Thesis Changes Log

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PhD Program: Materials Science and Engineering

Title of Thesis: FIRST-PRINCIPLES STUDY OF ADVANCED THERMOELECTRIC MATERIALS: METHODOLOGY AND APPLICATION

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The thesis document includes the following changes in answer to the external review process.

(1) p61… Modes with imaginary frequency point out that the corresponding compounds are unstable. Usually, the phonon spectrum with imaginary modes cannot be used to extract thermodynamic properties. This should be mentioned and discussed. Table 3.1 contains numerous compounds with positive E_above_hull. Do all of them have imaginary modes? Can you estimate the impact of imaginary modes on the accuracy of ZT calculation?

I did a modification of this paragraph and added more discussion:

"In Table 3.1, all novel compounds we found promising to be good thermoelectric materials are listed with their thermoelectric properties. The lattice thermal conductivity and figure of merit data of some compounds are missing in the table, because there is serious imaginary frequency in their phonon spectrum. Therefore, these compounds are dynamically unstable at least at 0 K and our model cannot calculate their lattice thermal conductivity properly. However, this doesn't mean these compounds cannot exist, since they could become stable and their phonon spectrum could have no minus frequency at high temperature. A representative compound like this is cubic-GeTe, it is unstable and its phonon spectrum has serious imaginary frequency at 0 K, However, it becomes stable and was also verified to have high figure of merit in experiment at high temperature. We still mark these compounds as promising due to their high power factor values."

In table 3.1, there are many compounds having positive energy above convex hull, but not all of them have imaginary frequency in their spectrum. For example, $Co_4P_4Se_4$, $Co_4As_4Se_4$, $Al_4Hg_2Se_8$, MgTe *et al*. they have small positive energy above the convex hull, but their phonon spectrums

totally have no imaginary frequency. Thus, their lattice thermal conductivity and figure of merit can be calculated without influence from imaginary frequency.

(2) The thesis is lacking a discussion/summary section covering advantages and disadvantages of the proposed materials in a concise way. It would be useful to give some insights regarding the physical reasons for improved thermoelectric properties of the newly proposed compounds. Which compound is the most promising one and should be considered for synthesis in the first place?

For "*a discussion/summary section covering advantages and disadvantages of the proposed materials in a concise way*", this is a good idea. In the revised manuscript, I added one more subsection "**4.16 Discussion**" in **Chapter 4**. In this subsection, I gave a short summary about some characteristics that good thermoelectric materials share according to our calculation. I also listed 10 most promising thermoelectric compounds founded in this work, with properties relevant for experimental synthesis:

"

The above sections introduce part of the promising thermoelectric materials founded in this work. From their data of structure and transport properties, we can get some clues about what makes a good thermoelectric material. For cubic compounds, due to their high symmetry, the conduction band or valence band along specific directions in the Brillouin zone could have high band degeneracy, which means there will be multiple carrier pockets involved in transport process. In this case, the DOS effective mass for conduction band or valence band could be large, while the conductivity effective mass of carriers could keep small. Therefore, both Seebeck coefficient and electrical conductivity of them could be high, leading to a high power factor. Meanwhile, if the cubic compounds contain some heavy elements, such as in $MAcTe_2$-like compounds, the phonons could be efficiently scattered and their lattice thermal conductivity could be greatly reduced. For tetragonal and orthorhombic compounds, the band degeneracy of their conduction or valence bands is not large ($N < 4$) because of their lower symmetry. Thus, the power factor of these compounds is not as high as that of cubic compounds. However, the tetragonal and orthorhombic compounds have much more chance to have low lattice thermal conductivity. According to our calculation, those materials, such as SnSe-like compounds, $Ba_4Cu_8Te_8$, $Cs_6Cu_4Bi_{10}S_{20}$, have their κ_L as low as the amorphous limit. Such a low κ_L originates from their structure: they are anisotropic, contain layers or voids with heavy atoms (such as Ba, Cs) loosely bonded to surrounding atoms. Thus, these compounds have strong anharmonicity intrinsically in their lattice. In order to accurately calculate their κ_L, in principle the high order interaction beyond three-phonon process should be

