THERMOELECTRIC PROPERTIES IN $Ga_2Te_3 - GaSb$ VACANCY COMPOUNDS

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ABSTRACT

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Thermoelectric materials with high figure of merit, which requires large Seebeck coefficient, large electrical conductivity and low thermal conductivity, are of great importance in solid state cooling and power generation. Solid solution formation is one effective method to achieve low thermal conductivity by phonon scattering due to mass and strain field fluctuation. This type of scattering is maximized in structures containing vacancies. The thermoelectric properties of the vacancy compounds of Ga₂Te₃ – GaSb are studied in this research. We find that the lattice thermal conductivity is reduced by over an order of magnitude with the addition of only very moderate amounts of Ga₂Te₃. Additionally, both the carrier type and concentration can be modified with the addition of Ga₂Te₃. While the vacancy structure induced by the addition of Ga₂Te₃ to GaSb can effectively reduce phonon conductivity, carrier mobility is also degraded. Thus the optimized thermoelectric properties require careful control of the vacancy content in these solid solutions. The effect of preparation methods on thermoelectric properties of these solid solutions has also been studied. The influence of extrinsic doping and isoelectronic substitution on thermoelectric performance of Ga₂Te₃ – GaSb is also discussed in this work.

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CHAPTER 1 Introduction to Thermoelectric Materials

With the rise in demand for energy and the increase in environmental problems caused by combustion of fossil fuels over the world, the thermoelectric materials are receiving more and more attention in recent years. Home heating, vehicle exhaust and industrial processes all generate enormous amount of heat. In our daily life, two third of the energy is emitted in the form of heat which results not only in the pollution of the environment, but also huge energy waste. Thermoelectric materials, which can absorb and liberate heat under current excitation and convert thermal energy into electric energy, are regarded as an environment-friendly solution to increasing energy efficiency.

1.1 Thermoelectric phenomena

The thermoelectric effect is a thermodynamically reversible process in conductors with flows of heat and electricity. The most important effects in thermoelectric phenomena are Seebeck effect, Peltier effect and Thomson effect.

The Seebeck effect was discovered by Thomas J. Seebeck in 1823. When a closed circuit is composed of two different kinds of conducting materials and the junctions are at different temperatures, an electromotive force will be observed between the two junctions and a current will be detected in the circuit. This electromotive force is called the Seebeck electromotive force and can be expressed by equation 1^1 :

$$E_{AB} = S_{AB} \times \Delta T \tag{1}$$

where S_{AB} is the relative Seebeck coefficient between the conducting material A and B.

The Peltier effect is a reverse process of Seebeck effect which was discovered by Jean C.A. Peltier in 1834. When a current is introduced into a closed circuit composed of two different kinds of conducting materials, heat is absorbed at one junction and liberated at the other. The heat absorbing rate is proportional to the current which is expressed by equation 2^{1} :

$$\dot{Q}_{AB} = \pi_{AB} I \tag{2}$$

where π_{AB} is the relative Peltier coefficient between material A and B.

The Thomson effect is discovered by William Thomson, who examined the effects of Seebeck and Peltier and concluded that a relation exists between these two coefficients which is expressed by equation 3^1 :

$$\pi = T \times S \tag{3}$$

The Thomson effect is a thermodynamically reversible process of heat absorbing and liberating in a circuit consisting of a single homogenous conducting material, rather than two conductors, when a current and a temperature gradient is in present.

1.2 Thermoelectric circuit

The thermoelectric effects are utilized in the thermoelectric circuit which consists of p-type and n-type semiconducting materials, as is shown in Figure 1^2 .



Figure 1² Thermoelectric circuits for heating/cooling (a) and power generation (b) (For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this thesis)

There are two kinds of thermoelectric circuits with different functions of heating, cooling and power generation. If the circuit is connected to an external power source, the holes and electrons in the two semiconductors will move in the direction shown in (a) and the circuit acts as a refrigerator or a heat pump which will absorb heat at the upper end and liberate the heat at the other, as is shown by Figure 1(a). If a load is placed in the circuit and the temperature difference is introduced at the two junctions, the holes and electrons will be driven down the temperature gradient and a current will be induced which makes the circuit a power generator, as is shown by Figure 1(b).

