Thermoelectric Properties of Binary Semiconducting Intermetallic Compounds Al$_2$Ru and Ga$_2$Ru Synthesized by Spark Plasma Sintering Process

Yoshiki Takagiwa$^1$, Yuka Matsubayashi$^1$, Akitoshi Suzumura$^1$, Junpei Tamura Okada$^2$ and Kaoru Kimura$^1$

$^1$Department of Advanced Materials Science, The University of Tokyo, Kashiwa 277-8561, Japan
$^2$Department of Space Biology and Microgravity Sciences, Japan Aerospace Exploration Agency, Tsukuba 305-8505, Japan

We synthesized sintered pellets of Al$_2$Ru and Ga$_2$Ru by the spark plasma sintering (SPS) method, resulted in a removal of small amount of a secondary phase and of cracks. The maximum Seebeck coefficient of Al$_2$Ru and Ga$_2$Ru shows a large positive value of 200 $\mu$V/K and 360 $\mu$V/K, respectively. In particular, a large power factor $\sim$2.8 mW/m-K$^2$ was obtained at 773 K in Ga$_2$Ru compound. The dimensionless figures of merit $ZT$ of sintered Al$_2$Ru and Ga$_2$Ru samples monotonically increase with increasing temperature and reach a maximum value of 0.20 and 0.45 at about 873 K and 773 K, respectively. [doi:10.2320/matertrans.E-M2010807]

1. Introduction

Thermoelectric materials can be used to create devices that generate power through the direct conversion of thermal energy to electrical energy. The potential of thermoelectric materials is defined by the dimensionless figure of merit, $ZT = S^2\sigma T/k$, where $S$, $\sigma$, $k$, and $T$ are the Seebeck coefficient, the electrical conductivity, the thermal conductivity, and the temperature, respectively. One of the criteria for the practical application of thermoelectric materials is that $ZT$ is desired to be above unity. To obtain a high $ZT$ value, the Seebeck coefficient and electrical conductivity should be large while the thermal conductivity should be low. Recently, a very large $ZT$ exceeding 2.0 has been reported in SrTiO$_3$ for two-dimensional electron gas. While low-dimensional materials are likely to exhibit a high $ZT$ value, bulk materials are also important for practical use in, for example, industrial processes.

Unconventional semiconductors such as FeSi have attracted attention for thermoelectric applications. While alloys composed of metallic constituents are naturally expected to be metallic, hybridization between transition metals (TM) and group III and IV elements, such as Al, Ga, and Si, leads to a band gap in the $d$ bands near the Fermi level, as confirmed by theoretical calculations. A comparatively narrow band gap, a few hundred meV, near the Fermi level is expected to cause a large absolute value of the Seebeck coefficient, which is desirable to obtain a high electric power.

Takeuchi et al. reported the composition dependence of the thermoelectric properties of $\alpha$-AlReSi alloy system, and discussed the cause of the strong composition dependence of the thermoelectric properties in terms of their electronic structure. In this material, strong covalent bonds between Al-Al atoms and Al-TM atoms are experimentally observed by the maximum entropy method (MEM)/Rietveld analysis, and are attributed to the formation of the pseudogap near the Fermi level. For Al-Pd-(Mn or Re) quasicrystals, the pseudogap is deeper than that for the approximant crystals because of a more isotropic structure. Therefore, these quasicrystals have a much higher $ZT$ value than the approximants. Nishino et al. revealed that the temperature dependence of the electrical resistivity for Heusler-type Fe$_2$VAl exhibited a semiconducting behavior. Recently, the electronic properties of Fe$_2$VAl$_{1-x}$M$_x$ (M: B, In, Si) alloys have been systematically investigated by Vasundhara et al. As pointed out by Mahan and Sofo, a narrow peak in the density of states (DOS) at a few $k_B T$ from the Fermi level can be beneficial for improving the thermoelectric performance. The above mentioned materials, indeed, possess relatively large Seebeck coefficients and high power factors $S^2\sigma$.

