Reduction of Thermal Conductivity for Icosahedral Al-Cu-Fe Quasicrystal through Heavy Element Substitution

Yoshiki Takagiwa 1,* , Ryota Maeda 1, Satoshi Ohhashi 2 and An-Pang Tsai 2

Abstract: Icosahedral Al-Cu-Fe quasicrystal (QC) shows moderate electrical conductivity and low thermal conductivity, and both p- and n-type conduction can be controlled by tuning the sample composition, making it potentially suited for thermoelectric materials. In this work, we investigated the effect of introducing chemical disorder through heavy element substitution on the thermal conductivity of Al-Cu-Fe QC. We substituted Au and Pt elements for Cu up to 3 at% in a composition of Al 63 Cu 25 Fe 12 , i.e., Al 63 Cu 25−x(Au,Pt) x Fe 12 (x = 0, 1, 2, 3). The substitutions of Au and Pt for Cu reduced the phonon thermal conductivity at 300 K (κ_{ph,300K}) by up to 17%. The reduction of κ_{ph,300K} is attributed to a decrease in the specific heat and phonon relaxation time through heavy element substitution. We found that increasing the Pt content reduced the specific heat at high temperatures, which may be caused by the locked state of phasons. The observed glass-like low values of κ_{ph,300K} (0.9–1.1 W m⁻¹ K⁻¹ at 300 K) for Al 63 Cu 25−x(Au,Pt) x Fe 12 are close to the lower limit calculated using the Cahill model.

Keywords: quasicrystals; thermal conductivity; Al-Cu-Fe; heavy element substitution; thermoelectric properties

1. Introduction

Thermoelectric materials can directly convert a temperature difference into electrical voltage. Home heating, automotive exhaust, and industrial processes all generate enormous waste heat. Thermoelectric materials can recover waste heat emitted from commercial and industrial cycles. The potential of thermoelectric materials can be evaluated by the dimensionless figure of merit zT, as expressed by

\[ zT = \frac{S^2\sigma}{k_t} \]  

(1)

where \( S \), \( \sigma \), \( k_t \), and \( T \) are the Seebeck coefficient, the electrical conductivity, the total thermal conductivity, and the temperature, respectively [1,2]. In general, \( k_t \) is the sum of two contributions, the phonon part \( k_{ph} \) and the electron part \( k_{el} \):

\[ k_t = k_{ph} + k_{el} \]  

(2)

To enhance \( zT \), it is necessary to simultaneously optimize \( S \), \( \sigma \), and \( k_t \). Icosahedral quasicrystals (QCs) have shown good thermoelectric properties because of the formation of the pseudogap and complex crystal structures [3]. We succeeded in an enhancement of \( zT \) for Al 71 Pd 29 Mn 9 QC from 0.18 to 0.26 through 3 at% Ga substitution for Al without reducing the power factor \( S^2\sigma \). Substitution of Ga at less than 4 at% for Al had less influence on both \( \sigma \) and \( S \), while \( k_t \) (in particular, \( k_{ph} \)) decreased through the combination of weakening of the intercluster bonds and an alloying effect [3–5].
Icosahedral Al-Cu-Fe QC shows the following attractive characteristics as a potential thermoelectric material:

(i) The magnitude and sign of the Seebeck coefficient strongly depend on the sample composition, i.e., the position of the Fermi level in the electronic density of states, indicating that both p- and n-type materials can be obtained in the same alloy [6–8].

(ii) As expected from a complex crystal structure, a low $\kappa_t$ of less than 2 W m$^{-1}$ K$^{-1}$ at 300 K has been reported [7–10].

(iii) The constituent elements are nontoxic, readily available, and show favorable costs for industrial use [11].

Although several advantageous physical properties are recognized in Al-Cu-Fe QC, there are only a few studies on the high-temperature thermoelectric properties [9,12]. Until now, the effect of elemental substitution on the thermoelectric properties of Al-Cu-Fe QC has not been clarified. In particular, lowering $\kappa_{ph}$ using an alloying effect, inspired from previous works [4,13,14] on Al-Pd-Mn and Al-Pd-Re QCs by transition metal substitutions, remains a possibility. We also expected that the suppression of phason flipping by heavy element substitution could reduce the thermal conductivity. In this work, we focus on icosahedral Al-Cu-Fe QC for lowering $\kappa_t$ and investigate the effects of Au and Pt substitutions for Cu on $\kappa_{ph}$. Here, we selected Au and Pt as substitution elements for Cu because of the large atomic radii, strong bond strength with Al, and a high melting point of Pt. From the experimental point of view, investigating high-temperature thermal conductivity is of great importance for controlling the unusual increase in the specific heat [15–19] for Al-based QCs and approximants, which provides an additional route to tune the thermoelectric [3] and thermal rectifier [12] properties.