1.3 Energy conversion efficiency and thermoelectric figure of merit

The energy conversion efficiency is the most important parameter of any thermoelectric materials. For the function of Peltier heating or cooling, we use coefficient of performance ϕ ,

which is rate of absorption or evolution of heat at certain temperature divided by total electric power consumed, to define the conversion efficiency³:

$$\phi_{\max} = \frac{T_{ave}(\sqrt{1 + ZT_{ave}} - 1)}{\Delta T(\sqrt{1 + ZT_{ave}} + 1)} - \frac{1}{2}$$
(4)

For the function of power generation, the efficiency is defined as useful electric power I^2R delivered to the external circuit divided by the rate of heat energy absorption at the source temperature³:

$$\varepsilon = \frac{\Delta T}{T_H} \frac{\sqrt{1 + ZT_{ave}} - 1}{\sqrt{1 + ZT_{ave}} + T_C / T_H}$$
(5)

Equation 5 shows that, with increasing value of ZT_{ave} , the energy conversion efficiency reaches its maximum of Carnot efficiency.

For both case of Peltier heating or cooling and power generation, the energy conversion efficiency increases with increasing ZT. ZT is dimensionless value which is called the figure of merit:

$$ZT = \frac{S^2 \times \sigma}{\kappa} \times T = \frac{P}{\kappa} \times T \tag{6}$$

where S is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, T is absolute temperature, P is called the power factor. So the main objective of study about thermoelectric materials is to increase the figure of merit so as to achieve higher conversion efficiency.

1.4 Design of thermoelectric materials

The figure of merit consists of three parts: Seebeck coefficient, electrical conductivity and thermal conductivity. Large Seebeck coefficient can maintain large electromotive force between the two junctions at certain temperature difference, which increases the electric power output at given rate of heat absorption. High electrical conductivity, that is low resistivity, can minimize the Joule heat generated by the conductors which decreases the energy loss and increases the energy conversion efficiency. Small thermal conductivity can prevent the temperature difference between the junctions from decreasing due to the thermal flow along the conductors. The maintained temperature difference can help to generate the electromotive force by Seebeck effect and convert thermal energy into electrical energy.

The relation between Seebeck coefficient and electrical conductivity and the value of power factor is shown in figure 2^4 . The Seebeck coefficient will decrease with the increasing electrical conductivity. So the highest power factor is achieved in the region of semiconductor.



Figure 2⁴ Nominal dependencies of the Seebeck coefficient, electrical conductivity, and power factor on carrier concentration in a solid

In intrinsic semiconductors, the Seebeck coefficient could be expressed by equation 7^5 :

$$S = \frac{S_e \sigma_e + S_h \sigma_h}{\sigma_e + \sigma_h} \tag{7}$$

where S_e/S_h is the Seebeck coefficient of electron/hole, σ_e/σ_h is the conductivity of electron/hole. Because S_e is negative and S_h is positive, the coexistence of electron and hole will decrease S. Extrinsic doping of semiconductors can increase the concentration of one kind of charge carriers and almost eliminate the other which will prevent the compensation of Seebeck coefficient by electrons and holes. In a doped semiconductor, the Fermi level is close to or even within the conduction band which makes the semiconductor partially degenerate. In this case, the carrier concentration should be expressed by equation 8 under the condition of Fermi-Dirac distribution rather than Boltzmann distribution⁵:

$$n = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi m^* k_B T}{h^2}\right)^{3/2} F_{1/2} \tag{8}$$

where m^* is carrier effective mass and $F_{1/2}$ is Fermi integral in the form of:

$$F_r = \int_0^\infty \frac{x^r}{1 + \exp(x - \eta)} dx \tag{9}$$

The Seebeck coefficient can be expressed by equation 10^5 :

$$S = \mp \frac{k_B}{e} \left[\frac{(\frac{5}{2} + \lambda)F_{3/2 + \lambda}}{(\frac{3}{2} + \lambda)F_{1/2 + \lambda}} - \eta \right]$$
(10)

where η is reduced Fermi energy which equals to E_F/k_BT and λ is carrier scattering parameter which equals -1/2 for lattice scattering and +3/2 for ionized impurity scattering. From equation 8 to 10, we can see that the value of S²n is only controlled by the location of Fermi level (η), the nature of electron scattering (λ) and carrier effective mass (m^{*}). The maximum of S²n is achieved when Fermi level slightly shifts into the conduction band, which indicates a partially degenerate semiconductor⁵.