included. However, such a calculation is always time-consuming. In our model, the overall anharmonicity is mainly reflected by the value of phonon velocity and Grüneisen coefficient. It seems our model tend to underestimate κ_L of those compounds with strong anharmonicity (as shown in Fig. 2.6, 4.33, 4.43, 4.47b), mainly because the calculated Grüneisen coefficients are quite large (Table 1 in Ref. [111], Table 4.9, 4.13). More accurate κ_L could be obtained if the accuracy of Grüneisen coefficients can be improved.

Furthermore, for the convenience of experimental verification, 10 compounds introduced in the previous sections, which we think as the most promising thermoelectric materials, are selected and shown in Table 4.20. Experimental investigation on these compounds is strongly encouraged.

Table 4.20. The most promising thermoelectric compounds founded in this work, expecting for experimental verification

Formula	Crystal system	Stability	doping	Including toxic element	Including expensive element	PF_{max} ($\mu W \cdot cm^{-1} \cdot K^{-1}$)	$\kappa_{L,300K}$ ($W \cdot m^{-1} \cdot K^{-1}$)	ZT_{max}
$Co_4P_4S_4$	Cubic	Stable	p	No	No	101.50	32.66	0.79
$Sn_4Pt_4Se_4$	Cubic	Stable	p	No	Yes	63.22	4.38	1.51
Cd_4Se_8	Cubic	Stable	n	Yes	No	21.77	2.06	1.35
$Hg_2In_4S_8$	Cubic	Stable	p	Yes	No	41.04	2.79	1.30
$Nb_6Sb_4Te_{10}$	Cubic	Stable	p	No	Yes	37.13	5.21	1.11
$Dy_8P_8S_8$	Orthor-hombic	Stable	n, p	No	No	10.52 (n) 17.63 (p)	2.29	1.11 (n) 1.21 (p)
Ge_4Se_4	Orthor-hombic	Stable	n	No	No	12.54	0.41	3.17
$Cu_4Sb_4Se_8$	Orthor-hombic	Stable	n	No	No	12.82	2.34	1.09
$Ba_2Hf_1S_4$	Tetragonal	Stable	n, p	No	No	16.68 (n) 34.08 (p)	0.89	2.63 (n) 3.70 (p)
Ga_2Te_5	Tetragonal	Stable	n	No	Yes	25.12	1.51	2.54

"

well, this "high band degeneracy is beneficial for improving power factor" theory is not proposed by me. Actually, it has been proposed more than 10 years and have been verified by many theoretical and experimental works [1-6]. For now, this theory is a kind of "golden standard" in thermoelectric community. I just use it to explain the results of my calculation. You remind me that I should give a clearer explanation about how it comes. Thus, I extended the third paragraph in Sec. 3.3 and gave more explanation.

"

What simple properties are strongly correlated with the thermoelectric properties, such as the power factor? As shown in Section 2.2, the effective mass (m^*) appears in many places and is the key parameter to determine the scattering rate of each scattering process involved. According to single parabolic band approximation, the Seebeck coefficient is proportional to the density of states effective mass m_d^* [74],

$$\alpha \approx \frac{2\pi^{2/3} k_B^2 T m_d^*}{3^{5/3} e n^{2/3} \hbar^2}(r+3/2)$$

whereas the carrier mobility is inversely proportional to the conductivity effective mass m_c^* (eq. 2.13). m_d^* can be increased either by increasing band degeneracy N or by increasing $m_\parallel^* m_\perp^{*2}$ (eq. 2.23). However, increasing the latter will also increase m_c^* (eq. 2.24). Therefore, the ideal situation would be the band degeneracy N is very large while $m_\parallel^*$ and $m_\perp^*$ keep small. In this case, a material should have large power factor. This is possible if the conduction band or valence band locates along specific directions in Brillouin zone for those high-symmetrical compounds (such as cubic ones), or make several different bands converge to the same energy level…

"