In this study, we focus attention on the binary semiconducting intermetallic compound Al$_2$Ru family because it has been investigated as a material related to the Al-TM-based quasicrystal. They possess the orthorhombic TiSi$_2$ structure, which has the space group $Fdd2$ with 24 atoms per unit cell. Basov et al. observed that the Al$_2$Ru is infrared active, indicating the presence of a gap. Mandrus et al. reported the temperature dependence of the thermoelectric properties of the Al$_2$Ru. However, they claimed that the Al$_2$Ru and this class of intermetallic compounds are probably not a fruitful place ($ZT\sim0.07$ at 800 K) to search for novel thermoelectric materials because of the comparatively high thermal conductivity of about 13 W/m-K at room temperature. To lower the thermal conductivity, we synthesized Ga$_2$Ru compound, formed by fully replacing Al with heavier Ga atoms in the Al$_2$Ru. The temperature dependence of the electrical conductivity under 673 K has been reported by Evers et al., and pioneering studies on the thermoelectric properties have been reported by Amagai et al. The maximum $ZT$ value of the hot-pressed Ga$_2$Ru showed 0.3 at 780 K, which was significantly smaller than that of practical thermoelectric materials. In this article, we report the thermoelectric properties of Al$_2$Ru and Ga$_2$Ru synthesized by using the spark plasma sintering (SPS) process.
2. Experimental Procedure

\( \text{Al}_2\text{Ru} \) and \( \text{Ga}_2\text{Ru} \) mother ingots were synthesized by an arc-melting technique under a purified argon atmosphere. The samples were annealed at 1273 K for 24 h. After annealing, the samples were quenched in water. However, there are some cracks and pores in the arc-melted and annealed sample, which should decrease the electrical conductivity. To improve the microstructure, we synthesized a sintered sample by the SPS method. As for the \( \text{Al}_2\text{Ru} \), \( \text{Al} \) and \( \text{Ru} \) powder was placed in a carbon die with a diameter of 10 mm for the SPS processing on SPS SYNTEX INC. (DR. SINTER. LAB., SPS-515S). The temperature of the specimen was increased from ambient temperature to 873 K in 5 min, and from 873 K to the consolidating temperature of 1223 K in 5 min, and then the consolidating temperature was held for 30 min. A pressure of 2.5 kN was applied during the heating process. After the SPS treatment, the specimen was cooled to ambient temperature under an argon atmosphere applying pressure of 2.5 kN. The sintered sample was annealed at 1023 K for 24 h and 1223 K for 24 h. To obtain a single phase of the \( \text{Al}_2\text{Ru} \), we reduced about 4 mass% of Ru powder from stoichiometric composition. As for the \( \text{Ga}_2\text{Ru} \), the arc-melted and annealed sample was crushed to an average particle size of below 20 \( \mu \)m. The powder was placed in a carbon die with a diameter of 10 mm. The temperature of the specimen was increased from ambient temperature to 873 K in 5 min, and from 873 K to the consolidating temperature of 1223 K in 5 min, and then the consolidating temperature was held for 10 min. A pressure of 3.3 kN was applied during the heating process. After the SPS treatment, the specimen was cooled to ambient temperature under an argon atmosphere applying pressure of 2.5 kN.

The characterization of the samples was performed by powder X-ray diffraction (XRD) measurements with Cu \( K\alpha \) radiation. The local compositions were examined by electron probe microanalysis (EPMA). The electrical conductivity and Seebeck coefficient were measured in a helium atmosphere at temperatures between 373 and 973 K by the four-probe method and the steady-state temperature gradient method, respectively. The thermal conductivity was obtained by measuring the density, specific heat and thermal diffusivity from 300 to 973 K by the laser flash method. Hall coefficient measurements were performed for the sintered \( \text{Ga}_2\text{Ru} \) at ambient temperature. The Debye temperatures were calculated from the transverse and longitudinal sound velocities measured by the ultrasonic pulse echo method (Nihon Matech Corp., Echometer 1062).

3. Sample Characterization

Figure 1 shows experimental and calculated XRD patterns of the \( \text{Al}_2\text{Ru} \). In the arc-melted and annealed (arc-melted) sample (a), there exist a secondary phase of \( \text{AlRu} \). On the other hand, we could obtain a pattern of single phase for \( \text{Al}_2\text{Ru} \) in sintered and annealed (sintered) sample (b), which agrees well with the calculated pattern (c). Figure 2 shows experimental and calculated XRD patterns of the \( \text{Ga}_2\text{Ru} \). Very weak peaks of a secondary phase of \( \text{Ga}_3\text{Ru} \) were observed in the arc-melted and annealed (arc-melted) sample (a). On the other hand, the amount of the secondary phase of \( \text{Ga}_2\text{Ru} \) significantly decreases in the arc-melted, annealed and sintered (sintered) \( \text{Ga}_2\text{Ru} \) samples. Pattern (c) is a calculated pattern. Arrows show the peak of a secondary phase of \( \text{AlRu} \).

