Enhancing high-temperature thermoelectric properties of PtAs$_2$ by Rh doping

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The effects of Rh doping on the thermoelectric properties of Pt$_{1-x}$Rh$_x$As$_2$ ($x = 0, 0.005$, and $0.01$) with pyrite structure were studied by conducting measurements of electrical resistivity $\rho$, Seebeck coefficient $S$, and thermal conductivity $\kappa$. The sample with $x = 0.005$ exhibited large $S$ and low $\rho$, resulting in a maximum power factor ($S^2/\rho$) of 65 $\mu$W/cmK$^2$ at 440 K. The peculiarly shaped “corrugated flat band” predicted for PtSb$_2$ might explain the enhanced thermoelectric properties of doped PtAs$_2$.

Thermoelectric power generation has attracted much recent attention as a means for directly converting waste heat into electricity; however, its successful commercial application will require the development of thermoelectric materials with high efficiency. Thermoelectric efficiency can be evaluated using the dimensionless figure of merit $ZT = S^2T/\rho\kappa$, where $S$ is the Seebeck coefficient, $\rho$ is electrical resistivity, $\kappa$ is thermal conductivity, and $T$ is absolute temperature. In this formula, the power factor (PF) $= S^2/\rho$ expresses the upper limit on the amount of electrical power that can be drawn from a material; to efficiently generate thermoelectricity, therefore, it is important to have both a large Seebeck coefficient $S$ and a low (metallic) electrical resistivity $\rho$. This is not easy to obtain, however, as a low $\rho$ requires a high carrier density (large Fermi surface), while a large $S$ will be associated with low carrier density.

Kuroki and Arita demonstrated theoretically that a large $S$ can be attained in metals having a peculiarly shaped band structure of the so-called “pudding mold” type,$^4$ which consists of both a dispersive and a flat region. When the chemical potential of the metal is located within the dispersive region but is close to the flat region, a large asymmetry appears in the velocities of carriers around the chemical potential, producing a large $S$ even in metals with large Fermi surfaces. Angle-resolved photoemission spectroscopy revealed the existence of a “pudding mold” band in the thermoelectric oxide Na$_x$CoO$_2$.$^2,3$ A substance simultaneously exhibits large $S$ ($\approx 100 \mu$V/K) and low $\rho$ ($\approx 200 \mu$Ωcm) at 300 K,$^5,6$ resulting in a large PF of $\approx 50 \mu$W/cmK$^2$, which is comparable to that of the typical thermoelectric material Bi$_2$Te$_3$ (PF $\approx 40 \mu$W/cmK$^2$).$^7$

More recently, Mori et al.$^8$ proposed another peculiarly shaped band structure, referred to as the “corrugated flat band” type, that can attain large values of $S$ in a metallic state. This structure exhibits band dispersion with an overall flatness that extends over the entire Brillouin zone while expressing a series of localized rises and dips that create multiple Fermi pockets (with large carrier density) and a large degree of carrier velocity asymmetry around the chemical potential. This model successfully explains the enhanced thermoelectric properties of Ir-doped PtSb$_2$ with a cubic pyrite structure (space group $Pa\bar{3}$), which exhibits a maximum power factor of 43 $\mu$W/cmK$^2$ at 400 K.$^9$ Importantl, Mori et al.$^8$ predicted that the power factor would continue to increase if the band gap of PtSb$_2$ could be increased, as thermally activated carriers beyond the gap serve to significantly degrade $S$ at high temperatures. This degradation factor is seen experimentally in PtSb$_2$, in which the value of $S$ starts to decrease with increasing temperature above 400 K owing to the narrow gap (0.06–0.08 eV).$^9$

In this Letter, we report on the enhanced thermoelectric properties of Rh-doped PtAs$_2$ at temperatures above 400 K. PtAs$_2$ is isotypic and isovalent to PtSb$_2$ but has a larger band gap (0.8 eV). As in doped PtSb$_2$,$^9$ a large Seebeck coefficient has been observed in the metallic state of doped Pt$_{1-x}$Rh$_x$As$_2$; unlike doped PtSb$_2$, however, the Seebeck coefficient of doped PtAs$_2$ continues to increase with increasing temperature up to 600 K, resulting in large values of PF (e.g., 65 $\mu$W/cmK$^2$ at 440 K) over this range.

