Enhancement of thermoelectric efficiency of CoSb$_3$-based skutterudites by double filling with K and Tl

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INTRODUCTION

Thermoelectric (TE) materials can be used for direct energy conversion from waste heat into electrical power, and have advantages of no moving parts and high reliability. The efficiency of the energy conversion of TE materials is governed by the material’s dimensionless figure of merit: $zT = S^2T/\rho\kappa$, where $S$ is the Seebeck coefficient, $T$ is the absolute temperature, $\rho$ is the electrical resistivity, and $\kappa$ is the total thermal conductivity ($\kappa = \kappa_{\text{lat}} + \kappa_{\text{el}}$), where $\kappa_{\text{lat}}$ and $\kappa_{\text{el}}$ are the lattice and electronic contributions, respectively (Ioffe, 1957; Slack, 1995; Nolas et al., 2001). Because the $zT$ value directly reflects the energy conversion efficiency, development of high-$zT$ materials is important for effective energy saving by recycling the waste heat by TE technology. It is considered that materials with $zT > 1$ should be obtained for practical application. To achieve such a high $zT$, a large $S$, low $\rho$, and low $\kappa$ are required. However, $S$, $\rho$, and $\kappa_{\text{el}}$ are strongly interconnected with each other in materials, therefore reduction of $\kappa_{\text{lat}}$ is required to maximize $zT$ (Ioffe, 1957; Nolas et al., 2001).

Skutterudite compounds have the composition MX$_3$, where $M$ is a transition metal, such as Co, and $X$ represents a pnictogen atom, such as Sb. These compounds are body-centered cubic with 32 atoms in the unit cell and the space group Im3. The structure contains two voids per unit cell. When a third atom $A$ is incorporated into the voids, the formula of the compounds, referred to as filled skutterudites, becomes $AM_nX_{12}$. The $A$ atom is weakly bonded to the other atoms and “rattles,” leading to strong scattering of heat-carrying phonons. Thus, the introduction of $A$ atoms into the voids of the skutterudite structure is an effective method for reducing $\kappa_{\text{lat}}$. Although skutterudites filled with alkali, alkaline-earth, or rare-earth metals with $zT > 1$ have been widely reported (Morelli et al., 1997; Nolas et al., 2000; Chen et al., 2001; Lamberton et al., 2002; Puyet et al., 2004; Pei et al., 2006; Zhao et al., 2006), skutterudites filled with other elements, such as group 13 elements such as thallium (Tl), have been scarcely reported (Harnwungmoung et al., 2010; Qiu et al., 2013; Tang et al., 2014). Recently, the vibrational frequencies of the filler atoms in cobalt antimonide (CoSb$_3$)-based skutterudites have been calculated by density functional theory. It was found that the vibrational frequencies were significantly different for different chemical groups of the periodic table (Yang et al., 2007). It has been suggested that only the lattice phonons with frequencies near the vibrational frequency of the fillers can be strongly scattered via phonon resonant scattering (Shi et al., 2011). Thus, introducing filler elements belonging to different chemical groups into the cages of CoSb$_3$ could introduce various distinctive filler vibrational frequencies for a broader range of lattice phonon scattering, leading to further $\kappa_{\text{lat}}$ reduction (Shi et al., 2011). In the present study, we selected Tl (one of the heaviest elements) and potassium (K) (one of the lightest elements) as the double-filling combination to achieve significant reduction of $\kappa_{\text{lat}}$ of CoSb$_3$-based skutterudites. Based on previous studies (Pei et al., 2006; Harnwungmoung et al., 2010) we selected the sample compositions Tl$_x$K$_{0.3}$Co$_4$Sb$_{12}$ ($x = 0.1 – 0.3$) and their high-temperature TE properties were investigated. The effect of Tl and K double-filling on the TE properties of CoSb$_3$ was also investigated.

