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Charge Transport and Thermoelectric Properties of Layered BiCuOCh (Ch = Se, Te) compounds

층상구조를 가진 BiCuOCh (Ch = Se, Te) 화합물의 전하 전송 및 열전 특성 연구

2016 년 8 월

서울대학교 대학원 재료공학부 안태호
Charge Transport and Thermoelectric Properties of Layered BiCuOCh (Ch = Se, Te) Compounds

지도교수 박 찬

이 논문을 공학박사학위 논문으로 제출함
2016 년 8 월

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Abstract

Charge Transport and Thermoelectric Properties of Layered BiCuOCh \((Ch = \text{Se, Te})\) Compounds

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The demand for alternative energy of fossil fuel is becoming a major social issue. Thermoelectric materials have received a lot of attention recently as one of the key technologies to solve energy problems because they can directly and reversibly convert waste heat into electrical power. The efficiency of a thermoelectric material is determined by the dimensionless figure of merit \(ZT = S^2\sigma T/\kappa\), where \(S\), \(\sigma\), \(T\), and \(\kappa\) are Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. All those parameters are interrelated with carrier concentration, band structure, and the dominant scattering mechanisms, for example, in terms of carrier concentration, the increase in carrier concentration leads to the increase in electrical conductivity, the decrease in Seebeck coefficient, and the increase in electronic thermal conductivity. Therefore, optimization of the carrier concentration is needed to improve the efficiency of a thermoelectric device.
BiCuO\textit{Ch} (\textit{Ch} = Se and Te) oxychalcogenide has been reported as a promising oxide thermoelectric material since 2010 due to intrinsically low thermal conductivity originated from its weak inter-layer bonding, low Young’s modulus, and anharmonicity and high Seebeck coefficient originated from the layered structure with alternately stacked (Bi\textsubscript{2}O\textsubscript{2})\textsuperscript{2+} insulating and (Cu\textsubscript{2}Ch\textsubscript{2})\textsuperscript{2-} conducting layers along the \textit{c}-axis. However, in case of BiCuOSe, the main limitation of undoped BiCuOSe for thermoelectric applications originates from its poor electrical conductivity. Therefore, enhancement of electrical conductivity has to be achieved in order to improve thermoelectric performances of BiCuOSe thermoelectric materials.

First, we report the density of state effective mass and related charge transport properties in K-doped BiCuOSe. As compared with undoped BiCuOSe, simultaneous increase in both the carrier concentration and the Hall mobility was achieved in the K-doped BiCuOSe. The origin of the enhancement was discussed in terms of the two-band structure in the valence band of the BiCuOSe. The decrease in thermal conductivity with increasing K doping amounts in Bi\textsubscript{1-x}K\textsubscript{x}CuOSe was observed due to the phonon scattering by K atoms. With optimized hole concentration and lower thermal conductivity than other compounds, the highest \textit{ZT} of 0.41 was obtained at 640K in Bi\textsubscript{0.948}K\textsubscript{0.052}CuOSe compound.

Second, the effects of Bi deficiency on thermoelectric properties in Bi\textsubscript{1-x}CuOSe (\textit{x} = 0-0.1) were investigated. The electrical conductivity of the compound increased with the increase in the Bi deficiency due to the increase in hole concentration by introducing Bi deficiencies. The drastic reduction in Seebeck coefficient was observed and it was discussed in terms of electronic structures calculated by density
functional theory (DFT) of Bi$_{1-x}$CuOSe compounds. Thermal conductivity increased due to the increase in hole concentration and reduced anharmonicity with increasing amounts of Bi-deficiency in the Bi$_{1-x}$CuOSe compounds. The highest figure of merit (0.4 at 810K) was obtained for Bi$_{0.975}$CuOSe through the optimized hole concentration, and this value was $\sim 8\%$ higher than that in the stoichiometric compound.

Third, we investigated point defect-assisted doping mechanism and related thermoelectric transport properties in Pb-doped BiCuOTe compounds. The substitution of trivalent Bi$^{3+}$ with divalent Pb$^{2+}$ led to the generation of more than one hole per single Pb atom. The origin of the extra charge carrier was discussed in terms of the formation energy of $p$-type native point defects, and it could be evidenced by the density functional theory calculations. Related charge transport properties indicated that control of the native point defect is critical to achieve high thermoelectric performance in BiCuOTe material system.

Finally, the effects of Pb doping on thermoelectric properties in Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ ($x = 0-0.06$) were investigated. The Pb doping in BiCuOSe$_{0.8}$Te$_{0.2}$ led to the increase in electrical and thermal conductivity and the decrease in Seebeck coefficient due to the increase in hole concentration. The generation of unexpected free hole was also observed in these compounds. It was confirmed that the change in temperature-dependent power factor of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds when comparing with temperature-dependent power factor of Bi$_{1-x}$Pb$_x$CuOSe and Bi$_{1-x}$Pb$_x$CuOTe compounds. The highest figure of merit of 1.06 at 910K was obtained for Bi$_{0.94}$Pb$_{0.06}$CuOSe$_{0.8}$Te$_{0.2}$ with enhance power factor.
Keywords: Oxychalcogenide, BiCuOCh, Charge transport, Thermoelectric properties, Doping, Vacancy formation

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Chapter 1. General Introduction

The demand for alternative energy of fossil fuel is becoming a major social issue. In recent years, thermoelectric materials have received a lot of attention as one of the key technologies to solve energy problems because they can directly and reversibly convert waste heat into electrical power. The efficiency of a thermoelectric material is determined by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $T$, and $\kappa$ are Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively [1-3]. The enhanced $ZT$ can be obtained with high Seebeck coefficient, high electrical conductivity, and low thermal conductivity; however, all those parameters are interrelated with carrier concentration, band structure, and the dominant scattering mechanisms [2,4-6]. For example, in terms of carrier concentration, the increase in the carrier concentration increases the electrical conductivity, decreases the Seebeck coefficient, and increases the electronic thermal conductivity [7]. Therefore, the optimization of the carrier concentration is needed to improve the efficiency of a thermoelectric device.

Thermoelectric materials based on Bi$_2$Te$_3$ [8,9], PbTe [10,11], CoSb$_3$ [12,13] and SiGe [1] have been commercially used because of their high efficiency compared to most other thermoelectric materials. However, these materials have limited applications owing to their high cost and toxicity. Therefore, many studies on alternative thermoelectric materials with high efficiency, low cost, and environmentally friendly characteristics have been reported. Oxide materials have received increasing attention as one of alternative thermoelectric materials owing to their low cost, high thermal and chemical stability, and environmentally friendly characteristics.
compatibility [14-16]. Although many promising oxides such as Ca$_3$Co$_4$O$_9$ [14], NaCo$_2$O$_4$ [15], and SrTiO$_3$ [16] have been studied in order to enhance their efficiency, their ZT values are not enough to be practically applicable.

BiCuOSe oxyselenide has been reported as a promising oxide thermoelectric material since 2010. It has a layered structure (space group: P4/nmm) with alternately stacked (Bi$_2$O$_2$)$^{2+}$ insulating layers and (Cu$_2$Se$_2$)$^{2-}$ conducting layers along the c-axis [17-19] and exhibits intrinsically very low thermal conductivity (0.40 Wm$^{-1}$K$^{-1}$ at 923 K), possibly because of its weak inter-layer bonding, low Young’s modulus, and anharmonicity [20]. The main limitation of undoped BiCuOSe for thermoelectric applications originates from its poor electrical conductivity (< 10 S/cm) [21]. The electrical conductivity of BiCuOSe can be significantly improved by doping with various divalent and monovalent ions (Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Pb$^{2+}$ and Na$^+$) or Cu-deficient self-doping [21-32]. Furthermore, thermoelectric performances have been remarkably enhanced in the doped BiCuOSe as compared to the undoped BiCuOSe, and the highest ZT value (1.4 at 923 K) has been reported for Ba-doped BiCuOSe [27].

Despite the significant achievements in the thermoelectric performance, the efficiency of doped BiCuOSe is still low as compared to other waste heat to power (WHP) system, and the behavior of electron and phonon in BiCuOSe has not yet been fully understood. In this respect, we report the density of state (DOS) effective mass and related charge transport properties in K-doped BiCuOSe in Chapter 5 in this dissertation. The K-doped BiCuOSe compounds exhibited typical metallic conduction behavior with improved $p$-type conduction properties both in the carrier concentration and the Hall mobility as compared to undoped BiCuOSe compound.
The DOS effective masses of the K-doped BiCuOSe compounds were significantly lower than that in the undoped compound, and this result was quite consistent with the enhanced Hall mobilities in the K-doped compounds. This result was explained by the two-band model in the valence band of the BiCuOSe. The thermal conductivity decreased with increasing K doping amounts in Bi$_{1-x}$K$_x$CuOSe compounds because of the phonon scattering by K atoms. The highest $ZT$ of 0.41 was obtained at 640K for Bi$_{0.948}$K$_{0.052}$CuOSe compound owing to optimized hole concentration and lower thermal conductivity than other compounds.

In Chapter 6, the effects of the Bi deficiency on the thermoelectric properties of Bi$_{1-x}$CuOSe compounds are discussed in this dissertation. The $p$-type conduction properties of Bi$_{1-x}$CuOSe compounds improved with increasing hole concentration introduced by Bi deficiency. A drastic decrease in the Seebeck coefficient was observed and is discussed in terms of electronic structures calculated by DFT of Bi$_{1-x}$CuOSe compounds. With increasing Bi-deficiency in the Bi$_{1-x}$CuOSe compounds, thermal conductivity increased owing to increasing hole concentration and reduced anharmonicity. The highest figure of merit (0.4 at 810K) was obtained in Bi$_{0.975}$CuOSe, and this value was ~ 8% higher than that for the stoichiometric compound.

In chapter 7 in this dissertation, the investigation of point defect-assisted doping mechanism and related thermoelectric transport properties in Pb-doped BiCuOTe compounds is discussed. Because BiCuOTe exhibited higher electrical conductivity and power factor than BiCuOSe, BiCuOTe was selected. Even undoped BiCuOTe compound exhibited degenerately doped semiconducting behavior up to extrinsic–intrinsic transition temperature, and this result indicates that native point defects are
the main source of the hole generation in BiCuOTe. The hole concentration increased with the increase with increasing amount of Pb, thus significantly increased the electrical conductivity of Pb-doped BiCuOTe. However, although at most one hole per single dopant atom could be generated owing to the divalency of Pb, more than one hole per a Pb atom were generated in the Pb-doped compound. The dependence of the formation energies of possible point defects ($V_{Cu}$ and $V_{Bi}$) on the amount of Pb-doping were calculated based on density functional theory (DFT), and the results were quite consistent with our observations. With these results, it can be concluded that the thermoelectric performance of BiCuOTe compound is critically determined by the native point defects.

Finally, in Chapter 8, the effects of the Pb doping on the thermoelectric properties of $\text{Bi}_{1-x}\text{Pb}_x\text{CuOSe}_{0.8}\text{Te}_{0.2}$ compounds are reported in this dissertation. Because the increase in the hole concentration is not an effective way to improve $ZT$ of BiCuOTe, which was mentioned in Ch. 7 and the lattice thermal conductivity can be reduced by alloying scattering, $\text{BiCuOSe}_{0.8}\text{Te}_{0.2}$ was selected. The electrical conductivity increased, and the Seebeck coefficient decreased with increasing doping amounts of Pb due to the increase in hole concentration. The change in the temperature-dependent power factor was observed when comparing with Pb-doped BiCuOSe and BiCuOTe. With increasing doping amounts of Pb in the $\text{Bi}_{1-x}\text{Pb}_x\text{CuOSe}_{0.8}\text{Te}_{0.2}$ compounds, the thermal conductivity increased because of increasing hole concentration although the alloying scattering affected the thermal conductivity. The highest figure of merit of 1.06 at 910K was obtained for $\text{Bi}_{0.94}\text{Pb}_{0.06}\text{CuOSe}_{0.8}\text{Se}_{0.2}$. 
References


Chapter 2. General Background

2.1 Thermoelectricity and Thermoelectric effects

The demand for alternative and renewable energy has become a major social issue because of the lack of the fossil fuels. Therefore, the energy should be used more efficiently, and alternative and renewable energy sourced must explored. Figure 2-1 shows the energy use in the US in 2008, conducted by the Lawrence Livermore National Laboratory [1]. As shown in Fig. 2-1, more than 50% of the energy used in the US was lost as waste heat; therefore, the waste heat has to be recovered to use energy in a more efficient way. Thermoelectricity, which is the one of waste heat to power (WHP) technology, can directly convert waste heat to electrical energy. It can also reversibly convert heat energy to electrical energy. Therefore, thermoelectricity can be used for both power generation and electronic refrigeration. Thermoelectric devices have many advantages such as a simple structure, no moving part, high power reliability, scalability, compactness, quietness and no need of maintenance as compared with other approaches to power generation or electronic refrigeration.

Thermoelectric effects refer to the three effects: Seebeck, Peltier, and Thomson effects [2]. Seebeck effect was discovered by Thomas Seebeck in 1821, and he found that electromagnetic field (EMF) was generated between the junctions of two dissimilar conductors, when the junctions were maintained at different temperatures as shown in Fig. 2-2 [2,3]. Majority charge carriers (electrons or holes) thermally diffuse from the hot side to the cold side and this phenomenon creates an electric field, which leads to a drift that actually balances the diffusion of the charges. The Seebeck coefficient is the ratio of the electric field and temperature gradient, and therefore can be expressed by $S = \frac{\Delta V}{\Delta T}$ where $S$, $\Delta V$, and $\Delta T$ are the Seebeck
coefficient, voltage gradient, and temperature gradient, respectively. The sign of the Seebeck coefficient is determined by the type of majority charge carriers (positive for a $p$-type material and negative for an $n$-type material).

In contrast to the Seebeck effect, when current flows through the loop formed by two dissimilar materials, the carriers attempt to return to the electron equilibrium that existed before the current was applied by absorbing energy at one connector and releasing it at the other (Fig. 2-3). This effect is called as the Peltier effect discovered by Jean Peltier in 1834 and it is defined as the ratio of the rate of heating or cooling to the electrical current passing through the junction. Peltier effect can be represented by $\Pi = Q_{\Pi}/I$ where $\Pi$, $Q_{\Pi}$, and $I$ are the Peltier coefficient, absorbed heat, and applied current, respectively [4].

The Thomson effect was discovered by William Thomson (Lord Kelvin) in 1854, and it is the phenomenon of cooling or heating by a current carrying material that has a temperature difference (Fig. 2-4) [5]. The Thomson effect led to a direct relationship between the Seebeck and Peltier coefficients and can be defined as the rate of heat transferred per unit of temperature gradient per unit of current. Therefore it can be defined by $dQ = \beta I dT$ where $dQ$, $\beta$, $I$, and $dT$ are the rate of heat generation, Thomson coefficient, applied current, and temperature gradient, respectively.
Figure 2-1. The flow chart of energy use in US in 2008 which is conducted by the Lawrence Livermore National Laboratory [1].
Figure 2-2. Instrument used by Seebeck to observe the deflection of a compass needle (a) due to a thermoelectric induced current from heating the junction of two different metals (n and o) [3].
Figure 2-3. A schematic of Peltier effect.

Figure 2-4. A schematic of Thomson effect.
2.2 Efficiency and Figure of Merit (ZT) of Thermoelectric

Figure 2-5 shows a schematic of a simple thermoelectric module consisted of $p$- and $n$- type thermoelectric materials [6]. The temperatures of the source and sink are $T_C$ and $T_H$, respectively. When heat flows from top to bottom, current $I$ pass the thermoelectric device. The efficiency of this device is the ratio of electrical energy supplied to the load to heat energy absorbed at a hot junction and is defined by Eq. 2.1

$$\eta = \frac{P}{Q}, \quad (2.1)$$

where $P$ and $Q$ are the electrical power output and the input heat required at the hot junction to maintain the junction at $T_H$, respectively. The electrical energy supplied to the load $P$ can be obtained by the difference in the thermal energy absorbed at the hot side $Q$ and the thermal energy drained at the cold side $Q_d$. $Q$ and $Q_d$ can be presented by Eqs.2.2 and 2.3, respectively.

$$Q = \Delta S T_H I - \frac{I^2 R}{2} + \kappa \Delta T, \quad (2.2)$$

$$Q_d = \Delta S T_C I + \frac{I^2 R}{2} + \kappa \Delta T, \quad (2.3)$$

where $\Delta S$ is the difference in the Seebeck coefficient between $p$- and $n$-type thermoelectric materials, $I$ is the current supplied to the load, $R$ is the internal electrical resistance, and $\kappa$ is the thermal conductivity. If the internal loss in the system is assumed to be negligible, $P$ can be presented be the following equation [2].

$$Q - Q_d = (\Delta S \Delta T - RI) I = I^2 R, \quad (2.4)$$

where $R_L$ is the resistance of the load, and thus the efficiency of the thermoelectric module cab be rewritten as Eq. 2.5.

$$\eta = \frac{P}{Q} = \frac{R_L S^2 \Delta T (R + R_L)^2}{\Delta S T_H I - \frac{I^2 R}{2} + \kappa \Delta T}, \quad (2.5)$$
Eq. 2.6 can be simplified using a new variable $Z$ as follows:

$$\eta = \frac{\Delta T}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}},$$  \hspace{1cm} (2.6)

$ZT$ called the dimensionless figure of merit determines the efficiency of thermoelectric devices and can be expressed by $ZT = S^2 \sigma T(\kappa_c + \kappa_L)$, where $\sigma$, $\kappa_c$ and $\kappa_L$ are the electrical, electronic, and lattice thermal conductivities, respectively [7-9]. The enhanced $ZT$ can be achieved with high Seebeck coefficient, high electrical conductivity, and low thermal conductivity; however, all those parameters are interrelated with carrier concentration, band structure, and the dominant scattering mechanisms [8,10-12]. The electrical conductivity, Seebeck coefficient (degenerated semiconductor), and thermal conductivity are represented by the following equations:

$$\sigma = qn \mu,$$  \hspace{1cm} (2.7)

$$S = \frac{8\pi^2 k^2 T^2}{3q^2 h^2} m^* \left( \frac{\pi}{3n} \right)^{2/3},$$  \hspace{1cm} (2.8)

$$\kappa = \kappa_c + \kappa_L = L \sigma T + \kappa_L = ne \mu LT + \kappa_L,$$  \hspace{1cm} (2.9)

where $q$, $n$, $\mu$, $k$, $h$, $m^*$, and $L$ are the carrier charge, carrier concentration, carrier mobility, Boltzmann constant, Planck constant, density of state (DOS) effective mass, and Lorenz number, respectively. With these equations, high Seebeck coefficient and low electronic thermal conductivity can be obtained at low carrier concentration. However, low carrier concentration also results in low electrical conductivity. In contrast, in the case of high carrier concentration, high electrical conductivity can be achieved but high carrier concentration also leads to low Seebeck coefficient and high electronic thermal conductivity. The dependence of parameters on the carrier concentration is plotted in Fig. 2-6 [13]. To obtain improved $ZT$, the carrier concentration has to be optimized. The range of optimized carrier concentration typically is between $10^{19}$ and $10^{21}$ cm$^{-3}$ (depending on the
material system), indicating that heavily doped semiconductors are best for the thermoelectric materials.