![Fig. 1 X-ray diffraction patterns of (a) arc-melted and annealed (arc-melted), (b) sintered and annealed (sintered) \( \text{Al}_2\text{Ru} \).](image1)

![Fig. 2 X-ray diffraction patterns of (a) arc-melted and annealed (arc-melted), (b) arc-melted, annealed and sintered (sintered) \( \text{Ga}_2\text{Ru} \) samples. Pattern (c) is a calculated pattern. Arrows show the peak of a secondary phase of \( \text{Ga}_3\text{Ru} \).](image2)

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the sintered Al$_2$Ru and Ga$_2$Ru are 95%. The (SPS) sintered bulk density (6.16 g/cm$^3$) of the Al$_2$Ru is significantly larger than that (5.765 g/cm$^3$) of hot-pressed sample by Mandrus et al. This is due to a high relative density and slightly Ru-rich sample (as listed in Table 2) for the (SPS) sintered sample.

Figure 3 shows back scattered electron images (BEI) of the sintered Al$_2$Ru and Ga$_2$Ru samples. While there are some pores (black area) in the Al$_2$Ru, few pores are observed in the Ga$_2$Ru. There are no cracks both in the sintered Al$_2$Ru and Ga$_2$Ru samples. We cannot observe the secondary phases of AlRu and Ga$_3$Ru in the sintered Al$_2$Ru and Ga$_2$Ru, respectively. Table 2 lists the nominal compositions and averaged microprobe compositions obtained by using EPMA.

### 4. Thermoelectric Properties

The electrical resistivity $\rho$ of the Al$_2$Ru and Ga$_2$Ru from 373 to 973 K is plotted in Fig. 4(A). The previous reported data of hot-pressed Al$_2$Ru$^{15}$ and Ga$_2$Ru$^{17}$ are also plotted. $\rho$ exhibits a semiconducting behavior both in the Al$_2$Ru and Ga$_2$Ru. As for the Al$_2$Ru, $\rho_{373K}$ of the sintered sample is significantly lower than that of the arc-melted sample or hot-pressed sample.$^{15}$ This is due to the fact that the (SPS) sintered sample does not contain any cracks. However, the trend of $\rho$ was changed above 573 K: the arc-melted sample shows lower electrical resistivity than the sintered sample, which comes from the existence of metallic secondary phase of AlRu as confirmed by XRD. As for the Ga$_2$Ru, $\rho$ of the sintered sample is markedly lower than that of the arc-melted sample in the overall temperatures, but is higher than the hot-pressed sample.$^{17}$ The former trend is because the arc-melted sample contains a lot of cracks and a nonmetallic secondary phase of Ga$_3$Ru. Indeed, Ga$_3$Ru exhibits relatively higher electrical resistivity ($\sim 10^5 \Omega \cdot cm$),$^{18}$ which is one-order higher than that of the Ga$_2$Ru. We cannot discuss the latter trend at this stage because the bulk density or microprobe composition of hot-pressed Ga$_2$Ru is not described in the Ref. 17).

Above 500 K, $\rho$ obeys the Arrhenius law $\rho(T) = \rho_0 e^{\Delta/k_BT}$. 

