LAYERED INORGANIC-ORGANIC HYBRID MATERIALS
WITH REDUCED THERMAL CONDUCTIVITY

by

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Dr. Jing Li

and approved by

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ABSTRACT OF THE THESIS

Layered Inorganic-Organic Hybrid Materials
with Reduced Thermal Conductivity

by Yu-Chu Chen

Thesis Director:
Professor Jing Li

New ternary inorganic-organic hybrid materials \((H_2\text{pda})_{0.5}Cu_2\text{SbSe}_3\) and
\([H_2\text{bda}]_{0.5}Cu_2\text{SbSe}_3\) (pda= propanediamine, bda= butanediamine) were synthesized by the hydrothermal method. Both structures are composed of \([Cu_2\text{SbSe}_3]^-\) 2D layer structures that are connected by the organic amines. A series of hybrid compounds \(Cu_2\text{SbSe}_3(L)_{x}\) (L= en, pda, bda; x=0.5, 1) were synthesized for an integrated study. Compared with the 3D structure compound \(Cu\text{SbSe}_2\), the thermal conductivity study shows that incorporation of incorporation of inorganic-organic interface can effectively reduce the thermal conductivity.
Acknowledgements

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I am grateful to the committee members Dr. Tewodros Asefa and Dr. John Brennan for serving on my committee.

I would like to thank our collaborators, Dr. Thomas J. Emge for the single crystal data analysis, Dr. Ten Yuen for her help in magnetic property measurements and Dr. Ronggui Yang for the thermal conductivity measurements.

I would like to gratefully thank Dr. Jing Li’s research group, for many helpful discussions, assistance and friendship. It was a great pleasure to work with you.

Last, I would like to express my deep gratitude to my mother, for her love and support.
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Chapter I: Introduction

Thermoelectric materials have drawn great attention recently due to their potential of converting waste heat to electricity. The efficiency of thermoelectric devices is determined by the figure of merit $ZT$ (Equation 1):

$$ZT = \frac{\alpha^2 \sigma T}{\kappa_E + \kappa_L} = \frac{\alpha^2 T}{\rho \kappa}, \quad (1)$$

where $\alpha$, $\sigma$, $\kappa$ and $\rho$ are the Seebeck coefficient, electrical conductivity, thermal conductivity and electrical resistivity, respectively. Thermal conductivity is attributed to the sum of the electronic thermal conductivity $\kappa_E$ and the lattice thermal conductivity $\kappa_L$. $ZT$ can be promoted by reducing the thermal conductivity or by enhancing the electrical conductivity. Reductions of thermal conductivity in thermoelectric materials have been reported, yet a decrease in $\sigma/\kappa_E$ is still difficult to achieve.

Studies have shown the layer-structured materials such as Bi$_2$Te$_3$ (Figure 1) have the ability to scatter the short-wavelength acoustic phonons hence further reduce the lattice thermal conductivity.$^{1,2}$ Introducing the interfaces in the materials can also help to reduce the thermal conductivity.$^3$

A new type of materials, inorganic-organic hybrid semiconductors, have drawn huge interests recently.$^4,5$ Incorporation of two distinctly different materials into a single crystal lattice often lead to enhance properties and functionalities.$^6$ Since the structure plays an important role of phonon scattering in the compounds, the formation of inorganic-organic hybrid materials can benefit thermoelectric property by their unique
structures. Our group had previously demonstrated the inorganic-organic hybrid materials have the advantages of low thermal conductivity and high flexibility.\textsuperscript{7,8} As shown in Figure 2, the incorporation of organic molecules semiconductor can create two-dimensional structures. By introducing the inorganic-organic interfaces to the structure, the thermal conductivity of the material can be reduced.