Meanwhile, the flat bands with high DOS at the Fermi surface, indicating the increase in the DOS effective mass \((m_d^*)\), can enhance Seebeck coefficient. However, high DOS effective mass can also reduce the carrier mobility because heavy carrier decreases low velocity and mobility \([7,11]\) although the exact relationship between the effective mass and mobility is complex, and depends on the electronic structure, scattering mechanisms and anisotropy \([11]\). Therefore, DOS effective mass also has to be optimized to obtain enhanced \(ZT\).
Figure 2-5. A schematic of a simple thermoelectric module consisted of $p$- and $n$-type thermoelectric materials [6].
Figure 2-6. The dependence of $ZT$ parameters on carrier concentration [13].
2.3 Commercial and Alternative Thermoelectric Materials

Figure 2-7 shows the temperature-dependent $ZT$ of commercially used $n$- and $p$-type thermoelectric materials [6]. As shown in Fig. 2.7, thermoelectric materials can be divided depending on the operating temperature range. Bi$_2$Te$_3$-based alloys are referred as low-temperature materials and can be used at the temperature up to around 450K. Thermoelectric refrigeration consists of Bi$_2$Te$_3$-based alloys. The intermediate temperature materials can be used at temperature range up to around 850 K and PbTe- and CoSb$_3$-based alloys are used for waste heat recovery of automotive or plants. SiGe-based alloys are high temperature materials usually used in the field of space. These materials have high efficiency compared to most other thermoelectric materials. However, these materials have limited applications because of their high cost and toxicity. The price of elements is plotted as a function of abundance in Fig. 2-8 [14]. Most elements such as Co, Bi, Sb, Se, and Te composing thermoelectric materials are expensive and have low abundance as shown in Fig. 2-8, whereas Pb even though not expensive and has low abundance is toxic. Therefore, many studies on alternative thermoelectric materials with high efficiency, low cost, and environmentally friendly characteristics have been carried out since 2010 (Fig. 2-9 [15]). Among alternative thermoelectric materials, oxide materials have received increasing attention as one of the alternative thermoelectric materials due to their low cost, high thermal and chemical stability, and environmental compatibility [16-18]. Although many promising oxides such as Ca$_3$Co$_4$O$_9$ [16], NaCo$_2$O$_4$ [17], and SrTiO$_3$ [18] have been studied in order to enhance their efficiency, their $ZT$ values are not enough to be practically applicable. However, recently, BiCuOSe oxyselenide has been reported as a promising oxide thermoelectric material, with
highest ZT value (1.4 at 923 K) of Ba-doped BiCuOSe, comparable with commercial thermoelectric materials (Fig. 2-10 [19]).
Figure 2-7. Temperature-dependent $zT$ of $n$- and $p$- type thermoelectric materials used commercially [6].
Figure 2-8. Price versus abundance for selected elements. Prices are mostly averages for the year 2009 from U.S. Geological Survey (2010) [14].
Figure 2-9. ZT of the current bulk thermoelectric materials as a function of year: The left part indicates the three conventional thermoelectric systems with ZT < 1.0 before 1990s, the middle part elucidates that the ZTs were enhanced to about 1.7 by nanostructures, and the right part shows the high performance realized in promising thermoelectric materials developed recently and characterized by low-cost, earth-abundant, and low thermal conductivity [15].
Figure 2-10. Dimensionless figure-of-merit $ZT$ vs. temperature of typical current thermoelectric materials [19].
References


Chapter 3. Reviews of BiCuOCh (Ch = Se and Te)

Thermoelectric Material

3.1 General Properties of BiCuOCh (Ch = Se and Te)

Figure 3-1 shows the schematic of crystal structure for BiCuOSe [1], indicating that BiCuOCh has a layered ZrCuSiAs structure type with the tetragonal unit cell (Space group = P4/nmm) and exhibits a two-dimensional (2D) layered structure with alternatively stacked [Bi$_2$O$_2$]$^{2+}$ insulating and [Cu$_2$Ch$_2$]$^{2-}$ conducting layers [2,3]. The [Bi$_2$O$_2$]$^{2+}$ layers consist of slightly distorted Bi$_4$O tetrahedral, and [Cu$_2$Ch$_2$]$^{2-}$ layers consist of slightly distorted CuCh$_4$ tetrahedral with Se–Se edges being shared. The Cu$_2$Ch$_2$ layer could be regarded as a reversed version of the Bi$_2$O$_2$ layer, because the position of Se atoms is the same as that of Bi atoms, whereas the position of Cu atoms is the same as that of O atoms in the Bi$_2$O$_2$ layer [2-7]. Figure 3-2 shows the transmission electron microscopy (TEM) images of BiCuSeO along (a) [001], (b) [100] and (c) [110] zone axes [8]. As expected, the layered structure with alternatively stacked [Bi$_2$O$_2$]$^{2+}$ and [Cu$_2$Se$_2$]$^{2-}$ layers was not observed in the lattice image along the [001] zone axis (c axis). In contrast, in Figs. 3-2(b) and (c), representing the lattice images along the [100] and [110] zone axes, respectively, clearly show a layered structure.

The electronic band structures of BiCuOSe and BiCuOTe calculated by Zou et al. are presented in Figure. 3-3 [9]. According to the band structure calculation, BiCuOSe and BiCuOTe are multiband materials with an indirect band gap. The calculated energy band gaps for BiCuOSe and BiCuOTe with PBE +U + SOC are 0.38 and 0.05 eV [9], respectively, whereas the energy band gap for BiCuOSe and BiCuOTe estimated experimentally are 0.8 and 0.4 eV [10]. The bottom of the conduction band and the top of the valence band mainly consist of Bi 6p states and
bonding hybridized Cu 3d–$Ch$ 4p states, respectively. The crystal structures, electronic structures, and chemical and physical properties of BiCuOSe are summarized in Table 3-1 [9,11-13].

Figure 3-1. The crystal structure of BiCuOCh [1].
Figure 3-2. HRTEM images of the BiCuSeO sample: (a–c) Lattice images of along [001], [100] and [110] zone axes, respectively. (d, f and h) Fast Fourier-transform images of (a), (b) and (c), respectively. (e, g and i) Crystal structures of BiCuSeO along [001], [100] and [110] zone axes, respectively [8].
Figure 3-3. Calculated band structures near the Fermi energy of (a) BiCuOSe and (b) BiCuOTe. The Fermi levels are set to zero [9].
Table 3-1. General properties of BiCuOCh (Ch = Se, Te) at RT [9, 11-13].

<table>
<thead>
<tr>
<th></th>
<th>BiCuOSe [11]</th>
<th>BiCuOTe [9, 12,13]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>367.4858</td>
<td>416.13</td>
</tr>
<tr>
<td>Crystal system</td>
<td></td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td></td>
<td>P4/nmm</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a =b= 0.3921 nm</td>
<td>a =b= 0.4041 nm [9]</td>
</tr>
<tr>
<td></td>
<td>c = 0.8913 nm</td>
<td>c = 0.9523 nm [9]</td>
</tr>
<tr>
<td>Theoretical density</td>
<td>8.9 g/cm³</td>
<td>8.88 g/cm³</td>
</tr>
<tr>
<td>Carrier concentration</td>
<td>1 x 10¹⁸ /cm³</td>
<td>6.9 x 10¹⁸ /cm³ [12]</td>
</tr>
<tr>
<td>Carrier mobility</td>
<td>22 cm²/V·s</td>
<td>13 cm²/V·s [12]</td>
</tr>
<tr>
<td>Band effective masses</td>
<td>Light hole band (0.18 mₐ)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Heavy hole band (1.1 mₐ)</td>
<td>-</td>
</tr>
<tr>
<td>Seebeck coefficient</td>
<td>349 µV/K</td>
<td>170 µV/K [13]</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>1.12 S/cm</td>
<td>289 S/cm [13]</td>
</tr>
<tr>
<td>Lattice thermal conductivity</td>
<td>0.55 W/m·K</td>
<td>0.47 W/m·K (373K)</td>
</tr>
<tr>
<td>Longitudinal sound velocity</td>
<td>3290 m/s</td>
<td>-</td>
</tr>
<tr>
<td>Transverse sound velocity</td>
<td>1900 m/s</td>
<td>-</td>
</tr>
<tr>
<td>Average sound velocity</td>
<td>2107 m/s</td>
<td>-</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>76.5 GPa</td>
<td>-</td>
</tr>
<tr>
<td>Debye temperature</td>
<td>243K</td>
<td>-</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>Grüneisen parameter</td>
<td>1.5</td>
<td>-</td>
</tr>
</tbody>
</table>
3.2 Advantage of BiCuOCh \((Ch = \text{Se and Te})\) for Thermoelectric Applications

BiCuOCh materials have been received significant attentions as one of the promising middle-temperature (600-900 K) thermoelectric materials since 2010, because of their advantages for thermoelectric applications. The advantages for thermoelectric materials are as follows:

First, BiCuOCh compounds have a competitive price, because Cu and O, the elements of BiCuOCh compounds, are one of the most inexpensive materials in the Earth’s crust. Fig. 3-4 shows the price ($/Kg) of BiCuOCh and commercial thermoelectric materials (Source: [14]). BiCuOSe and BiCuOTe are inexpensive than commercial thermoelectric materials expect CoSb3.

Second, BiCuOCh compounds have an intrinsically low thermal conductivity. Fig. 3-5 shows the comparison of the total thermal conductivity for BiCuOCh and commercial thermoelectric materials [8,13,15,16,17,18]. The lower total thermal conductivity of BiCuOCh than commercial thermoelectric materials is confirmed in Fig. 3-5. The origin of the low thermal conductivity for the BiCuOCh is because of its layered structure, weak bonding, and anharmonicity. The layered structure of BiCuOCh shown in Fig. 3-1 results in phonon scattering by the interface between layers. Moreover, the weak interatomic bonding leads to slow transport for phonons, thus resulting in lower lattice thermal conductivity. The weak interatomic bonding can be determined by Young’s modulus, because it generally results in lower stiffness and lower Young's modulus [19,20]. Fig. 3-6 shows the Young's modulus of BiCuOSe with oxide compounds [11]. As shown in Fig. 3-6, the Young’s modulus of BiCuOSe is lower than other oxide compounds. Besides Young’s modulus, the
anharmonicity of the material is related to the thermal conductivity, because the anharmonicity of the chemical bond drives the phonon–phonon umklapp and normal processes that intrinsically limit the lattice thermal conductivity [21,22]. The Grüneisen parameter is often referred as a temperature dependent anharmonicity parameter that reflects the phonon vibrations in crystal lattices that deviate from harmonic oscillation [11]. The Grüneisen parameter for BiCuOSe was reported to be 1.5, indicating high anharmonicity of the lattice vibrations [11]. The bond anharmonicity of BiCuOSe may originate from the presence of the lone pair electrons of Bi, as reported Sallis by et al. [23]. This lone-pair electron gives rise to extra electron clouds surrounding Bi atoms and causes nonlinear repulsive forces, leading to the stronger lattice anharmonic vibration.

Third, BiCuOCh compounds have higher Seebeck coefficient as compared to other commercial materials (Fig. 3-7 [8,13,15,16,17,18]). The high Seebeck coefficient is related to their layered crystal structure with alternately stacked insulating and conducting layers. Those layers were supposed to form a natural superlattice with the 2D confinement of the charge carriers [24]. Dresshaus and Hicks reported that it was possible to cause dramatic differences in the density of electronic states, as shown in Fig. 3-8, when the dimensionality of the material was decreased [25]. A low-dimensional materials system was shown to enhance the thermoelectric performance of a 2D superlattice consisting of PbTe quantum wells and Pb_{1-x}Eu_{x}Te barriers [26]. The effect of this local increase in the DOS on the Seebeck coefficient is given by the Mott expression represented by Eq. 3.1 [27].

\[
S = \frac{\pi^2 k_B^2 T}{3q} \left[ \frac{g(E)}{n(E)} + \frac{d\mu(E)}{\mu(E)} \right]_{E=E_F}, \tag{3.1}
\]
where \( g(E) \) is the DOS, \( n(E) \) is the carrier density at the energy level \( E_F \), and \( \mu(E) \) is the carrier mobility at the energy level \( E_F \). As shown in Eq. 3.1, a local increase in \( g(E) \) can enhance the Seebeck coefficients. Ohta et al. reported the two dimensional electron gas structure of \( \text{SrTiO}_3/\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3/\text{SrTiO}_3 \), containing artificial insulating/conductive/insulating layers, exhibited a high Seebeck coefficient [28] and is very similar to the natural layered structure of BiCuOCh. Therefore, 2D like electronic structure of BiCuOCh leads to high Seebeck coefficients.

Finally, BiCuOCh compounds have enough thermal stability for middle-temperature thermoelectric materials. BiCuOSe and BiCuOTe are thermally stable at < 773K [29] and < 620K, and confirmed by differential scanning calorimetry (DSC) as shown in Fig. 3-9. Table 3-2 summarizes the thermally stable temperature of BiCuOCh compounds and middle-temperature thermoelectric materials used commercially [29-31]. As listed in Table 3-2, BiCuOCh compounds are stable enough to be used in the middle-temperature range.
Figure 3-4. Price ($/Kg) of BiCuOCh and commercial thermoelectric materials (Source: J. G. Price, The society of Economic Geologists Newsletter, 82 (2010)).

Figure 3-5. The comparison of total thermal conductivity for BiCuOCh and commercial thermoelectric materials [8,13,15,16,17,18].
Figure 3-6. Young’s modulus of BiCuOSe with oxide compounds [11].

Figure 3-7. The comparison of Seebeck coefficient for BiCuOCh and commercial thermoelectric materials [8,13,15,16,17,18].
Figure 3-8. Electronic density of states for a bulk 3D crystalline semiconductor, a 2D quantum well, a 1D nanowire or nanotube and a 0D quantum dot [25].
Figure 3-9. DSC results of BiCuOTe.

Table 3-2. Thermal stability of BiCuOCh (Ch = Se, Te) and middle-temperature thermoelectric materials used commercially [29-31].

