Journal of Alloys and Compounds 509 (2011) 1084–1089

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effects of Tl-filling into the voids and Rh substitution for Co on the thermoelectric properties of $CoSb_3$

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ARTICLE INFO

Article history:
Received 2 September 2010
Received in revised form
25 September 2010
Accepted 29 September 2010
Available online 8 October 2010

Keywords:
Thermoelectric
Skutterudite
$CoSb_3$
Thallium
Rhodium
Thermal conductivity

ABSTRACT

In order to enhance the thermoelectric (TE) properties of $CoSb_3$, we tried to reduce the lattice thermal conductivity (κ_{lat}) by filling Tl into the voids and substitution of Rh for Co. We prepared polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0, 0.05, 0.10, 0.15, 0.20$ and $y = 0.1, 0.2$) and examined their TE properties from room temperature to 750 K. All the samples indicated negative values of the Seebeck coefficient (S). Both the electrical resistivity and the absolute values of the S decreased with increasing the Tl-filling ratio. The Tl-filling and Rh substitution reduced the κ_{lat}, due to the rattling and the alloy scattering effects. The minimum value of the κ_{lat} was 1.54 W m^{-1} K^{-1} at 550 K obtained for $Tl_{0.20}(Co_{0.8}Rh_{0.2})_4Sb_{12}$. $Tl_{0.20}(Co_{0.8}Rh_{0.2})_4Sb_{12}$ exhibited the best TE performance; the maximum value for the dimensionless figure of merit ZT was 0.58 at around 600 K.

1. Introduction

The thermoelectric (TE) technology, used for direct conversion of waste heat into electrical power will contribute substantially to future power supply and sustainable energy management [1,2]. The efficiency of a material used in TE devices is determined by the dimensionless figure of merit, $ZT = S^2T/\rho/\kappa$, where S is the Seebeck coefficient, ρ is the electrical resistivity, T is the absolute temperature, and κ is the total thermal conductivity ($\kappa = \kappa_{lat} + \kappa_{el}$, the lattice and electronic contributions, respectively). Therefore, to maximize ZT of a material, large S and low ρ as well as low κ are required. As these transport properties are interrelated each other, a number of parameters need to be optimized to maximize ZT. The ZT value of the materials used in current devices is approximately 1. In recent years, several classes of bulk materials [3,4] with high ZT have been discovered, including filled skutterudites [5–7].

Skutterudite compounds have the composition MX_3 where M is a metal atom such as Co, Rh, or Ir and X represents a pnicogen atom such as P, As, and Sb. These compounds are body-centered cubic with 32 atoms in the unit cell and space group $Im3$. There are two voids per unit cell in the structure. When the third atom incorporates into the void, the formula of the compounds turns out to be RM_4X_{12}, where R is most often a rare-earth element, called filled-skutterudite structure [8]. The R atom is bonded weakly with the other atoms and rattles. Therefore, the introduction of R atoms into the voids of the skutterudites is an effective method of reducing the lattice thermal conductivity (κ_{lat}) such as thallium-filled skutterudites [9,10]. In addition to the rattling effect, the κ_{lat} could be reduced by the alloy scattering effect. The alloying can reduce the κ_{lat} by the point defect phonon scattering while giving little influence on the electrical transport, because it does not introduce charge disorder in the crystal lattices. For example, in the systems of Si–Ge alloy [11], (Zr,Hf)NiSn [12], and Ti(Co,Rh)Sb [13] the reduction of the κ_{lat} through the alloy scattering effect have been achieved. In the $CoSb_3$ system, the κ_{lat} reduction has been observed in $Co(Sb,As)_3$ [14] and $(Co,Rh)Sb_3$ [15,16].

In the present study, we tried to reduce the κ_{lat} of $CoSb_3$ by combining the rattling and the alloying effects in the system of Tl-filled $(Co,Rh)Sb_3$. Polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ were prepared and their TE properties were examined from room temperature to 750 K. Effects of Tl-filling into the voids and Rh substitution for Co on the TE properties of $CoSb_3$ were investigated.