This thesis exhibits a series of ternary inorganic-organic hybrid materials with different lengths of diamines cooperated in order to understand optimization of thermoelectric property by introducing the inorganic-organic interfaces to semiconductors. We discuss the roles of organic diamines in optical and thermal transport properties. Furthermore, several new hybrid compounds have been developed and their physical properties have been investigated.
Figure 1. Crystal structure of the thermoelectric material, Bi$_2$Te$_3$. The Bi and Te layers are held together by strong covalent bonds, whereas the bonding between adjacent Te layers is of the van der Waals type. This weak binding between the Te layers accounts for the ease of cleavage along the plane perpendicular to the c-axis and the anisotropic thermal and electrical transport properties of Bi$_2$Te$_3$.\textsuperscript{9}

Figure 2 The 2D layer hybrid materials can be obtained by introducing organic ligands into the 3D bulk materials.
Chapter II: Sample Preparation

2.1 Reagents

Ethylenediamine (en, 99%, Aldrich), propanediamine (pda, 98%, Alfa Aesar), 1,2-diaminopropane, butanediamine (bda, 98%, Alfa Aesar), CuCl (chemically pure, ICN Biomedicals), SbCl$_3$ (99+%, Alfa Aesar), Se (99.5%, Alfa Aesar), Cu, Sb (99.5%, Strem Chemical). K$_2$Se was prepared from the reactions of potassium metal and selenium in a 2:1 ratio in liquid ammonia.

2.2 Sample Synthesis

2.2.1 (H$_2$pda)$_{0.5}$Cu$_2$SbSe$_3$

Orange needle-like crystals of (H$_2$pda)$_{0.5}$Cu$_2$SbSe$_3$ were synthesized by the solvothermal reaction. The reagents CuCl (25mg), SbCl$_3$ (57mg), Se (60mg) and pda (3mL, propanediamine) were placed into a Teflon-lined stainless autoclave. The reaction was placed in 150 °C for 7 days. The sample was collected and washed successively with distilled water and absolute ethanol.

2.2.1 (H$_2$bd$_{2}$a)$_{0.5}$Cu$_2$SbSe$_3$

Orange plate-like crystals were synthesized by the solvothermal reaction. The reagents CuCl (25mg), SbCl$_3$ (57mg), Se (60mg) and bda (3mL, butanediamine) were placed into a Teflon-lined stainless autoclave. The reaction was placed in 150 °C for 7 days. The sample was collected and washed successively with distilled water and absolute ethanol.

2.2.2 Cu$_2$SbSe$_3$(en)$_{0.5}$

Orange needle-like crystals of Cu$_2$SbSe$_3$(en)$_{0.5}$ were synthesized by the solvothermal reaction. The reagents CuCl (25mg), SbCl$_3$ (57mg), Se (60mg) and ethylenediamine (3mL) were placed into a Teflon-lined stainless autoclave. The reaction was placed in 180 °C for 7 days. The sample was collected and washed successively with distilled water and absolute ethanol.
2.2.3 Cu$_2$SbSe$_3$(en)

Orange plate-like crystals of Cu$_2$SbSe$_3$(en)$_{0.5}$ were synthesized by the solvothermal reaction. The reagents CuCl (25mg), SbCl$_3$ (57mg), Se (60mg) and ethylenediamine (3mL) were placed into a Teflon-lined stainless autoclave. The reaction was placed in 150 °C for 7 days. The sample was collected and washed successively with distilled water and absolute ethanol.

2.2.3 Cu$_2$SbSe$_3$(bda)$_{0.5}$

Orange plate-like crystals were obtained by the solvothermal reaction. The reagents CuCl (25mg), SbCl$_3$ (57mg), Se (60mg) and butanediamine (3mL) were placed into a Teflon-lined stainless autoclave. The reaction was placed in 150 °C for 7 days. The sample was collected and washed successively with distilled water and absolute ethanol.

2.2.4 CuSbSe$_2$

The black crystals were synthesized by the solvothermal reaction. The reagents Cu (38.1mg), Sb (73.2mg), Se (118.4mg), H$_2$O (0.6mL) and 1,2-diaminopropane (3mL) were placed into a Teflon-lined autoclave. The reaction was placed in 160 °C for 10 days. The sample was collected and washed successively with distilled water, absolute ethanol.

2.3 Pellet preparation

Pellets were prepared from the powder obtained after reaction. Due to different natures of the compounds, pellets were annealed at different temperature in order to get the similar porosity. The density of each sample was calculated, for all of the samples the density was greater than 80% of the theoretical density.