2. Experimental Procedure and Sample Characterization

Mother ingots of Al$_{63}$Cu$_{25-x}$(Au,Pt)$_x$Fe$_{12}$ ($x = 0, 1, 2, 3$) were synthesized by an arc melting technique and annealed at 1073 K for 48 h under a purified argon atmosphere. The obtained ingots were crushed to a particle size of less than 45 $\mu$m. The regulated powder samples were put into a carbon die with an inner diameter of 10 mm for spark plasma sintering with a heating rate of ~150 K min$^{-1}$ (LABOX-110MC; SinterLand, Inc., Niigata, Japan). A pressure of 57 MPa was applied under a purified argon atmosphere during the sintering process. The consolidating temperature was maintained for 10 min for all samples. Table 1 lists applied consolidating temperatures, bulk densities obtained from geometric calculations, and crystalline sizes using Scherrer’s formula for Al$_{63}$Cu$_{25-x}$(Au,Pt)$_x$Fe$_{12}$ ($x = 0, 1, 2, 3$). The resulting relative densities were over 95%. The bulk density increased with increasing Au and Pt fraction $x$, which can be understood as increasing the average mass through heavy element substitution. The estimated crystalline sizes were slightly larger than the value (850 Å) of the NIST Si standard powder sample. The phase purity of the samples was evaluated by X-ray diffraction (XRD) (SmartLab; Rigaku, Inc., Tokyo, Japan), as shown in Figure 1a,b. We observed peak shifting to a lower degree with increasing (Au,Pt) concentrations, indicating that the quasilattice constant increased (Figure 2). This behavior can be qualitatively explained by the substitution of larger atomic radii of Au (1.37Å) and Pt (1.39Å) for Cu (1.28Å). Only the sample of Al$_{63}$Cu$_{22}$Au$_3$Fe$_{12}$ contained a small amount of the excess phase of Al$_2$Au. The precipitates can affect the thermoelectric properties; thus, we excluded the results and discussion for Al$_{63}$Cu$_{22}$Au$_3$Fe$_{12}$. Composition analyses were performed using inductively coupled plasma atomic emission spectroscopy (ICP) analysis (Table 2). We found that the analyzed Au/Pt concentration increased with increasing nominal fraction, except for the sample of Al$_{63}$Cu$_{22}$Au$_3$Fe$_{12}$, in which the secondary phase of Al$_2$Au was precipitated. From ICP analysis, we found that Au hardly substitutes for Cu, while Pt can substitute for Cu up to 3 at%.
Table 1. List of applied consolidating temperatures, bulk densities, crystalline sizes for $\text{Al}_{63}\text{Cu}_{25-x}(\text{Au,Pt})_x\text{Fe}_{12}$ ($x = 0, 1, 2, 3$).

| Samples | Consolidating Temperature (K) | Bulk Density (g cm$^{-3}$) | Crystalline Size (Å) |
|---------|-------------------------------|-----------------------------|----------------------|
| $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ | 898 | 4.43 | 1256(62) |
| $\text{Al}_{63}\text{Cu}_{24}\text{Au}_1\text{Fe}_{12}$ | 1013 | 4.58 | 1090(58) |
| $\text{Al}_{63}\text{Cu}_{23}\text{Au}_2\text{Fe}_{12}$ | 1018 | 4.70 | 824(70) |
| $\text{Al}_{63}\text{Cu}_{22}\text{Au}_3\text{Fe}_{12}$ | 1033 | 4.80 | 379(13) |
| $\text{Al}_{63}\text{Cu}_{23}\text{Pt}_1\text{Fe}_{12}$ | 948 | 4.66 | 1062(16) |
| $\text{Al}_{63}\text{Cu}_{22}\text{Pt}_2\text{Fe}_{12}$ | 968 | 4.86 | 979(17) |
| $\text{Al}_{63}\text{Cu}_{22}\text{Pt}_3\text{Fe}_{12}$ | 1083 | 4.88 | 974(16) |

Figure 1. X-ray diffraction patterns of (a) $\text{Al}_{63}\text{Cu}_{25-x}(\text{Au,Pt})_x\text{Fe}_{12}$ ($x = 0, 1, 2, 3$), together with peak indices and calculated peak positions of $\text{Al}_2\text{Au}$, and (b) $\text{Al}_{63}\text{Cu}_{25-x}\text{Pt}_x\text{Fe}_{12}$ ($x = 0, 1, 2, 3$). Arrows indicate peaks of excess phase of $\text{Al}_2\text{Au}$. 
Figure 1. X-ray diffraction patterns of (a) Al$_{63}$Cu$_{25-x}$(Au,Pt)$_x$Fe$_{12}$ and (b) Al$_{63}$Cu$_{25}$Al$_2$Fe$_{12}$, $x = 0, 1, 2, 3$.

Figure 2. Quasilattice constant of Al$_{63}$Cu$_{25-x}$(Au,Pt)$_x$Fe$_{12}$ ($x = 1, 2, 3$).