Polycrystalline samples of Pt$_{1-x}$Rh$_x$As$_2$ with $x = 0, 0.005$, and $0.01$ were synthesized by means of a solid-state reaction in two steps. First, stoichiometric amounts of the starting materials Pt (99.99%), Rh (99.98%), and As (99.9999%) were mixed, ground, and then heated in an evacuated quartz tube at 500$^\circ$C for 10 h and at 700 $^\circ$C for 40 h. The product was powdered, pressed into pellets, and sintered at 1100$^\circ$C for 10 h. The resulting samples were characterized by means of powder X-ray diffraction (XRD), and it was confirmed that they consisted of single-phase Pt$_{1-x}$Rh$_x$As$_2$. Thermoelectric properties, namely, electrical resistivity $\rho$, Seebeck coefficient $S$, and thermal conductivity $\kappa$ were measured over the temperature range from 2 to 300 K using a physical property measurement system (PPMS, Quantum Design). High-temperature values of $S$ and $\rho$ were measured over the temperature range from 300 to 600 K by using, respectively, a commercial thermopower measurement appara-

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consistent with previous reports, x of PtAs$_2$ exhibits a semiconducting behavior that is consistent with previous reports, while Rh doping causes both the magnitude and temperature dependence of $\rho$ to change abruptly from semiconducting to metallic. Values of $\rho$ on the order of 100 $\mu\Omega$cm at 300 K and the positive temperature coefficient of resistivity for Pt$_{1-x}$Rh$_x$As$_2$ ($x = 0.0, 0.005$ and $0.01$) suggest that these samples have attained a metallic state with the metallic temperature dependence of $\rho$ remaining up to 600 K. Figure 1(b) shows that the Seebeck coefficient $S$ is negative for $x = 0.0$, indicating that the majority of the charge carriers in this sample are electrons. In the non-doped PtAs$_2$, the absolute value of $S$ decreases with decreasing temperature, although this temperature dependence is altered abruptly by Rh doping. For $x = 0.005$ and $0.01$, the Seebeck coefficient $S$ exhibits a positive value (Fig. 1(b)), which indicates that the majority of charge carriers are holes. It can be seen that, for $x = 0.005$, $S$ increases with increasing temperature up to 600 K, at which point it reaches 260 $\mu$V/K; this contrasts strongly with the behavior of Pt$_{1-x}$Ir$_x$Sb$_2$, in which $S$ decreases with increasing temperature above 400 K. The difference might be attributable to the differential in energy gap magnitudes predicted by Mori et al., which would allow metallic values of $\rho$ to coexist with a large $S$ in Pt$_{1-x}$Rh$_x$As$_2$.

The observed continuous increase in $S$ with increasing temperature results in high values of PF at high temperatures, as can be seen in Fig. 2(a), which shows the temperature dependence of PF. Of the samples, $x = 0.005$ exhibits the highest PF of 65 $\mu$W/cmK$^2$ at approximately 440 K, a value that is higher than those of Pt$_{1-x}$Ir$_x$Sb$_2$ (43 $\mu$W/cmK$^2$) and Bi$_2$Te$_3$ (40 $\mu$W/cmK$^2$). This high PF value is maintained up to 600 K, in marked contrast to Pt$_{1-x}$Ir$_x$Sb$_2$, in which PF decreases significantly above 400 K. It is therefore apparent that a drastic improvement in the high temperature thermoelectric properties of Pt-based pyrites can be attained by replacing Sb with As.

Finally, we examined the thermoelectric efficiency of the doped Pt$_{1-x}$Rh$_x$As$_2$ sample. Figure 2(b) shows the
temperature dependence of the dimensionless figure of merit \( ZT \). Reflecting the high value of \( \rho \) shown in Fig. 1(a), \( ZT \) is negligibly small at \( x = 0 \); as \( x \) increases, \( ZT \) is enhanced until \( x = 0.005 \). At \( x = 0.005 \), \( ZT \) increases with increasing temperature until it reaches a maximum value of 0.18 at 600 K. This high-temperature behavior is drastically enhanced relative to Pt\(_{1-x}\)Rh\(_x\)As\(_2\) in which \( ZT \) shows a broad maximum (0.17) at 480 K. From the measured thermoelectric properties, it was partially supported by a Grant-in-Aid for Scientific Research (C) (25400372) from the Japan Society of the Promotion of Science (JSPS) and the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program) from JSPS.