EXPERIMENTAL

Polycrystalline samples of Tl and K double-filled skutterudites, Tl$_x$K$_{0.3}$Co$_4$Sb$_{12}$ ($x = 0.1 – 0.3$), were synthesized by a combination of melting, quenching, and long-term high-temperature annealing. The high-purity elements Tl (99.9%), K (99%), Co (99.99%), and Sb (99.999%) were weighed in appropriate ratios and placed in a carbon crucible in a silica tube. Considering that...
K rapidly evaporates at high temperatures, appropriate amounts of excess K were added to the mixtures of the starting materials. The silica tubes were sealed under vacuum, heated slowly up to 1323 K, and then quenched to room temperature. The silica tubes were then heated again up to 873 K and annealed for 1 week. The obtained ingots were crushed into powders, followed by spark plasma sintering at 923 K under a pressure of 50 MPa for 15 min in an Ar flow atmosphere.

Structural characterization was conducted using X-ray diffraction (XRD) analysis in air at room temperature with Cu Kα radiation. The microstructure and chemical composition of the samples were investigated by field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray (EDX) analysis in vacuum at room temperature. S and ρ were measured using a commercially-available apparatus (ULVAC ZEM-1) in a He atmosphere. The thermal diffusivity (α) was measured by the laser flash method in a vacuum using a commercially available, thermal constant analyzer (ULVAC TC-7000). α was evaluated via the standard equation of \( \kappa = \alpha C_p d \), where \( C_p \) and \( d \) are the heat capacity and density, respectively. \( C_p \) was estimated using the Dulong–Petit model: \( C_p = 3nR \), where \( n \) is the number of atoms per formula unit and \( R \) is the gas constant. All of the TE properties were measured from room temperature to 773 K.

The Hall coefficient (\( R_{H} \)) was measured at room temperature by the van der Pauw method under vacuum with an applied magnetic field of 0.5 T. The Hall carrier concentration (\( n_{H} \)) and Hall mobility (\( \mu_{H} \)) were calculated from \( R_{H} \) assuming a single band model and a Hall factor of 1, i.e., \( n_{H} = 1/(eR_{H}) \) and \( \mu_{H} = R_{H}/\rho \), where \( e \) is the elementary electric charge. The density of the bulk samples was calculated based on the samples' weight and dimensions.

**RESULTS AND DISCUSSION**

The powder XRD patterns of the polycrystalline samples of \( \text{Tl}_x\text{K}_0.3\text{Co}_4\text{Sb}_{12} \) (\( x = 0.1 - 0.3 \)) are shown in Figure 1A, together with the peak positions of CoSb₃. All of the peaks in the XRD patterns were identified as peaks derived from the skutterudite phase. The lattice parameters (\( a \)) of the samples calculated from the XRD patterns almost linearly increased with increasing TI content, as summarized in Table 1. The densities of the samples are summarized in Table 1. All of the samples had high densities equivalent to approximately 98% of the theoretical densities. The FE-SEM and EDX mapping images of the sample with \( x = 0.3 \) are shown in Figure 1B. The FE-SEM image confirmed that the sample was homogeneous. EDX analysis revealed that Ti, K, Co, and Sb were uniformly distributed on the sample surface. The chemical compositions of all of the samples determined by the quantitative EDX analysis are summarized in Table 1. The K contents in the EDX compositions were clearly lower than in the nominal compositions, probably because of the volatilization loss of K during the synthesis. The XRD and FE-SEM/EDX results revealed that all of the TI and K added to CoSb₃ filled the voids of the skutterudite structure, and thus all of the samples prepared in the present study were skutterudite single phases with no impurity phases.

The room temperature values of \( n_{H} \) and \( \mu_{H} \) for the samples are summarized in Table 1. It was confirmed that increasing the TI content increased \( n_{H} \). Owing to the large amounts of the filler elements TI and K, very high \( n_{H} \) values (e.g., \( 4.3 \times 10^{20} \text{cm}^{-3} \)) for the sample with \( x = 0.3 \) were obtained. The \( \mu_{H} \) of the samples slightly decreased with increasing \( n_{H} \), mainly because of the increase of carrier–carrier scattering.