Table 2. Nominal compositions and ICP results for Al$_{63}$Cu$_{25-x}$(Au,Pt)$_x$Fe$_{12}$ ($x = 1, 2, 3$).

| Nominal Compositions | Phase | ICP Analysis of Chemical Composition |
|----------------------|-------|-------------------------------------|
| Al$_{63}$Cu$_{34}$Al$_2$Fe$_{12}$ | $i$ | Al$_{63}$Cu$_{24.2}$Au$_{0.9}$Fe$_{11.8}$ |
| Al$_{63}$Cu$_{34}$Al$_2$Fe$_{12}$ | $i$ | Al$_{63}$Cu$_{22.4}$Au$_{1.9}$Fe$_{11.7}$ |
| Al$_{63}$Cu$_{22}$Au$_2$Fe$_{12}$ | $i$ | Al$_{65.2}$Cu$_{21.2}$Au$_{1.7}$Fe$_{11.4}$ |
| Al$_{63}$Cu$_{34}$Pt$_1$Fe$_{12}$ | $i$ | Al$_{63.2}$Cu$_{24.2}$Pt$_{0.9}$Fe$_{11.3}$ |
| Al$_{63}$Cu$_{24}$Pt$_2$Fe$_{12}$ | $i$ | Al$_{63.2}$Cu$_{23.8}$Pt$_{1.7}$Fe$_{11.3}$ |
| Al$_{63}$Cu$_{22}$Pt$_3$Fe$_{12}$ | $i$ | Al$_{63.1}$Cu$_{22.3}$Pt$_{2.6}$Fe$_{12}$ |

The total thermal conductivity $κ_t$ was calculated from the density $d$, the specific heat at constant pressure $C_p$, and the thermal diffusivity $λ$ using the relationship $κ_t = dC_pλ$. Both $C_p$ and $λ$ were measured by the laser flash method (TC-7000; Advance Riko, Inc., Kanagawa, Japan) from 300 to 873 K. The transverse and longitudinal speeds of sound were measured by ultrasonic pulse-echo method (Echometer 1062; Nihon Matech Corp., Tokyo, Japan). The electrical conductivity was measured between 300 K and 873 K by the four-probe method (ZEM-3; Advance Riko, Inc., Kanagawa, Japan) for a rough estimation of the electron thermal conductivity $κ_{el}$ using the Wiedemann–Franz law. The Seebeck coefficient was obtained by the steady-state temperature gradient method using a ZEM-3 instrument.

3. Results and Discussion

Figure 3a,b show the temperature dependences of $C_p$ and $λ$ from 300 to 873 K for Al$_{63}$Cu$_{25-x}$(Au,Pt)$_x$Fe$_{12}$ ($x = 0, 1, 2, 3$). The measured $C_p$ of Al$_{63}$Cu$_{25}$Fe$_{12}$ increased with increasing temperature and reached between 4$R$ and 5$R$ at 873 K, as shown in Figure 3a. This behavior is quantitatively consistent with a previous report by Prekul et al. [16]. An unusual increase in the $C_p$ of icosahedral and decagonal QCs was discussed in terms of the introduction of chemical disorder and anharmonicity in lattice vibration [15] and the localized electronic nature [16] of QCs. Edagawa et al. first mentioned that excess specific heat can be attributed to the excitation of phasons [15], which will be discussed below. The values of $C_p$ at 300 K for both Au- and Pt-substituted samples decreased with increasing $x$ because of an increase in mean atomic weight. However, the trend of $C_p$ at high temperatures is rather complex; the $C_p$ values of Au- and Pt-substituted samples, except for a sample with $x = 3$ (Pt), were larger than that of pristine Al-Cu-Fe. Here, we exclude the detailed discussion on $C_p$ of Au-substituted samples because Au did not systematically substitute for Cu, as already mentioned in Section 2. It is easily expected that increasing Pt fraction will bring chemical disorder in the atomic arrangement. Therefore, the observed increase in $C_p$ at high temperatures for samples with $x = 1$ and 2 can be caused by introducing chemical disorder. On the contrary, the systematic decrease in $C_p$ at 873 K...
with increasing Pt fraction was observed; in particular, the \( C_P \) of the sample with \( x = 3 \) was lower than that of \( \text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12} \) QC. The observed reduction of \( C_P \) at high temperatures may be attributed to the locked state of phasons, that is, a pinning effect of phasons through heavy element substitution for Cu sites. However, there is room for further discussion on the effect of excited or locked phasons on the high-temperature specific heat, which will enhance our knowledge of the specific features of QCs. On the other hand, as expected, the \( \lambda \) values were reduced by both Au and Pt substitutions throughout the measurement temperature region because of the alloying effect, as shown in Figure 3b.

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The values of \( C_P \) at 300 K for both Au- and Pt-substituted samples decreased with increasing \( x \) because of an increase in mean atomic weight. However, the trend of \( C_P \) at high temperatures is rather complex; the \( C_P \) values of Au- and Pt-substituted samples, except for a sample with \( x = 3 \) (Pt), were larger than that of pristine \( \text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12} \) QC. Here, we exclude the detailed discussion on \( C_P \) of Au-substituted samples because Au did not systematically substitute for Cu, as already mentioned in Section 2. It is easily expected that increasing Pt fraction will bring chemical disorder in the atomic arrangement. Therefore, the observed increase in \( C_P \) at high temperatures for samples with \( x = 1 \) and 2 can be caused by introducing chemical disorder. On the contrary, the systematic decrease in \( C_P \) at 873 K with increasing Pt fraction was observed; in particular, the \( C_P \) of the sample with \( x = 3 \) was lower than that of \( \text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12} \) QC. The observed reduction of \( C_P \) at high temperatures may be attributed to the locked state of phasons, that is, a pinning effect of phasons through heavy element substitution for Cu sites. However, there is room for further discussion on the effect of excited or locked phasons on the high-temperature specific heat, which will enhance our knowledge of the specific features of QCs. On the other hand, as expected, the \( \lambda \) values were reduced by both Au and Pt substitutions throughout the measurement temperature region because of the alloying effect, as shown in Figure 3b.

