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Thermal Rectification in Bulk Material Through Unusual Behavior of Electron Thermal Conductivity of Al-Cu-Fe Icosahedral Quasicrystal

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In this study, a new thermal rectifier working at high temperatures above 300 K was developed using $Al_{61.5}Cu_{26.5}Fe_{12}$ icosahedral quasicrystal and Ag_2Te. The thermal conductivity of $Al_{61.5}Cu_{26.5}Fe_{12}$ increased drastically with temperature and, at 1000 K, reached a value nine times larger than that at 300 K. The thermal conductivity of Ag_2Te showed a sudden decrease at around 400 K, and the thermal conductivity at 423 K became 60% smaller than that at 300 K. By making a composite consisting of $Al_{61.5}Cu_{26.5}Fe_{12}$ icosahedral quasicrystal and Ag_2Te, we succeeded in obtaining a large thermal rectification ratio (TRR) of $|\mathbf{J}_{\mathrm{large}}|/|\mathbf{J}_{\mathrm{small}}| = 1.63$ using two heat reservoirs maintained at $T_{\mathrm{H}} = 543$ K and $T_{\mathrm{L}} = 300$ K. The obtained TRR value is the largest among those ever reported for bulk thermal rectifiers.

Key words: Thermal rectification, thermal conductivity, electronic structure, electron transport properties

INTRODUCTION

Heat management, whereby waste heat generally emitted into the environment is collected and used in systems that require heating power, has attracted considerable interest for saving energy, reducing global warming gases, and contributing to a sustainable society. The thermal rectifier,[1] which is considered to act as a thermal diode and depends significantly on the direction of the heat flux flowing in it, could become a major technology for optimum heat management.

Among the several types of thermal rectifier,[1] we focus upon the bulk thermal rectifier,[2,3] which is a composite consisting of two solid materials possessing thermal conductivities with different temperature dependence, as shown in Fig. 1. The principle of the bulk thermal rectifier was theoretically proposed by two groups in 2006,[2,3] and its validity was subsequently confirmed by experiment,[4] in which the observed thermal rectification ratio (TRR = $|\mathbf{J}_{\mathrm{large}}|/|\mathbf{J}_{\mathrm{small}}|$) was small but finite at 1.43. This type of thermal rectifier could be very useful because the amount of heat flux can be optimized as a function of the rectifier's thickness, the shape of the device is not limited by any significant condition, and it can be used as a mechanical part.

Despite experimental confirmation of bulk thermal rectification, several problems prevent the use of such rectifiers in practical applications. One of the most serious problems is their very low working temperature. Thermal rectification in a bulk material was first observed at low temperatures below 150 K,[4] because the bulk thermal rectifier used the significant temperature dependence of the lattice thermal conductivity generally observable in crystalline materials at low temperatures below 150 K. Unfortunately, it is very difficult to increase the temperature range of this large variation in the lattice thermal conductivity to high temperatures above 300 K. Another problem is the small magnitude of the TRR observed for the bulk thermal rectifier; the largest value observed was less than 1.5.

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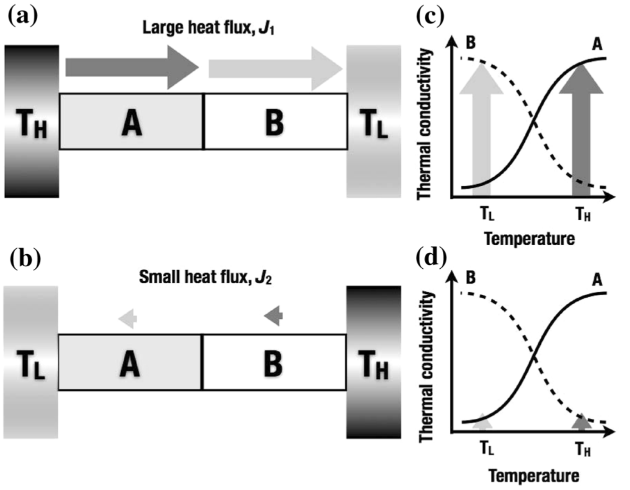

Fig. 1. (a) and (b) Schematic illustration of a thermal rectifier consisting of material A and material B, whose thermal conductivity is drawn schematically in (c) and (d). When material A is located on the high-temperature side, both materials possess a relatively large thermal conductivity, and a large heat flux is consequently generated. If the position of the two heat reservoirs is exchanged, both materials possess a relatively small thermal conductivity, and the heat flux also becomes smaller than in the other case.