2.3.1 (H$_2$pd$_{0.5}$Cu$_2$SbSe$_3$

The as-made (H$_2$pd$_{0.5}$Cu$_2$SbSe$_3$ powder was poured into a circular die (13 mm diameter) and pressed under 4 tons of pressure for 30 mins follow by annealing under 80°C for 2 hours.
2.3.2 Cu$_2$SbSe$_3$(en)$_{0.5}$

The as-made Cu$_2$SbSe$_3$(en)$_{0.5}$ powder was poured into a circular die (13 mm diameter) and pressed under 4 tons of pressure for 30 mins follow by annealing under 80°C for 2 hours.

2.3.3 Cu$_2$SbSe$_3$(en)

The as-made Cu$_2$SbSe$_3$(en) powder was poured into a circular die (13 mm diameter) and pressed under 4 tons of pressure for 30 mins follow by annealing under 80°C for 2 hours.

2.3.4 (H$_2$bda)$_{0.5}$Cu$_2$SbSe$_3$

The as made Cu$_2$SbSe$_3$(bda)$_{0.5}$ powder was poured into a circular die (13 mm diameter) and pressed under 4 tons of pressure for 30 mins follow by annealing under 80°C for 2 hours.

2.3.5 CuSbSe$_2$

The as made Cu$_2$SbSe$_3$(en)$_{0.5}$ powder was poured into a circular die (13 mm diameter) and pressed under 4 tons of pressure for 30 mins follow by annealing under 280°C in vacuum for 2 hours.
Chapter III: Analysis Techniques

3.1. X-ray Diffraction Techniques

X-ray diffraction has been widely used to determine the crystal structure. In this study, single-crystal X-ray diffraction data were collected on a Siemens (Bruker) SMART APEX II diffractometer with graphite-monochromated Mo Kα radiation ($\lambda=0.71073$ Å) at room temperature. This analysis was only employed on a few samples in this study. The powder X-ray diffraction measurements were also used to identify the structures and the purity of the samples of known structures. Powder X-ray diffraction data were obtained by Rigaku Ultima IV. The source of X-rays was generated from copper. The sample was ground to fine powders and spread to a thin layer on the glass. Data was collected at room temperature with 4 seconds per step and a step size of 0.2° at the operating power of 44kV/40mA.

3.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a qualitative method to determine the changes in weight in upon sample heating. The thermal stability of the materials can be observed with TGA, which is useful in the preliminary determination of the sample structure. The data was collected by a thermal analyzer (TGA2050, TA Instruments, USA). 10-20 mg of sample was loaded in the aluminum pan. The heating procedure was set from 25 °C to 500 °C at a heating rate of 10°C/min and at a nitrogen gas rate of 80mL/min.

3.3. UV-vis diffuse reflectance measurement

Optical diffuse reflectance spectra were measured using Shimadzu UV-3101PC double beam, double monochromator spectrophotometer. The samples were ground into
powder. The spectra was collected in the wavelength range 250-2000nm. BaSO₄ was used as the reference (100% reflectance). The spectra were converted by Kubelka-Munk function (F-Function), which assumes the scattered radiation is distributed isotropically therefore the scattering factor (S) can be taken as a constant. The formula for the Kubelka-Munk function is:

\[ F(R_\infty) = \frac{\alpha}{S} = \frac{(1-R_\infty)^2}{2R_\infty}. \]

Where, \( R_\infty \) = reflectance at given wavelength = \( \frac{R_{\text{sample}}}{R_{\text{standard}}} \)

\( \alpha \) = absorption coefficient

S = scattering coefficient.

In the semiconducting materials, band gap energy is related to the extrapolation of this line of optical absorption edge to the photon energy (\( hv \)) as shown in Figure 3.

![Figure 3. Spectrum of Kubelka-Munk function vs. photo energy (hv).](image)

**3.4. Magnetic measurement**

Magnetic or spin properties are useful in the determination of structural features in transition metal compounds. In this study, magnetic measurements were performed on Quantum Design SQUID (Superconducting Quantum Interference Device). A
superconducting electromagnet provides the magnetizing field in a SQUID magnetometer. Paramagnetic compounds that contain unpaired electrons are attracted into magnetic fields, and diamagnetic compounds are those with no unpaired electrons are repelled by a magnetic field. The sensor converts the magnetic flux threading the SQUID loop into a voltage across the device.\textsuperscript{10, 11}

The magnetic susceptibility $\chi(T)$ is defined as $M(T)/H$, where $M(T)$ is temperature dependent magnetization and $H$ is magnetic field strength. By the temperature dependency of magnetic susceptibility, one can distinguish the magnetic property of the material is paramagnetic, ferromagnetic or antiferromagnetic as shown in Figure 4.