Figure 3. (a) Specific heat at constant pressure \( C_P \), (b) thermal diffusivity \( \lambda \), and (c) total thermal conductivity \( \kappa_t \) as a function of temperature for \( \text{Al}_{63}\text{Cu}_{25−x}(\text{Au, Pt})_x\text{Fe}_{12} \) (\( x = 0, 1, 2, 3 \)). The dashed and dotted lines represent the Dulong–Petit limit (3\( R \)) and 5\( R \), respectively. \( \text{Al}_{63}\text{Cu}_{22}\text{Au}_3\text{Fe}_{12} \) is excluded because of secondary phase precipitation.

The temperature dependence of obtained \( \kappa_t \) for all samples is displayed in Figure 3c. The value of \( \kappa_t \) at 300 K (\( \kappa_{t,300K} \)) for \( \text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12} \) is 1.42 W m\(^{-1}\) K\(^{-1}\); previously reported \( \kappa_{t,300K} \) of Al-Cu-Fe QC is distributed in the range of 1–2 W m\(^{-1}\) K\(^{-1}\) [7–10], which is caused by the difference in the sample composition because \( \kappa_t \) (in particular, \( \kappa_{el} \)) is sensitive to the actual composition, as observed in Al-Pd-Re QC [20]. However, the details are not clear at this stage because the analyzed composition and each parameter of \( \kappa_t \), \( C_P \), and \( \lambda \) were not described in the literature [7–10]. Compared with other Al-based QCs, the measured \( \kappa_{t,300K} \) of \( \text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12} \) is significantly higher than those of Al-Pd-Mn and Al-Pd-Re QCs [3,20] because of the relatively light constituent elements Fe and Co, compared with Pd and Re. A detailed comparison will be discussed below.
Table 3 lists the $\kappa_{t,300K}$ for all samples investigated. While the $\kappa_{t,300K}$ for Au-substituted samples increased by up to 2.8%, the $\kappa_{t,300K}$ for Pt-substituted samples decreased by up to 7.7%. To understand the different behaviors of $\kappa_{t,300K}$ with Au and Pt substitutions, we evaluated the lattice component of $\kappa_{\text{ph}}$ after subtracting $\kappa_{\text{el}}$ from $\kappa_{t}$ using the Wiedemann–Franz law:

$$\kappa_{\text{ph}} = \kappa_{t} - \kappa_{\text{el}} = \kappa_{t} - L_0 \sigma T$$

(3)

where $L_0$ is the Lorenz number. We estimated $L_0$ value using a model proposed by Kim et al., $L_0 = 1.5 + \exp[-1.16]*10^{-8}$ $\Omega$ $\cdot$ $m$ $^2$ $K^{-2}$ [21]. The electrical conductivity $\sigma$ and calculated $\kappa_{\text{el}}$ as a function of temperature are displayed in Figure 4a,b. All samples show semiconductor-like behavior, i.e., $\sigma$ increases with increasing temperature [Figure 4a]; thus, the estimated $\kappa_{\text{el}}$ also increases monotonically [Figure 4b]. The measured $\sigma$ at 300 K ($\sigma_{300K}$) for $\text{Al}_3\text{Cu}_{25-x}\text{Fe}_{12}$ was approximately 400 $\Omega^{-1}$ $cm^{-1}$, which is consistent with previous data of similar sample compositions of Al-Cu-Fe QC [6–8, 10]. Contrary to expectation, $\sigma$ significantly increased with Au substitution ($\sigma_{300K}$ $\sim$700 $\Omega^{-1}$ $cm^{-1}$), although Cu and Au have the same number of electrons per atom ratio ($e/a$) of +1 [22]. Referring to the results of ICP composition analyses (Table 2), the Al concentration of Au-substituted samples increased as $x$ increases. Therefore, the measured enhancement of $\sigma$ will be caused by the different $\text{Al}/(\text{Cu}+\text{Au})$ ratios, i.e., shifting the position of the Fermi level in the electronic density of states. On the other hand, Pt substitution for Cu succeeds in more precise composition control with almost constant Al concentration. The sample with $x = 1$ (Pt) possessed a higher $\sigma_{300K}$ of 550 $\Omega^{-1}$ $cm^{-1}$, probably because of an increase in the carrier concentration, compared with the sample with $x = 0$. In turn, the carrier mobility of samples with higher Pt fractions of $x = 2, 3$ will be largely suppressed by introducing chemical disorder, resulting in a decrease in $\sigma$ for the samples with $x = 2$ and 3. Although the microstructure (such as defect, strain, and grain size) can also affect $\sigma$, the observed non-monotonic change in $\sigma$ cannot be explained only by such extrinsic factors.