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doi:10.1016/j.jallcom.2010.09.207

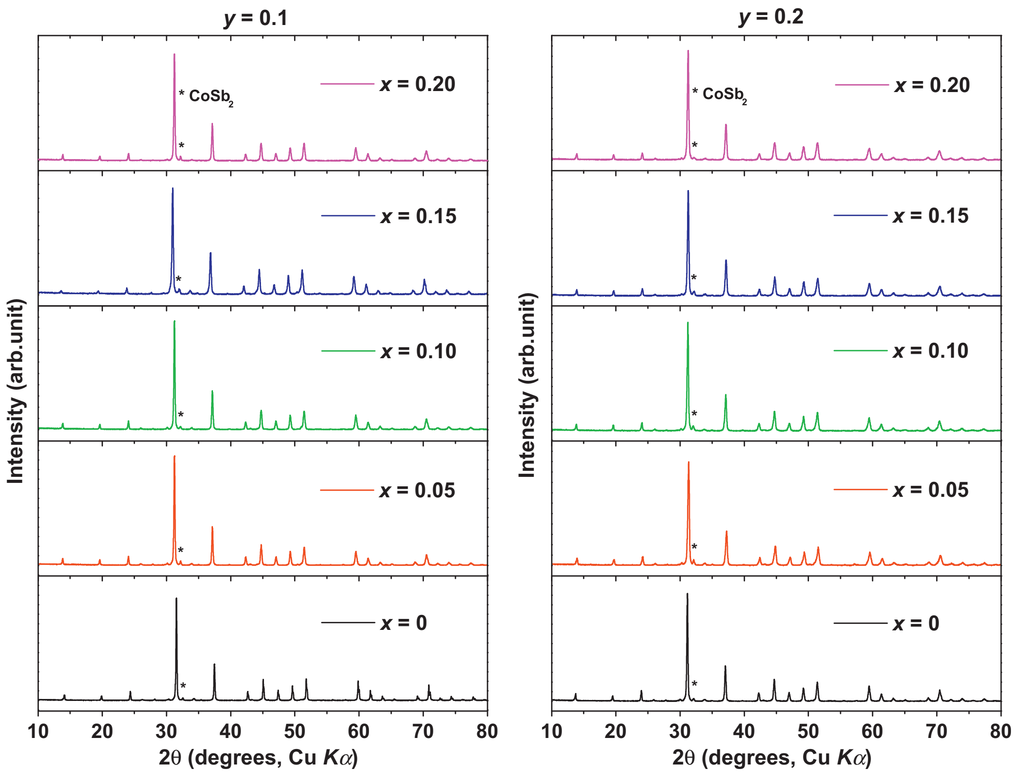

Fig. 1. Powder XRD patterns of the polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and $y = 0.1$, 0.2).

2. Experiment

Since up to approximately 22% of the voids in $CoSb_3$ can be filled with Tl [9,10] and the TE properties of $(Co_{1-y}Rh_y)_4Sb_{12}$ ($y = 0.1$, 0.2, 0.3) have been studied [16], we determined the composition of the samples prepared in the present study as $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and $y = 0.1$, 0.2). The polycrystalline samples were prepared from stoichiometric amounts of Tl, Rh, Co, and Sb chunks by direct reactions in sealed silica tubes. The sealed silica tubes were heated slowly up to 1323 K and quenched in water bath followed by annealing at 773 K for one week. The obtained ingots were crushed into fine powders, followed by hot-pressing in graphite dies at 973 K for 3 h in an argon flow atmosphere. Column-shaped (10 mm in diameter and 15 mm in height) and disc-shaped (10 mm in diameter 1 mm in thickness) pellets were prepared. The obtained samples were characterized with a powder X-ray diffraction (XRD) method using Cu $K\alpha$ radiation at room temperature. The density of the bulk samples was calculated based on the measured weight and dimensions. ρ and the S were measured by using a commercially available apparatus (ULVAC, ZEM-1) in a helium atmosphere. Thermal conductivity (κ) was evaluated from thermal diffusivity (α), heat capacity (C_p), and sample density (d) based on the relationship $\kappa = \alpha C_p d$. C_p was estimated from the Dulong-Petit model, $C_p = 3nR$, where n is the number of atoms per formula unit and R is the gas constant. The α was measured by the laser flash technique in a vacuum using a commercially available apparatus (ULVAC TC-7000). These TE properties were evaluated from room temperature to 750 K.

