Al_5 and $\text{Fe}_4\text{Al}_{13}$ are 1.5 W/mK and 0.8 W/mK respectively. Figure 6 shows the temperature dependence of the Seebeck coefficient; S decreases with increasing temperature. The absolute maximum value of S is 25 $\mu\text{V/K}$ at 973 K for all samples except for $\text{Fe}_4\text{Al}_{9.0}$. In spite of low phonon thermal conductivity, the obtained maximum ZT value of these compounds is only 0.02 because of the low Seebeck coefficient.

Figure 8 shows the variation of phonon thermal conductivities for Fe-Al compounds. We obtained phonon thermal conductivities of FeAl ($x_{\text{Al}} = 0.50$) and FeAl_2 , and the previous studies provide the values of the others.^{9,10} The values of FeAl_2 , Fe_2Al_5 and $\text{Fe}_4\text{Al}_{13}$, which have partially occupied sites in the unit cell, are lower than the values of the others. The unit cell volume of $\text{Fe}_4\text{Al}_{13}$ is seven times larger than that of Fe_2Al_5 . However, the value of $\text{Fe}_4\text{Al}_{13}$ is only half of that of Fe_2Al_5 .

3.3 The origin of low phonon thermal conductivity

From eq. (3), the phonon thermal conductivity originates from the specific heat, the group velocity and the phonon relaxation time. As mentioned above, the specific heat does not play a main role in the low phonon thermal conductivity.

We measured the speed of sounds of synthesized samples to estimate the group velocity. Table 2 shows the speed of sounds of FeAl , FeAl_2 , Fe_2Al_5 , and $\text{Fe}_4\text{Al}_{13}$ respectively. The difference in the speed of sounds is within only 10%, which

Table 2 The speed of sounds for Al-Fe system.

	FeAl	FeAl_2	Fe_2Al_5	$\text{Fe}_4\text{Al}_{13}$
Longitudinal wave, v_L / ms^{-1}	6896	6818	7200	7176
Transverse wave, v_T / ms^{-1}	3834	3870	4186	4186

Fig. 9 Electrical conductivity vs number of atoms per unit cell.

is not enough to explain the difference in the phonon thermal conductivity.

Figure 9 shows the electrical conductivity as a function of the number of atoms in the unit cell. The fact that Fe_2Al_5 has the low electrical conductivity as well as the low phonon thermal conductivity may suggest partially occupied sites scattering not only phonon but electron suppress phonon and electron relaxation time. Although the phonon thermal conductivity of Fe_2Al_5 is twice as large as that of $\text{Fe}_4\text{Al}_{13}$, electrical conductivity is almost identical. In the case of $\text{Fe}_4\text{Al}_{13}$, the lower phonon thermal conductivity can be understood through the increased phonon scattering rate due to the larger unit cell. In conclusion, low relaxation time caused by phonon scattering at partially occupied sites plays a main role in low phonon thermal conductivity.

4. Conclusion

This study focuses on thermoelectric properties for Fe_2Al_5 and $\text{Fe}_4\text{Al}_{13}$, both of which have anomalous crystal structures, and on the origin of low phonon thermal conductivity for Fe_2Al_5 . The experimental findings are concluded as follows: (i) the room-temperature phonon thermal conductivity of Fe_2Al_5 and $\text{Fe}_4\text{Al}_{13}$ are 1.5 W/mK and 0.8 W/mK respectively, (ii) despite Fe_2Al_5 contains only 15 atoms in the unit cell without heavy elements, the lattice thermal conductivity is low. Considering the chained crystal structure model of Fe_2Al_5 , the observed low phonon thermal conductivity can be explained by such atomic disordering which suppresses the phonon relaxation time, (iii) in the case of $\text{Fe}_4\text{Al}_{13}$, lower phonon thermal conductivity can be understood through the increasing phonon scattering rate due to 102 atoms in the unit cell, (iv) the maximum dimensionless figure of merit was approximately 0.02 for both Fe_2Al_5 and $\text{Fe}_4\text{Al}_{13}$ at 973 K.

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