Although the TRR value guaranteeing applicability of a rectifier remains unclear, it is natural to consider that TRR = 1.5 is still too small for practical applications. To make a practical bulk thermal rectifier, we need to greatly increase both the working temperature and the magnitude of the TRR.

A more recent report stated that the electron thermal conductivity increases drastically at high temperatures above 300 K, provided that one considers an aperiodic material possessing a narrow pseudogap of a few hundred meV in width at the Fermi energy (E_F).[5] This was proven by using $Al_{72.6}Re_{17.4}Si_{10}$ and $Al_{71.6}Mn_{17.4}Si_{11}$ approximants of icosahedral quasicrystal, and by successfully developing a thermal rectifier working at high temperatures above 300 K.[5,6] However, the magnitude of the TRR was still limited to a value of less than 1.1, which is definitely too small for practical applications.

Although the experimentally observed TRR was too small, theoretical calculations suggested that a bulk thermal rectifier consisting of $Al_{62}Cu_{25.5}Fe_{12.5}$ icosahedral quasicrystal and a simple semiconducting material, Si or Ge, could possess a large TRR exceeding 2.[6] The large TRR presumably arises from the significantly varying electron thermal conductivity of the quasicrystal,[7,8] which is closely related to its quasiperiodicity and the narrow, deep pseudogap at E_F. Here "pseudogap" means a dip in the electronic density of states such as that observed near E_F in semimetals. In the present study, therefore, we attempted to develop a thermal rectifier possessing a large TRR by using an Al-based icosahedral quasicrystal as a main component.

We selected an Al-Cu-Fe icosahedral quasicrystal from the group of Al-based icosahedral quasicrystals, mainly because its constituent elements are inexpensive, environmentally friendly, and ubiquitous, and therefore preferable for practical applications, and partly because these icosahedral quasicrystals possess an appropriately shaped pseudogap at E_F. The latter is confirmed by the very small value of the electron specific heat coefficient,[9] the gradually decreasing electrical resistivity with increasing temperature,[10] and the temperature dependence of the Seebeck coefficient possessing a maximum at around room temperature.[11]

For the second material to use together with the Al-Cu-Fe icosahedral quasicrystal, we employed Ag_2Te because of its significant drop in thermal conductivity at around 420 K with increasing temperature due to a phase transition.[12–16] At high temperatures above 420 K, silver ions start to wander in this material. These mobile silver ions presumably prevent phonon wave packets from freely propagating in the sample or directly prohibit the existence of well-defined wave packets, and therefore the lattice thermal conductivity shows very small values. Although this material contains tellurium, which is rare, expensive, and toxic, we considered that it would be good as a test material to obtain a large TRR value at high temperatures above 300 K.

In this paper, we report that significant thermal rectification was indeed observed for the thermal rectifier consisting of Al-Cu-Fe icosahedral quasicrystal and Ag_2Te using heat reservoirs maintained at 300 K and 543 K.

EXPERIMENTAL PROCEDURES

Al-Cu-Fe icosahedral quasicrystals were prepared using arc melting in a pressurized argon gas atmosphere, and the prepared ingots were annealed at 950 K for 72 h. Ag_2Te was prepared by induction melting in a pressurized argon gas atmosphere, and the mother ingot was annealed at 870 K for 24 h. All the ingots were crushed into powder and sintered into a cylindrical shape of 10 mm diameter by pulsed current sintering (PCS).

Using the laser flash method, we measured the temperature dependence of the thermal conductivity of both the Al-Cu-Fe icosahedral quasicrystals and Ag_2Te in the temperature range of 300 K to 1000 K and 300 K to 650 K, respectively. We also measured the temperature dependence of the Seebeck coefficient for Al-Cu-Fe icosahedral quasicrystals at 100 K to 600 K using a Seebeck measurement system developed by MMR Technologies, Inc. (Mountain View, CA).