The electrical conductivity is defined by equation 11:

$$\sigma = ne\mu$$
 (11)

where μ is carrier mobility. Large carrier effective mass may result in high carrier concentration, but also low mobility, because heavy carriers move at low speed. Equation 6 shows that the power factor equals (S² σ), that is (S²ne μ). The value of n× μ leads to the concept of effective mobility which is expressed by equation 12:

$$\mu^* = \mu(m^*)^{3/2} \tag{12}$$

The semiconductor with high effective mobility will have large electrical conductivity.

Thermal energy in solids is transferred primarily by electrons and phonons. So the thermal conductivity κ consists of two parts: κ_E – electronic thermal conductivity and κ_L – lattice thermal conductivity. The electronic thermal conductivity is related to electrical conductivity by Wiedemann-Franz law⁶:

$$\kappa_E = L\sigma T \tag{13}$$

where L is the Lorentz constant. The value of lattice thermal conductivity is usually obtained by subtracting electronic thermal conductivity from the total thermal conductivity. The lattice thermal conductivity could also be expressed by equation 14^{1} :

$$\kappa_L = \frac{1}{3} C_v v_{ph} l_{ph} \tag{14}$$

where C_v is heat capacity per unit volume, v_{ph} is phonon velocity, l_{ph} is phonon mean free path which is equal to phonon velocity times relaxation time for phonon scattering process τ . Phonons in the lattice can be scattered by other phonons, point defects, grain boundaries, charge carriers and so on. The total rate of scattering process, which is the reciprocal of relaxation time τ , equals to the sum of that of different scattering process⁷.

$$\tau^{-1} = \sum_{i} \tau_{i}^{-1} = \tau_{phonon-phonon}^{-1} + \tau_{point-defect}^{-1} + \tau_{grain-boundary}^{-1} + \dots$$
(15)

At high temperature, which is near or above Debye temperature, the phonon – phonon scattering process is predominant. The specific heat is constant at the Dulong-Petit value and the mean free path decreases exponentially with temperature. So the lattice thermal conductivity decreases with increasing temperature. At low temperature, which is well below Debye temperature, the grain boundary scattering is predominant. The mean free path is constant and equals to the grain size, and the specific heat is proportional to T^3 at low temperature. So the lattice thermal conductivity increases as T^3 . As is pointed out above, the lattice thermal conductivity over Debye temperature will decrease with increasing temperature due to the increasing of intensity of vibrations of the lattice. So, at certain temperature, the lattice thermal

conductivity should be smaller for the material with lower Debye temperature. The Debye temperature for an element or compound will decrease with increasing atomic weight, which indicates that, for the elements in the same column of the periodic table, the element with higher atomic weight will have the lower lattice thermal conductivity³.

For the point defect scattering of phonons, the scattering rate is proportional to the concentration of the impurity atom and the square of mass difference between host lattice atom and the impurity atom. So an effective method to increase the phonon scattering by point defect is to make isoelectronic substitution for the host atom with the impurity atom of very different mass.

Because the Seebeck coefficient and carrier concentration could be expressed by Fermi level and the nature of electron scattering, we can write the equation for figure of merit in terms of reduced Fermi energy and electron scattering parameter⁵:

$$z = \frac{\left(\frac{5}{2} + \lambda - \eta\right)^2}{\left(2\frac{k_B^2}{e}FG\exp\eta\right)^{-1} + \left(\frac{5}{2} + \lambda\right)T}$$
(16)

where
$$F = \frac{\mu}{\kappa_L} (m^*)^{3/2}$$
 (17) $G = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$ (18)

Equation 16 shows that that the value of figure of merit depends on the reduced Fermi energy, the electron scattering parameter and factor F. The Fermi level could be controlled and optimized by doping. The variation of electron scattering parameter is small. So the predominant factor to determine the plausibility of thermoelectric application is the value of F, which requires large effective mobility and small lattice thermal conductivity.

In conclusion, the three parameters of Seebeck coefficient, electrical conductivity and thermal conductivity are interrelated, it is difficult to change one without affecting the other two. The most effective way to improve ZT is to use the semiconducting materials with high effective mobility and optimize the Fermi level by doping to achieve large power factor, and at the same time, to scatter phonons (but not electrons) by point defects, grain boundaries, charge carriers, and so on to decrease lattice thermal conductivity without affecting carrier mobility significantly.