Table 3. Total thermal conductivity at 300 K ($\kappa_{t,300K}$) and its rate of change ($\Delta\kappa_{t,300K}/\kappa_{t,300K}$), phonon thermal conductivity at 300 K ($\kappa_{\text{ph},300K}$) and its rate of change ($\Delta\kappa_{\text{ph},300K}/\kappa_{\text{ph},300K}$), rate of change in specific heat at 300 K ($\Delta\gamma_{300K}/\gamma_{300K}$), rate of change in speed of sound ($\Delta\nu_s/\nu_s$), and minimum thermal conductivity at 300 K ($\kappa_{\text{min},300K}$) for $\text{Al}_3\text{Cu}_{25-x}(\text{Au},\text{Pt})_x\text{Fe}_{12}$ ($x = 0, 1, 2, 3$). $\text{Al}_3\text{Cu}_{25-x}\text{Au}_2\text{Fe}_{12}$ is excluded because of secondary phase precipitation.

| Samples | $\kappa_{t,300K}$ | $\Delta\kappa_{t,300K}/\kappa_{t,300K}$ | $\kappa_{\text{ph},300K}$ | $\Delta\kappa_{\text{ph},300K}/\kappa_{\text{ph},300K}$ | $\Delta\gamma_{300K}/\gamma_{300K}$ | $\Delta\nu_s/\nu_s$ | $\kappa_{\text{min},300K}$ |
|---------|-----------------|--------------------------------|-----------------|--------------------------------|-----------------|-----------------|-----------------|
| $x = 0$ | 1.42            | -                              | 1.12            | -                              | -               | -               | -               |
| Au: $x = 1$ | 1.41          | -0.7                           | 0.96            | -14.3                          | -               | -               | -               |
| Au: $x = 2$ | 1.46          | 2.8                            | 1.06            | -5.4                           | -               | -               | -               |
| Pt: $x = 1$ | 1.33          | -6.3                           | 0.93            | -17.0                          | -               | -               | -               |
| Pt: $x = 2$ | 1.35          | -4.9                           | 1.03            | -8.0                           | -               | -               | -               |
| Pt: $x = 3$ | 1.31          | -7.7                           | 1.03            | -8.0                           | -               | -               | -               |

| Samples | $\Delta\gamma_{300K}/\gamma_{300K}$ | $\Delta\nu_s/\nu_s$ | $\kappa_{\text{min},300K}$ |
|---------|--------------------------------|-----------------|-----------------|
| $x = 0$ | -                              | -               | -               |
| Au: $x = 1$ | -3.9                         | -0.2            | 1.11            |
| Au: $x = 2$ | -4.5                         | -5.2            | 1.08            |
| Pt: $x = 1$ | -8.7                         | -0.2            | 1.13            |
| Pt: $x = 2$ | -13                          | -2.3            | 1.12            |
| Pt: $x = 3$ | -11                          | 0               | 1.14            |
Returning to the estimation of $\kappa_{el}$, the Wiedemann–Franz law applied for pseudogap and narrow-gap compounds is found to be invalid because it assumes that the spectral conductivity varies linearly with energy [17]. The validity of the Wiedemann–Franz law was also discussed by Maciá [23]. Hitherto, there is no empirical relation to calculate $\kappa_{el}$ for QCs; thus, we adopted the conventional Equation (3) and $L_{0}$ values using an empirical model [21] for a rough estimation of $\kappa_{ph}$.

The calculated $\kappa_{ph}$ as a function of temperature are shown in Figure 5a,b. It should be noted that although the apparent increase in $\kappa_{ph}$ at high temperatures originates from conduction carriers [17], room-temperature $\kappa_{ph}$ may not be largely under- or over-estimated. We found that the increase in $\kappa_{el,300K}$ for Au-substituted samples (Table 3) is attributed to an increase in $\kappa_{el}$, as shown in Figure 4b, probably because of an increase in the carrier concentration because the electrical conductivity increases for Au-substituted Al-Cu-Fe [Figure 4a]. The $\kappa_{ph}$ at 300 K ($\kappa_{ph,300K}$) for both Au- and Pt-substituted samples decreased by up to 14.3% and 17.0%, respectively (Table 3), which is caused by the alloying effect. For a better understanding of the decrease in $\kappa_{ph,300K}$, we performed speed-of-sound measurements for pristine and Au- and Pt-substituted samples. The obtained speeds of sound $v_{s}$ are distributed between 4150–4400 m s$^{-1}$, and no composition dependence of $v_{s}$ is observed. Here, $\kappa_{ph}$ is expressed using the specific heat at constant volume $C_{V}$, $v_{s}$, and the phonon relaxation time $\tau_{ph}$,

$$\kappa_{ph} = \frac{1}{3} C_{V} v_{s}^{2} \tau_{ph}$$  \hspace{1cm} (4)

We now compare each parameter change of $C_{P}$ and $v_{s}$, as listed in Table 3. Here, we should discuss $C_{V}$ rather than $C_{P}$ using the following relationship [15]:

$$C_{V} = C_{P} - 9VB\alpha^{2}T$$  \hspace{1cm} (5)

where $V$, $B$, and $\alpha$ are the atomic volume, the bulk modulus, and the linear thermal expansion coefficient, respectively. Although we did not perform measurements of $B$ and $\alpha$, qualitative analysis can be performed using the parameter $C_{P}$. The rate of change in $C_{P}$, $\Delta C_{P,300K}/C_{P,300K}$, increased with increasing Au/Pt fraction; the reduction of $C_{P}$ at 300 K for Pt-substituted samples is larger than that for Au-substituted samples. On the other hand, the rate of change in $v_{s}$, $\Delta v_{s}/v_{s}$, had less influence on $\kappa_{ph,300K}$. However, the additional reduction of $\tau_{ph}$ should be considered to explain $\Delta \kappa_{ph,300K}/\kappa_{ph,300K}$ of 14.3% and 17.0% for Au- and Pt-substituted samples, respectively. The reduction of $\tau_{ph}$ is estimated to be up to ~11%, and the alloying effect through heavy element substitution, in particular, worked in dilute Au- and Pt-substituted Al-Cu-Fe QC.