The thermal rectifier, having a total length of $L = 20$ mm and diameter of $d = 10$ mm, was made by connecting cylindrical Al-Cu-Fe and Ag_2Te samples. The heat flux $|\mathbf{J}|$ flowing in the sample was estimated using a newly developed, simple apparatus in which the composite sample together with a copper block were placed between a heater maintained at 543 K and a water-cooled block (Fig. 2). To

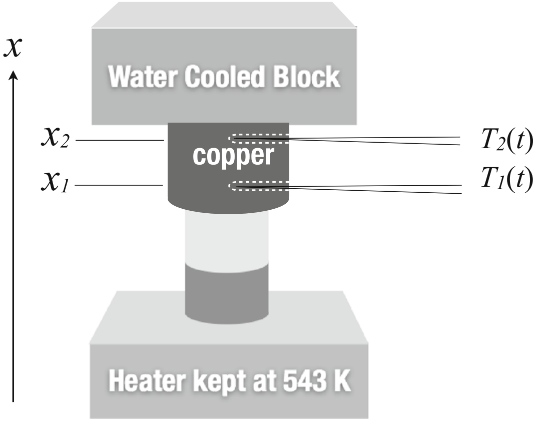

Fig. 2. Schematic illustration of the system used for evaluating the heat flow. By measuring the temperature gradient in the copper block, the heat flow through the thermal rectifier is estimated.

achieve good thermal contact, all the components were placed in a hand-press apparatus and mechanically pressed with force of ~150 N. The pressure at the sample interface was estimated to be ~1.9×10^6 Pa. We also used a small amount of thermal grease, a small amount of silver paste, and a thin carbon sheet of 0.2 mm thickness at the interfaces of the water-cooled block/sample A, sample A/sample B, and sample B/heater, respectively. The heat current J flowing though the composite also passed through the copper block, in which two thermocouples were placed at positions x_1 and x_2. By using the thermal conductivity of copper (κ_{Cu}), the difference in the positions of the thermocouples ($\Delta x = x_2 - x_1$), and the measured temperature difference ($-\Delta T = T_1 - T_2$), we estimated the magnitude of J from Fourier's law as $J = |\mathbf{J}| = -\kappa|\nabla T| = \kappa_{\mathrm{Cu}}(x_2 - x_1)/(T_1 - T_2)$, ignoring the radiation emitted from the side walls of the sample. The whole measurement system was sealed in a vacuum chamber, and measurements were conducted under vacuum for more than 10 times to confirm reproducibility.

RESULTS

Figure 3 shows the powder x-ray diffraction (XRD) patterns of $Al_{61.5}Cu_{26.5}Fe_{12}$ icosahedral quasicrystal, $Al_{62}Cu_{25.5}Fe_{12.5}$ icosahedral quasicrystal, and Ag_2Te. The XRD pattern of Ag_2Te calculated from crystal structure data[17] is also plotted with the measured one. The XRD patterns confirm that the prepared samples consisted solely of the desired phase, and therefore the samples were used to construct the thermal rectifier.