1.5 Promising thermoelectric materials and application

In the past decades of research, several promising thermoelectric materials have been developed in the laboratory and applied to industrial and commercial use.



Figure 3⁸ Common n- (a) and p-type (b) thermoelectric materials

As is shown by Figure 3^8 , for room temperature application, the most widely used thermoelectric material is the alloys of Bi₂Te₃ and Sb₂Te₃ with the peak ZT value between 0.8 to 1.1. For mid-temperature application (500 ~ 1000 K), the state-of-the-art materials are PbTe and skutterudite materials. These skutterudite materials are in the form of AB₃ (A=Co, Ni, Fe; B=P, Sb, As) with cage-like structure into which some low-coordination ions, like rare-earth elements, can be filled. The filled atoms will "rattle" within the cage to scatter phonons so as to reduce the thermal conductivity but not affect the electron mobility very much⁹. The solid solution of Ge-Si is suitable for high temperature application (over 1000 K). With the development of nanotechnology, researchers have achieved enhanced ZT in some new materials such as nanocomposites, superlattice thin films, quantum dot superlattices, and nanowires.

Thermoelectric devices are solid-state devices. They are reliable, scalable, silent and environment-friendly. They have no moving parts and do not require refrigerant liquids, such as chlorofluorocarbons, for cooling. They could be applied as thermoelectric generators in the vehicle exhaust pipe or radioisotope thermoelectric generator in aerospace applications. They could be used as thermocouples and thermopiles for temperature measurement. Thermoelectric materials can also be used as refrigerators, such as the climate control seat in vehicles. With further investigation, more promising TE materials and application will be found in the future.

CHAPTER 2 Vacancy compound of thermoelectric materials

Since the total thermal conductivity has electron and lattice components and the electrical thermal conductivity is related to the electrical conductivity by Wiedemann-Franz law, so an effective method to decrease thermal conductivity is to minimize κ_L by scattering phonons. There are several different phonon scattering mechanisms in materials including phonon-phonon scattering, grain boundary scattering, point defect scattering, resonance scattering and charge carrier scattering, and the total rate of scattering equals to the sum of that of different processes⁷. Solid solution formation is one effective way to achieve low thermal conductivity because of point defect scattering which is caused by the mass and strain filed fluctuation^{10,11}. It is proved that the atomic mass difference between the guest and the host and the concentration of the impurity play an important role in the reduction of κ_L . The scattering parameter A can be expressed by equation 19^6 :

$$A = \frac{\Omega_0}{4\pi v^2} x (1 - x) (\frac{\Delta M}{M})^2$$
⁽¹⁹⁾

where Ω_0 , v, x, ΔM , and M stand for the volume of the unit cell, the lattice sound velocity, the fraction of guest atom, the atomic mass difference between the guest and the host and the average mass of the cell respectively. The lattice thermal conductivity is inversely proportional¹² to A^{1/2}. The solid solution of compounds with same crystal structure can help to reduce the lattice thermal conductivity. The isoelectronic substitution, which means the guest and host atom have the same valence, can further increase the figure of merit by preventing the mobility from decreasing. Because the replacing atom remains neutral in the lattice, there is no Coulomb force

that will scatter electrons thus to decrease the electrical conductivity. The examples of solid solution involving isovalent substitution are InSb – GaSb and GaAs – GaSb.

2.1 Introduction of vacancy compound

A vacancy compound is one kind of solid solution with some lattice sites vacant or unoccupied by atoms. Under such a condition, the value of $\Delta M/M$ is maximized at a value of unity ¹³, and this kind of defect structure can be achieved on many lattice sites throughout the crystal, so we can expect strong phonon scattering by point defect in vacancy compound.



Figure 4 The zinc-blende structure of InSb

The solid solution of In_2Te_3 – InSb is one kind of vacancy compound. InSb is a

semiconducting material for infrared detector application, like thermal imaging cameras. InSb possesses the zinc-blende structure. As is shown by figure 4, the lattice sites of the face-centered cubic system are occupied by antimony atoms and the four interstitial sites which are not adjacent are occupied by indium atoms. InSb has excellent power factor due to its highest carrier mobility among all the III – V semiconductors, which is about 80000 cm²/V*s^{7,14}. But the large thermal conductivity of pure InSb at both low and high temperature makes it inappropriate for