Figure 4. (a) Electrical conductivity $\sigma$ and (b) electron thermal conductivity $\kappa_{el}$ as a function of temperature for Al$_{63}$Cu$_{25-}$(Au,Pt)$_{2}$Fe$_{12}$ ($x = 0, 1, 2, 3$). Al$_{63}$Cu$_{22}$Au$_{1}$Fe$_{12}$ is excluded because of secondary phase precipitation.
Indeed, the values of $\Delta P$ at 300 K for $\text{Al}_{63}\text{Cu}_{25-x}\text{Au}_{x}$ Fe$_{12}$ (x = 0, 1, 2, 3) are already close to the value of ternary Al-Pd-Mn QC [3], in which a heavier mean atomic weight is expected.

The reduction of $C_P$ and $\tau_{ph}$ for amorphous solids and disordered crystals. The thermal conductivity is calculated using the model proposed by Cahill et al. [24, 25], which provides the lower limit of the lattice thermal conductivity $\kappa_{\text{min}}$ for cubic-Au-Al-RE ACs and extra phonon engineering such as nanostructuring [26] will not be beneficial for further reduction of $\kappa_{\text{ph}}$ of the present materials.

Next, we evaluated the minimum thermal conductivity $\kappa_{\text{min}}$ using the model proposed by Cahill et al. [24, 25], which provides the lower limit of the lattice thermal conductivity for amorphous solids and disordered crystals. The $\kappa_{\text{min}}$ can be calculated as the following equation,

$$\kappa_{\text{min}} = \left(\frac{\pi}{6}\right)^\frac{1}{2} k_B n^\frac{3}{2} \sum l_t v_{l,t} \left(\frac{T}{\theta_{l,t}}\right)^2 \int_0^{\theta_{l,t}} \frac{x^3 e^x}{(e^x - 1)^2} dx$$  \hspace{0.5cm} (6)

Here, $k_B$ is the Boltzmann constant, $n$ is the number density of atoms, $v_l$ is the longitudinal speed of sound, $v_t$ is the transverse speed of sound, $T$ is the temperature, and $\theta_{l,t}$ is the cut off temperature, $\theta_{l,t} = v_{l,t}\left(\frac{h}{k_B}\right)(6\pi^2N)^\frac{1}{3}$, where $h$ is Planck's constant. The calculated $\kappa_{\text{min}}$ is listed in Table 3. Note here that the values of $\kappa_{\text{ph,300K}}$ for $\text{Al}_{63}\text{Cu}_{25-x}(\text{Au,Pt})_x\text{Fe}_{12}$ are already close to the $\kappa_{\text{min}}$, indicating that extra phonon engineering such as nanostructuring [26] will not be beneficial for further reduction of $\kappa_{\text{ph}}$ of the present materials.

Finally, we compare $\kappa_{\text{ph,300K}}$ for various three-dimensional icosahedral QCs and related approximant crystals (AC): Al-Cu-Fe QC, Al-Cu-(Au,Pt)-Fe QCs, Al-Pd-Mn QC [3], Al-Pd-Re QC, and Tsai-type cubic-Au-Al-Gd AC [27], as shown in Figure 6. Compared with Al-based ternary QCs, Al-Cu-Fe QC having a lighter mean atomic weight shows the highest $\kappa_{\text{ph,300K}}$, while Al-Pd-Re QC shows the lowest one. A significant increase in $d$ results in a low $\nu_s$, $\nu_s = \sqrt{B/d}$. Indeed, the values of $\nu_s$ are 4340, 3770, and 3590 m s$^{-1}$ for Al-Cu-Fe QC, Al-Pd-Mn QC [4], and Al-Pd-Re QC, respectively. Note here again that the decrease in $\kappa_{\text{ph,300K}}$ of Au- and Pt-substituted Al-Cu-Fe QCs is attributed to the reduction of both $C_P$ and $\tau_{ph}$. Recently discovered Tsai-type Au-based approximant ACs have rather heavy atomic weight, close to 130 g mol$^{-1}$. One example is cubic-Au-Al-RE ACs; a glass-like low $\kappa_{\text{ph,300K}}$ of $\approx 0.6$ W m$^{-1}$ K$^{-1}$ was observed for Au-Al-Gd AC. Cubic-Au-Al-RE ACs may be a good starting point for enhancing thermoelectric properties because they possess wide composition ranges [28]. Compared with pristine Al-Cu-Fe, the Au/Pt substitution brings a heavier atomic weight of up to 10%. The $\kappa_{\text{ph,300K}}$ of Au/Pt-substituted quaternary Al-Cu-Fe has a value close to that of ternary Al-Pd-Mn QC [3], in which a heavier mean atomic weight is expected.