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermally stable temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiCuOSe</td>
<td>&lt; 773K [29]</td>
</tr>
<tr>
<td>BiCuOTe</td>
<td>&lt; 620K</td>
</tr>
<tr>
<td>CoSb3</td>
<td>&lt; 693K [30]</td>
</tr>
<tr>
<td>PbTe</td>
<td>&lt; 700K [31]</td>
</tr>
</tbody>
</table>
3.3 Disadvantage of BiCuOCh (Ch = Se and Te) for Thermoelectric Applications and Approaches to Improve ZT of BiCuOCh in Previous Reports

BiCuOSe compounds have advantages such as high Seebeck coefficients and low thermal conductivity for thermoelectric applications; however, they also have a disadvantage owing to their low electrical conductivity of <10 S/cm [8]. Enhanced \( ZT \) can be obtained by enhancing the Seebeck coefficient, electrical conductivity, and lower thermal conductivity. However, because the lattice thermal conductivity (0.4-0.6 W/mK at 300-923K) is already low, it doesn’t seem that the lattice thermal conductivity can be effectively reduced [11]. Therefore, the best way to enhance \( ZT \) is to improve the power factor by optimizing the carrier concentration. Because the carrier concentration of BiCuOSe at RT is around \( 10^{18} / \text{cm}^3 \), which is lower than the optimum range of carrier concentration \( (10^{19}-10^{21}/\text{cm}^3) \), the carrier concentration has to be increased for improving power factor. There are several ways to increase the carrier concentration. First way of increasing carrier concentration is divalent or monovalent ion doping into Bi sites because of the charge valence for Bi of 3+. When divalent or monovalent ions are doped into Bi sites, one or two free holes can be generated to keep the charge balance in BiCuOSe, and it can increase the carrier concentration. The defect equations for divalent and monovalent doping into Bi sites are as follows:

Divalent ions doping : \( \text{Bi}^x_{\text{Bi}} + x\text{M} \leftrightarrow (1-x)\text{Bi}^x_{\text{Bi}} + x\text{M}^x_{\text{Bi}} + x\text{h}^+ + x\text{Bi}^\uparrow \), \hspace{1cm} (3.2)  
Monovalent ions doping : \( \text{Bi}^x_{\text{Bi}} + x\text{M} \leftrightarrow (1-x)\text{Bi}^x_{\text{Bi}} + x\text{M}^x_{\text{Bi}} + 2x\text{h}^+ + x\text{Bi}^\uparrow \), \hspace{1cm} (3.3)

In previous reports, Bi ions were substituted with divalent (Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\), Pb\(^{2+}\)) or monovalent ions (Na\(^+\)), leading to increase in the carrier concentration [8,24,32-39]. Furthermore, the carrier concentration was optimized by controlling
doping amounts. Second way to increase the carrier concentration is by the formation of vacancy. The achievement of enhancing $ZT$ through the formation of Cu vacancy was reported by Liu et al. [40]. Because the charge valence of Cu is 1+, one free hole can be generated to keep the charge balance in BiCuOSe when forming Cu vacancy. The defect equation for the formation of Cu vacancy in BiCuOSe is as follows:

$$\text{Bi}_{Bi}^x \leftrightarrow V_{Bi}'' + 3h^* + \text{Bi} \uparrow,$$

(3.4)

Besides optimizing carrier concentration, another option to enhance the $ZT$ of BiCuOSe is by enhancing the mobility through producing textured microstructure by applying a hot-forging process [41]. The texturation of BiCuOSe increases the electrical conductivity by increasing the carrier mobility and improving $ZT$ (1.4 at 923 K) for the textured Bi$_{0.875}$Ba$_{0.125}$CuOSe after three hot-forging steps. Although the best $ZT$ of 1.4 at 923 K was achieved for BiCuOSe, the efficiency has to be improved for waste heat to power application. Figure 3-10 shows the efficiency of the best practice mechanical heat engines compared to an optimistic thermoelectric estimate [42]. As shown in Fig. 3-10, the efficiency is still lower than other WHP applications.

In contrast, in the case of BiCuOTe, only Pb doping was reported to improve $ZT$, and Pb doping was not an effective way to improve $ZT$ although the electrical conductivity was enhanced by Pb doping [13]. In previous report, Pb doping was not reported to be an effective way to enhance $ZT$. Therefore, the behavior of electron and phonon in Pb-doped BiCuOTe has to be investigated to find another ways to improve $ZT$ through the behavior of electron and phonon in Pb-doped BiCuOTe.
Figure 3-10. Efficiency of ‘best practice’ mechanical heat engines compared with an optimistic thermoelectric estimate [41,42].
References


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Chapter 4. Experimental

4.1 Solid-state Reaction Method

The solid-state reaction method is one of the methods for the synthesis of polycrystalline compounds. In order for the reactions of solids to occur at an appreciable rate, heating them at higher temperatures is necessary. In general, Tamman’s Rule suggests that at the temperature of about two-thirds of the melting point of the lower melting reactant is needed for reaction to occur in a reasonable time [1]. Therefore, the reactions of solids occur in the solid state by diffusion among solid particles. In a typical solid-state reaction process, the reactants are first mixed in a mortar after the reactants have been weighed out in the required amounts. Then, the mixed powders are pressed into pellets at high pressure. Finally, the pellets are annealed in a furnace at a reasonable temperature in a reasonable time. The factors on which the feasibility and rate of a solid-state reaction depend include reaction conditions, structural properties of the reactants, surface area of the solids, their reactivity, and the thermodynamic free energy change associated with the reaction [2,3].
4.2 Spark Plasma Sintering

Spark plasma sintering (SPS) is a rapid sintering technique and has many advantages such as ease of operation and accurate control of sintering energy, high sintering speed (a high heating and cooling rate), high reproducibility, sintering less additives, safety and reliability over conventional systems using hot press (HP) sintering, hot isostatic pressing (HIP), or atmospheric furnaces [4]. Figs. 4-1[5] and 4-2 show the schematic and photograph of an SPS apparatus consisting of a chamber, power supply, and mechanical loading system, which act at the same time as high-power electrical circuit. SPS is a process involving the consolidation of powders under the simultaneous action of a pulsed DC current and an appropriate uniaxial pressure. When pulsed DC current is applied to graphite mold, Joule heating is generated, and then the necks are formed around the area of contact between particles (Fig. 4-3 [4]). In contrast to the conventional hot pressing, where the heat is provided by external heating elements, the heat generation is internal, resulting in a very high heating or cooling rate, hence generally the sintering process is very fast (within a few minutes). Because of short sintering time, it has the potential of densifying powders with nanosize or nanostructure while avoiding coarsening, which accompanies standard densification routes [6]. In general, SPS process depends upon sintering temperature, applied pressure, heating rate, holding time, and total sintering time and those parameters are essential for the optimization of consolidation conditions for each material type.
Figure 4-1. A schematic of the SPS apparatus [5].
Figure 4-2. A photograph of the SPS apparatus.
Figure 4-3. A mechanism of SPS [4].
4.3 X-ray Diffraction Analysis

X-ray diffraction (XRD) is the one of the most widely used characterization technique for determining the crystal structure, phase composition, lattice parameter, gain size, and orientation of the samples. The XRD technique is based on diffraction governed by Bragg’s law, represented by the following equation [7]:

\[ n\lambda = 2d \sin \theta, \]  \hspace{1cm} (4.1)

where \( n \) is an integer indicating the order of reflection, and \( \lambda \) is the wavelength of the X-ray beam, \( d \) is the inter-planar spacing, and \( \theta \) is the incident angle. Bragg’s Law is one of the most important physical laws used for interpreting XRD data. X-rays with wavelengths of the same order are generated by a cathode ray tube, filtered, and then directed toward the sample to investigate the structure of crystals. It is important to realize that the wavelength of the wave should be about the same as the repeat distance of the periodic structure for diffraction to occur [7]. X-ray beam constructively interacts with the parallel plane of atoms when Bragg’s law is satisfied as shown in Fig. 4-4.

In this study, the bulk of X-ray characterization was performed using a Rigaku D/MAX-2500/PC and Bruker D8 Advance diffractometer equipped with Cu Ka radiation.
Figure 4-4. Bragg analysis for X-ray diffraction by crystal planes [8].

$$2d \sin \theta = n \lambda$$
4.4 Electrical Conductivity and Seebeck Coefficient Measurement

4.4.1 Electrical Conductivity Measurement

The four-probe method was used to measure the electrical conductivity. The four-probe method has been developed to minimize the contact resistance between the metal electrode and sample. The contact resistance depends on the resistance of samples. Two copper leads inject the current through the sample, and the resistive voltage \( V_r \) along the longitudinal direction of the sample is measured using the Pt leg of the Pt and Pt-Rh thermocouple. Voltage leads should be positioned away from the current leads to ensure uniform current flow through the voltage probes. There are some additional concerns for thermoelectric materials, because of the generation of \( \Delta V \) by the Seebeck effect [9]. This generation of \( \Delta V \) can be added to the voltage \( V_r \) during the measurement of electrical conductivity. In order to measure \( V_r \) more accurately and minimize the effect of Seebeck voltage, the current flow should be reversed high speed and high resolution [10]. Moreover, the electrical conductivity should be calculated from multiple measurements at different currents in both the directions. Before measuring the electrical conductivity, the ohmic contact between the probes and the surface of the samples has to be ensured for accurate measurement. The electrical conductivity is calculated by the following equation:

\[
\sigma = \frac{L}{A} R ,
\]

(4.1)

where \( L \) is the distance between the two voltage proves, \( A \) is the cross sectional area of the sample, and \( R \) is the resistance of the sample. Figs. 4-5 and 4-6 show the photograph of RZ-2001i (Ozawa Science) and ZEM-3 system (Ulvac-Riko technologies) used for the measurement of electrical conductivity and Seebeck coefficient.

4.4.2 Seebeck Coefficient Measurement
Seebeck coefficient is defined as the ratio of an open-circuit potential difference to the temperature difference [11]. During the Seebeck coefficient measurement, it is difficult to measure the accurate voltage and real temperatures at voltage probes. In order to more accurately measure the Seebeck coefficient, the current flow is stopped to take account of Peltier voltage, and the temperature dependence of the Seebeck coefficient is measured by measuring data at different temperatures using a heater. By using the slope of \( \Delta V/\Delta T \), the total Seebeck coefficient of sample and Pt is obtained and can be expressed by Eq. 4.2.

\[
S_{Total} = S_{Sample} - S_{Pt},
\]  

(4.2)

where \( S_{Sample} \) and \( S_{Pt} \) are the Seebeck coefficient of sample and Pt, respectively. The Seebeck coefficient of sample can be obtained by correcting the Seebeck coefficient of Pt reported by Cusack and Kendall [12]. The sign of the Seebeck coefficient indicates the dominant charge carrier type. For general and \( p \)-type materials the Seebeck coefficient is positive, whereas \( n \)-type materials have negative Seebeck coefficient. RZ-2001i (Ozawa Science) and ZEM-3 (Ulvac-Riko technologies) as shown in Figs. 4-5 and 4-6, respectively, were used to measure Seebeck coefficients.
Figure 4-5. A photograph of RZ-2001i (Ozawa Science).

Figure 4-6. A photograph of ZEM3 (Ulvac-Riko).
4.5 Hall Effect Measurement

In order to understand the charge transport of materials, the Hall effect measurement is performed. With a Hall effect measurement system, carrier concentration and Hall mobility of materials can be obtained. The Hall effect is the production of voltage difference across an electrical conductor, transverse to an electric current in the conductor, and a magnetic field perpendicular to current [13]. Fig. 4-7 shows the schematic of the mechanism for Hall effect. After current $I$ passes through the conductor, the magnetic field is applied to the conductor, and then the Hall voltage is produced in conductor. The Hall coefficient is calculated by using Eq. 4.3, and the sign of the Hall coefficient indicates the type of major carrier.

$$R_H = \frac{V_H w}{IB},$$  \hspace{1cm} (4.3)

where $R_H$ is the Hall coefficient, $V_H$ is the Hall voltage produced, $w$ is width of sample, $I$ is the current applied, and $B$ is the magnetic field applied. Moreover, the electrical conductivity and carrier concentration are obtained by using the Hall coefficient as represented by the following equations.

$$\sigma = \frac{V_H wd}{Il},$$  \hspace{1cm} (4.4)

$$R_H = \frac{1}{ne},$$  \hspace{1cm} (4.5)

where $\sigma$ is the electrical conductivity, $d$ is the thickness of a sample, $l$ is the length of a sample, $n$ is the carrier concentration, and $e$ is the charge carrier. Hall mobility, $\mu_H$, is also calculated by Eq. 4.6.

$$\mu = \frac{\sigma}{ne},$$  \hspace{1cm} (4.6)

Figure 4-8 shows the photograph of the Hall measurement system (ResiTest 8300, Toyo Corporation) used to obtain the carrier concentration and Hall mobility of the sample.
Figure 4-7. A schematic of mechanism of Hall effect [14].
Figure 4-8. A photograph of Hall measurement system (ResiTest 8300, Toyo Corporation).
4.6 Thermal Conductivity Measurement

Thermal conductivity is related to the transfer of heat through a material and is evaluated primarily in terms of Fourier's Law for heat conduction. Heat transfer of a material having low thermal conductivity is lower than a material with high thermal conductivity. Thermal conductivity is expressed by Eq. 4.7.

\[ \kappa_{\text{Tot}} = \rho \alpha C_p, \]  

\( (4.7) \)

where \( \kappa_{\text{Tot}}, \rho, \alpha, \) and \( C_p \) are the total thermal conductivity, density, thermal diffusivity, and the specific heat of a sample. In this study, the density was determined by using the volume and weight of a sample, and the thermal diffusivity and the specific heat were measured by laser flash technique and differential scanning calorimetry (DSC). The measurement principle and techniques are explained in the following subsections.

4.6.1 Thermal Diffusivity Measurement (Laser Flash Technique)

A laser flash technique was used to measure the thermal diffusivity of the samples. Fig. 4-9 shows the photograph of a laser flash analysis system (DLF1300, TA). The disk samples with the diameter and thickness of 12.7 and 1~2 mm were used, respectively. All the samples were coated with graphite to improve the absorptivity and then placed with one side facing the laser beam and the other side IR detector. The temperature would rise monotonically to a limiting temperature value in the complete absence of heat loss from the sample; however, the measured temperature peak will appear at a certain \( T_{\text{max}} \) and then return to the ambient value in real situations. The thermal diffusivity is calculated by using the time to reach half of \( T_{\text{max}} \), which is expressed by Eq. 4.8 [15].
\[ t_{0.5} = \frac{0.1388d^2}{\alpha} \] (4.8)

where \( d \) is the thickness of a sample. Even though the laser flash technique is the most favored one for measuring thermal diffusivity, there are some issues to more accurate measurements of thermal diffusivity. Because the heating of the front surface cannot be considered instantaneous relative to the time to diffuse through the sample, a finite width of the laser pulse with thin or high thermal diffusivity can affect the measurement of samples [16-19]. Therefore, the software used in the measurement system has been developed and contains a set of theoretical analysis techniques to correct this problem.

### 4.6.2 Specific Heat Capacity

Specific heat capacity was measured by DSC, because the laser flash system is not as accurate as the DSC method. Fig. 4-10 shows the photograph of the apparatus used in DSC techniques. In this method, three measurements of baseline, reference sample, and a sample were performed, and the specific heat capacity of a sample is calculated by the following relationship. \( C_p = \frac{\text{Signal}_{\text{sample}} - \text{Signal}_{\text{baseline}}}{(\text{sample mass} \times \text{heating rate} \times \text{sensitivity})} \).

In each measurement, a DSC signal is observed with respect to time and temperature. In order to measure specific heat accurately, all the three measurements should be performed using the same crucibles under the same conditions.
Figure 4-9. A photograph of laser flash analysis system (DLF1300, TA).
Figure 4-10. A photograph of differential scanning calorimetry (STA 409 PC, Netzsch).
References


[8] https://commons.wikimedia.org/wiki/File:Bragg%27s_Law.PNG


Chapter 5. Density of State Effective Mass and Related Charge Transport Properties in K-doped BiCuOSe

5.1 Introduction

LnCuOCh (Ln: lanthanide, Ch: chalcogenide) quaternary oxycarbonides have attracted much attention owing to their versatile applications such as ionic conductors and $p$-type transparent conducting films [1–3]. LnCuOCh has a layered structure (space group: P4/nmm) with alternately stacked $(Ln_2O_2)^{2+}$ insulating layers and $(Cu_2Ch_2)^{2-}$ conducting layers along the $c$-axis [1,4,5]. Hiramatsu et al. reported the significant decrease in the bandgap energy of BiCuOCh (0.84-1.1 eV) as compared to LaCuOCh (2.4-3.1 eV), when the lanthanum ions ($Ln^{3+}$) in the insulating layer were replaced with non-lanthane Bi$^{3+}$ ions [6]. This bandgap narrowing is due to the fact that the conduction band minima (CBM) in BiCuOCh is composed of Bi 6p, while that of LaCuOCh is determined by Cu 4s [6]. Because of the decrease in the bandgap of BiCuOCh, which has potential for thermoelectric applications, in 2010, Zhao et al. measured the thermoelectric properties of BiCuOSe and reported that it exhibited great potential for thermoelectric applications [7]. The performance of a thermoelectric material is determined by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $T$, and $\kappa$ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. The performance of a thermoelectric material is determined by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $T$, and $\kappa$ are the Seebeck coefficient, the electrical conductivity, the absolute temperature, and the thermal conductivity, respectively [8-
Since the first report on the thermoelectric properties of BiCuOSe by the Zhao’s group [7], it has been attracted as a promising $p$-type thermoelectric material owing to its low thermal conductivity and high Seebeck coefficient. Recently, improved $p$-type conduction properties have been achieved for BiCuOSe by doping with various divalent ions ($\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Sr}^{2+}$, $\text{Ba}^{2+}$, and $\text{Pb}^{2+}$) and also by Cu-deficient self-doping [7, 11-16]. Furthermore, remarkable thermoelectric performances have been recently discovered in the doped BiCuOSe [7, 11-16], and the highest ZT value (1.14 at 823 K) has been reported for Pb-doped BiCuOSe [16]. Notably, the thermoelectric and charge transport properties are critically dependent on the DOS effective mass ($m^*_d$), i. e., the effective mass at the Fermi level. Therefore, the study of the effective mass of the doped BiCuOSe is of great significance not only for understanding its conduction behavior but also for improving the thermoelectric performance of this material system.