3. Results and discussion

Powder XRD patterns of polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and $y = 0.1$, 0.2) are shown in Fig. 1. All the samples were identified as skutterudite compounds, although they contained $CoSb_2$ as an impurity phase. Shi et al. [17] studied the phase diagrams for skutterudite solid solutions made by alloying at the Co site of $CoSb_3$ skutterudite structure by density functional theory. In Ref.

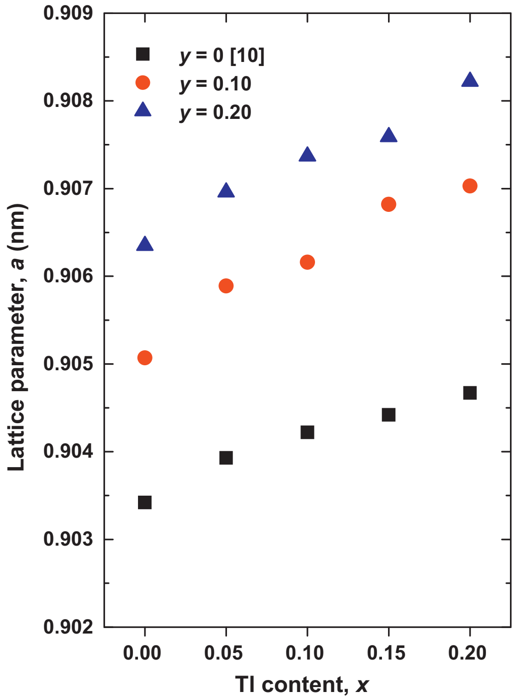

Fig. 2. Lattice parameters of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and $y = 0.1$, 0.2) as a function of Tl content (x), together with the data for $Tl_xCo_4Sb_{12}$ [10].

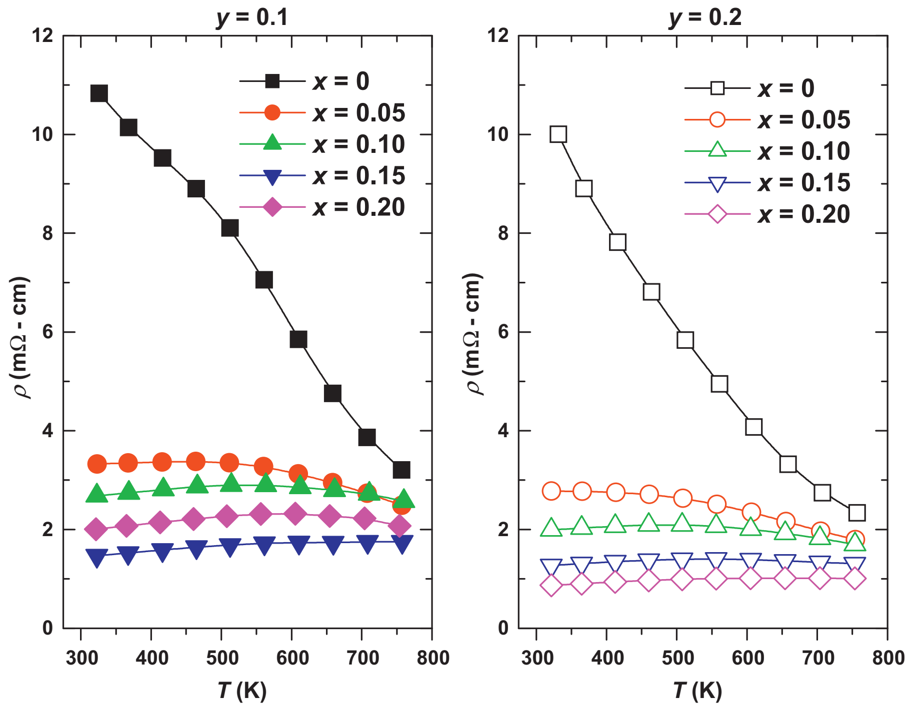

Fig. 3. Temperature dependences of the electrical resistivity (ρ) of the polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and $y = 0.1$, 0.2).