![Figure 5. Phonon thermal conductivity $\kappa_{\text{ph}}$ as a function of temperature for (a) $\text{Al}_{63}\text{Cu}_{25-x}\text{Au}_{x}$ Fe$_{12}$ (x = 0, 1, 2) and (b) $\text{Al}_{63}\text{Cu}_{25-x}\text{Pt}_{x}$ Fe$_{12}$ (x = 0, 1, 2, 3). The dashed lines represent the minimum thermal conductivity $\kappa_{\text{min}}$ for $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$.](image-url)
Figure 6. Phonon thermal conductivity at 300 K $\kappa_{ph,300K}$ versus mean atomic weight for various undoped icosahedral quasicrystals (QCs) and related approximant crystals (ACs): Al-Cu-Fe QC, Al-Cu-(Au,Pt)-Fe QCs, Al-Pd-Mn QC [4], Al-Pd-Re QC, and cubic-Au-Al-Gd AC [27]. The Au/Pt substitution reduced $\kappa_{ph,300K}$ down to that of Al-Pd-Mn QC [4]. The dashed curve is drawn to guide the eye.

4. Conclusions

We investigated the effects of Au and Pt substitutions on the thermal conductivity above 300 K for $\text{Al}_{63}\text{Cu}_{25-x}(\text{Au,Pt})_{x}\text{Fe}_{12}$ ($x = 0, 1, 2, 3$). High-density Au- and Pt-substituted Al-Cu-Fe samples were successfully synthesized by the combination of arc melting and spark plasma sintering. We found that increasing the Pt content reduced the specific heat at high temperatures, which may be caused by the locked state of phasons. The substitution of Pt for Cu reduced $\kappa_{ph,300K}$ by up to 17%. The reduction of $\kappa_{ph,300K}$ was attributed to a decrease in the specific heat and phonon relaxation time through heavy element substitution and the alloying effect. The present results show that the substitution of Pt for Cu sites can reduce the $\kappa_{ph}$ down to 0.93 W m$^{-1}$ K$^{-1}$ at 300 K, which is comparable with that of ternary Al-Pd-Mn QC with heavier mean atomic weight.

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**References**

1. Snyder, G.J.; Toberer, E.S. Complex Thermoelectric Materials. *Nat. Mater.* 2008, 7, 105–114. [CrossRef]
2. Ren, Z.; Chen, G.; Dresselhaus, M. Nanostructured thermoelectric materials. In *Thermoelectrics and Its Energy Harvesting: Modules, Systems, and Applications in Thermoelectrics*; Rowe, D.M., Ed.; CRC Press: Boca Raton, FL, USA, 2012; Chapter 1.
3. Takagiwa, Y.; Kimura, K. Metallic-covalent bonding conversion and thermoelectric properties of Al-based icosahedral quasicrystals and approximants. *Sci. Technol. Adv. Mater.* **2014**, *15*, 044802. [CrossRef]

4. Takagiwa, Y.; Kamimura, T.; Hosoi, S.; Okada, J.T.; Kimura, K. Thermoelectric properties of polygrained icosahedral Al$_{71-x}$Ga$_x$Pd$_{25}$Mn$_9$ (x = 0, 2, 3, 4) quasicrystals. *J. Appl. Phys.* **2008**, *104*, 073721. [CrossRef]

5. Takagiwa, Y.; Kamimura, T.; Okada, J.T.; Kimura, K. Thermoelectric Properties of Icosahedral Al-Pd-(Mn or Re) Quasicrystals: Improvement of the ZT Value by Ga Substitution for Al Atoms. *J. Electron. Mater.* **2010**, *39*, 1885–1889. [CrossRef]

6. Pierce, F.S.; Bancel, P.A.; Biggs, B.D.; Guo, Q.; Poon, S.J. Composition dependence of the electronic properties of Al-Cu-Fe and Al-Cu-Ru-Si semimetallic quasicrystals. *Phys. Rev. B* **1993**, *47*, 5670–5676. [CrossRef] [PubMed]

7. Bilušić, A.; Smontara, A.; Lasjaunias, J.C.; Ivkov, J.; Calvayrac, Y. Thermal and thermoelectric properties of icosahedral Al$_{64}$Cu$_{23}$Fe$_{12}$ quasicrystal. *Mater. Sci. Eng. A* **2020**, *794*, 294–296, 711–714. [CrossRef]

8. Bilušić, A.; Pavuna, D.; Smontara, A. Figure of merit of quasicrystals: The case of Al-Cu-Fe. *Vacuum* **2001**, *61*, 345–348. [CrossRef]

9. Nakayama, R.; Takeuchi, T. Thermal Rectification in Bulk Material Through Unusual Behavior of Electron Thermal Conductivity of Al-Cu-Fe Icosahedral Quasicrystal. *J. Electron. Mater.* **2015**, *44*, 356–361. [CrossRef]