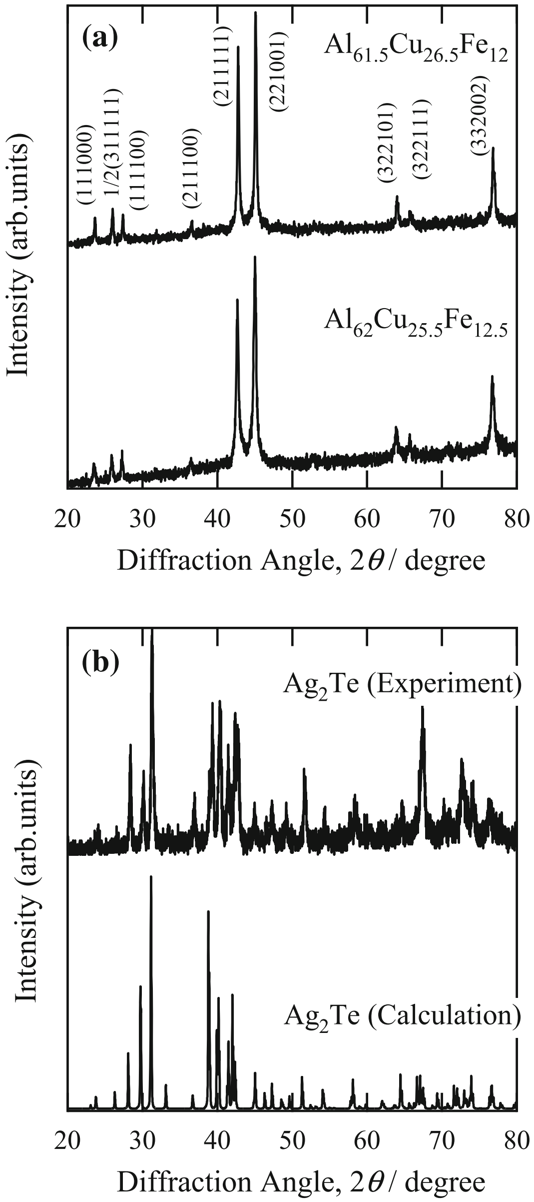

Fig. 3. (a) Powder x-ray diffraction patterns of $Al_{61.5}Cu_{26.5}Fe_{12}$ and $Al_{62}Cu_{26.5}Fe_{12.5}$ icosahedral quasicrystals. All peaks were successfully identified as those from the quasicrystalline phase. (b) Powder x-ray diffraction pattern of Ag_2Te. The rather complicated structure and large lattice constants of Ag_2Te make the number of diffraction peaks larger. The calculated x-ray diffraction pattern of Ag_2Te is also plotted at the bottom. Although the peak intensities are slightly different from the calculated values, all peaks could be safely attributed to Ag_2Te.

According to the previously reported quantitative analyses on the Seebeck coefficient[11] and electron thermal conductivity,[18] an unusual increase of the electron thermal conductivity at high temperatures is thought to become evident in materials possessing a small Seebeck coefficient under the condition of a pseudogap at E_{F}. To confirm this prediction, we measured the Seebeck coefficient of two samples of icosahedral quasicrystal. As is clearly shown from the Seebeck coefficient results in Fig. 4, $Al_{61.5}Cu_{26.5}Fe_{12}$ possesses a smaller Seebeck coefficient than $Al_{62}Cu_{25.5}Fe_{12.5}$ at low temperatures below 400 K and probably at high temperatures above 600 K. From the thermal conductivity of Al-Cu-Fe icosahedral quasicrystals shown in Fig. 5, the ratio of the thermal conductivity at 1000 K to that at

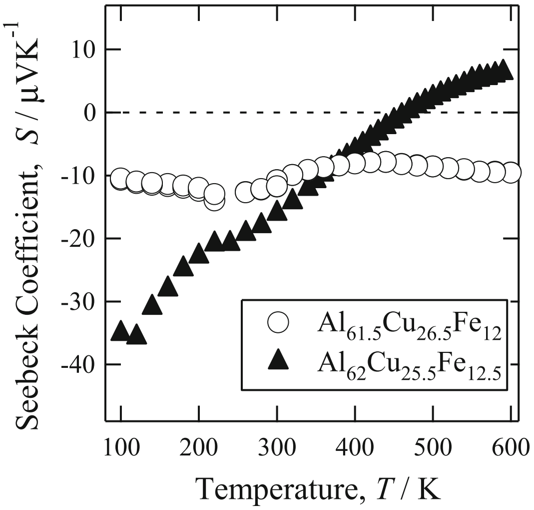

Fig. 4. Seebeck coefficient of $Al_{61.5}Cu_{26.5}Fe_{12}$ and $Al_{62}Cu_{25.5}Fe_{12.5}$ icosahedral quasicrystals. $Al_{61.5}Cu_{26.5}Fe_{12}$ possesses a smaller magnitude than $Al_{62}Cu_{25.5}Fe_{12.5}$ over a wide temperature range.