![Image](image1.png)
The Seebeck coefficient $S$ of the $\text{Al}_2\text{Ru}$ and $\text{Ga}_2\text{Ru}$ from 373 to 973 K is plotted in Fig. 5. A large positive $S$ was observed in the overall temperatures except for the arc-melted $\text{Al}_2\text{Ru}$. The maximum $S$ value of the $\text{Al}_2\text{Ru}$ and $\text{Ga}_2\text{Ru}$ are $\sim 200$ and $\sim 360 \mu \text{V/K}$, respectively. As $S$ of $\text{Ga}_2\text{Ru}$ below 500 K exhibits negative value,\(^{18}\) therefore, it is reasonable to state that the difference in $S$ between arc-melted and sintered $\text{Ga}_2\text{Ru}$ samples is caused by the secondary phase of $\text{Ga}_2\text{Ru}$. On the other hand, comparative large difference in $S$ between the arc-melted and sintered $\text{Al}_2\text{Ru}$ samples will be caused by a metallic secondary phase of $\text{Al}_2\text{Ru}$. From the shape of the density of states (DOS) of the $\text{Al}_2\text{Ru}$ and $\text{Ga}_2\text{Ru}$,\(^{19}\) it is easily expected that $S$ and $\sigma$ is strongly affected by the position of the Fermi level. Therefore, the discrepancy in $S$ between our results and the previous data\(^{5,17}\) will be attributed to the sample’s compositions. Because the room-temperature Hall coefficient is positive for the $\text{Ga}_2\text{Ru}$, it is obvious that holes dominantly contribute to the conduction. The carrier density and mobility of the $\text{Ga}_2\text{Ru}$ are $1.13 \times 10^{18} \text{cm}^{-3}$ and 129 cm$^2$/V-s at 300 K, respectively. This result is consistent with the band-structure calculations, which predict that the $\text{Al}_2\text{Ru}$ and $\text{Ga}_2\text{Ru}$ compounds are narrow-band-gap semiconductors with a light hole pocket and heavier electron pockets.\(^{19,22,25}\)

Figure 6 shows the power factor $S^2\sigma$ of the $\text{Al}_2\text{Ru}$ and $\text{Ga}_2\text{Ru}$ as a function of temperature. A large positive $S^2\sigma$ (2.8 mW/m-K$^2$ around 700 K) was observed in the sintered $\text{Ga}_2\text{Ru}$, which is significantly higher than the previous reported data ($\sim 2.2$ mW/m-K$^2$) by Amagai et al.\(^{17}\) This $S^2\sigma_{\text{max}}$ value is comparable with the practical thermoelectric materials. On the other hand, $S^2\sigma$ value of the sintered $\text{Al}_2\text{Ru}$ shows 1.6 mW/m-K$^2$ around 800 K whose value is slightly higher than that of the result by Muta et al.\(^{24}\) The thermoelectric performance dramatically increases more than one and a half times by replacing Al with Ga atoms for sintered single phase samples. The origin of higher $\sigma$ of the $\text{Ga}_2\text{Ru}$ than that of the $\text{Al}_2\text{Ru}$ is caused by fewer pores. A comparative low $S^2\sigma$ of the arc-melted and annealed $\text{Ga}_2\text{Ru}$ (1.1 mW/m-K$^2$) is originated from the high electrical resistivity, brought by an extrinsic origin such as cracks.

We measured the specific heat $C_p$ of the $\text{Al}_2\text{Ru}$ and $\text{Ga}_2\text{Ru}$ by using the laser flash method. Figure 7 represents $C_p$ as a function of temperature from 300 to 973 K. Because an error of $C_p$ is considered to be about $\pm 10\%$, there is no significant difference in $C_p$ between the arc-melted and sintered samples.
of the Al$_2$Ru and Ga$_2$Ru. $C_p$ of the Al$_2$Ru and Ga$_2$Ru exhibit about 0.4 and 0.3 J/g-K at 300 K, respectively. The difference in $C_p$ can be explained by the difference in the mass between the Al$_2$Ru (6.16 g/cm$^3$) and Ga$_2$Ru (9.02 g/cm$^3$). We readily see that the curves approach asymptotically the value of 3R, that is, the Dulong and Petit limit. As the temperature is further increased, they cross this limit and continue to increase. This phenomenon is also observed in pure metals such as aluminum and copper.