![Figure 4. Characteristic plots of temperature dependence of magnetic susceptibility.\textsuperscript{12}](image)
Chapter IV: Studies on Cu₂SbSe₃(L)ₓ (L=ethylenediamine, propanediamine, butanediamine; x=0.5, 1)

4.1. Introduction

Cu₂SbSe₃(en)₀.₅ and Cu₂SbSe₃(en) of mixed-valent Cu had been reported previously by our group.¹³ These compounds are composed of two-dimensional intermetallic Cu₂SbSe₃ layers separated by free en molecules. The isostructural hybrid compound Cu₂SbS₃(en)₀.₅ was reported in 2000 by Powell et al.¹⁴ This type of hybrid materials exhibited semiconducting properties, which shows the organic spacers give limits effect on the band-gap-related electronic properties. By incorporating the organic amines, the inorganic-organic interfaces were introduced into the structures which can effectively reduce thermal conductivity, making this type of hybrid materials good candidates for thermoelectric applications.

4.2 Result and discussion

Cu₂SbSe₃(en)₀.₅ and Cu₂SbSe₃(en)

Cu₂SbSe₃(en)₀.₅ and Cu₂SbSe₃(en) were obtained by the same starting materials with different reaction temperatures. The optimal reaction temperature for Cu₂SbSe₃(en)₀.₅ is 180°C while the optimal reaction temperature for Cu₂SbSe₃(en) is 150°C. The crystal structures of the two compounds are depicted in Figure 5. The ethylenediamine molecules are positioned between the inorganic layers with different orientations in Cu₂SbSe₃(en)₀.₅ and Cu₂SbSe₃(en). The PXRD patterns are shown in Figure 6 and Figure 7, which match well with the simulated patterns from the reported single crystal structures. Thermogravimetric analysis (TGA) data is plotted in Figure
Figure 9. Cu$_{2}$SbSe$_{3}$(en)$_{0.5}$ shows a single-step weight loss, whereas Cu$_{2}$SbSe$_{3}$(en) shows three-steps weight loss starting at lower temperature. The lower thermal stability of Cu$_{2}$SbSe$_{3}$(en) is caused by the orientation of en molecules. The optical properties are shown in Figure 10 (a)(b), the results are consistent with the reported value of 1.58eV and 1.68eV.

$$(\text{H}_2\text{pda})_{0.5}\text{Cu}_2\text{SbSe}_3$$

$(\text{H}_2\text{pda})_{0.5}\text{Cu}_2\text{SbSe}_3$ crystallizes in the monoclinic space group $P2_1/n$, the compound is composed of two-dimensional intermetallic Cu$_2$SbSe$_3$ separated by protonated pda molecules as shown in Figure 11. The Cu$_2$SbSe$_3$ layers is very similar to the Cu$_2$SbSe$_3$(en)$_X$ compound. The average Sb-Se distance, 2.570Å. Figure 12 depicts the local coordination of the framework atoms, while selected bond lengths and angles are presented in Table 2. The Cu$_2$SbSe$_3$ layer is depicted in Figure 13, and the interlayer distance is about 5.8 Å. The PXRD spectrum of the sample after reaction is displayed in Figure 14. The pattern matches with the simulated patterns of reported single crystal structures, however, the crystallinity is poorer than Cu$_2$SbSe$_3$(en)$_{0.5}$ and Cu$_2$SbSe$_3$(en).