In this chapter, we report the thermoelectric and charge transport properties of the K-doped BiCuOSe compounds. The K-doped BiCuOSe compounds exhibited typical metallic conduction behavior with improved $p$-type conduction properties both in the carrier concentration and the Hall mobility as compared to the undoped BiCuOSe compound. The DOS effective masses in the K-doped BiCuOSe compounds were significantly lower than that of the undoped compound, and this behavior was quite consistent with the enhanced Hall mobilities of the K-doped compounds. This result was explained by the two-band model in the valence band of the BiCuOSe. Finally, the thermal conductivity of the compounds is also discussed in terms of electronic and lattice thermal conductivities obtained using Lorenz numbers calculated by the single parabolic band (SPB) model.
5.2 Experimental Procedure

5.2.1 Synthesis of Bi$_{1-x}$K$_x$CuOSe Compounds

Bi$_{1-x}$K$_x$CuOSe (x=0, 0.026, 0.052, and 0.104) compounds were fabricated by solid state reaction. Bi$_2$O$_3$ (99.999%, Sigma Aldrich), Bi (99.999%, 5N Plus), Se (99.999%, 5N Plus), Cu (99.99%, Alfa Aesar), and KO$_2$ (97%, Sigma Aldrich) were used as starting materials. It was determined that little amount of Na impurity (<1 wt. %), which can be negligible, was in the KO$_2$ powder by using induction coupled plasma (ICP). Mixtures of starting materials were ground by using an alumina mortar and pestle, then the powders were pressed into pellets under uniaxial stress (80MPa). The compacted powders were annealed at 973K for 15 h in evacuated silica tubes. The obtained samples were pulverized into powders again.

5.2.2 Consolidation of Bi$_{1-x}$K$_x$CuOSe Compounds

The Bi$_{1-x}$K$_x$CuOSe (x=0, 0.026, 0.052, and 0.104) powders were consolidated by spark plasma sintering. The powders were loaded into a graphite mold and placed into the sintering chamber. The mold was heated up to 923K with the heating rate of 100K/min and held for 5 min in a vacuum of $10^{-3}$ Torr. During the heating and sintering process, a uniaxial constant pressure of 50 MPa was applied. After finishing holding time, the pressure was released, and then the sample was furnace quenched to room-temperature. Graphite foils were used to transmit electric current effectively to the sample during the spark plasma sintering. After the sintering process, the graphite foils were completely removed by polishing with a sand paper.
5.2.3 Characterization

Phase analyses of the compounds were performed by using an X-ray diffractometer (D/Max-2500/PC, Rigaku, Japan) with Ni filtered Cu Kα radiation. The operation voltage and current were kept at 40 kV and 200 mA, respectively. Microstructural characterizations were also carried out by using a scanning electron microscope (JSM-6700, JEOL, Japan). Electrical conductivity and Seebeck coefficient were measured by using a thermoelectric property measurement system (RZ-2001i, Ozawa Science, Japan) with a four-probe method from room temperature to 650K. High-temperature charge transport properties were characterized up to 445K by using a high-temperature Hall measurement system (ResiTest 8400, Toyo Corporation, Japan) under a magnetic field of 0.57 T. The thermal conductivity was calculated from $\kappa=\alpha C_p \rho$, where the thermal diffusivity ($\alpha$) was measured using the laser flash diffusivity method (DLF1300, TA, USA). The specific heat capacity ($C_p$) was estimated by Dulong-Petit law and the density ($\rho$) was determined by using direct measurement of volume and weight samples.
5.3 Result and Discussion

5.3.1 Phase Analysis and Microstructures of Bi$_{1-x}$K$_x$CuOSe Compounds

Figure 5-1 shows the XRD patterns in log scale of the as-prepared Bi$_{1-x}$K$_x$CuOSe ($x = 0, 0.026, 0.052,$ and $0.104$) powders. In this experiment, K-doping was carried out using the decomposition of potassium superoxide (KO$_2$) into K and O$_2$. Regardless of the incorporation of K, the XRD patterns for Bi$_{1-x}$K$_x$CuOSe ($x = 0, 0.026,$ and $0.052$) indicate that the compounds consist of a single phase of BiCuOSe (PDF #45-0296) without any secondary phase. When $x = 0.104$, slight trace of Bi$_2$O$_3$ secondary phase was detected. The lattice constants of the compounds monotonically increased along both $a$ and $c$ directions with increasing amounts of K as shown in Fig. 5-2, probably because of the fact that the ionic radius of K$^+$ (0.151 nm) is considerably larger than that of Bi$^{3+}$ (0.117 nm) [17]. In literature, this type of lattice expansion has also been reported for other BiCuOSe compounds doped with divalent ions such as Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, and Pb$^{2+}$ into Bi sites [7,12-14]. Therefore, the XRD result clearly shows that KO$_2$ is an effective starting material for K-doping in BiCuOSe from the structural point of view. The microstructures of Bi$_{1-x}$K$_x$CuOSe compounds are shown in Fig. 5-3. Any preferred orientation and noticeable differences were not observed in the SEM images, and all the compounds have a similar relative density of 94-95%. This result indicates that the thermoelectric transport properties of the samples can be directly compared without further considering the additional effects of the microstructure.

5.3.2 Charge Transport Properties of Bi$_{1-x}$K$_x$CuOSe Compounds

Figure 5-4 shows the temperature-dependent electrical conductivities ($\sigma$) of the
Bi$_{1-x}$K$_x$CuOSe compounds. The electrical conductivities of the compounds increased with increasing amount of the dopant, and this result clearly indicates that the monovalent K$^+$ ion is also an effective dopant for BiCuOSe as well as the divalent ions. The electrical conductivities of the K-doped BiCuOSe compounds exhibited negative temperature-dependence, i.e., metallic conduction behavior, whereas the undoped BiCuOSe exhibited semiconducting behavior. It is noteworthy that a clear tendency of $\sigma \propto T^{-1.5}$ was observed for 5.2 and 10.4 at.% K-doped BiCuOSe compounds as shown in the inset of Fig. 5-4. This tendency could also be observed in 2.6 at. % K-doped compound at a relatively low temperature. In a degenerately doped $p$-type semiconductor where its Fermi level is located below the valence band maxima, the carrier concentration is independent of temperature up to extrinsic-intrinsic transition temperature [18]. In this case, the electrical conductivity should decrease with increasing temperature due to the reduction in the carrier mobility through the carrier-acoustic phonon scattering ($\mu \propto T^{-1.5}$) [18,19]. Therefore, the observed temperature-dependence of $\sigma \propto T^{-1.5}$ clearly demonstrates that the K-doped BiCuOSe compounds are degenerate semiconductors, and that the hole-acoustic phonon scattering is the dominant mechanism for the metallic conduction behavior in the degenerately K-doped BiCuOSe compounds.

Figure 5-5 and Figure 5-6 show the hole concentrations and the Hall mobilities respectively, of the BiCuOSe compounds at room temperature as a function of the amount of K, and the results are listed in Table 5-1. The hole concentrations at 10.4 at. % K-doped BiCuOSe compounds ($4.78 \times 10^{19}$/cm$^3$) were almost one order higher than that in the undoped compound ($5.10 \times 10^{18}$/cm$^3$). However, the measured carrier concentrations were much lower than the nominal carrier concentrations ($8.12 \times 10^{20}$,
1.62 × 10^{21}, and 3.25 × 10^{21}/cm$^3$ for $x = 0.026, 0.052$, and 0.104, respectively), and this result suggests that the designed amount for K atoms was not fully doped into Bi sites due to the large difference in their ionic radius. The doping mechanism can be explained in a similar manner to the case of divalent doping in the literature as follows; the substitution of Bi$^{3+}$ by K$^+$ generates hole carriers in the insulating layer of [Bi$_2$O$_2$]$^{2+}$, and then the holes are transferred into the conducting layer of [Cu$_2$Se$_2$]$^{2-}$ in the K-doped BiCuOSe compounds [7,12-14]. In general, the increase in the carrier concentration by doping of foreign atoms entails the decrease in the mobility due to the ionized scattering [20,21]. However, as shown in Figs. 5-5 and 5-6, the mobilities in the K-doped compounds were significantly higher than that for the undoped compound (2.35 cm$^2$/V·s). Therefore, K-doping has been found to be beneficial to the charge transport in BiCuOSe not only by increasing the hole concentration but also by enhancing the Hall mobility.

5.3.3 Calculation of Density of State Effective Mass and Power Factor of Bi$_{1-x}$K$_x$CuOSe Compounds

In order to understand the origin of the enhanced Hall mobility in the K-doped BiCuOSe compounds, the effective masses were estimated by using the Pisarenko relation as expressed by the following equation:

$$S = \frac{8\pi^2 k^2 T}{3qh^2} m_d \left( \frac{\pi}{3n} \right)^{2/3},$$

(5.1)

where $S$ is the Seebeck coefficient, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $q$ is the carrier charge, $h$ is the Plank constant, $m_d^*$ is the effective mass at the Fermi level, and $n$ is the hole concentration [22,23]. Fig. 5-7 shows the Seebeck
coefficients of the BiCuOSe compounds, and the effective mass can be estimated from Pisarnko’s relation. For the calculation, the Seebeck coefficients and hole concentrations of Bi_{1-x}K_xCuOSe were used.

The estimated DOS effective masses of the BiCuOSe compounds are shown in Fig. 5-8. The effective masses of the K-doped BiCuOSe compounds were significantly lower than that of the undoped compound. However, in the K-doped compounds, the effective mass increases with the amount of K-doping as guided with a red arrow. Interestingly, the results are consistent with the Hall measurement results. Although the Hall mobilities in the K-doped BiCuOSe compounds were significantly enhanced by K-doping as compared to the undoped case, the mobility decreased monotonically by K-doping in the K-doped compounds as shown in Fig. 5-6. Therefore, it is elucidated that the reduction of the effective mass can be the origin of the enhanced Hall mobilities in the K-doped compounds. Because the valence band maxima (VBM) of BiCuOSe is composed of the mixture of heavy and light hole bands as schematically drawn in the inset [24], our result implies that the K-doping in the BiCuOSe compound changes the dominant band for the hole transport from the heavy hole to the light hole. Furthermore, the increase in the effective mass along with the K-doping means that there is non-parabolicity in the light-hole band. In the non-parabolic system, the DOS effective mass is dependent on the carrier concentration, and it can be expressed by Eq. 5.2 [25].

\[
(m_d^*)^2 = (m_{d0}^*)^2 + 4 \frac{m_{d0}^*}{E_1} \left(\frac{3}{8\pi}\right)^{2/3} \frac{h^2}{2} P^{2/3},
\]

where \(m_{d0}^*\) is the DOS effective mass at VBM, which can be determined by the extrapolation of a plot of \((m_d^*)^2\) vs. \(P^{2/3}\), and \(E_1\) is a constant which can be calculated.
by the slope of the plot. The DOS effective mass at the VBM of the light hole was estimated to be 0.18 m_e by Eq. 5.2, and this value is quite lower than that of the heavy hole (~1.1m_e) in the undoped BiCuOSe. Therefore, the charge transport in the K-doped compound is critically determined by the light-hole band, and it can be the origin of the simultaneously enhanced carrier concentration and Hall mobility in the degenerately K-doped BiCuOSe compounds. Figure 5-9 shows the temperature-dependent thermoelectric power factors (PF, \( S^2\sigma \)) of the Bi_{1-x}K_xCuOSe compounds.

In a thermoelectric material, the enhancement of the carrier mobility can increase the electrical conductivity (\( \sigma \)), whereas the decrease in the effective mass can decrease the Seebeck coefficient (S). In this experiment, the K-doped compounds exhibited significantly improved power factors than the undoped compound in all the temperature range. Interestingly, the temperature dependence of the power factors exhibited quite similar behavior to those of the electrical conductivities shown in Fig. 5-4. Therefore, this result indicates that the power factor of BiCuOSe is critically affected by the enhanced carrier mobility through the K-doping regardless of the reduction of the Seebeck coefficient. However, the effect of the effective mass on the thermoelectric performance could also be observed in the K-doped compounds where the charge transport is dominantly determined by the light-hole band. As shown in the inset, the room-temperature power factor of the K-doped BiCuOSe compound increases with increasing effective mass as guided with a red arrow. Therefore, the thermoelectric performance of BiCuOSe was observed to be critically dependent on the effective mass through the contrary effects on the electrical conductivity and the Seebeck coefficient.
5.3.4 Thermal Conductivity and ZT of Bi$_{1-x}$K$_x$CuOSe Compounds

Figure 5-10 shows the temperature-dependent total thermal conductivity of Bi$_{1-x}$K$_x$CuOSe compounds. With the increase in $x$, the total thermal conductivity decreased. The total thermal conductivity is the sum of the electronic thermal conductivity ($\kappa_{\text{el}}$) and lattice thermal conductivity ($\kappa_{\text{lat}}$). The electronic thermal conductivity can be calculated according to Wiedemann–Franz equation ($\kappa_{\text{el}} = L\sigma T$), where $L$ is the Lorentz number [26]. In order to obtain reliable electronic and lattice thermal conductivity, temperature-dependent Lorenz factor should be estimated by SPB model as follows [27,28]:

$$L = \left( \frac{k_B}{e} \right)^2 \left( \frac{(r + 7/2)F_{r,5/2}(\xi)}{(r + 3/2)F_{r,3/2}(\xi)} - \left[ \frac{(r + 5/2)F_{r,3/2}(\xi)}{(r + 3/2)F_{r,1/2}(\xi)} \right]^2 \right), \quad (5.3)$$

where $r$ is the scattering parameter (+1/2 for optical phonon scattering, -1/2 for acoustic phonon scattering and +3/2 for ionized impurity scattering), $F_n$ is the Fermi integral, and $\xi$ is the reduced Fermi energy. $F_n$ and $\xi$ are expressed by Eqs. 5.4 and 5.5, respectively.

$$F_n = \int_0^\infty \frac{x^n}{1 + \exp(x - \xi)} \, dx, \quad (5.4)$$

$$\xi = \frac{E_V - E_F}{k_B T}, \quad (5.5)$$

where $E_V - E_F$ is the Fermi energy level with respect to the top of the valence band. As shown by the above equations, the Lorenz number is dependent on the scattering mechanism and hole concentration. Because it is confirmed that the dominant scattering mechanism is hole-acoustic phonon scattering through the temperature dependence of $\sigma \propto T^{1.5}$, scattering parameter for Bi$_{1-x}$K$_x$CuOSe is -1/2. Using Eqs. 5.4 and 5.5 and the values of Seebeck coefficients obtained by experiment, the
temperature-dependent Lorenz number was estimated and plotted as shown in Fig. 5-11. The Lorenz numbers of Bi$_{1-x}$K$_x$CuOSe ranged from $1.50 \times 10^{-8}$ to $1.57 \times 10^{-8}$ W/Ω/K$^2$ at all the measured temperatures. Temperature-dependent electronic and lattice thermal conductivity are shown in Figs. 5-12 and 5-13, respectively. Electronic thermal conductivity increased with increasing amounts of K atoms because of increasing hole concentration. However, lattice thermal conductivity decreased with increasing doping amount of K due to the fact that K atoms act as the phonon scattering centers because of the difference in the mass between Bi (208.98 g/mol) and K (39.10 g/mol) [29]. Moreover, the decrease in the lattice thermal conductivity decreased the total thermal conductivity. Fig. 5-14 shows the temperature-dependence $ZT$ of Bi$_{1-x}$K$_x$CuOSe compounds. Combining the results of the electrical and thermal transport properties, the highest $ZT$ value of 0.41 was obtained for Bi$_{0.948}$K$_{0.052}$CuOSe at 640K attributing to lower lattice thermal conductivity and higher power factor compared to those of other compounds.
Figure 5-1. X-ray diffraction patterns in a log scale of the Bi$_{1-x}$K$_x$CuOSe compounds.
Figure 5-2. Lattice constant $a$, $c$ of the Bi$_{1-x}$K$_x$CuOSe compounds.
Figure 5-3. Microstructures of the Bi$_{1-x}$K$_x$CuOSe compounds.
Figure 5-4. Temperature-dependent electrical conductivities of the Bi$_{1-x}$K$_x$CuOSe compounds. A plot of $\sigma$ vs. $10000/T^{1.5}$ is shown in the inset.
Figure 5-5. Dependence of hole concentration on the atomic percent of K in the BiCuOSe compound.

Figure 5-6. Dependence of Hall mobility on the atomic percent of K in the BiCuOSe compound.
Figure 5-7. Temperature-dependent Seebeck coefficients of the Bi$_{1-x}$K$_x$CuOSe compounds.
Figure 5-8. Dependence of density of state (DOS) effective masses on the atomic percent of K in the BiCuOSe compounds. A schematic for the two-band structure is shown in the inset.
Figure 5-9. Temperature-dependent thermoelectric power factors of the Bi$_{1-x}$K$_x$CuOSe compounds. Room temperature power factors as a function of the effective mass are shown in the inset.
Figure 5-10. Temperature-dependent total thermal conductivities of the Bi$_1$-$x$K$_x$CuOSe compounds.
Figure 5-11. Temperature-dependent Lorenz number of the Bi$_{1-x}$K$_x$CuOSe compounds.

Figure 5-12. Temperature-dependent electronic thermal conductivities of the Bi$_{1-x}$K$_x$CuOSe compounds.
Figure 5-13. Temperature-dependent lattice thermal conductivities of the Bi$_{1-x}$K$_x$CuOSe compounds.

Figure 5-14. Temperature-dependent ZT of the Bi$_{1-x}$K$_x$CuOSe compounds.
Table 5-1. Electrical properties of the undoped and K-doped BiCuOSe compounds.