In this assessment, we assumed that \( \kappa \) is independent of temperature at \( T > 300 \) K and used a value of \( \kappa = 0.207 \) W/cmK at 300 K to estimate \( ZT \) in this upper range. As shown in Fig. 1(c), the values of \( \kappa \) is increased slightly by Rh doping. The increased value of \( \kappa = 0.207 \) W/cmK for \( x = 0.005 \), which is approximately one order of magnitude larger than that for Bi\(_2\)Te\(_3\), is the primary reason that the dimensionless figure of merit \( (ZT = S^2T/\rho\kappa) \) is suppressed in this result.

Because larger values of PF can be obtained at high temperatures, it is meaningful to reduce the thermal conductivity \( \kappa \) in order to enhance \( ZT \). From the measured values of \( \rho \), we estimated the electronic thermal conductivity values \( (\kappa_e = L_0T/\rho) \), where \( L_0 \) is the Lorenz number \( 2.44 \times 10^{-8} \) WΩ/K\(^2\) and found that, for Pt\(_{1-x}\)Rh\(_x\)As\(_2\) \( (x = 0.005) \), \( \kappa_e = 0.013 \) W/cmK at 300 K, with a resultant lattice component, \( \kappa_{\text{lattice}} \), of 0.194 W/cmK. If this value can be further reduced, the thermoelectric properties of Rh-doped PtAs\(_2\) could be improved. PtAs\(_2\) tolerates a variety of chemical substitutions, and the replacement of the As\(_2\) molecule, for instance, with the hetero-nuclear diatomic GeSe molecule, which is isovalent to As\(_2\), might be useful in suppressing \( \kappa_{\text{lattice}} \). If \( ZT \) can be enhanced, the present compound could be applied to thin-film thermoelectric devices, though the use of Pt and Rh is not compatible with the applications in a large scale.

In this study, polycrystalline samples of Pt\(_{1-x}\)Rh\(_x\)As\(_2\) with \( x = 0.0, 0.005, \) and 0.01 were prepared and their thermoelectric properties were investigated at 2–600 K. The doped samples exhibited metallic conductivity and a large Seebeck coefficient, which combined to enhance the power factor to approximately 65 µW/cmK\(^2\) at 440 K for Pt\(_{1-x}\)Rh\(_x\)As\(_2\) with \( x = 0.005 \). As predicted by Mori et al., materials that combine a “corrugated flat” band structure with a wider band gap have high thermoelectric properties. Such a peculiarly shaped band structure has been predicted in PtAs\(_2\) by the first principles calculation.\(^{11}\)

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1 K. Kuroki and R. Arita, J. Phys. Soc. Jpn. 76, 083707 (2007).
2 H.-B. Yang, S.-C. Wang, A. K. P. Sekharan, H. Matsui, S. Souma, T. Sato, T. Takahashi, T. Takeuchi, J. C. Campuzano, R. Jin, B. C. Sales, D. Mandrus, Z. Wang, and H. Ding, Phys. Rev. Lett. 92, 246403 (2004).
3 H.-B. Yang, Z.-H. Pan, A. K. P. Sekharan, T. Sato, S. Souma, T. Takahashi, R. Jin, B. C. Sales, D. Mandrus, A. V. Fedorov, Z. Wang, and H. Ding, Phys. Rev. Lett. 95, 146401 (2005).
4 T. Arakane, T. Sato, T. Takahashi, T. Fujii, and A. Asamitsu, New J. Phys. 13, 043021 (2011).
5 I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B 56, R12685 (1997).
6 T. Motohashi, E. Naujalis, R. Ueda, K. Isawa, M. Karppinen, and H. Yamauchi, Appl. Phys. Lett. 79, 1480 (2001).
7 T. Caillat, M. Carle, P. Pierrat, H. Scherrer, and S. Scherrer, J. Phys. Chem. Solids 53, 1121 (1992).
8 K. Mori, H. Usui, H. Sakakibara, and K. Kuroki, AIP Advances 2, 042108 (2012).
9 Y. Nishikubo, S. Nakano, K. Kudo, and M. Nohara, Appl. Phys. Lett. 100, 252104 (2012).
10 W. D. Johnston, R. C. Miller, and D. H. Damon, J. Less-Common Met. 8, 272 (1965).
11 K. Mori, H. Usui, H. Sakakibara, and K. Kuroki, arXiv:1308.3414.