$(\text{H}_2\text{pda})_{0.5}\text{Cu}_2\text{SbSe}_3$ and Cu$_2$SbS$_3$(en)$_{0.5}$ have the same inorganic layer with different diamine molecules parallel to the layers. However, Cu$_2$SbSe$_3$(en)$_{0.5}$ and Cu$_2$SbS$_3$(en) possess the neutral inorganic layers containing Cu$^I$/Cu$^{II}$ and non-protonated amine in the structure. While the X-ray diffraction analysis was incapable of detecting the degree of, the conclusion was supported by magnetic susceptibility and EPR measurements. The paramagnetic behavior indicated Cu$^I$ and Cu$^{II}$ both exist in Cu$_2$SbSe$_3$(en)$_{0.5}$ and Cu$_2$SbSe$_3$(en), and the mix-valance coppers render the neutral layers.
However, diamagnetic property was observed in \((\text{H}_2\text{pda})_{0.5}\text{Cu}_2\text{SbSe}_3\) compound by magnetic susceptibility measurement displayed in Figure 15. Therefore, an anionic layer \([\text{Cu}_2\text{SbSe}_3]^\text{−}\) is rendered by monovalent copper and trivalent antimony. This type of negatively charged inorganic layer had also been observed on the isostructural compound \((\text{H}_2\text{pda})_{0.5}\text{Cu}_2\text{SbS}_3\) with \([\text{Cu}_2\text{SbSe}_3]^\text{−}\) layers separated by protonated amines\(^{15}\). Similar anionic layer was also found in \([\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_2][\text{Ag}_2\text{SbS}_3]\).\(^{16}\)

The optical property of \((\text{H}_2\text{pda})\text{Cu}_2\text{SbSe}_3\) is shown in Figure 16. The absorption edge appears at 1.71 eV. Thermogravimetric analysis result is presented in Figure 17. The 7.13% weight loss before 200°C indicates the organic amines is coordinated in the compound and is similar to the estimated structure with 7.27% of propanediamine.

\((\text{H}_2\text{bda})_{0.5}\text{Cu}_2\text{SbSe}_3\)

The red plate crystals were obtained by the same starting materials of \(\text{Cu}_2\text{SbSe}_3(\text{en})_x\ (x=0.5\ or\ 1)\) and \((\text{H}_2\text{pda})_{0.5}\text{Cu}_2\text{SbSe}_3\) but changing the solvent to butanediamine. The powder X-ray diffraction pattern of this red plate crystal is shown in Figure 18. The first low-angle peak is located at similar position with \([\text{H}_2\text{pda}]\text{Cu}_2\text{SbSe}_3\), which indicates the b-axis of the two compounds has very small difference due to the similarity of propanediamine and butanediamine.

The optical property is shown in Figure 19. The band-gap is estimated to be 1.81 eV from the sharp absorption edge which exhibits the nature of semiconductors. Thermogravimetric analysis was carried out on this sample. The result is illustrated in Figure 20. This compound has one-step weight loss around 200°C and starts to decompose after 350°C. The weight loss is about 7.28%, and the calculated weight loss
for (H$_2$bda)$_{0.5}$Cu$_2$SbSe$_3$ is 8.32%. Diamagnetic behavior is shown in magnetic susceptibility measurement which can be seen in Figure 21. The isostructural compound (H$_2$bda)$_{0.5}$Cu$_2$SbS$_3$ was also reported by Bensch et al.$^{15}$
4.3. Summary

Hybrid materials Cu$_2$SbSe$_3$(L)$_x$ (L=ethylenediamine, propanediamine, butanediame; x=0.5 and 1) were synthesized with different organic amines by the mild solvothermal method. The structure where amines perpendicularly hang in between the inorganic layers can only be obtained with en molecules because of their relatively small chain length. Moreover, the en molecules are perpendicular to the layers in Cu$_2$SbSe$_3$(en) leading to the largest interlayer distance among the hybrid materials. This Cu$_2$SbSe$_3$(en) can only be obtained at lower temperature than Cu$_2$SbSe$_3$(en)$_{0.5}$, suggesting that the structure with en molecule horizontally separating the layer is the thermodynamically stable compound. For 1propanediamine and butanediame, the organic amines tend to be cooperated horizontally. The hybrid materials with neutral charged inorganic layers can be obtained in Cu$_2$SbSe$_3$(en)$_{0.5}$ and Cu$_2$SbSe$_3$(en). All the hybrid compounds have their band gap at 1.6eV-2.0eV, demonstrating their semiconducting nature.
Figure 5. (Left) Crystal structure of Cu$_2$SbSe$_3$(en)$_{0.5}$ and (Right) Cu$_2$SbSe$_3$(en).$^{13}$
Figure 6. PXRD patterns of Cu$_2$SbSe$_3$(en)$_{0.5}$ (black) and simulated pattern from single crystal structure (red).
Figure 7. PXRD patterns of Cu$_2$SbSe$_3$(en) (black) and simulated pattern from single crystal structure (red).