You talked about absolute uncertainties or error bar of the calculation. Actually, in Sec. 2.3.2, one of the quantities we used to measure the agreement between experimental data and calculated data is RMSrD (Root Mean Square relative Deviation), which can be seen as uncertainty. The RMSrD of our lattice thermal conductivity model is around 30%, which means generally the calculated value is 30% different from the experimental value. For electronic transport properties model it is much more complex, since there are more parameters influencing the calculated results, such as the input carrier concentration from experiment. It is hard to give a quantitative estimation about the error bar of the calculation. About adding discussions of accuracy of ZT, I think this is a good suggestion. In the revised manuscript, I added one more subsection "**2.3.4. Testing of the figure of merit**" in **Chapter 2**,

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The above shows the tests for model of lattice thermal conductivity and model of electronic transport properties, respectively. However, the thermoelectric figure of merit is the combination of these quantities; thus, how accurate of the program for this combinatorial property? we calculated the figure of merit for 3 well-known thermoelectric materials and compared the results with the experimental values. The Table 2.6 lists the compounds and their experimental conditions.

Fig. 2.9 shows the calculated figure of merit compared with experimental values for the testing set. The situation could be quite different for different compounds. For example, for PbTe, the calculated *ZT* matches with the experimental values quite well for both n-type and p-type transport. For SnSe, the calculation agrees with the experiment well below 700 K. Above 700 K, the difference becomes larger. That's because, first, SnSe goes through a phase transition from α-phase (s.g. *Pnma*) to β phase (s.g. *Cmcm*) at around 700 K; second, the concentration of holes increases due to the thermal excitation instead of the constant value ($3.3e17$ cm^{-3}) used in the calculation. However, if using a higher hole concentration ($5e18$ cm^{-3}, from the experimental measurement) for α-phase SnSe, the calculated *ZT* is close to the average experimental values measured along different directions in the high temperature range. Thus, the calculation is still reasonable. For Bi_2Te_3, *ZT* is overestimated greatly by the calculation. It is mainly because our calculated lattice thermal conductivity is much lower than that from the experiment (for example, Cal. 0.36 W·m^{-1}·K^{-1} versus Exp. 1.7 W·m^{-1}·K^{-1}, at 300 K). Moreover, Bi_2Te_3 is a typical narrow-gap semiconductor, in which both electrons and holes are excited at an elevated temperature. It has been shown in experiment that the concentrations of both electrons and holes increase greatly above 300 K [143]. This bipolar effect diminishes the Seebeck coefficient and increases the electronic thermal conductivity. In our method, this bipolar effect is not included, and the trends at higher

temperatures cannot be correctly reflected. Therefore, this case reminds us, for a compound with narrow bandgap and very low lattice thermal conductivity (< 1 W·m^{-1}·K^{-1} at 300 K), its figure of merit values are most probably being overestimated by our methods.

Table **Error! No text of specified style in document.**.1. Temperature and doping conditions used for calculating the figure of merit