[17], it was reported that the calculated formation enthalpy ΔH values for the $Co_{1-x}Rh_xSb_3$ system were all positive, suggesting that the solid solution was not thermodynamically stable at 0 K. The consolute temperature for $Co_{1-x}Rh_xSb_3$ was estimated to be around 510 K, and the estimated solubility at room temperature was 0.05. Although the $Co_{1-x}Rh_xSb_3$ solid solution was not thermodynamically stable theoretically, the skutterudite phase of the compositions of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and $y = 0.1$, 0.2) were obtained in the present study. The sample preparation procedure such as the cooling time would be an important factor to determine the solid solubility of the system.

Fig. 2 shows the lattice parameters of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ as a function of Tl content, together with the data for $Tl_xCo_4Sb_{12}$ [10]. The lattice parameters of all the samples increased almost linearly with increasing Tl content and the slope were similar in the samples with different Rh content. High-density samples (>97% of the theoretical density) were obtained in the present study. The SEM

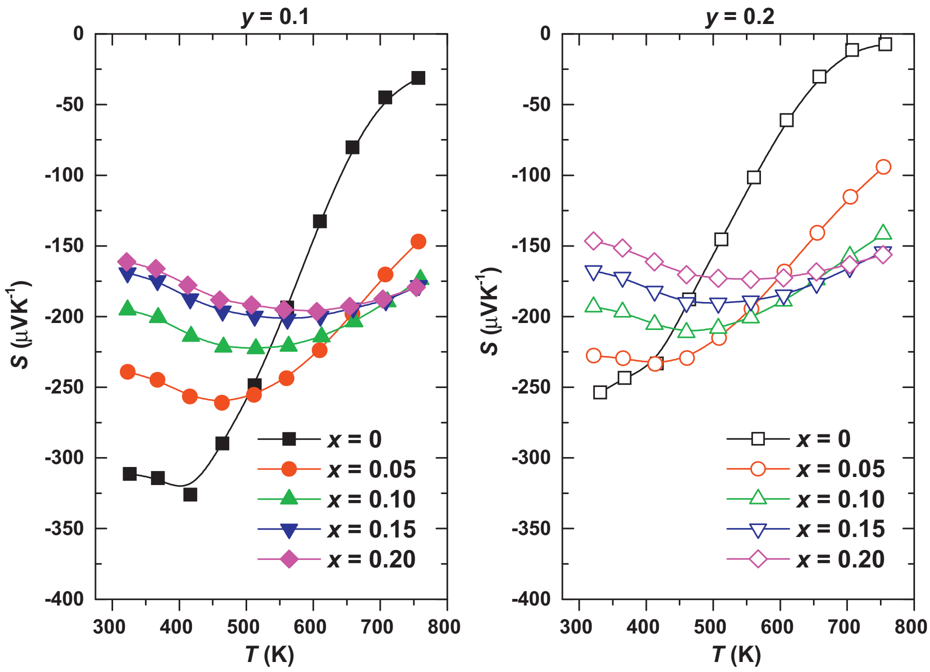

Fig. 4. Temperature dependences of the Seebeck coefficient (S) of the polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and $y = 0.1$, 0.2).