Figure 8. Thermogravimetric analysis of Cu$_2$SbSe$_3$(en)$_{0.5}$.

Figure 9. Thermogravimetric analysis of Cu$_2$SbSe$_3$(en).
Figure 10. Optical absorption spectra of (a) $\text{Cu}_2\text{SbSe}_3$($\text{en}$)$_{0.5}$ and (b) $\text{Cu}_2\text{SbSe}_3$(en).
<table>
<thead>
<tr>
<th>Crystallographic data for $[\text{H}<em>2\text{pda}]</em>{0.5}[\text{Cu}_2\text{SbSe}_3]$.</th>
</tr>
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<td><strong>Empirical formula</strong></td>
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<td><strong>Goodness-of-fit on F²</strong></td>
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<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
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<td><strong>R indices (all data)</strong></td>
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Figure 11. Perspective views of $[\text{H}_2\text{pda}]_{0.5}[\text{Cu}_2\text{SbSe}_3]$ along the $c$ direction. Pink balls represent Sb atoms, yellow balls represent Cu, and light blue balls represent Se. The H and O atoms are omitted for clear views.
Figure 12. Local coordination of the framework atoms in (H$_2$pda)$_{0.5}$Cu$_2$SbSe$_3$.

Table 2. Bond lengths [Å] and angles [°] for (H$_2$pda)$_{0.5}$Cu$_2$SbSe$_3$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
<th>Angle [°]</th>
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<tr>
<td>Sb(1)-Cu(2)#2</td>
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<td>Cu(1)-Se(1)</td>
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<td></td>
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<tr>
<td>Cu(1)-Sb(1)#5</td>
<td>2.6759(9)</td>
<td></td>
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<tr>
<td>Cu(2)-Se(1)</td>
<td>2.3732(10)</td>
<td></td>
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<tr>
<td>Cu(2)-Se(3)#5</td>
<td>2.4072(9)</td>
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<tr>
<td>Cu(2)-Se(2)#6</td>
<td>2.4195(9)</td>
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#1 x-1/2,-y+1/2,z+1/2  #2 x-1/2,-y+1/2,z-1/2
#3 x,y,z-1             #4 x+1,y,z             #5 x+1/2,-y+1/2,z-1/2
#6 x+1/2,-y+1/2,z+1/2
Figure 13. The inorganic layer Cu$_2$SbSe$_3$ projected along the b-axis.

Figure 14. PXRD patterns of [H$_2$pda]$_{0.5}$[Cu$_2$SbSe$_3$]$_{0.5}$ (red) and simulated pattern from single crystal structure (black).
Figure 15. The magnetic susceptibility $\chi$ vs temperature for $[\text{H}_2\text{pda}]_{0.5}[\text{Cu}_2\text{SbSe}_3]$. 

Figure 16. Optical absorption spectra of $[\text{H}_2\text{pda}]_{0.5}[\text{Cu}_2\text{SbSe}_3]$. 

Figure 17. Thermogravimetric analysis (TGA) of $[\text{H}_2\text{pda}]_{0.5}[\text{Cu}_2\text{SbSe}_3]$. 

Figure 18. PXRD patterns of $\text{Cu}_2\text{SbSe}_3(\text{bda})_{0.5}$ (red) and $[\text{H}_2\text{pda}]_{0.5}\text{Cu}_2\text{SbSe}_3$ (black).
Figure 19. Optical absorption spectra of $[\text{H}_2\text{bda}]_{0.5}\text{Cu}_2\text{SbSe}_3$.