The temperature dependences of \( \rho \), \( S \), \( \kappa \), and \( zT \) are shown in Figures 2A–D, respectively. As shown in Figure 2A, \( \rho \) increased with increasing temperature, showing the typical heavily-doped semiconductor behavior reported by Mallik et al. (2008). As shown in Figure 2B, \( n_{H} \) greatly increased while \( \mu_{H} \) slightly decreased with increasing TI content, leading to a decrease in \( \rho \) with increasing TI content. \( S \) was negative for all of the samples, as shown in Figure 2B, indicating that the majority of charge carriers were electrons. The absolute values of \( S \) decreased with increasing TI content. The results for both \( \rho \) and \( S \) can be explained by \( n_{H} \) increasing by adding TI. As shown in Figure 2C, all of the samples showed very low \( \kappa \) values. The sample with \( x = 0.3 \) showed higher \( \kappa \) than the sample with \( x = 0.2 \) because of the large \( \kappa_{el} \) of the sample with \( x = 0.3 \). Owing to sufficiently reduced \( \kappa \), all of the samples exhibited relatively high \( zT \) values, as shown in Figure 2D. The maximum \( zT \) of around one was obtained at 773 K for the nominal compositions \( \text{Tl}_0.3\text{K}_0.3\text{Co}_4\text{Sb}_{12} \) and \( \text{Tl}_0.5\text{K}_0.5\text{Co}_4\text{Sb}_{12} \).

Figure 3A shows the temperature dependence of \( \kappa_{lat} \) for \( \text{Tl}_x\text{K}_0.3\text{Co}_4\text{Sb}_{12} \) (\( x = 0.1 - 0.3 \)), which was obtained by subtracting the \( \kappa_{el} \) value from the total (measured) \( \kappa \) value. The value of \( \kappa_{el} \) can be calculated using \( \kappa_{el} = \sigma L \), where \( \sigma \) is the electrical conductivity and \( L \) is the Lorenz number (\( = 2.45 \times 10^{-8} \text{W} \text{ΩK}^{-2} \)). The sample with \( x = 0.3 \) had the lowest \( \kappa_{lat} \) in the entire temperature range. Furthermore, the bipolar effect, which is observed as a rapid increase in the \( \kappa_{lat} \) value at high temperatures, can be seen in the sample with \( x = 0.1 \). It is considered that the large \( n_{H} \) in the samples of \( x = 0.2 \) and 0.3 effectively depresses the bipolar effect at high temperatures. The bipolar effect is also observed in the temperature dependence of \( S \) in Figure 2B, i.e., the \( S \) of the sample with \( x = 0.1 \) first decreases with temperature and then increases with temperature above about 600 K. A \( \kappa_{lat} \) value as low as 0.9 W m⁻¹ K⁻¹ was obtained for the sample with \( x = 0.3 \). The \( \kappa_{lat} \) values obtained
Table 1: Nominal and EDX compositions, lattice parameter ($a$), carrier concentration ($n_H$), carrier mobility ($\mu_H$), and density ($d$) of the samples.

| Nominal composition     | EDX composition     | $a$ (nm) | $n_H$ ($10^{20}$ cm$^{-3}$) | $\mu_H$ (cm$^2$ V$^{-1}$ s$^{-1}$) | $d$ (g/cm$^3$) | $d$ (%T.D.) |
|-------------------------|--------------------|---------|-----------------------------|-----------------------------------|----------------|-------------|
| Tl$_{0.1}$K$_{0.3}$Co$_4$Sb$_{12}$ | Tl$_{0.1}$K$_{0.2}$Co$_{3.8}$Sb$_{12.4}$ | 0.9041 (2) | 1.5 | 52 | 760 | 98 |
| Tl$_{0.2}$K$_{0.3}$Co$_4$Sb$_{12}$ | Tl$_{0.2}$K$_{0.2}$Co$_{3.8}$Sb$_{12.3}$ | 0.9059 (2) | 3.0 | 42 | 763 | 98 |
| Tl$_{0.3}$K$_{0.3}$Co$_4$Sb$_{12}$ | Tl$_{0.3}$K$_{0.2}$Co$_{3.8}$Sb$_{12.3}$ | 0.9068 (2) | 4.3 | 39 | 767 | 97 |

The data were obtained at room temperature. Considering the uncertainty in the EDX analysis, the error bars of the EDX compositions are a maximum of 5%.