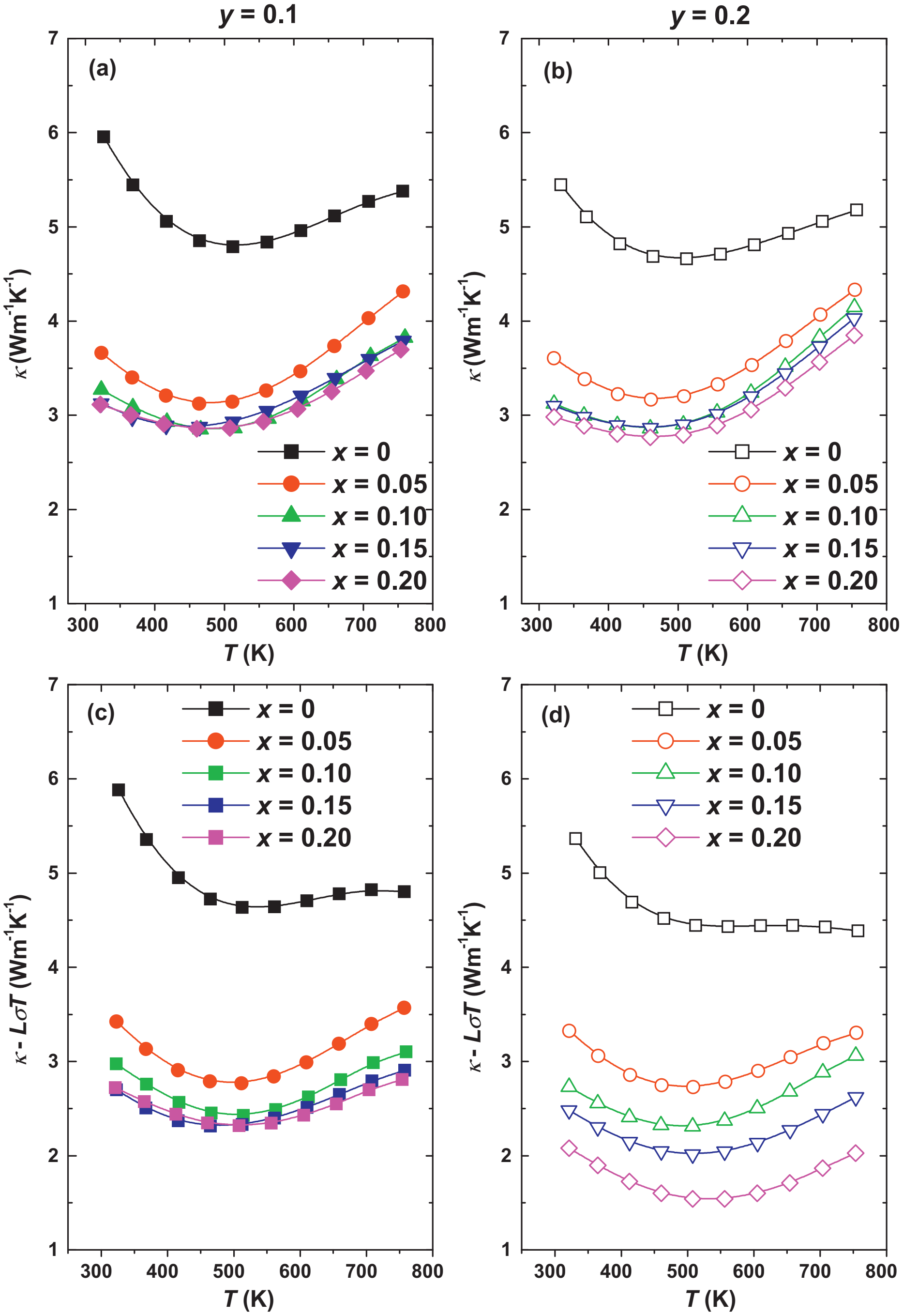

Fig. 5. Temperature dependences of the thermal conductivity of the polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and $y = 0.1$, 0.2); (a) and (b) total (measured) thermal conductivity κ and (c) and (d) lattice thermal conductivity κ_{lat}.

images of all samples confirm that the samples were homogeneous. EDX analysis on all the samples revealed that Co, Rh, Sb, and Tl were uniformly distributed on the sample surface. Quantitative EDX analysis confirmed that the chemical compositions of the hot-pressed samples corresponded to the nominal target compositions.

Temperature dependences of the ρ and the S for polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and $y = 0.1$, 0.2) are shown in Figs. 3 and 4, respectively. The S values were negative for all samples, indicating that the majority of charge carriers were electrons. Both the ρ and absolute S values of $y = 0.2$ samples were lower than those of $y = 0.1$ samples, indicating that the carrier concentration of $y = 0.2$ samples was larger than that of $y = 0.1$ samples. With increasing the Tl-filling ratio x, the magnitude of ρ and absolute S of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ decreased. These results obtained in the cases of both ρ and S implied that Tl-filling led to an increase of the electron carrier concentration. The similar carrier concentration increase was observed in the Tl-filled $CoSb_3$ system, viz. the carrier concentration for $Tl_{0.25}Co_4Sb_{12}$ ($23.9 \times 10^{19}\ cm^{-3}$) was more than ten times that of $CoSb_3$ ($1.56 \times 10^{19}\ cm^{-3}$) [10].