Figure 20. Thermogravimetric analysis (TGA) of $[\text{H}_2\text{bda}]_{0.5}\text{Cu}_2\text{SbSe}_3$. 
Figure 21 The magnetic susceptibility $\chi$ vs temperature for [H$_2$bd]**{0.5}[Cu$_2$SbSe$_3$].
Chapter V: Thermal conductivity study of Cu$_2$SbSe$_3$(L)$_x$ hybrid materials and the CuSbSe$_2$ semiconductor

Thermal conductivity is obtained by experimental measurements of thermal diffusivity and specific heat. The thermal diffusivity measurements were performed on Netzsch Instrument laser flash apparatus LFA 457 Microflash, and the specific heat measurements were carried out using Netzsch Instruments DSC204F1. Thermal conductivity is defined by the following equation:

$$\lambda(T) = d(T) \times \rho(T) \times c_p(T) \quad \textbf{Equation 1}$$

Where, $\lambda = \text{thermal conductivity}$

$d = \text{thermal diffusivity}$

$c = \text{specific heat}$

$\rho = \text{density}$

In order to understand the role of organic amines in hybrid material on the effects of thermal conductivity, a ternary inorganic semiconductor CuSbSe$_2$ was selected as a reference to be compared with the hybrid materials. CuSbSe$_2$ exhibits the semiconducting nature with relatively small band gap 1.05eV. CuSbSe$_2$ has been recently studied on the thermoelectric properties and solar energy applications. The synthesis and crystal structure of this compound was reported by many workers. The structure of CuSbSe$_2$ is composed by double-layered arrangement with the Sb$^{III}$ bonded to 3Se atoms forming a trigonal pyramidal structure. And Cu$^I$ is bonded to 4 Se atoms forming tetrahedral structure. Interestingly, there are secondary Sb-Cu interactions and Sb-Se interactions between the layers as shown in Figure 22. The distances of the interactions are less than
the sum of the respective van der Waals radii. The neighboring CuSbSe\textsubscript{2} layers are interconnected by the secondary interactions, giving a 3-D structure of CuSbSe\textsubscript{2}.\textsuperscript{18} On the other hand, the hybrid materials Cu\textsubscript{2}SbSe\textsubscript{3}(L)\textsubscript{x} (L=ethylenediamine, propanediamine and butanediamine) are composed by copper thioantimonates layers, the interlayer distances can be tuned by using amine ligands with different length.

The results of thermal diffusivities and heat capacities of Cu\textsubscript{2}SbSe\textsubscript{3}(en)\textsubscript{0.5}, Cu\textsubscript{2}SbSe\textsubscript{3}(en), (H\textsubscript{2}pda)Cu\textsubscript{2}SbSe\textsubscript{3}, (H\textsubscript{2}bda)Cu\textsubscript{2}SbSe\textsubscript{3} and CuSbSe\textsubscript{2} are shown in Figure 23-24. The thermal conductivities of the four semiconductors were obtained by the Equation 1. The calculated results are plotted in Figure 25.

Table 3 shows the thermal diffusivities, heat capacities, densities and thermal conductivities of Cu\textsubscript{2}SbSe\textsubscript{3}(en)\textsubscript{0.5}, Cu\textsubscript{2}SbSe\textsubscript{3}(en), (H\textsubscript{2}bda)Cu\textsubscript{2}SbSe\textsubscript{3} and CuSbSe\textsubscript{2} at room temperature. For hybrid materials, the thermal conductivity decrease when longer organic alkyldiamins chains are employed. This is because the interlayer distances of the hybrid materials increase as a function of organic alkyldiamines chain length. While Cu\textsubscript{2}SbSe\textsubscript{3}(en)\textsubscript{0.5} and Cu\textsubscript{2}SbSe\textsubscript{3}(en) have the same organic amine in their structures, the perpendicular ethylenediamine accounts for the bigger distance between the layers of Cu\textsubscript{2}SbSe\textsubscript{3}(en) than Cu\textsubscript{2}SbSe\textsubscript{3}(en)\textsubscript{0.5} causing the lower thermal conductivity observed. The interlayer distances of Cu\textsubscript{2}SbSe\textsubscript{3}(en)\textsubscript{0.5} and Cu\textsubscript{2}SbSe\textsubscript{3}(en) are 5Å and 6.8Å, respectively. In the isostructural system, [H\textsubscript{2}bda]\textsubscript{0.5}Cu\textsubscript{2}SbS\textsubscript{3} exhibited shorter interlayer distances than [H\textsubscript{2}pda]\textsubscript{0.5}Cu\textsubscript{2}SbS\textsubscript{3} despite the higher number of carbon atoms of butanediamine. This phenomenon was explained by Bensch as following, the position of N atoms and S atoms seem to favor the N-H···S bonds and decrease the interlayer distance.\textsuperscript{15} However, Se is less electronegative, the N-H···Se bonds are less favored in our [H\textsubscript{2}bda]\textsubscript{0.5}Cu\textsubscript{2}SbSe\textsubscript{3}
hybrid compounds. Therefore, the increase of interlayer spacing with longer alkylidiamines chain length can be predicted.