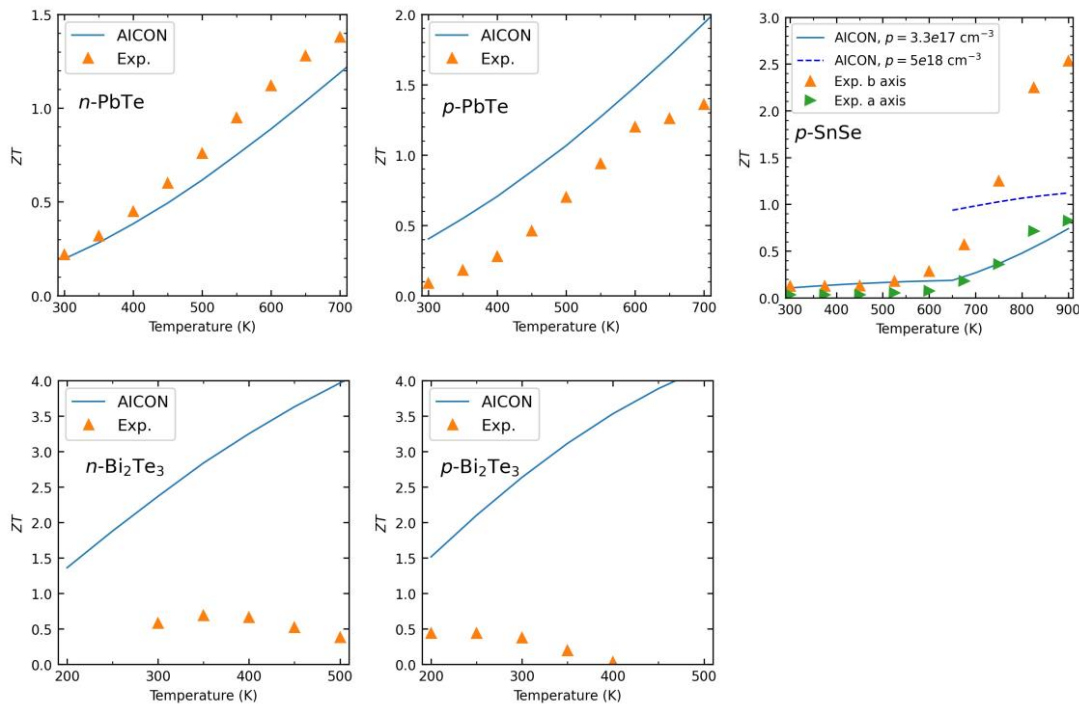| Materials	Doping	T (K)	n (cm^{-3})	Exp. Ref.
PbTe	n-type	300–800	1.8×10^{19}	[77]
PbTe	p-type	300–800	1.4×10^{20}	[136]
SnSe	p-type	300–900	3.3×10^{17} 5.0×10^{18}	[36]
Bi$_2$Te$_3$	n-type	300–500	3.3×10^{19}	[142]
Bi$_2$Te$_3$	p-type	200–500	1.1×10^{19}	[143]

Figure **Error! No text of specified style in document.**.1. Calculated and experimental figure of merit for the test materials at temperatures and carrier concentrations specified in Table 2.6.

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(5) A two-lines introduction to the features of MPJ vs PBE method as for the band gap evaluation could be inserted at page 68 of the thesis.

In the revised manuscript, the last paragraph of **Sec. 3.2**, I added a short introduction about the features of MBJ vs PBE method,

"… we selected two representative compounds, $Co_4As_4S_4$ and Cd_4Se_8, and recalculated their band-structure-related key parameters, including the band gap, deformation potential constant, and band effective mass, using the modified Becke–Johnson (MBJ) method [157,158]. The MBJ potential in combination with LDA-correlation yields band gaps with an accuracy similar to hybrid functional, but computationally less expensive (although still expensive than PBE functional). …"

(6) "In addition, the carrier concentration could change with temperature, whereas we use a fix value in calculation for simplicity." - This sounds like a very crude unphysical approximation. The carrier concentration in semiconductors usually strongly depends on temperature. Clarify why such a crude approximation is considered.

For an extrinsic semiconductor above the room temperature, the carrier concentration could keep stable within some temperature range, because it mainly decided by concentration of donor or acceptor. Meanwhile, for many testing materials I used, the literatures just gave a carrier concentration number and didn't show the change of carrier concentration with respect to temperature. I modified this sentence and gave more explanation at the end of the second paragraph in Sec. 2.3.3,

"… In addition, the carrier concentration could change with temperature, whereas we use a fixed value from the experimental measurement in calculation. Noting such an arrangement is reasonable, since for extrinsic semiconductor above certain temperature, the carrier concentration is decided by the concentration of donor or acceptor (suppose fully ionized), before the intrinsic excitation becomes dominant."

(7) Table 2.1 and other tables - all notations should be clearly explained; even if they seem obvious; \kappa_{cal_cor} is not obvious at all; is this the value with the scaling factor?