<table>
<thead>
<tr>
<th>Atomic percent of K (at%)</th>
<th>$\sigma$ (S/cm)</th>
<th>$p$ (1/cm$^3$)</th>
<th>$\mu_H$(cm$^2$/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.27</td>
<td>$5.05 \times 10^{18}$</td>
<td>2.35</td>
</tr>
<tr>
<td>2.6</td>
<td>47.49</td>
<td>$2.34 \times 10^{19}$</td>
<td>12.6</td>
</tr>
<tr>
<td>5.2</td>
<td>56.83</td>
<td>$3.51 \times 10^{19}$</td>
<td>9.98</td>
</tr>
<tr>
<td>10.4</td>
<td>76.45</td>
<td>$4.78 \times 10^{19}$</td>
<td>9.95</td>
</tr>
</tbody>
</table>
5.4 Summary

In summary, the thermoelectric and charge transport properties of Bi$_{1-x}$K$_x$CuOSe compounds were investigated. Enhanced $p$-type conduction properties were achieved by doping with potassium superoxide into the BiCuOSe lattice. The K-doped BiCuOSe compounds were degenerately doped, exhibiting a typical metallic conduction behavior ($\sigma \propto T^{-1.5}$). Improved Hall mobilities were also achieved for the K-doped BiCuOSe compounds, attributed to the reduction in the effective mass due to the two-band structure in the valence band of BiCuOSe. Based on the Pisarenko relation, the effective masses of the heavy hole (undoped BiCuOSe) and those of the light hole (K-doped compounds) were estimated. The light-hole band was non-parabolic, and the effective mass at the VBM was estimated to be 0.18 m$_e$. The thermal conductivity decreased with increasing K doping in the Bi$_{1-x}$K$_x$CuOSe compounds, because of the phonon scattering by K atoms. The highest $ZT$ of 0.41 was obtained at 640K for Bi$_{0.948}$K$_{0.052}$CuOSe compound owing to the higher power factor and lower thermal conductivity than other compounds. With these results, it can be concluded that K-doping is an effective way to improve $ZT$ through the $p$-type conduction properties in BiCuOSe by increasing both the carrier concentration and the Hall mobility.
References


[27] W.-S. Liu, Q. Zhang, Y. Lan, S. Chen, X. Yan, Q. Zhang, H. Wang, D. Wang,


Chapter 6. Effects of Bi-deficiency on Thermoelectric Properties of Bi-deficient BiCuOSe

6.1 Introduction

The efficiency of a thermoelectric material is determined by the dimensionless figure of merit \( ZT = S^2 \sigma T / \kappa \), where \( S \), \( \sigma \), \( T \), and \( \kappa \) are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively [1–3].

Because of high thermoelectric performance, thermoelectric materials based on \( \text{Bi}_2\text{Te}_3 \), PbTe, CoSb\(_3\), and SiGe have been commercially used [1, 4–9] although they have high cost and toxic. However, many studies on alternative thermoelectric materials, with low cost and environmentally friendly characteristics have been reported, and oxides [10-12] such as \( \text{Ca}_3\text{Co}_4\text{O}_9 \), \( \text{NaCo}_2\text{O}_4 \), and \( \text{SrTiO}_3 \) have received increasing attention as one of alternative thermoelectric materials. Although oxide materials have low cost, high thermal and chemical stability, and environmental compatibility [10-12], good for thermoelectric applications, the improvement in the thermoelectric efficiency is still needed.

BiCuOSe oxyselenide, which is one of the oxide thermoelectric materials, has been reported as a promising oxide thermoelectric material owing to its high Seebeck coefficient and low thermal conductivity. However, its poor electrical conductivity originated by its low hole mobility is disadvantageous for thermoelectric application [13]. The enhanced electrical conductivity of BiCuOSe can be achieved through the doping of various divalent or monovalent ions (\( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \), \( \text{Sr}^{2+} \), \( \text{Ba}^{2+} \), \( \text{Pb}^{2+} \), \( \text{Na}^+ \), and \( \text{K}^+ \)) and also through the formation of Cu-deficiency in BiCuOSe [14-27]. The
formation of Bi-deficiency is reported to increase the hole concentration of BiCuOSe in Chapter 6. However, a detailed systematic study on the effects of Bi-deficiency of thermoelectric properties of BiCuOCh compounds has been hardly reported. From this point of view, it is necessary to study the effect of Bi-deficiency on BiCuOCh system to extend our understanding of BiCuOCh system.

In this chapter, we also report the effects of the Bi deficiency on the thermoelectric properties of Bi$_{1-x}$CuOSe compounds. The $p$-type conduction properties of Bi$_{1-x}$CuOSe compounds improved with increasing hole concentration introduced by Bi deficiency. A drastic reduction in Seebeck coefficient was observed, and it is discussed in terms of electronic structures calculated by DFT of Bi$_{1-x}$CuOSe compounds. With increasing Bi-deficiency in the Bi$_{1-x}$CuOSe compounds, the thermal conductivity increased because of increasing hole concentration and reduced anharmonicity. The highest figure of merit (0.4 at 810K) was obtained in Bi$_{0.975}$CuOSe, and this value was ~8% higher than that of the stoichiometric compound.
6.2 Experimental Procedure

6.2.1 Synthesis and Consolidation of Bi$_{1-x}$CuOSe Compounds

Bi$_{1-x}$CuOSe compounds ($x = 0, 0.025, 0.05, 0.075$ and $0.01$) were synthesized by a one-step solid state reaction. Bi$_2$O$_3$ (99.999%, Sigma Aldrich), Bi (99.999 %, 5N Plus), Se (99.999 %, 5N Plus) and Cu (99.99%, Alfa Aesar) were used as starting materials. Mixtures of starting materials were ground with an alumina mortar and pestle, and the pressed into pellets under uniaxial stress (80MPa). The pressed pellets were annealed at 973K for 15 h in evacuated silica tubes to obtain BiCuOSe phase. The annealed samples were pulverized into powders, and then the powders were consolidated by spark plasma sintering at 948K under 50 MPa of pressure for 5 min in a $10^{-3}$ torr vacuum. The prepared samples were sliced with a low-speed diamond saw and then polished before measuring the thermoelectric properties.

6.2.2 Characterization

The phase analyses at room temperature and high temperature were performed using X-ray diffraction (XRD) method (New D8 Advance, Bruker, Germany) and high temperature X-ray diffraction (HTXRD) method (D/ MAX-2500/PC, Rigaku, Japan). Microstructural characterizations were also carried out by using a scanning electron microscope (SU70, Hitachi, Japan). Electrical conductivities and Seebeck coefficients were investigated by using a four-point probe method (ZEM-3, ULVAC-RIKO, Japan) and thermal conductivity was measured using a laser flash technique (DLF 1300, TA, USA) from room temperature to 810K. Carrier concentrations and mobility were determined by using a high-temperature Hall measurement system (ResiTest 8300, Toyo Corporation, Japan) under a magnetic field of 0.57 T. The
thermal conductivity was calculated from $\kappa = \alpha C_p \rho$, where the thermal diffusivity ($\alpha$) was measured using the laser flash diffusivity method (DLF1300, TA, USA). The specific heat capacity ($C_p$) was obtained by differential scanning calorimetry (STA 409 PC, Netzsch, Germany) and the density ($\rho$) was determined by using direct measurement of volume and weight samples.

### 6.2.3 Computation Details

In order to explore effects of Bi vacancy on the thermoelectric transport and electronic structures of BiCuOSe system, we were calculated electric thermal transport coefficients by employing BoltzTrap code [28] and electronic band calculation based on the DFT approach. On our electronic band calculation, we adopt BiCuOSe, Bi$_{0.97}$CuOSe, and Bi$_{0.94}$CuOSe configuration. In this calculation, we consider 2×2×1 and 3×3×1 extended cells for Bi$_{0.97}$CuOSe and Bi$_{0.97}$CuOSe, respectively. We were carrying out structure optimization for pure BiCuOSe as well as Bi-vacancy introduced BiCuOSe compounds using a set of 80 k-points for the irreducible Brillouin zone, and the self-consistent-field convergence thresholds of $10^{-5}$ eV and 0.001 eV/Å for the total electronic energy and force, respectively. Our DFT calculations employed the frozen-core projector augmented wave (PAW) method [29, 30] encoded in the Vienna ab-initio simulation package (VASP) [31]. The generalized-gradient approximation (GGA) [32] of Perdew, Burke and Ernzerhof (PBE) is used for the exchange-correlation functional with the plane-wave-cut-off energy of 450 eV.

We also calculated thermoelectric coefficient for pure BiCuOSe as well as Bi-vacancy introduced BiCuOSe compounds by solving Boltzmann thermal transport equations which is implemented in The BoltzTraP code. The BoltzTraP code solves the semi-classical Boltzmann equation using the rigid band approach [33]. This
method has been successful in calculating transport properties and predicting the optimal doping levels for thermoelectric materials [34-37]. For the calculation of thermoelectric properties, we consider dense k-mesh (a set of 4000 k-points in IBZ) to ensure the convergence of the calculated thermoelectric properties. The BoltzTrap code allows one to calculate the electrical conductivity $\sigma$, the Seebeck coefficient $S$, and the thermoelectric power factors (TPFs) $S^2\sigma/\tau$ under the assumption that the relaxation time $\tau$ is energy-independent.
6.3 Results and Discussion

6.3.1 Phase Analysis and Microstructures of Bi$_{1-x}$CuOSe Compounds

Figure 6-1 shows the XRD patterns in a log scale of the as-prepared Bi$_{1-x}$CuOSe ($x = 0, 0.025, 0.05, 0.075,$ and 0.01) compounds. The XRD patterns of all the Bi$_{1-x}$CuOSe compounds indicate that all the peaks can be indexed to the BiCuOSe (PDF#45-0296); however, a trace of CuSe secondary phase were detected when $x \geq 0.025$. The CuSe secondary phase can be because of the formation of Bi deficiency, and it may be possible to form Bi$_2$O$_3$ phase although that phase is not detected in the XRD patterns. The microstructures of Bi$_{1-x}$CuOSe compounds are shown in Fig. 6-2. Any preferred orientation and noticeable differences were not observed in the SEM images, and all the compounds have a similar relative density in the range of 93-95%.

6.3.2 Charge Transport of Bi$_{1-x}$CuOSe Compounds

Figure 6-3 shows the temperature-dependent electrical conductivities of the Bi$_{1-x}$CuOSe compounds. As shown in Fig. 6-3, the electrical conductivities of the compounds increased from 1.54 S/cm for BiCuOSe to 41.18 S/cm for Bi$_{0.95}$CuOSe at 300K with increasing Bi deficiency. This result indicates that the Bi deficiency in BiCuOSe is also an effective way to enhance electrical conductivity similar to the doping with divalent (Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ and Pb$^{2+}$) or monovalent ions (Na$^+$ and K$^+$) or Cu-deficient self-doping [14-27]. The enhanced electrical conductivity of Bi-deficient BiCuOSe compounds can be attributed to the hole carriers, which are induced by Bi deficiencies in the (Bi$_2$O$_3$)$^{2+}$ layers. And BiCuSeO exhibited a semiconducting behavior, which is the increase of electrical conductivity with
increasing temperature, and Bi-deficient BiCuOSe compounds also showed semiconducting behavior except Bi$_{0.9}$CuOSe. Fig. 6-4 shows the electrical conductivities of the compounds as a function of $1/T$, and there are three zones. The behavior of electrical conductivities of zone I and zone III can be explained by the extrinsic and intrinsic behavior of a semiconductor. In the extrinsic region of a semiconductor, the carrier concentration is independent of temperature. In contrast, the carrier concentration increases with increasing temperature in the intrinsic region of a semiconductor. However, as shown in Fig. 6-4, a dramatic change in the behavior of temperature-dependent electrical conductivities of Bi$_{1-x}$CuOSe compounds was observed between zone II and zone III. This result can be attributed to the formation of secondary phase or phase transition. Fig. 6-5 shows the XRD patterns of the as-prepared BiCuOSe and Bi$_{0.9}$CuOSe compounds from 300K to 800K. Both for BiCuOSe and Bi$_{0.9}$CuOSe compounds, the main phase can be indexed with BiCuOSe phase at 300K, and the peaks of the XRD patterns shifted to lower angle because of thermal expansion. However, a phase transition from BiCuOSe to CuSe phase was observed in Bi$_{0.9}$CuOSe compound while a trace of CuSe secondary phase was detected with maintaining BiCuOSe phase in BiCuOSe compound above 700K. The behavior of electrical conductivity for Bi$_{1-x}$CuOSe at around 650K can be explained with the phase transition for that compound.

Figure 6-6 and Figure 6-7 show the hole concentrations and Hall mobilities at room temperature as a function of the amount of Bi deficiency in the Bi$_{1-x}$CuOSe compounds. The hole concentration increased with increasing Bi deficiency, and the value in Bi$_{0.9}$CuOSe compound ($7.58 \times 10^{20}$/cm$^3$) was more than one order higher than that of the BiCuOSe compound ($2.34 \times 10^{18}$/cm$^3$). The generation of free holes
can be explained in a similar manner to the case of Cu-deficient self-doping in the literature as follows [27]:

$$\text{Bi}^x_{\text{Bi}} \leftrightarrow \text{V}^\circ_{\text{Bi}} + 3h^* + \text{Bi} \uparrow,$$

(6.1)

where $\text{V}^\circ_{\text{Bi}}$ is the Bi vacancy, and $h^*$ is the produced holes. This means that the formation Bi deficiency introduces three free holes, and the hole concentration can be increased by Bi deficiencies. However, the measured carrier concentrations were much lower than the nominal carrier concentrations ($1.17 \times 10^{21}, 2.34 \times 10^{21}, 3.51 \times 10^{21} \text{, and } 4.68 \times 10^{21} \text{ cm}^{-3}$ for $x = 0.025, 0.05, 0.075, \text{ and } 0.1$, respectively), and this result suggests that three free holes per Bi deficiency were not generated. As shown in Fig. 6-7, the Hall motilities of Bi$_{1-x}$CuOSe compounds decreased with increasing fraction of Bi deficiency. The reduction in the mobility can be because of the ionized scattering. In general, the increase in the carrier concentration by doping of foreign atoms entails the decrease in the mobility because of the ionized scattering [38,39].

6.3.3 Change of Electronic Structure and Related Seebeck Coefficient of Bi$_{1-x}$CuOSe Compounds

Figure 6-8 shows the temperature-dependent Seebeck coefficients of the Bi$_{1-x}$CuOSe compounds. The Seebeck coefficients of Bi$_{1-x}$CuOSe compounds show positive Seebeck coefficients, which indicate a $p$-type electrical transport behavior. Bi deficiency also has a significant effect on the Seebeck coefficients. The Seebeck coefficients of Bi$_{1-x}$CuOSe compounds are positive, indicating a $p$-type electrical transport behavior. Bi deficiency also has a significant effect on the Seebeck coefficients. The Seebeck coefficient of the compounds decreased with increasing Bi deficiency fraction, and this result can be attributed to increasing hole
concentration. In general, the Seebeck coefficient is proportional to $p^{2/3}$ by Pisarenko’s relation as represented in Eq. 6.2.

$$S = \frac{8\pi^2 k_B^2 T}{3qh^2} m^*_d \left( \frac{\pi}{3p} \right)^{2/3}, \quad (6.2)$$

where $S$ is the Seebeck coefficient, $k_B$ is the Boltzmann’s constant, $T$ is the absolute temperature, $q$ is the carrier charge, $h$ is the Plank’s constant, and $m^*_d$ is the effective mass and $p$ carrier concentration [40]. However, when $x$ was higher than 0.05, the temperature dependence of Seebeck coefficient changed, and the Seebeck coefficient of the compounds drastically decreased with the increasing Bi deficiency fraction, for example, the Seebeck coefficient decreased from 567.81 μV/K for BiCuOSe to 16.08 μV/K for Bi$_{0.9}$CuOSe at 300K. In order to compare with the Seebeck coefficients of BiCuOSe compounds in previous reports [15,16,18,20,22,24,26,27,41], the Seebeck coefficients at RT of this work and previous reports were plotted as a function of carrier concentration in Fig. 6-9. The drastic reduction in the Seebeck coefficient was not reported previously and can be related to the change in the electronic structure. Fig. 6-10 shows the electronic structures calculated by DFT (a,b) and the schematics of electronic structures (c,d) of BiCuOSe and Bi$_{0.97}$CuOSe compounds. BiCuOSe has high Seebeck coefficient related to its layered crystal structure with alternately stacked insulating and conducting layers. Those layers were supposed to form a natural superlattice with 2D confinement of the charge carriers [19]. However, as shown in Fig. 6-10, [Bi$_2$O$_2$]$^{2+}$ insulating layers and [Cu$_2$Se$_2$]$^{2-}$ conducting layers can be related to the charge transfer in Bi$_{0.97}$CuOSe, whereas the charge transfer can be related to only [Cu$_2$Se$_2$]$^{2-}$ conducting layers in BiCuOSe. This result can be because of the change
in the electronic structure from 2D-like electronic structure to 3D-like electronic structure. When comparing with the Seebeck coefficients calculated by the Boltzmann thermal transport, the trend of the experimental values of Seebeck coefficient is similar to the calculated values shown in Fig. 6-11.