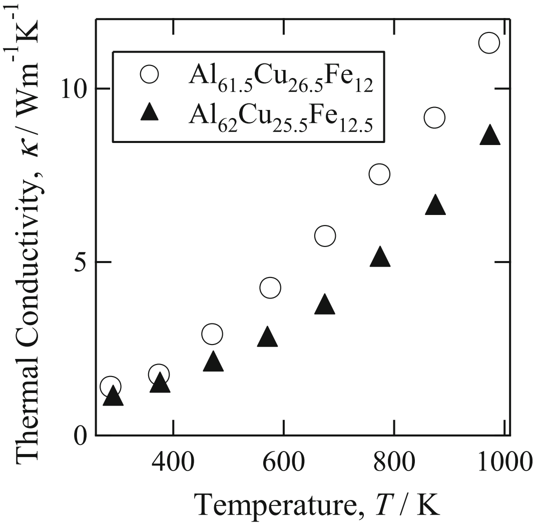

Fig. 5. Thermal conductivity of $Al_{61.5}Cu_{26.5}Fe_{12}$ and $Al_{62}Cu_{25.5}Fe_{12.5}$.

300 K, $\kappa(1000\,K)/\kappa(300\,K)$, clearly becomes larger for $Al_{61.5}Cu_{26.5}Fe_{12}$, which has a smaller Seebeck coefficient over a wide temperature range.

Figure 6 shows the thermal conductivity of Ag_2Te prepared in this study. In the heating process, the thermal conductivity suddenly dropped to 0.5 W m^{-1} K^{-1} at around 420 K, the same as previously reported.[12] This sudden drop encouraged us to use Ag_2Te in a thermal rectifier together with the Al-Cu-Fe quasicrystal possessing a significant increase in thermal conductivity with increasing temperature.

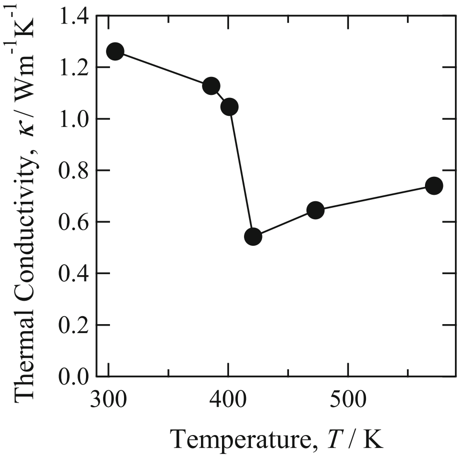

Fig. 6. Thermal conductivity of Ag_2Te.

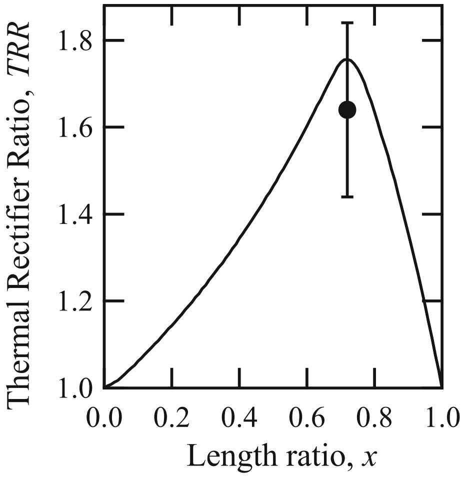

Fig. 7. Thermal rectification ratio (TRR) of the thermal rectifier consisting of $Al_{61.5}Cu_{26.5}Fe_{12}$ icosahedral quasicrystal and Ag_2Te. The calculated value (solid line) and the experimentally determined value (solid circle, TRR = 1.63) are plotted as a function of the length ratio $x = L_{\text{Al-Cu-Fe}}/L_{\text{Ag2Te}}$.