I have added the explanation of each notation of Table 2.1 in its caption,

"Table **Error! No text of specified style in document.**.2. Calculated and experimental lattice thermal conductivity [88,117,118] of the test compounds at 300 K ($W·m^{-1}·K^{-1}$). κ_{exp} is the experimental value, κ_{cal} is the calculated value without multiplying scale factor, κ_{cal_cor} is the calculated value with scaling"

(8) Table 3.1 - clarify for which temperature these data are calculated

I added one sentence explanation in the caption of Table 3.1,

"Table **Error! No text of specified style in document.**.3. Novel compounds found to be good thermoelectric materials. Maximum power factor and figure of merit were calculated within temperature range from 300 K to 1000 K"

(9) Why were hexagonal crystal structures excluded from the consideration? There is no explanation in the text.

The hexagonal crystal system was not included in the criteria used for extracting structures from Materials Project database. Because, if including the hexagonal structure, the total amount of structure would be over 2000. For now, we don't have enough resources and time to finish all the calculation. Thus, we decided to start from cubic, tetragonal and orthorhombic structures. In the future, the hexagonal structures will also be calculated. To clarify this, we modified the first paragraph in Sec. 3.1,

"… (5) nonferromagnetic phase, because the band structures of ferromagnetic phases need a special consideration within the DFT and are thus unsuitable for an automatic approach like the one used here. These criteria resulted in over 1000 entries out of the database. Currently, 463 structures (127 cubic, 336 tetragonal and orthorhombic) have been sent to run the transport properties calculation. In the future, more compounds, belonging to hexagonal or other low symmetrical crystal system, will also be calculated."

(10) The description of the crystal structure of DyPS (or $Dy_8P_8S_8$), which belongs to the GdPS type is misleading. The candidate states that phosphorus atoms form layers in the a-b plane that alternate with the two-atom-thick Dy-S blocks. In fact, the analysis of the bond distances shows that phosphorus atoms form zigzag chains withing the a-b plane with the P-P distance of about 2.2 Å, prerequisite of a single P-P bond. Therefore, one of the structural units is the $_1(P^{-1})$ chain anion, and the compound can be rationalized as $Dy^{3+}P^{-1}S^{-2}$ leading to expected semiconducting properties.

Thank you for this clarification. In the revised manuscript, we modified the first paragraph in Sec. 4.7 as,

"This compound adopts a layered orthorhombic structure with a space group *Pnma* (Fig. 4.27). There are two-atom-thick DyS slabs (along the *a-b* plane) with strong Dy–S bonding within the plane of the slabs. Each Dy (or S) atom is bonded to five neighboring S (or Dy) atoms in a distorted zig-zag-type structure. The P atoms form zigzag chain along the *a* axis direction within the *a-b* plane. The bond length of P-P atoms is about 2.23 Å, prerequisite of a single P-P bond. Therefore, one of the structural units is the $_1(P^{-1})$ chain anion, and the compound can be rationalized as $Dy^{3+}P^{-1}S^{-2}$…"

It is true that band gap is a good indicator for good thermoelectric materials. The ideal band gap for a compound should be $6\,k_BT - 10\,k_BT$ at temperature T. I consider this point at the beginning of the research. One of the selection rules used to extract structures from database is the band gap should be larger than 0 eV but smaller than 1.2 eV. It is known that GGA-PBE functional usually underestimate the band gap (averagely 50%). However, a more accurate band gap doesn't mean more accurate transport properties. Two main reasons: first, band gap is not the only key parameter from band structure. We could use a more accurate functional, such as MBJ, to calculate the band gap. As shown in Sec. 3.2, however, the improvement of power factor using a more accurate functional is not large compared with using PBE, because the band effective mass can also be enlarged by MBJ, which is harmful for carrier mobility and may reduce the power factor. Second, the main function of band gap in our model is indicating the band nonparabolicity, as shown in the eq. 2.21. The larger the band gap, the closer the energy band to single parabolic band model. Usually, single parabolic band model tends to underestimate the scattering rate of carriers because it doesn't involve the interaction from other energy bands. In our relaxation time model, we only consider acoustic phonon, polar optical phonon and ionized impurity scattering processes, while other scattering processes, such as nonpolar optical phonon scattering, inter-valley scattering, grain boundary, are omitted. Therefore, we intentionally hope the nonparabolicity could be stronger so that the scattering rate of the current implemented model could be larger to offset the deficiency of the model itself. By this way, the calculated transport properties could be closer to the experimental values.