### 6.3.4 Thermal conductivity and ZT of Bi$_{1-x}$CuOSe Compounds

Figure 6-12 shows the temperature-dependent total thermal conductivity of the Bi$_{1-x}$CuOSe compounds. For all the samples, the total thermal conductivity decreased with increasing temperature. Oxides generally have high thermal conductivity due to their strong chemical bonding characteristics. On the contrary, their total thermal conductivity is very low and comparable to other high-performance thermoelectric materials [10-12]. The total thermal conductivity increased with increasing Bi deficiency, but still maintains low over the entire measuring temperature range. In general, the total thermal conductivity is the sum of lattice and electronic thermal conductivity and is proportional to the electronic thermal conductivity by the Wiedemann–Franz relation [42]. The temperature-dependent lattice thermal conductivities of the Bi$_{1-x}$CuOSe compounds are presented in Fig. 6-13. The increase in the lattice thermal conductivity was observed, because of the reduced anharmonic interactions. The 6S$^2$ lone pair of Bi, which is the one of the elements for BiCuOSe, leads to the anharmonicity in BiCuOSe [27]. When the fraction of Bi in BiCuOSe is decreased by the formation of Bi-deficiency, the anharmonicity in BiCuOSe compounds can be reduced. Therefore, the reason for the increase in the total thermal conductivity is the increase in the hole concentration and the decrease in the anharmonicity in BiCuOSe.
Figure 6-14 presents the figure of merit for the Bi$_{1-x}$CuOSe compounds. With the optimized power factor and intrinsically low thermal conductivity, the $ZT$ value improved to 0.4 at 810K for the Bi$_{0.975}$CuOSe, which is ~ 8% higher than that for BiCuOSe. These results indicate that the thermoelectric properties of BiCuOSe can be improved by increasing the Bi deficiency in BiCuOSe. However, the increasing the Bi-deficiency can drastically decrease the Seebeck coefficients because of the change in the electronic structure. Therefore, the amounts of Bi-deficiency in BiCuOSe has to be considered to efficiently improve $ZT$. 
Figure 6-1. X-ray diffraction patterns in a log scale of the Bi$_{1-x}$CuOSe compounds.
Figure 6-2. Microstructures of the Bi$_{1-x}$CuOSe compounds.
Figure 6-3. Temperature-dependent electrical conductivities of the Bi$_{1-x}$CuOSe compounds.
Figure 6-4. Electric conductivities of the Bi$_{1-x}$CuOSe compounds as function of 1/$T$. 
Figure 6-5. XRD patterns of BiCuOSe and Bi$_{0.9}$CuOSe compounds from 300K to 800K.
Figure 6-6. Dependence of carrier concentration on the atomic percent of Bi-deficiency in the Bi$_{1-x}$CuOSe compounds.

Figure 6-7. Dependence of Hall mobility on the atomic percent of Bi-deficiency in the Bi$_{1-x}$CuOSe compounds.
Figure 6-8. Temperature-dependent Seebeck coefficients of the Bi$_{1-x}$CuOSe$_x$ compounds.
Figure 6-9. Dependence of Seebeck coefficients on carrier concentration in the BiCuOSe compounds.
Figure 6-10. Electronic structures calculated with DFT (a,b) and schematics of electronic structures (c,d) of BiCuOSe and Bi$_{0.97}$CuOSe compounds.
Figure 6-11. Dependence of Seebeck coefficients on carrier concentration in the BiCuOSe compounds compared with Seebeck coefficients calculated by Boltzmann thermal transport.
Figure 6-12. Temperature-dependent thermal conductivities of the Bi$_{1-x}$CuOSe compounds.

Figure 6-13. Temperature-dependent lattice thermal conductivities of the Bi$_{1-x}$CuOSe compounds.
Figure 6-14. Temperature-dependent ZT of the Bi$_{1-x}$CuOSe compounds.
6.4 Summary

In summary, the effects of Bi deficiency on the thermoelectric properties of Bi$_{1-x}$CuOSe ($x = 0-0.1$) were investigated. The electrical conductivity of these compounds increased, and their Seebeck coefficient decreased with increasing Bi deficiency. These results were because of the increase in the hole concentration by introducing Bi deficiencies. Except Bi$_{0.9}$CuOSe, these compounds showed semiconducting behavior, and high-temperature XRD patterns revealed the formation of Cu$_2$Se secondary phase in BiCuOSe and the phase transition from BiCuOSe to Cu$_2$Se in Bi$_{0.9}$CuOSe, which can explain the electrical conductivity behavior at around 650K. The drastic reduction in the Seebeck coefficient was observed and it was led to the change in the electronic structure. With the optimized hole concentration and intrinsically low thermal conductivity, maximum $ZT$ value of 0.4 of at 810 K was obtained for Bi$_{0.975}$CuOSe, which is ~8% higher than that for BiCuOSe. These results indicate that Bi deficiency in BiCuOSe system is an effective way to improve $ZT$. 
References


Chapter 7. Point Defect-Assisted Doping Mechanism and Related Thermoelectric Transport Properties in Pb-doped BiCuOTe

7.1 Introduction

In recent years, BiCuOCh (Ch = chalcogen) oxycarbides have attracted much attention as promising thermoelectric materials for power generation using waste heat. They exhibit extremely low lattice thermal conductivity (\(\kappa_{\text{lat}} < 1.0 \text{ W/m-K}\)) [1-3], while the electrical conductivity (\(\sigma\)) of BiCuOCh is relatively poor due to its low hole mobility [4-8]. The electrical conductivity, however, can be significantly improved by doping with various elements (Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\), Pb\(^{2+}\), Na\(^{+}\), and K\(^{+}\)), which can remarkably enhance the thermoelectric performance [1,2,3,9-16]. Sui et al. reported the highest thermoelectric figure-of-merit \(ZT(= S^2\sigma T/\kappa)\), where \(S\) is the Seebeck coefficient, \(\kappa\) is the thermal conductivity, and \(T\) is the absolute temperature) of 1.4 at 923 K in the textured Ba-doped BiCuOSe [12], and it was superior to the state-of-the-art \(ZT\) value reported for \(p\)-type skutterudite system (\(ZT = 1.2\) at 800K), which is one of the middle-temperature thermoelectric materials [17].

Compared with other thermoelectric materials, the achieved high thermoelectric performance of BiCuOSe mainly originates from its very low thermal conductivity rather than its power factor. Actually, the power factors (\(PF = S^2\sigma\)) of BiCuOSe (< \(1 \times 10^{-3}\) W/cm-K\(^2\)) [1,2,3,9-16] were reported to be considerably smaller than that of the \(p\)-type skutterudite (> \(4.5 \times 10^{-3}\) W/cm-K\(^2\)) [17]. In this respect, BiCuOTe is one of the suitable thermoelectric materials to obtain high power factor in BiCuOCh.
system. Because the antibonding orbital of Cu 3d-Te 5p state is stronger than the Cu 3d-Se 4p states at the same doping level, the hole mobility of BiCuOTe can be significantly improved [18]. Therefore, the power factors in the undoped BiCuOTe are superior to that in the undoped BiCuOSe, leading to high ZT (0.66 at 673K) [19] compared to that for the undoped BiCuOSe (~ 0.4 at 673K) [1,2,3,9-16]. However, in contrast to BiCuOSe, the carrier optimization for the improvement of ZT by doping has not been successful for BiCuOTe. The electrical conductivity could be enhanced by Pb-doping in the BiCuOTe, whereas the power factors did not significantly improved because of the drastic reduction in the Seebeck coefficient. Moreover, the strengthened electrical contribution to the thermal conductivity ($\kappa_{\text{elec}}$) by Pb-doping decreased the ZT values [19]. Therefore, understanding the effect of doping on the thermoelectric properties is of great significance for enhancing the thermoelectric performance of BiCuOTe.

In this chapter, point defect-assisted doping mechanism and related thermoelectric transport properties of Pb-doped BiCuOTe compounds are presented. Even undoped BiCuOTe compound exhibited degenerately doped semiconducting behavior up to extrinsic-intrinsic transition temperature, and this result indicates that the native point defects are the main source of the hole generation in BiCuOTe. The hole concentration increased with increasing amount of Pb, significantly increasing the electrical conductivity of Pb-doped BiCuOTe. However, although at most one hole per single dopant atom could be generated because of the divalency of Pb, more than one hole per a Pb atom was generated in the Pb-doped compound. The dependence of the formation energies of possible point defects ($V_{\text{Cu}}$ and $V_{\text{Bi}}$) on the amount of Pb-doping were calculated based on DFT, and the results were quite consistent with
our observations. Detail thermoelectric transport properties of the Pb-doped BiCuOTe compounds are also discussed.
7.2 Experimental Procedure

7.2.1 Synthesis and Consolidation of Bi$_{1-x}$Pb$_x$CuOTe Compounds

Bi$_{1-x}$Pb$_x$CuOTe ($x = 0, 0.01, 0.02, 0.04$ and $0.06$) compounds were synthesized by one step solid state reaction. Bi$_2$O$_3$ (99.999%, Sigma Aldrich), Bi (99.999 %, 5N Plus), Te (99.999 %, 5N Plus), Cu (99.99%, Alfa Aesar) and Pb (99.9%, Alfa Aesar) were used as starting materials. Mixtures of starting materials were ground with an alumina mortar and pestle, and they were pressed into pellets under uniaxial stress (80 MPa). The pressed pellets were annealed at 788K for 12 h in evacuated silica tubes to obtain a homogeneous BiCuOTe phase. The annealed samples were pulverized into powders, and then the powders were consolidated by spark plasma sintering at 748K under 50 MPa of pressure for 5 min in a $10^{-3}$ Torr vacuum.

7.2.2 Characterization

Phase analyses of the compounds were performed using an X-ray diffractometer (New D8 Advance, Bruker, Germany) with Ni filtered Cu Kα radiation. The operation voltage and current were kept at 40 kV and 40 mA, respectively. Electrical conductivities and Seebeck coefficients were measured by a thermoelectric property measurement system (RZ-2001i, Ozawa Science, Japan) from room temperature to 600K, and carrier concentration and mobility at RT were determined using a Hall measurement system (Hall, ResiTest 8300, Toyo Corporation) under a magnetic field of 0.57 T. The thermal conductivity was calculated from $\kappa=\alpha C_p \rho$, where the thermal diffusivity ($\alpha$) was measured using the laser flash diffusivity method (DLF1300, TA, USA). The specific heat capacity ($C_p$) was obtained by differential scanning calorimetry (STA 409 PC, Netzsch, Germany) and the density ($\rho$) was determined.
by using direct measurement of volume and weight samples.

7.2.3 Computation Details

The crystal structure optimization for the Pb-doped BiCuOTe compound was carried out using a set of 200 k-points for the irreducible Brillouin zone. Calculation of vacancy formation energy for Pb-doped and undoped case and calculation of the change of lattice parameter as a function of Pb-doping concentration were also performed. In the calculation, a set of 200 k-points for the irreducible Brillouin zone was used, and the self-consistent-field convergence thresholds were $10^{-5}$ eV and 0.001 eV/Å for the total electronic energy and force, respectively. The DFT calculations employed the frozen-core projector augmented wave (PAW) method [20,21] encoded in the Vienna ab initio simulation package (VASP) [22]. The generalized-gradient approximation (GGA) [23] of Perdew, Burke and Ernzerhof (PBE) was used for the exchange-correlation functional with the plane-wave-cut-off energy of 550 eV.
7.3 Results and Discussion

7.3.1 Phase Analysis of Bi$_{1-x}$Pb$_x$CuOTe Compounds

Figure 7-1 shows the XRD patterns of the as-prepared Bi$_{1-x}$Pb$_x$CuOTe (x = 0, 0.01, 0.02, 0.04 and 0.06) compounds. The XRD patterns reveal that the compounds consist of a single phase of BiCuOTe with little trace of Bi$_2$O$_3$ secondary phase. The peak-to-peak ratios between the Bi$_2$O$_3$ and BiCuOTe phase in Fig. 7-2 confirmed that the formation of Bi$_2$O$_3$ secondary phase was not affected by the amount of Pb-doping. As shown in Fig. 7-3, the lattice parameters along a- and c-axis increased with increasing amount of Pb as listed in Table 7-1. The increase in the lattice parameter is because of the ionic radius of Pb$^{2+}$ (0.129 nm), which is larger than that of Bi$^{3+}$ (0.117 nm) [24]. The increase in the lattice parameter along the c-axis is more significant than that along the a-axis, and the calculated values based on DFT calculations also exhibited the same tendency. This behavior can be related to the decrease in the Columbic attraction among (Bi$_2$O$_2$)$^{2+}$ insulating layers and (Cu$_2$Ch$_2$)$^{2-}$-conducting layer as proposed by Barreteau et al. [25]. Figure 7-4 presents the relative intensities of (004) to (102) and (110) to (102) peaks in the XRD patterns, and the relative intensities were not strongly dependent on the amount of Pb-doping.

7.3.2 Point Defect-assisted Doping Mechanism and Related Charge Transport Properties of Bi$_{1-x}$Pb$_x$CuOTe Compounds

Figure 7-5 shows the temperature-dependent electrical conductivities of the Bi$_{1-x}$Pb$_x$CuOTe compounds. The electrical conductivities of the compounds increased with increasing amount of Pb-doping, indicating that Pb atom is an effective acceptor for BiCuOTe. To understand the effect of Pb-doping on the electrical conductivity,
Hall measurements of the compounds were performed at room temperature. As shown in Table 7-2, the electrical conductivities characterized by thermoelectric properties measurement system were in reasonably good agreement with those by the Hall measurements. Figure 7-6 presents the hole concentrations at room temperature as a function of the amount of Pb-doping in the Bi$_{1-x}$Pb$_x$CuOTe compounds. The hole concentration increased with increasing amount of Pb, and the value in 6 at% Pb-doped BiCuOTe compound ($1.4 \times 10^{21}$/cm$^3$) was more than one order higher than that in the undoped compound ($6.9 \times 10^{19}$/cm$^3$). The doping mechanism can be simply explained by the substitution of Bi$^{3+}$ by Pb$^{2+}$ as same as in Pb-doped BiCuOSe compounds [13-15]. The Bi$^{3+}$ substitution with Pb$^{2+}$ results in the generation of hole carriers in the insulating layer of [Bi$_2$O$_2$]$^{2+}$, and then the holes are transferred to the conducting layer of [Cu$_2$Se$_2$]$^{2-}$ of the Pb-doped BiCuOTe compounds. However, notably, the carrier concentrations in the Pb-doped compounds are higher than the nominal carrier concentration (indicated by dashed line; the case when a single dopant atom in the site of Bi provides only one hole through the mechanism described above). This tendency is more clearly observed in the compounds with high Pb content as shown in Fig. 7-7.

The anomalous doping effect of Pb has also been reported for BiCuOSe compounds. Dopants such as Pb$^{2+}$ (0.133 nm) and Sr$^{2+}$ (0.132 nm) with ionic radii larger than that of Bi$^{3+}$ (0.117 nm) exhibited strong doping efficiency in this material system [13,25]. In contrast, the doping yield was far below unity in the case of Mg$^{2+}$ (0.086 nm) [9]. Actually, because a considerably high hole concentration ($6.9 \times 10^{19}$/cm$^3$) was observed even in the undoped compound, it is obvious that the native point defects play an important role in this material system. Therefore, it can be reasonably
proposed that the doping mechanism is closely related to the formation of extra point defects because of the existence of foreign ions at Bi\(^{3+}\) sites.

Moreover, the mobility continuously decreased with increasing amount of Pb as shown in Table 7-2 and Fig. 7-8(a). In Chapter 5, it was revealed that the mobility is critically affected by the two-band structure in BiCuOCh [20]. The charge transport in the undoped BiCuOSe \((p = 5.1 \times 10^{18} \text{ /cm}^3)\) was determined by the heavy-hole band, whereas that in the degenerately doped BiCuOSe \((p = 2.3 \times 10^{19} \text{ /cm}^3)\) was governed by light-hole band as schematically drawn in Fig. 7-8(b). Therefore, it abruptly increased the mobility from 2.4 (undoped) to 12.6 cm\(^2\)/V∙s (doped) by increasing hole concentration. In this experiment, even the undoped BiCuOTe exhibited degenerately doped conducting behavior because of the native point defects with considerably high mobility \((1.3 \times 10^1 \text{ cm}^2/\text{V}∙\text{s})\), demonstrating that the charge transport in BiCuOTe is governed by the light-hole band as depicted in Fig. 7-8(c), and the decrease in the mobility by Pb-doping is affected by the ionized impurity scattering.

Based on the DFT calculations, the formation energies of possible point defects were calculated to understand the detailed doping mechanism, and the results are shown in Fig. 7-9 and Table 7-3. To describe the formation energy, 4×4×2 extended cell was considered. The atomic positions of all the considered systems were optimized based on the DFT calculations keeping the cell parameters constant as found in the experimental structure. In the undoped BiCuOTe, the formation energies of Cu and Bi vacancy were calculated to be 55 and 66 meV/formula unit (FU), respectively. Although both types of vacancy could contribute to the hole generation together because of their very low formation energies, the vacancy formation energy
at the Cu site was slightly lower than that of Bi site. Therefore, the $p$-type character in undoped BiCuOTe is mainly attributed to the formation of Cu vacancy. As the amount of Pb increases in BiCuOTe, both the vacancy formation energies in the Bi and Cu sites decrease; however, the decrease in the formation energy of $V_{Bi}$ is much steeper than that of $V_{Cu}$. Because of the large ionic size of Pb$^{2+}$, Pb-doping causes a structural strain in the $(Bi_2O_2)^{2+}$ layer, and this strain can be alleviated by introducing Bi vacancy. As a consequence, Pb-doping in Bi sites can trigger the generation of extra hole carrier by reducing the formation energy of $p$-type point defects, especially $V_{Bi}$ for the strain relaxation.