Temperature dependences of the κ and the κ_{lat} for polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20 and $y = 0.1$, 0.2) are shown in Fig. 5. κ_{lat} was obtained by subtracting electronic thermal conductivity ($\kappa_{el} = L\sigma T$, where

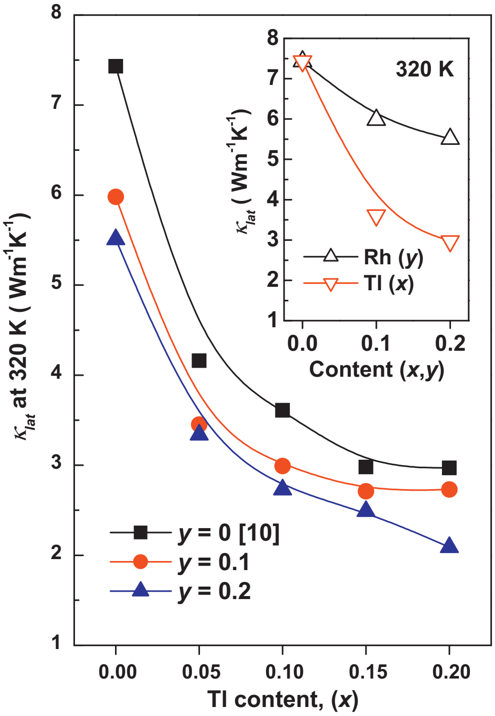

Fig. 6. Temperature dependences of the lattice thermal conductivity (κ_{lat}) of the polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0, 0.05, 0.10, 0.15, 0.20$ and $y = 0.1, 0.2$) at 320 K as a function of Tl content (x), together with the data for $Tl_xCo_4Sb_{12}$ [10]. Inset: the κ_{lat} at 320 K data for $Tl_xCo_4Sb_{12}$ and $(Co_{1-y}Rh_y)_4Sb_{12}$ as a function of Tl content x or Rh content y.

σ is the electrical conductivity and L is the Lorentz number $= 2.45 \times 10^{-8}$ WΩ K^{-2}) from the measured κ, i.e. $\kappa_{lat} = \kappa - L\sigma T$. The κ_{lat} of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ drastically decreased with Tl-filling and Rh substitution. Fig. 6 shows the relationship between the κ_{lat} at 320 K and Tl content for $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$, together with the literature data for $Tl_xCo_4Sb_{12}$ [10]. In the case of non-Tl system: $(Co_{1-y}Rh_y)_4Sb_{12}$, the κ_{lat} at 320 K decreased from 7.43 to 5.51 W m^{-1} K^{-1} by 20% substitution of Rh for Co. On the other hand, in the case of non-Rh system: $Tl_xCo_4Sb_{12}$, it was reported in Ref. [10] that the κ_{lat} at 320 K decreased from 7.43 to 2.97 W m^{-1} K^{-1} by 20% filling of Tl into the voids of the $CoSb_3$ crystal. In the inset of Fig. 6, the κ_{lat} at 320 K data for $Tl_xCo_4Sb_{12}$ and $(Co_{1-y}Rh_y)_4Sb_{12}$ are plotted as a function of Tl content x or Rh content y. From this figure, it was clear that the κ_{lat} of $Tl_xCo_4Sb_{12}$ was lower than that of $(Co_{1-y}Rh_y)_4Sb_{12}$. Therefore, it can be said that the rattling effect resulting from Tl-filling is more effective for κ_{lat} reduction than the alloy scattering effect between Co and Rh. By combining Tl-filling and Rh substitution in the $CoSb_3$ system, significant reduction of κ_{lat} was achieved. $Tl_{0.20}(Co_{0.8}Rh_{0.2})_4Sb_{12}$ exhibited the lowest κ_{lat} (2.09 W m^{-1} K^{-1} at 320 K).