Figure 8(A) shows the temperature dependence of the total thermal conductivity $\kappa_{\text{total}}$, together with the electronic contribution $\kappa_{\text{electronic}}$ estimated using the well-known Wiedemann-Franz law expressed by $\kappa_{\text{electronic}} = L_0 \sigma T$, where $L_0$ is the Lorentz number. We assumed $L_0$ to be 2.45 $\times$ 10$^{-8}$ V$^2$/K$^2$. $\kappa_{\text{total}}$ of the Ga$_2$Ru is 7–8 W/m-K at 300 K, which is beneficially lower than that (10–12 W/m-K) of the Al$_2$Ru. The room temperature magnitude of $\kappa_{\text{total}}$ of the sintered Ga$_2$Ru is $\sim$7 W/m-K that is consistent with the previous result of hot-pressed sample.\(^{(17)}\) $\kappa_{\text{total}}$ first decreases with increasing temperature up to 600 K, and then slightly increases with increasing temperature; this is mainly brought by the increase in the electronic contribution. It should be mentioned here that the samples for the thermal conductivity measurement were different from the samples for the electrical resistivity and Seebeck coefficient measurement, which means that, for the arc-melted samples, the situation of cracks and second phases, and their effects to the physical properties are different in the two samples. This causes that $\kappa_{\text{electronic}}$ of the arc-melted samples cannot be evaluated accurately. Thus, we estimate and compare the lattice thermal conductivity $\kappa_{\text{phonon}}$ ($= \kappa_{\text{total}} - \kappa_{\text{electronic}}$) for only the sintered samples as shown in Fig. 8(B). As for the sintered samples, it was observed that the Ga$_2$Ru with heavier atomic weight have the lower $\kappa_{\text{phonon}}$. This can be understood by the difference in the Debye temperature $\theta_D$, 520 K and 450 K, of the sintered Al$_2$Ru and Ga$_2$Ru samples, respectively. We calculated the minimum lattice thermal conductivity $\kappa_{\text{min}}$ for the Ga$_2$Ru using the model proposed by Cahill et al.\(^{(25)}\) The calculated $\kappa_{\text{min}}$ is about 1.0 W/m-K above 373 K as plotted in Fig. 8(B), which is about one-third of the sintered Ga$_2$Ru sample.

5. Estimation of Figure of Merit

Finally, we present the dimensionless figure of merit $ZT$ of the Al$_2$Ru and Ga$_2$Ru from 373 to 973 K in Fig. 9. The maximum $ZT$ value $ZT_{\text{max}}$ of the sintered Al$_2$Ru exhibits 0.20 above 900 K, which is significantly higher than the previous report (0.07 at 800 K).\(^{(15)}\) This is mainly brought by the decrease in the electrical resistivity because of removing cracks. On the other hand, the sintered Ga$_2$Ru exhibits $ZT_{\text{max}} = 0.45$ at 773 K, which is higher than the previous report (0.3 at 780 K)\(^{(17)}\) because of better microstructure and is over twice higher than that of the sintered Al$_2$Ru measured in this study because of heavier mass of Ga than that of Al and the better microstructure. The potential $ZT_{\text{max}}$ of the Ga$_2$Ru compound is $\sim$0.74, as estimated using the ideal minimum thermal conductivity ($= \kappa_{\text{min}} + \kappa_{\text{electronic}}$). This result indicates that the Ga$_2$Ru compound is a potential candidate for a novel
Thermoelectric material. Substitution of multiple elements with different masses will reduce $k_{\text{phonon}}$ via induced mass fluctuations and strain field effects.\textsuperscript{26,27} Furthermore, the power factor will increase to optimize the electronic structure via hole-doped substitutions.

6. Conclusions

In this study, the temperature dependence of the thermoelectric properties and the dimensionless figure of merit $ZT$ of binary semiconducting intermetallic $\text{Al}_2\text{Ru}$ and $\text{Ga}_2\text{Ru}$ compounds were investigated. We successfully synthesized the single-phase of the $\text{Al}_2\text{Ru}$ and $\text{Ga}_2\text{Ru}$ synthesized by using the SPS process. In particular, the SPS process is more favorable than the arc-melted and annealed process because the small amounts of secondary phase and a lot of cracks can be removed. We beneficially reduced the thermal conductivity by fully replacing Ga for Al atoms in the $\text{Al}_2\text{Ru}$. Also a large value ($\approx2.8\text{ mW/m-K}^2$) of $S^2\sigma$ was obtained in the sintered $\text{Ga}_2\text{Ru}$. $ZT$ increases with increasing temperature and reaches a maximum value of 0.45 at about 773 K. The potential $ZT_{\text{max}}$ is about 0.74, as estimated using the ideal minimum thermal conductivity, indicating that the $\text{Ga}_2\text{Ru}$ compound is a potential candidate for a novel thermoelectric material. Substitution of multiple elements with different masses will reduce the phonon thermal conductivity and the power factor will increase to optimize the electronic structure, which can obtain a higher $ZT$ value.

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