### 7.3.3 Thermoelectric properties of Bi$_{1-x}$Pb$_x$CuOTe Compounds

Figure 7-10 and Figure 7-11 show the effects of Pb-doping on the Seebeck coefficient and power factor of the Bi$_{1-x}$Pb$_x$CuOTe compounds, respectively. As the Pb content increased in these compounds, the Seebeck coefficient rapidly decreased because of increasing hole concentration through the anomalous doping mechanism. Consequently, significant enhancement in the power factor could not be achieved by Pb-doping in this experiment. When $x \geq 0.4$, the Seebeck coefficients were linearly proportional to temperature, indicating that the carrier concentrations in the compounds are almost constant in the temperature range used in this study. Meanwhile, the Seebeck coefficients of the compounds ($x \leq 0.2$) deviated from the linearity at relatively high temperature because of the extrinsic-intrinsic transition.

The Seebeck coefficients at room temperature are plotted as a function of carrier concentration as shown in Fig. 7-12, and they were compared to the calculated Seebeck coefficients. In the inset, the Fermi energy level indicates that even the
undoped BiCuOTe is degenerately doped at room temperature owing to the native point defects. This result is also consistent with the temperature dependence of its electrical conductivity below the extrinsic-intrinsic temperature, thus exhibiting the importance of the native point defects on the thermoelectric performance in this material system. Theoretically, Seebeck coefficients can be calculated by Eq. 7.1 in the case of SPB structure [26-28]. In this study, the charge transport in BiCuOTe is dominantly governed by a single band of light-hole regardless of Pb-doping as discussed above.

\[
S = -\frac{k_B}{e} \left( \frac{(r + 5/2)F_{r+3/2}(\xi)}{(r + 3/2)F_{r+1/2}(\xi)} - \xi \right),
\]  

(7.1)

where \( k_B \) is the Boltzmann constant, \( e \) is the electron charge, \( r \) is the scattering parameter (+1/2 for optical phonon scattering, -1/2 for acoustic phonon scattering and +3/2 for ionized impurity scattering), \( F_n \) is the Fermi integral in Eq. 7.2, and \( \xi \) is the reduced Fermi energy as represented by Eq. 7.3.

\[
F_n = \int_0^\infty \frac{x^n}{1 + \exp(x - \xi)} \, dx,
\]

(7.2)

\[
\xi = \frac{E_V - E_F}{k_BT},
\]

(7.3)

where \( E_V \) - \( E_F \) is the Fermi energy level with respect to the top of the valence band. For the calculation, effective mass was treated as a free parameter. As shown in Fig. 7-12, the calculated Seebeck coefficients based on the acoustic phonon scattering model \( (r = -1/2) \) are well fitted to the experimental values, indicating that the degree of non-parabolicity in BiCuOTe could be negligible for the calculation using Eq. 7.1. This result is consistent with the previous reports in doped BiCuOSe compounds [9,13,25].
Figure 7-13 and Figure 7-14 show the thermal conductivities and resulting $ZT$ values of the $\text{Bi}_{1-x}\text{Pb}_x\text{CuOTe}$ compounds, respectively. Undoped BiCuOTe compound exhibited a quite low thermal conductivity (0.834 W/m·K at RT). The thermal conductivity increased with increasing Pb-doping and could be explained by the increased electrical contribution to the thermal conductivity. When $x \geq 0.4$, the thermal conductivity monotonously decreased with increasing temperature. However, in the case of $x \leq 0.02$, there was a transition in its temperature dependence of the thermal conductivity at around 450 ~ 500K due to the onset of the bipolar conduction. Eventually, the $ZT$ values decreased monotonically with the increase in the amount of Pb and the highest $ZT$ value (0.51 at 600K) was obtained for undoped BiCuOTe compound.
Figure 7-1. X-ray diffraction patterns of the Bi$_{1-x}$Pb$_x$CuOTe compounds.
Figure 7-2. Relative intensities of the main peak for Bi$_2$O$_3$ (111) to that for Bi$_{1-x}$Pb$_x$CuOTe (102) in the XRD patterns of Fig. 7-1.
Figure 7-3. Lattice parameter $a, c$ of the Bi$_{1-x}$Pb$_x$CuOTe compounds.
Figure 7-4. Relative intensities of (110) to (102) and (004) to (102) peaks in the XRD patterns.
Figure 7-5. Temperature-dependent electrical conductivities of the Bi$_{1-x}$Pb$_x$CuOTe compounds.
Figure 7-6. Dependence of carrier concentration on the atomic percent of dopants in the BiCuOTe (filled blue) and BiCuOSe compounds (open)
Figure 7-7. Hole generation per a Pb atom (doping yield) as a function of the atomic percent of Pb in the Bi$_{1-x}$Pb$_x$CuOTe compounds.
Figure 7-8. (a) Hall mobilities of the Bi$_{1-x}$Pb$_x$CuOTe compounds as a function of carrier concentration at room temperature, (b) and (c) are schematics of the two band structure in BiCuOSe and BiCuOTe, respectively. (HH: heavy hole, LH: light hole, $E_F$: Fermi level).
Figure 7-9. Bi and Cu vacancy formation energy calculated with DFT as a function of atomic percent of Pb.
Figure 7-10. Temperature-dependent Seebeck coefficients of the Bi$_{1-x}$Pb$_x$CuOTe compounds.

Figure 7-11. Temperature-dependent power factor of the Bi$_{1-x}$Pb$_x$CuOTe compounds.
Figure 7-12. Carrier concentration-dependent Seebeck coefficients of the Bi$_1-x$Pb$_x$CuOTe compounds at room temperature and calculated Seebeck coefficients (solid line: $r = -1/2$, dashed line: $r = 1/2$ and 3/2). Calculated Fermi energy levels ($E_V - E_F$) are shown in the inset.
Figure 7-13. Temperature-dependent thermal conductivity of the Bi$_{1-x}$Pb$_x$CuOTe compounds.

Figure 7-14. Temperature-dependent $ZT$ of the Bi$_{1-x}$Pb$_x$CuOTe compounds.
Table 7-1. Experimental (Exp.) and calculated (Calc.) lattice parameters along $a$- and $c$-axis.

<table>
<thead>
<tr>
<th>Pb (at%)</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.4035</td>
<td>0.4058</td>
</tr>
<tr>
<td>1</td>
<td>0.4037</td>
<td>0.4059</td>
</tr>
<tr>
<td>2</td>
<td>0.4039</td>
<td>0.4060</td>
</tr>
<tr>
<td>4</td>
<td>0.4047</td>
<td>0.4061</td>
</tr>
<tr>
<td>6</td>
<td>0.4043</td>
<td>0.4061</td>
</tr>
</tbody>
</table>

Table 7-2. DFT calculations of the formation energies of Bi and Cu vacancy in Bi$_{1-x}$Pb$_x$CuOTe.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vacancy formation energy (meV/FU)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bi vacancy</td>
</tr>
<tr>
<td>BiCuOTe</td>
<td>66</td>
</tr>
<tr>
<td>Bi$<em>{0.985}$Pb$</em>{0.015}$CuOTe</td>
<td>34</td>
</tr>
<tr>
<td>Bi$<em>{0.97}$Pb$</em>{0.03}$CuOTe</td>
<td>18</td>
</tr>
<tr>
<td>Bi$<em>{0.955}$Pb$</em>{0.045}$CuOTe</td>
<td>3</td>
</tr>
<tr>
<td>Bi$<em>{0.94}$Pb$</em>{0.06}$CuOTe</td>
<td>-10</td>
</tr>
</tbody>
</table>
7.4 Summary

In summary, point defect-assisted doping mechanism and related thermoelectric properties of Pb-doped BiCuOTe compounds were investigated. Undoped BiCuOTe exhibited degenerately doped p-type semiconducting behavior owing to the native point defects, and the formation of the point defect was accelerated by the substitution of Bi with Pb. The DFT calculations demonstrate that Pb-doping generated extra charge carrier by reducing the formation energy of $V_{Bi}$ for the strain relaxation, resulting from the larger ionic radius of Pb$^{2+}$ than Bi$^{3+}$. The electrical conductivity of Pb-doped BiCuOTe could be significantly enhanced because of the unexpected increase in the hole concentration, while it drastically decreased the Seebeck coefficient. Therefore, the point defect-assisted doping in the Bi$_{1-x}$Pb$_x$CuOTe compounds inevitably entailed the increase in the thermal conductivity, consequently decreasing $ZT$. These results indicate that the thermoelectric performance of BiCuOTe compound is critically determined by the native point defects, and finding a suitable donor to compensate the holes can be a possible way to improve the thermoelectric performance.
References


Chapter 8. Effects of Pb Doping on Thermoelectric Properties in Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds

8.1 Introduction

BiCuOCh ($Ch$ = chalcogen) oxychalcogenides have attracted much attention as a promising thermoelectric material for power generation using waste heat due to their intrinsically high Seebeck coefficient and low thermal conductivity related with the crystal structure of BiCuOCh [1-5]. Many approaches to improve the thermoelectric efficiency of BiCuOCh have been reported. In the case of BiCuOSe compounds, the enhanced $ZT$ can be achieved by doping with various elements (Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Na$^+$, and K$^+$) or self-doping with Cu-vacancy or dual vacancies of Cu and Bi [1,2,4,5,7-16]. In the case of BiCuOTe compounds, the $ZT$ was not successfully enhanced although Pb doping was attempted to improve the $ZT$ of BiCuOTe [17].

BiCuOSe-BiCuOTe solid solution can be one of the ways to improve the $ZT$ of BiCuOCh because the lattice thermal conductivity can be lower. When Se was substituted by Te, the lattice thermal conductivity can be reduced because of alloying scattering, and the reduction in lattice thermal conductivity was reported for Bi$_2$Te$_3$$_x$Se$_{3-x}$ in previous reports [18]. Although there have been numerous reports on the thermoelectric properties of BiCuOSe$_{1-x}$Te$_x$, only electrical conductivity, Seebeck coefficients, and power factor of BiCuOSe$_{1-x}$Te$_x$ ($x = 0 - 1$) from 50K to 300K and those properties of Bi$_{0.9}$Sr$_{0.1}$CuOSe$_{1-x}$Te$_x$ at RT were reported by Barreteau et al.[19] and thermoelectric properties of BiCuOSe$_{1-x}$Te$_x$ ($x = 0 - 0.2$) from 300K to 923K were reported by Liu and coworkers [20]. Therefore, the simultaneous and
systematic understanding the temperature-dependent thermoelectric properties of a $p$-typed dopant-doped BiCuOSe$_{1-x}$Te$_x$ is necessary.

In this chapter, the effects of Pb doping on the thermoelectric properties of BiCuOSe$_{1-x}$Te$_x$ were investigated. Pb doping in BiCuOSe$_{1-x}$Te$_x$ compounds can increase the electrical and thermal conductivity and decrease the Seebeck coefficients. Therefore, BiCuOSe$_{0.8}$Te$_{0.2}$ was selected because it has higher $ZT$ than BiCuOSe while having low electrical and thermal conductivity and Seebeck coefficients. With increasing amount of Pb, hole concentration increased, thus increasing the electrical conductivity and the decreasing the Seebeck coefficients. The increase in the thermal conductivity was observed although the alloying scattering affected the thermal conductivity. The highest $ZT$ 1.06 at 910K was obtained for Bi$_{0.94}$Pb$_{0.06}$CuOSe$_{0.8}$Se$_{0.2}$, and the origin of the enhanced $ZT$ is discussed in terms of temperature-dependent power factor.
8.2 Experimental Procedure

8.2.1 Synthesis and Consolidation of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ Compounds

Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ ($x = 0, 0.01, 0.02, 0.04$ and $0.06$) compounds were synthesized by one step solid state reaction. Bi$_2$O$_3$ (99.999%, Sigma Aldrich), Bi (99.999%, 5N Plus), Se (99.999%, 5N Plus), Te (99.999%, 5N Plus), Cu (99.99%, Alfa Aesar) and PbO (99.9%, Kojundo) were used as starting materials. Mixtures of starting materials were ground with an alumina mortar and pestle, and they were pressed into pellets under uniaxial stress (80 MPa). The pressed pellets were annealed at 973K for 15 h in evacuated silica tubes. The annealed samples were pulverized into powders, and then the powders were consolidated by spark plasma sintering at 948K under 50 MPa of pressure for 10 min in a $10^3$ Torr vacuum.

8.2.2 Characterization

Phase analyses of the compounds were performed using an X-ray diffractometer (New D8 Advance, Bruker, Germany) with Ni filtered Cu Kα radiation. The operation voltage and current were kept at 40 kV and 40 mA, respectively. Microstructural characterizations were also carried out by using a scanning electron microscope (SU70, Hitachi, Japan). Electrical conductivities and Seebeck coefficients were measured by a thermoelectric property measurement system (RZ-2001i, Ozawa Science, Japan) from room temperature to 910K, and carrier concentration and mobility at RT were determined using a Hall measurement system (ResiTest 8300, Toyo Corporation, Japan) under a magnetic field of 0.57 T. The thermal conductivity was calculated from $\kappa=\alpha C_p\rho$, where the thermal diffusivity ($\alpha$) was measured using the laser flash diffusivity method (LFA457, Netzsch, Germany).
8.3 Results and Discussion

8.3.1 Phase Analysis and Microstructures of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ Compounds

Figure 8-1 shows the XRD patterns of the as-prepared BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ ($x = 0, 0.01, 0.02, 0.04$ and $0.06$) compounds. The XRD patterns of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds shifted to lower angles as compared to the XRD patterns of BiCuOSe because of the difference in the ionic radius between Se$^{2-}$ (0.198 nm) and Te$^{2-}$ (0.221 nm) [21], indicating that the XRD patterns of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds consist of a single phase of BiCuOSe$_{1-x}$Te$_x$. The lattice parameters of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds are presented in Fig. 8-2, indicating that the lattice parameters along $a$- and $c$-axis increased when Se$^{2-}$ atoms were substituted by Te$^{2-}$ atoms, and the lattice parameters along $a$- and $c$-axis slightly increased with increasing amount of Pb. The increase in the lattice parameter is because of the larger ionic radius of Pb$^{2+}$ (0.129 nm) than that of Bi$^{3+}$ (0.117 nm) [21] as mentioned in Chapter 7. The Lotgering factor, indicating the degree of orientation, can be obtained from the XRD patterns, and it can be expressed by the following equation

$$F = \frac{P - P_0}{1 - P_0},$$

(8.1)

where $P$ and $P_0$ are the ratio of the sum of (00l) intensities to (hkl) intensities from the XRD data and from XRD PDF # 45-0296, respectively. As shown in Fig. 8-3, the Lotgering factor for BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds has similar values in the range 0.04–0.07, indicating that all the compounds have random texture. Figure 8-4 shows the microstructures of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds. Any
preferred orientation and noticeable differences were not observed in the SEM images, and all the compounds have similar relative density in the range 94-96%.

8.3.2 Charge Transport of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ Compounds

Figure 8-5(a) shows the hole concentrations of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ at room temperature, and the hole concentrations at room temperature of doped BiCuOSe [7,11,22] and BiCuOTe (Ch. 7) are plotted as a function of doping amounts in the inset of Fig. 8-5(a). As shown in Fig. 8-5(a), the hole concentration increased when Te was substituted into Se site due to the decrease in the bandgap, because the intrinsic carrier concentration generally increases when with decreasing bandgap energy [23]. Moreover, the hole concentration also increased with increasing doping amount of Pb and can be explained in a manner similar to that of Pb-doped BiCuOSe [11,13] and BiCuOTe (in Chapter 7). In contrast, the anomalous doping effect of Pb as mentioned in Chapter 7 was also been observed for Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds as shown in the inset of Fig. 8-5(a). The Hall mobilities at room temperature of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds are shown in Fig. 8-5(b). The Hall mobility of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ decreased as compared to BiCuOSe because of the alloying scattering caused by the substitution of Te for Se; however, the Hall mobilities slightly increased with increasing doping amounts of Pb.

Figure 8-6(a) shows the temperature-dependent electrical conductivities of the BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds. The electrical conductivities of the BiCuOSe and BiCuOSe$_{0.8}$Te$_{0.2}$ were similar, although the hole concentration of BiCuOSe$_{0.8}$Te$_{0.2}$ was higher than that of BiCuOSe. This can result from the reduction
in the mobility caused by the change in the bonding angle [19]. The electrical conductivities of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ increased with increasing amount of Pb doping because of the increase in hole concentration. The electrical conductivities of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ ($x \leq 0.01$) compounds decreased and then increased as the temperature increased, while the electrical conductivities of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ ($x \geq 0.02$) compounds decreased with increasing temperature. The temperature-dependent electrical conductivity behavior of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds was related to the intrinsic-extrinsic transition. Fig. 8-6(b) shows the temperature-dependent Seebeck coefficients of the Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds. The Seebeck coefficient decreased with Te substitution for Se and increasing doping amounts of Pb because of increasing hole concentration. The Seebeck coefficients of undoped BiCuOSe and BiCuOSe$_{0.8}$Te$_{0.2}$ compounds decreased as the temperature increased, whereas the Seebeck coefficients were linearly proportional to temperature when $x \geq 0.01$, and this results were also related to the intrinsic-extrinsic transition.