Temperature dependence of the ZT for polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0, 0.05, 0.10, 0.15, 0.20$ and $y = 0.1, 0.2$) is shown in Fig. 7, together with the literature data for $CoSb_3$ [10,16]. Since Tl-filling and Rh substitution resulted in significant reduction of κ_{lat}, the enhancement of ZT was achieved. In particular, $Tl_{0.20}(Co_{0.8}Rh_{0.2})_4Sb_{12}$ exhibited the best TE performance and a maximum ZT value of 0.58 was obtained at around 600 K.

4. Summary

In this study, fully dense samples of polycrystalline $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0, 0.05, 0.10, 0.15, 0.20$ and $y = 0.1, 0.2$) were prepared and their high-temperature TE properties were examined. All samples exhibited negative S values. Tl filling and Rh substitution reduced the ρ, absolute S, and κ_{lat}. It was revealed that the rattling effect resulting from Tl-filling was more effective for κ_{lat} reduction than the alloy scattering effect between Co and Rh. The ZT was enhanced by Tl-filling and Rh substitution, and the maximum ZT obtained for $Tl_{0.20}(Co_{0.8}Rh_{0.2})_4Sb_{12}$ was 0.58 at around 600 K. By tuning the carrier concentration, further enhancement of ZT could be achieved. We are now performing TE characterizations on multi-filled skutterudites such as Tl and In double-filled $CoSb_3$. The results will be reported in near future.

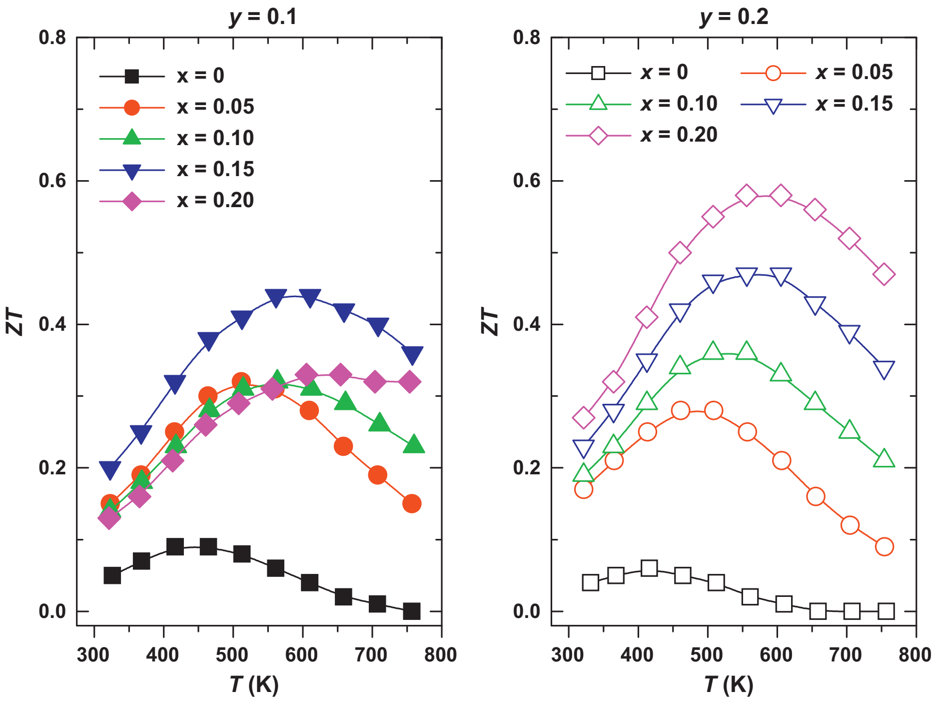

Fig. 7. Temperature dependences of the dimensionless figure of merit (ZT) of the polycrystalline samples of $Tl_x(Co_{1-y}Rh_y)_4Sb_{12}$ ($x = 0, 0.05, 0.10, 0.15, 0.20$ and $y = 0.1, 0.2$).

Acknowledgments

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 21760519) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. Additional support was kindly provided by The Thermal & Electric Energy Technology Foundation and the Murata Science Foundation. This work was also supported by the Rajamangala University of Technology Suvarnabhumi and the Government of Thailand.

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