We calculated the TRR from the measured thermal conductivities for a thermal rectifier consisting of $Al_{61.5}Cu_{26.5}Fe_{12}$ icosahedral quasicrystal and Ag_2Te, using the method reported by Takeuchi et al.[6] The calculated TRR under the condition of T_H = 543 K and T_L = 300 K is plotted in Fig. 7 as a function of the length ratio $x = L_{\text{Al-Cu-Fe}}/L_{\text{Ag2Te}}$. The TRR reaches a maximum when the temperature at the interface between the two materials becomes the same in the two different heat reservoir configurations. This situation occurs at x = 0.65 for the present thermal rectifier consisting of $Al_{61.5}Cu_{26.5}Fe_{12}$ icosahedral quasicrystal and Ag_2Te, and the estimated TRR reaches 1.75, which is much larger than the largest value of 1.43[4] ever reported for bulk thermal rectifiers.

Figure 8a, b shows the temperature of the copper block as a function of heating time when connected to the heat reservoir maintained at 543 K through

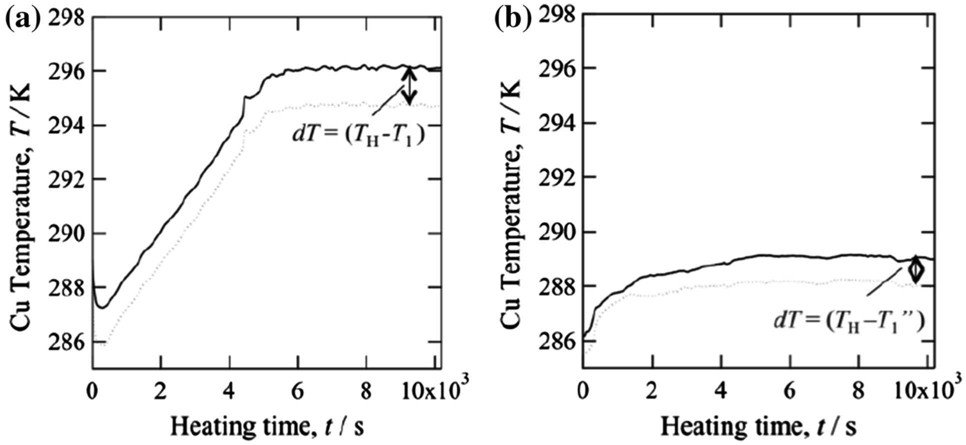

Fig. 8. Transient curves of the copper block temperature observed for (a) heater/$Al_{61.5}Cu_{26.5}Fe_{12}$/$Ag_2Te$/Cu and (b) heater/$Ag_2Te$/$Al_{61.5}Cu_{26.5}Fe_{12}$/Cu. When the icosahedral quasicrystal was located near the heater, the temperature difference became larger, indicating that rectification of heat flux indeed occurred in the thermal rectifier.

the thermal rectifier consisting of $Al_{61.5}Cu_{26.5}Fe_{12}$ icosahedral quasicrystal and Ag_2Te. The temperature difference $\Delta T = T_2 - T_1$ in the copper block was definitely larger when the $Al_{61.5}Cu_{26.5}Fe_{12}$ icosahedral quasicrystal was located near the 543 K heat reservoir, while it became smaller in the opposite configuration. This tendency clearly indicates the existence of thermal rectification caused by the thermal rectifier.

The estimated value of the TRR was 1.63 ± 0.2, which is slightly smaller than the calculated value (1.75) but is still the largest among those ever reported for bulk thermal rectifiers. We performed the measurement over five times, but all the data fell in the error bar range. The difference between the experiment and calculation could be caused by (a) radiation effect, (b) variation in T_1, (c) errors in determining temperatures, and/or (d) thermal resistance at the interfaces between the components.

We calculated the amount of heat loss due to radiation using the temperature distribution of the sample as estimated from the thermal conductivity. The amount was smaller than 10%. This value is not negligibly small, but it does not seriously affect the value of the TRR because the amount of radiation loss in one sample configuration is almost the same as in the other.