10. Dolinšek, J.; Vrtnik, S.; Klanjšek, M.; Jagličič, Z.; Smontara, A.; Smiljanič, I.; Bilušić, A.; Yokoyama, Y.; Inoue, A.; Landauero, C.V. Intrinsic electrical, magnetic, and thermal properties of single-crystalline Al$_{64}$Cu$_{23}$Fe$_{12}$ icosahedral quasicrystal: Experiment and modeling. *Phys. Rev. B* **2007**, *76*, 054201. [CrossRef]

11. Hurd, A.J.; Kelley, R.L.; Eggert, R.G.; Lee, M.-H. Energy-critical elements for sustainable development. *MRS Bull.* **2012**, *37*, 405–410. [CrossRef]

12. Takeuchi, T. Very large thermal rectification in bulk composites consisting partly of icosahedral quasicrystals. *Sci. Technol. Adv. Mater.* **2014**, *15*, 064801. [CrossRef] [PubMed]

13. Nagata, T.; Kirihara, K.; Kimura, K. Effect of Ru substitution for Re on the thermoelectric properties of AlPdRe icosahedral quasicrystals. *J. Appl. Phys.* **2003**, *94*, 6560–6565. [CrossRef]

14. Okada, J.T.; Hamamatsu, T.; Hosoi, S.; Nagata, T.; Kimura, K. Improvement of thermoelectric properties of icosahedral AlPdRe quasicrystals by Fe substitution for Re. *J. Appl. Phys.* **2009**, *101*, 103702. [CrossRef]

15. Edagawa, K.; Kajiyama, K.; Tamura, R.; Takeuchi, S. High-temperature specific heat of quasicrystals and a crystal approximant. *Mater. Sci. Eng. A* **2001**, *321*, 293–298. [CrossRef]

16. Prekul, A.F.; Kazantsev, V.A.; Shchegoleikhina, N.I.; Gulyaeva, R.I.; Edagawa, K. High-Temperature Heat Capacity of the Al$_{64}$Cu$_{23}$Fe$_{12}$ icosahedral quasicrystal. *Phys. Solid State* **2008**, *50*, 2013–2015. [CrossRef]

17. Tamura, S.; Fukushima, K.; Tokumoto, Y.; Takagiwa, Y.; Edagawa, K. High-Temperature Specific Heat of Al-Cu-Icosahedral Quasicrystals and 1/1 Crystal Approximants. *Mater. Trans.* **2021**, *62*, 356–359. [CrossRef]

18. Fukushima, K.; Suyama, H.; Tokumoto, Y.; Kamimura, Y.; Takagiwa, Y.; Edagawa, K. Comparative study of high-temperature specific heat for Al-Pd-Mn icosahedral quasicrystals and crystal approximants. *J. Phys. Commun.* **2021**, *5*, 085002. [CrossRef]

19. Takeuchi, T. Unusual Increase of Electron Thermal Conductivity Caused by a Pseudogap at the Fermi Level. *J. Appl. Phys.* **2019**, *125*, 041506. [CrossRef]

20. Nakayama, R.; Takeuchi, T. Improvement of thermoelectric properties of icosahedral AlPdRe quasicrystals by Fe substitution for Re. *J. Appl. Phys.* **2007**, *101*, 103702. [CrossRef]

21. Kim, H.-S.; Gibbs, Z.M.; Tang, Y.; Wang, H.; Snyder, G.J. Characterization of Lorenz number with Seebeck coefficient measurement. *APL Mater.* **2015**, *3*, 041506. [CrossRef]

22. Mizutani, U.; Sato, H.; Inukai, M.; Zijlstra, E.S. e/a determination for 4d- and 5d-transition metal elements and their intermetallic compounds with Mg, Al, Zn, Cd and In. *Philos. Mag.* **2013**, *93*, 3353–3390. [CrossRef]

23. Maciá, E.; Rodríguez-Oliveros, R. Theoretical assessment on the validity of the Wiedemann–Franz law for icosahedral quasicrystal. *Phys. Rev. B* **2007**, *75*, 104210. [CrossRef]

24. Cahill, D.G.; Pohl, R.O. Heat flow and lattice vibrations in glasses. *Solid State Commun.* **1989**, *70*, 927–930. [CrossRef]

25. Cahill, D.G.; Watson, S.K.; Pohl, R.O. Lower limit to the thermal conductivity of disordered crystals. *Phys. Rev. B* **1992**, *46*, 6131–6140. [CrossRef] [PubMed]

26. Kanatzidis, M.G. Nanostructured Thermoelectrics: The New Paradigm? *Chem. Mater.* **2010**, *22*, 648–659. [CrossRef]

27. Takagiwa, Y.; Kimura, K.; Sawama, K.; Hiroto, T.; Nishio, K.; Tamura, R. Thermoelectric properties of Tsai-type Au-Al-RE (RE: Yb, Tm, Gd) quasicrystals and approximants. *J. Alloys Compd.* **2015**, *652*, 139–144. [CrossRef]

28. Ishikawa, A.; Takagiwa, Y.; Kimura, K.; Tamura, R. Probing the pseudogap via thermoelectric properties in the Au-Al-Gd quasicrystal approximant. *Phys. Rev. B* **2017**, *95*, 104201. [CrossRef]