Figure 2: Temperature dependences of (A) electrical resistivity $\rho$, (B) Seebeck coefficient $S$, (C) thermal conductivity $\kappa$, and (D) dimensionless figure of merit $zT$ of polycrystalline bulk samples of Tl$_x$K$_{0.3}$Co$_4$Sb$_{12}$ ($x = 0.1 - 0.3$).

Figure 3: (A) Temperature dependence of the lattice thermal conductivity $\kappa_{lat}$ of polycrystalline bulk samples of Tl$_x$K$_{0.3}$Co$_4$Sb$_{12}$ ($x = 0.1 - 0.3$). (B) $\kappa_{lat}$ at 300 K vs. the total filling fraction $y$ in $M_x$Co$_4$Sb$_{12}$ ($M = $ Ti, K, or Ti and K). The data for Ti- and K-filled skutterudites were obtained from Harnwungmoung et al. (2010) and Pei et al. (2006), respectively.
in the present study are relatively low compared with those of other reported filled-skutterudite compounds. These results indicate that Tl and K double-filling is an effective way to scatter heat-carrying phonons and thus achieve sufficiently low $\kappa_{\text{lat}}$.

**Figure 3B** shows the $\kappa_{\text{lat}}$ value at 300 K vs. the total filling fraction $y$ in $M_x\text{Co}_4\text{Sb}_{12}$ ($M = \text{Tl}, \text{K}, \text{or Tl and K}$). Note that, here, the filling fraction of the Tl and K double-filling system, i.e., the $y$ values in $(\text{Tl}, \text{K})_2\text{Co}_4\text{Sb}_{12}$, were calculated based on the EDX compositions. In the case of the single element-filled system, it has been reported that the maximum filling limit $y$ is around 0.2 (Harnwunggmoung et al., 2010) and 0.45 (Pei et al., 2006) for $\text{Tl}_x\text{Co}_4\text{Sb}_{12}$ and $\text{K}_x\text{Co}_4\text{Sb}_{12}$, respectively. However, in the case of the Tl and K double-filling system, the total filling fraction was as high as 50% in the voids of the skutterudite structure, in other words, $y = 0.5$ in $(\text{Tl}, \text{K})_2\text{Co}_4\text{Sb}_{12}$. This large filling fraction led to significantly reduced $\kappa_{\text{lat}}$, and thus very high $zT$ values around one were obtained.

**SUMMARY**

In the present study, polycrystalline samples of Tl and K double-filled skutterudites with nominal compositions $\text{Tl}_x\text{K}_{0.5}\text{Co}_4\text{Sb}_{12}$ ($x = 0.1 - 0.3$) were prepared and their high-temperature TE properties were investigated. This is the first attempt to co-fill group 13 elements and alkaline metals into CoSb$_3$-based skutterudites. All of the samples showed the skutterudite single phase, although the maximum filling limits in the single-filled systems were $y = 0.2$ and 0.45 for $\text{Tl}_x\text{Co}_4\text{Sb}_{12}$ and $\text{K}_x\text{Co}_4\text{Sb}_{12}$, respectively. Owing to the large filling fraction of Tl and K, high $\eta_T$ ($\sim 4.3 \times 10^{20} \text{cm}^{-3}$) and low $\kappa_{\text{lat}}$ ($\sim 0.9 \text{Wm}^{-1}\text{K}^{-1}$) values were obtained. It can be concluded that Tl and K double-filling increases the maximum filling limit, and thus it is an effective way to reduce the $\kappa_{\text{lat}}$ value of CoSb$_3$. The maximum $zT$ of around one was obtained at 773 K for the samples with nominal compositions $\text{Tl}_{0.7}\text{K}_{0.3}\text{Co}_4\text{Sb}_{12}$ and $\text{Tl}_{0.2}\text{K}_{0.8}\text{Co}_4\text{Sb}_{12}$.

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**Conflict of Interest Statement**

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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