Relative density can be used as a criterion to estimate the porosity of the pellet. Ideally, the best annealing condition can make a pellet 100% of its molecular density. Due to the nature of our hybrid materials, high relative densities can be achieved under low annealing temperature (80°C). However, for an inorganic material such as CuSbSe₂, it is difficult to reach ideal annealing condition under 280°C. The highest relative density of CuSbSe₂ obtained was 77.6%, resulting the thermal conductivity lower than the reported thermal conductivity (~2.5 W/mK at room temperature). The relative density of (H₂bda)₀.₅Cu₂SbSe₃ was not calculated because the molecular density is unknown.
Summary

New inorganic-organic hybrid materials composed by 2D copper-antimony selenides layers have been synthesized and characterized. Low thermal conductivity is achieved in the inorganic-organic hybrid materials, as a result of the increase in the inorganic-organic interfaces. Compared with the inorganic semiconductor CuSbSe$_2$, the hybrid compounds have the lower thermal conductivity due to the presence of inorganic-organic interfaces. The thermal conductivity value decreases along with the increase of the length of organic amines. The optimization of thermoelectric performance by utilizing the hybrid materials may be a promising strategy and certainly more in-depth studies are needed to fully understand the origin of the reduction in their thermal conductivity.
Figure 22. 3-D extended network structure of CuSbSe$_2$, the secondary Cu-Sb interactions are connected and Sb-Se interactions are omitted for clarity.

Table 3. Thermal diffusivity, specific heat, density, relative density and thermal conductivity of Cu$_2$SbSe$_3$($L_x$) and CuSbSe$_2$ at room temperature (25°C).

<table>
<thead>
<tr>
<th></th>
<th>Thermal diffusivity (mm$^2$/S)</th>
<th>Specific heat (J/g/K)</th>
<th>Density (g/cm$^3$)</th>
<th>Relative density percentage</th>
<th>Thermal conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$SbSe$<em>3$(en)$</em>{0.5}$</td>
<td>0.157</td>
<td>0.478</td>
<td>3.68</td>
<td>80.8%</td>
<td>0.276</td>
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<tr>
<td>Cu$_2$SbSe$_3$(en)</td>
<td>0.177</td>
<td>0.449</td>
<td>3.34</td>
<td>88.9%</td>
<td>0.265</td>
</tr>
<tr>
<td>(H$_2$bd$<em>a$)$</em>{0.5}$Cu$_2$SbSe$_3$</td>
<td>0.128</td>
<td>0.493</td>
<td>3.41</td>
<td>NA</td>
<td>0.216</td>
</tr>
<tr>
<td>CuSbSe$_2$</td>
<td>0.483</td>
<td>0.390</td>
<td>4.71</td>
<td>77.6%</td>
<td>0.889</td>
</tr>
</tbody>
</table>
Figure 23. Thermal diffusivities of Cu$_2$SbSe$_3$(en)$_{0.5}$, Cu$_2$SbSe$_3$(en), (H$_2$bd)$_{0.5}$Cu$_2$SbSe$_3$ and CuSbSe$_2$.

Figure 24. Specific heats of Cu$_2$SbSe$_3$(en)$_{0.5}$, Cu$_2$SbSe$_3$(en), (H$_2$bd)$_{0.5}$Cu$_2$SbSe$_3$ and CuSbSe$_2$. 
Figure 25. Thermal conductivities of Cu$_2$SbSe$_3$(en)$_{0.5}$, Cu$_2$SbSe$_3$(en), (H$_2$bd$_a$)$_{0.5}$Cu$_2$SbSe$_3$ and CuSbSe$_2$. 
References