The absolute value of T_1, which nearly represents the lowest temperature of the sample, in one configuration is definitely different from that in the other configuration. This temperature difference of T_1 between the two configurations indicates that the temperature gradient in the rectifier in one configuration was different from that in the other, and a finite error arose in estimating $\mathrm{TRR} = |\mathbf{J}_1|/|\mathbf{J}_2|$. Nevertheless, we consider that the error caused by the variation in T_1 was not particularly large because the temperature gradient in the rectifier, which was estimated from $dT/dx \approx (T_H - T_1)/L_{\mathrm{sample}}$, varied by less than 3% between the two configurations of the heat reservoirs.

We could also eliminate the effect of errors in determining temperatures from the list of possible factors reducing the value of the TRR. The absolute value of the temperature definitely has errors due to errors in calibration. Nevertheless, such errors in temperature would vanish when calculating the $\mathrm{TRR} \approx (T_2 - T_1)_{\mathrm{AB}}/(T_2 - T_1)_{\mathrm{BA}}$ because of their presence in both the denominator and numerator.

We considered, therefore, that the thermal resistance at the interfaces would be dominantly responsible for the reduction in the TRR because the interface resistance, which was estimated from the measured heat flux using the measured thermal conductivity of the constituent materials, reached nearly 40% of the bulk heat resistance. This large heat resistance naturally makes the effectively applied temperature difference $\Delta T = T_2 - T_1$ smaller and reduces the value of the TRR. We calculated the TRR value by assuming that the highest temperature and lowest temperature were modified to 510 K and 320 K, respectively, roughly considering that 13% (=40% divided between the three boundaries) of the temperature variation occurred at each boundary. In this estimation, we ignored the effect of interface resistance between the two samples because the value of the TRR in the bulk thermal rectifier is dominantly determined by the thermal conductivity of the component in the highest temperature and lowest temperature region. The resulting reduced value was TRR = 1.65, notably almost coinciding with the measured one. This consideration definitely suggests that, if the interface thermal resistances could be effectively reduced, we would achieve a slightly larger TRR value, as estimated by the initial calculation.

DISCUSSION

As discussed in the previous section, the observed value of TRR = 1.63 ± 0.2 is the largest among those reported for bulk thermal rectifiers,[4–6,19,20] and the very high working temperature exceeding 300 K is another advantage. These characteristics could lead to the conception of new applications utilizing the thermal rectifier.

However, the volume change of Ag_2Te that occurred at the phase transition would make it difficult to use the rectifier in practical applications, because repeated thermal loading will produce severe strain and the sample would collapse in practice. This thermal rectifier is therefore not suitable for use under severe conditions with large and frequent changes in temperature gradient. To make practical thermal rectifiers, we need to find other materials possessing a significant variation of thermal conductivity without a significant change in volume over the working temperature range.

In sharp contrast to the significant volume change of Ag_2Te, the thermal, electrical, and mechanical properties of Al-Cu-Fe icosahedral quasicrystals show moderate changes with varying temperature. Although the volume change occurring in Ag_2Te makes it difficult to utilize the present rectifier in practical applications, our results confirm that the Al-Cu-Fe icosahedral quasicrystal is one of the best constituent materials for bulk thermal rectifiers. If we could identify other materials whose thermal conductivity decreases with increasing temperature, we could develop new thermal rectifiers suitable for practical applications. We have already developed such bulk thermal rectifiers, as reported elsewhere.[21]

CONCLUSIONS

In this study, we developed a new thermal rectifier working at high temperatures above 300 K using $Al_{61.5}Cu_{26.5}Fe_{12}$ icosahedral quasicrystal and Ag_2Te. The thermal conductivity of $Al_{61.5}Cu_{26.5}Fe_{12}$ at 1000 K was nine times larger than that at 300 K. The thermal conductivity of Ag_2Te suddenly decreased at around 400 K, and the thermal conductivity at 423 K became 60% smaller than that at 300 K. By making a composite consisting of $Al_{61.5}Cu_{26.5}Fe_{12}$ icosahedral quasicrystal and Ag_2Te, we succeeded in obtaining a TRR of 1.63 for two heat reservoirs maintained at $T_H = 543$ K and $T_L = 300$ K.

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