Figure 8-7 shows the power factor of the Pb-doped BiCuOSe, BiCuOTe and BiCuOSe$_{0.8}$Te$_{0.2}$ compounds as a function of doping amounts of Pb at (a) room temperature, (b) 600K and (c) 800K [11,13,17]. Due to the thermal stability of BiCuOTe compounds, the power factor of BiCuOTe at 800K was not compared. As shown in the Figs. 8-7(a) and (b), Pb-doped BiCuOTe compounds have higher power factor at RT and 600K than Pb-doped BiCuOSe and BiCuOSe$_{0.8}$Te$_{0.2}$ compounds, and it was related to the fact that the antibonding of Cu 3d-Te 5p state for BiCuOTe is stronger than Cu 3d-Se 4p states of BiCuOSe at the same doping level [24]. A comparison between BiCuOSe and BiCuOSe$_{0.8}$Te$_{0.2}$ compounds indicates that Pb-
doped BiCuOSe compounds have higher power factor at RT and 600K than Pb-doped BiCuOSe$_{0.8}$Te$_{0.2}$ compounds, whereas Pb-doped BiCuOSe compounds have higher power factor at 800K than Pb-doped BiCuOSe$_{0.8}$Te$_{0.2}$. This result indicates that Pb-doped BiCuOSe$_{0.8}$Te$_{0.2}$ compounds have enhanced thermoelectric efficiency at relatively high temperature as compared to Pb-doped BiCuOSe compounds.

### 8.3.3 Thermal Conductivity and $ZT$ of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ Compounds

Figure 8-8 shows the temperature-dependent (a) total thermal conductivities, (b) Lorenz number and (c) lattice thermal conductivities of the BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds. The total thermal conductivity is the sum of the electronic thermal conductivity ($\kappa_{\text{el}}$) and lattice thermal conductivity ($\kappa_{\text{lat}}$). In addition, the electronic thermal conductivity can be calculated according to Wiedemann–Franz equation ($\kappa_{\text{el}} = L\sigma T$), where $L$ is the Lorentz number [25]. In order to obtain reliable electronic and lattice thermal conductivity, temperature-dependent Lorenz factor was obtained by the SPB model [26,27].

As shown in Fig.8-8(a), the total thermal conductivity decreased when Te was substituted into Se sites due to the alloying scattering, as clearly shown by the lattice thermal conductivity (Fig. 8-8(c)). Although the lattice thermal conductivity decreased with increasing doping amounts of Pb due to the phonon scattering by Pb atoms, the total thermal conductivity increased with increasing amount of Pb-doping. This result can be explained by the increased electrical contribution to the thermal conductivity. Figure 8-8(d) shows the temperature-dependent $ZT$ of the BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds. The highest $ZT$ of 1.06 at 900K was obtained.
for the Bi$_{0.99}$Pb$_{0.01}$CuOSe$_{0.8}$Te$_{0.2}$ compounds with the optimized hole concentration.
Figure 8-1. X-ray diffraction patterns of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds.
Figure 8.2. Lattice parameter $a, c$ of BiCuOSe and $\text{Bi}_{1-x}\text{Pb}_x\text{CuOSe}_{0.8}\text{Te}_{0.2}$ compounds.
Lotgering factor of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds.

Figure 8-3. Lotgering factor of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds.
Figure 8-4. Microstructures of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds.
Figure 8-5. (a) hole concentration of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ at room temperature. Hole concentrations at room temperature of doped BiCuOSe and BiCuOTe (Ch. 7) are plotted as a function of doping amounts in the inset. (b) Hall mobility of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ at room temperature. Microstructures of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds.
Figure 8-6 Temperature-dependent (a) electrical conductivities and (b) Seebeck coefficients of Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$
Figure 8-7. The power factor of the Pb-doped BiCuOSe, BiCuOTe and BiCuOSe$_{0.8}$Te$_{0.2}$ compounds as a function of doping amounts of Pb at (a) room temperature, (b) 600K and (c) 800K.
Figure 8-8. Microstructures of BiCuOSe and Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds.
8.4 Summary

In summary, the effects of Pb doping on the thermoelectric properties of BiCuOSe$_{0.8}$Te$_{0.2}$ were investigated. With the increase in the amount of Pb, the electrical conductivity increased and the Seebeck coefficient decreased because of increasing hole concentration. The change in the temperature-dependent power factor was observed when comparing with Pb-doped BiCuOSe and BiCuOTe. With increasing doping amounts of Pb in the Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds, the thermal conductivity increased because of increasing hole concentration although the alloying scattering affected the thermal conductivity. The highest ZT of 1.06 at 910K was obtained for Bi$_{0.94}$Pb$_{0.06}$CuOSe$_{0.8}$Se$_{0.2}$ with enhanced power factor. These results indicate that Pb doping in BiCuOSe$_{0.8}$Te$_{0.2}$ system is an effective way to improve the figure of merit, and BiCuOSe$_{0.8}$Te$_{0.2}$ has improved thermoelectric efficiency at relatively high temperature because of the alloying scattering effects.
References


Chapter 9. Summary and suggestions for future work

BiCuO\textit{Ch} (\textit{Ch} = Se and Te) oxychalcogenide have been reported as a promising oxide thermoelectric material due to their low thermal conductivity and high Seebeck coefficient. However, they exhibited poor electrical conductivity, which is the main limitation for thermoelectric applications. Therefore, in this dissertation, poor electrical conductivity was enhanced through doping or the formation of vacancy and carrier concentration was optimized in order to improve the thermoelectric efficiency. Moreover, the charge transport and thermoelectric properties of BiCuO\textit{Ch} compounds were also investigated.

First, the DOS effective mass and related charge transport properties of K-doped BiCuOSe is reported. The K-doped BiCuOSe compounds exhibited typical metallic conduction behavior with improved \textit{p}-type conduction properties both in the carrier concentration and the Hall mobility as compared to the undoped BiCuOSe compound. The DOS effective masses in the K-doped BiCuOSe compounds were significantly lower than that in the undoped compound, and this result was quite consistent with the enhanced Hall mobilities of the K-doped compounds. This result was explained by the two-band model in the valence band of the BiCuOSe. The thermal conductivity decreased with increasing K doping in Bi\textsubscript{1-x}K\textsubscript{x}CuOSe compounds because of the phonon scattering by K atoms. The highest \textit{ZT} of 0.41 was obtained at 640K for Bi\textsubscript{0.948}K\textsubscript{0.052}CuOSe compound because of the higher power factor and lower thermal conductivity than other compounds. With these results, it can be concluded that K-doping is an effective way to improve \textit{ZT} through the \textit{p}-type conduction properties in BiCuOSe by increasing both the carrier concentration.
and the Hall mobility.

Second, the effects of the Bi deficiency on the thermoelectric properties of Bi\textsubscript{1-x}CuOSe compounds are reported. The $p$-type conduction properties of Bi\textsubscript{1-x}CuOSe compounds were improved with increasing hole concentration introduced by Bi deficiency. The drastic reduction in the Seebeck coefficient was observed, and it was discussed in terms of electronic structures calculated by DFT of Bi\textsubscript{1-x}CuOSe compounds. With increasing amounts of Bi-deficiency in the Bi\textsubscript{1-x}CuOSe compounds, the thermal conductivity increased because of increasing hole and reduced anharmonicity. The highest $ZT$ (0.4 at 810K) was obtained in Bi\textsubscript{0.975}CuOSe, and this value was $\sim$8% higher than that in the stoichiometric compound. These results conclude that Bi deficiency in BiCuOSe system is an effective way to improve the figure of merit.

Third, point defect-assisted doping mechanism and related thermoelectric transport properties in Pb-doped BiCuOTe compounds were investigated. Because BiCuOTe exhibited higher electrical conductivity and power factor than BiCuOSe, BiCuOTe was selected. The hole concentration increased with increasing amount of the Pb, significantly increasing the electrical conductivity of Pb-doped BiCuOTe. However, although at most one hole per single dopant atom could be generated due to the divalency of Pb, more than one hole per a Pb atom was generated in the Pb-doped compound. The dependence of the formation energies of possible point defects ($V_{Cu}$ and $V_{Bi}$) on the amount of Pb-doping were calculated based on DFT, and the results were quite consistent with our observations. These results indicate that the thermoelectric performance of BiCuOTe compound is critically determined by the native point defects, and that finding a suitable donor to compensate the holes
can be a possible way to improve the thermoelectric performance.

Finally, the effects of Pb doping on the thermoelectric properties of BiCuOSe$_{0.8}$Te$_{0.2}$ were investigated. With increasing amount of Pb, the electrical conductivity increased and the Seebeck coefficient decreased because of increasing hole concentration. The change in the temperature-dependent power factor was observed when compared to Pb-doped BiCuOSe and BiCuOTe. With increasing doping amounts of Pb in the Bi$_{1-x}$Pb$_x$CuOSe$_{0.8}$Te$_{0.2}$ compounds, the thermal conductivity increased due to the increase in hole concentration although the alloying scattering affected the thermal conductivity. The highest figure of merit of 1.06 at 910K was obtained for Bi$_{0.94}$Pb$_{0.06}$CuOSe$_{0.8}$Te$_{0.2}$ with enhanced power factor. Thus, Pb doping in BiCuOSe$_{0.8}$Te$_{0.2}$ system is an effective way to improve the figure of merit, and BiCuOSe$_{0.8}$Te$_{0.2}$ exhibited enhanced thermoelectric efficiency at relatively high temperature owing to the effects of alloying scattering.

The thermoelectric performance efficiency of BiCuOCh compounds remains still low for thermoelectric applications; therefore, the enhancement in the thermoelectric performance is still challenging. From the literature review and the study presented here, some suggestions for the further study are as follows:

1. In the case of BiCuOSe compounds:
   - Studying the effects of nanostructuring, carrier filtering, and resonant state on the thermoelectric properties of BiCuOSe.
   - For modulation, confirmation of electrothermal stability and finding n-type materials as a counterpart.
2. In the case of BiCuOTe compounds:
   - Finding a suitable donor to compensate the holes to improve the thermoelectric performance.
   - Finding another $p$-type dopants, which do not generate unexpected hole concentration.

3. In the case of BiCuOSe$_{1-x}$Te$_x$ compounds:
   - Finding a suitable dopant to improve the thermoelectric performance.
   - Trying approaches, which are effective to enhance the thermoelectric properties of BiCuOSe.
Publications


국문초록

층상구조를 가진 BiCuOCh (Ch = Se, Te) 화합물의 전하 전송 및 열전 특성 연구

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최근 에너지 부족 및 환경 문제가 사회적 이슈로 대두됨에 따라 폐열을 이용해 전력을 생산하는 열전재료의 연구가 관심을 받고 있다. 열전재료의 효율은 $ZT = S^2 \sigma T / \kappa$로 나타내어지며 제백계수 (S), 전기전도도 ($\sigma$), 열대운동도 ($T$), 열전도도 ($\kappa$)로 구성된다. 높은 열전변환효율을 확보하기 위해서는 높은 제백계수와 전기전도도, 그리고 낮은 열전도도를 가지면 되지만, 이들은 서로 상호작용적인 특성을 지니고 있어 독립적으로 제어하기가 힘들다. 예를 들면 전하농도의 경우, 전하농도가 증가하면 전기전도도가 증가하지만 제백계수는 감소하고 전자에 의한 열전도도는 증가한다. 따라서 높은 열전효율을 갖기 위해서는 전하농도의 최적화가 필요하다.

BiCuOCh 열전재료는 2010년도에 처음 열전재료로 보고되었으며 이 열전재료는 다른 열전재료에 비해 높은 제백계수와 낮은 열전도도를 가지고 있어 유망한 $\rho$형 중고온 열전재료 중 하나로 각광받고 있다.
하지만 BiCuOCh 열전재료는 낮은 전기전도도를 가지고 있어 높은 열전변환효율을 확보하는 데 있어 큰 장해가 되고 있다. 따라서 이 재료는 낮은 전기전도도를 개선하여 열전 효율을 향상시켜야 한다. 본 연구에서는 BiCuOCh 열전재료의 전기전도도를 증진시키기 위해 불순물 도핑하거나 Bi 정공을 형성하여 BiCuOCh의 전기전도도를 증진시키며, 도핑 또는 정공 형성 시 BiCuOCh 열전재료의 전하 전송과 열전 특성에 미치는 영향에 대하여 분석하였다.

먼저 BiCuOSe에 K를 도핑하여 K도핑이 BiCuOSe의 전하 전송과 열전 특성에 미치는 영향에 대한 연구를 진행하였다. 고상법으로 상합성하였으며 통전 활성 소결법을 통하여 소결하였다. BiCuOSe는 온도가 증가함에 따라 전기전도도가 증가하는 반도체적 거동을 보인 반면 K가 도핑된 BiCuOSe는 온도가 증가함에 따라 전기전도도가 감소하는 금속적 거동을 보였다. K 도핑 시 전기전도도가 증가하는 것을 확인하였고 이는 홀 농도 및 이동도의 증가로 인한 것이다. 이동도의 증가는 상태밀도의 유효질량이 K가 도핑 되었을 때 낮아지게 되는데 이로 인한 것으로 보인다. 그리고 이 상태밀도의 유효질량의 거동은 BiCuOSe의 가전자대의 다중 밴드로 인한 것으로 보인다. 열전도도의 경우 K 도핑 되었을 때 전자에 의한 열전도도가 높아졌음에도 불구하고 전체 열전도도는 낮아지는 것을 확인하였으며 이는 K가 포논을 산란시켰기 때문 이다. 가장 높은 ZT는 Bi_{0.948}K_{0.052}CuOSe 조성에서 0.41 (640K)의 값
을 나타내었으며 이는 최적화된 전하 농도 및 K에 의해 열전도도가 감소하였기 때문이다. 또한 BiCuOSe에 Bi 정공을 형성하여 Bi 정공이 BiCuOSe의 전하 전송과 열전 특성에 미치는 영향에 대한 연구를 진행하였다. Bi 정공 형성을 통해 BiCuOSe의 홀 농도 증가를 통해 전기전도도를 증진시켰다. 반면에 제백계수의 경우 급격한 감소를 보였는데 이는 Bi 정공 형성으로 인해 BiCuOSe의 전자 구조가 변했기 때문이다. 최적화된 전하 농도 및 본질적으로 낮은 열전도도로 인해 Bi0.975CuOSe 조성에서 810K에서 0.4의 ZT 값을 보였다. 이러한 결과로 Bi 정공 형성이 BiCuOSe의 열전효율을 향상시키는데 효과적인 방법 중에 하나라는 것을 알 수 있었다.

두번째로 전기전도도와 출력인자가 BiCuOSe 보다 높은 BiCuOTe 열전재료를 선택하여 Pb를 도핑하였으며 Pb 도핑이 BiCuOTe의 전하 전송과 열전 특성에 미치는 영향에 대해 연구하였다. 고상법으로 상합성 하였으며 통전 활성 소결법을 통하여 소결하였다. BiCuOTe에 Pb를 도핑하였을 때 전하농도가 증가하여 전기전도도의 증가, 제백계수의 감소, 열전도도의 증가를 야기하였다. Pb도핑시 BiCuOTe의 열전효율을 향상시키지 못하였는데 이는 예상치 못한 전하농도 증가로 인한 것으로 보인다. 이 예상치 못한 전하농도는 Pb^{2+}가 Bi^{3+}자리에 치환될 때 각각의 이온반경 크기에 차이로 인한 것이다. Pb^{2+}의 이온반경이 Bi^{3+}의 이온반경보다 크며 이로 인해 BiCuOTe에 변형이 생기게 되고 이 변형을 완화하기 위해 Bi나 Cu 정공을 형성하게 된다. 밀도범함수 이
론을 이용하여 Bi 및 Cu 정공 형성 에너지 계산을 하였으며 Pb 도핑 시 Bi나 Cu 정공이 생길 확률을 확인하였다. 따라서 Bi나 Cu 정공 형성이 예상치 못한 전하농도의 증가를 야기하였고 BiCuOTe의 열전특성에 영향을 미치는 것을 확인하였다.

마지막으로, BiCuOSe$\textsubscript{0.8}$$\text{Te}_{0.2}$에 Pb 도핑 시 Pb 도핑이 BiCuOSe$\textsubscript{0.8}$$\text{Te}_{0.2}$의 전하 전송과 열전 특성에 미치는 영향에 대한 연구를 진행하였다. 고상법으로 상합성 하였으며 통전 활성 소결법을 통하여 소결하였다. Pb 도핑을 통해 BiCuOSe$\textsubscript{0.8}$$\text{Te}_{0.2}$의 흑 높도 증가를 야기시켰다. 이로 인해 전기전도도 및 열전도도는 증가하였고 체백계수는 감소하였다. BiCuOSe$\textsubscript{0.8}$$\text{Te}_{0.2}$에 Pb 도핑 했을 때도 BiCuOSe와 BiCuOTe의 경우와 마찬가지로 예상치 못한 전하농도가 증가하였다. Pb가 도핑된 BiCuOSe와 BiCuOTe의 출력인자의 온도 의존성을 비교해본 결과 Pb가 도핑된 BiCuOSe$\textsubscript{0.8}$$\text{Te}_{0.2}$의 출력인자가 고온에서 우수함을 알 수 있었다. 향상된 출력인자로 인해 Bi$\textsubscript{0.94}$$\text{Pb}_{0.06}$CuOSe$\textsubscript{0.8}$$\text{Te}_{0.2}$ 조성에서 1.06 (910K)의 가장 높은 값을 얻었다.

이러한 연구 결과를 통해 BiCuOCh의 전하 전송과 열전 특성에 대해 좀 더 깊은 이해를 할 수 있었으며 이 연구 결과는 앞으로 BiCuOCh의 열전효율을 향상시키고 특성을 이해하는 데 크게 이바지할 것으로 예상한다.

핵심어: BiCuOCh, 칼코겐화합물, 전하 전송, 열전 특성, 도핑, 정공 형성