In the revised manuscript, I added more discussion of this issue at the last paragraph of **Sec. 3.2**,

"… As can be seen, the gain is quite small using a more accurate gap value. Moreover, the main function of band gap in our model is indicating the band nonparabolicity, as shown in the eq. 2.21. The larger the band gap, the closer the energy band to single parabolic band model. Usually, single parabolic band model tends to underestimate the scattering rate of carriers because it doesn't involve the interaction from other energy bands. In our relaxation time model, we only consider acoustic phonon, polar optical phonon and ionized impurity scattering processes, while other scattering processes, such as nonpolar optical phonon scattering, inter-valley scattering, grain

boundary, are omitted. Therefore, we intentionally hope the nonparabolicity could be stronger so that the scattering rate of the current implemented model could be larger to offset the deficiency of the model itself. By this way, the calculated transport properties could be closer to the experimental values. Therefore, the PBE method is still the best choice providing a balance between accuracy and speed."

(12) Currently, thermal transport, i.e. the lattice thermal conductivity, is mainly based on nonlinear phonon interaction (3 phonons). This is good for many packed systems such as Si or similar systems. But, for Cs- and Ba-containing systems, some loosely packed systems, and/or SnSe-like materials, there may exist rattling modes or phonon interaction beyond 3-phonon scattering. In that way, lattice thermal conductivity should be evaluated in a modified way. Accurate evaluation of this point could be very difficult, but a relatively in-depth discussion for certain materials with this character should be included in the thesis.

Yes, the current implemented model for lattice thermal conductivity only considers the three-phonon process. For those compounds with strong anharmonicity, such as SnSe-like compounds, the contribution from high-order interaction also have large proportion. However, such a calculation is always time-consuming. In our model, the effect of high-order interaction is included in the values of phonon velocity and Grüneisen coefficient, that is, strong anharmonicity should result in low phonon velocity and large Grüneisen coefficient. According to our test, the lattice thermal conductivity of compounds with strong anharmonicity is usually underestimated by our model, mainly because of the large Grüneisen coefficient. I added one more subsection "**4.16 Discussion**" in **Chapter 4**. In the first paragraph of this subsection, I added more discussion for certain materials with strong anharmonicity,

"… For tetragonal and orthorhombic compounds, the band degeneracy of their conduction or valence bands is not large ($N < 4$) because of their lower symmetry. Thus, the power factor of these compounds is not as high as that of cubic compounds. However, the tetragonal and orthorhombic compounds have much more chance to have low lattice thermal conductivity. According to our calculation, those materials, such as SnSe-like compounds, $Ba_4Cu_8Te_8$, $Cs_6Cu_4Bi_{10}S_{20}$, have their κ_L as low as the amorphous limit. Such a low κ_L originates from their structure: they are anisotropic, contain layers or voids with heavy atoms (such as Ba, Cs) loosely bonded to surrounding atoms. Thus, these compounds have strong anharmonicity intrinsically in their lattice. In order to accurately calculate their κ_L, in principle the high order interaction beyond three-phonon process should be included. However, such a calculation is always time-consuming. In our model, the overall anharmonicity is mainly reflected by the value of phonon velocity and Grüneisen

coefficient. It seems our model tend to underestimate κ_L of those compounds with strong anharmonicity (as shown in Fig. 2.6, 4.33, 4.43, 4.47b), mainly because the calculated Grüneisen coefficients are quite large (Table 1 in Ref. [111], Table 4.9, 4.13). More accurate κ_L could be obtained if the accuracy of Grüneisen coefficients can be improved."

(13) Corrected some typos.

(14) Update the Table of Contents, List of Figures and List of Tables.