the thermoelectric application⁶. The compound of In₂Te₃ also possesses the zinc-blende structure with one lattice site in three on the indium sub-lattice vacant, which means one in every three of the interstitial sites is not occupied by indium atom^{15,16}. Because one vacancy defect is achieved in every three indium sub-lattices throughout the crystal and the value of Δ M/M from equation 19 equals unity, the lattice thermal conductivity of In₂Te₃ is very low compared with that of InSb due to the strong phonon scattering by these vacancy point defects. A solid solution of In₂Te₃ and InSb will introduce the vacancy structure into the material to scatter phonons more effectively thus to decrease the lattice thermal conductivity greatly, and at the same time, optimize the carrier concentration of InSb so as to achieve higher power factor. It is reasonable to expect this formation of solid solution with vacancies can improve the thermoelectric performance.

The stoichiometric composition of this solid solution is $(In_2Te_3)_x(In_3Sb_3)_{1-x}$, and several researchers^{6,17,18} have demonstrated that the solid solution of In_2Te_3 -InSb also crystallizes in the zinc-blende structure with solubility of In_2Te_3 up to 15 mol% (x=0.15). The addition of In_2Te_3 increases the phonon scattering effect by point defect and thus greatly decreases the lattice thermal conductivity both at low and room temperature. Figure 5⁶ shows the change of κ_L of different In_2Te_3 content at 80 K and 300 K respectively. Because the mass and atomic size difference between antimony and tellurium is negligible, little mass and strain field fluctuation is caused by just replacing antimony atom with tellurium atom, so the obvious reduction of κ_L should be due to the occurrence of vacancy structure.



Figure 5⁶ Dependence of κ_L on content of In₂Te₃ Figure 6⁶ Temperature dependence of κ_L

Because Te atom has one more valence electron than Sb atom, the addition of In_2Te_3 into InSb not only introduces vacancy structure but also dopes the solid solution n-type¹⁹. So this solid solution becomes n-type and the electron concentration⁶ in InSb increases from ~10¹⁶ to ~10¹⁹ cm⁻³. The increasing carrier concentration can improve the electrical conductivity, but the Seebeck coefficient will decrease with the increasing σ . Additionally, an increase of σ increases the electronic thermal conductivity, which leads to the increasing of total thermal conductivity and reduction of ZT. Some researchers⁶ studied the deficiency on the In site, which is in the stoichiometric composition of (In_{2.85})_{1- δ}Sb_{2.55}Te_{0.45}. This will result in an even higher vacancy concentration to scatter phonons so as to further reduce lattice thermal conductivity. And because both InSb and In₂Te₃ are ionic compounds, the decreasing amount of In atom will reduce the electrons contributed to the conduction band. The deficiency on the In sites further reduces the thermal conductivity, decreases the carrier concentration and optimizes the Fermi level to achieve higher power factor, which results in an enhanced ZT. Figure 6^6 shows the temperature dependence of κ_L for InSb, In_{2.85}Sb_{2.55}Te_{0.45}, (In_{2.85})_{1- δ}Sb_{2.55}Te_{0.45} and a typical PbTe. As can be seen from figure 6, the κ_L of (In_{2.85})_{1- δ}Sb_{2.55}Te_{0.45} is further reduced and can be comparable to that of the typical state-of-art TE materials, PbTe.

The vacancy compound of In₂Te₃-InSb can achieve higher figure of merit because of effective phonon scattering by vacancies. But there are still some disadvantages of this solid solution. The lattice vacancy in In₂Te₃ is disordered. Although the vacancy can be transformed to order at temperature of approximately 893 $K^{20,21,22}$, this ordering requires special preparation techniques or very long annealing time because of the low diffusivity²³. This will increase the cost and complexity of manufacture process. If the lattice vacancy is disordered, there will be additional scattering center in the materials that lower both the thermal conductivity as well as the electron mobility. The reduced mobility will decrease the electrical conductivity which will harm the ZT. But an ordered state of vacancy, on the other hand, can increase the mobility²⁴ and the energy $gap^{25,26,27}$ which is due to the reduction in entropy and increment in strength of some bonds. The ordering vacancy can improve electrical conductivity and power factor without increasing thermal conductivity. But it is very difficult to achieve ordering state in In₂Te₃ unfortunately.

Another disadvantage of this solid solution is the low solubility of In_2Te_3 which is only 15 mol%. Because every three sites on the In sub-lattice contributes one vacancy, the actual vacancy

concentration is only 5 mol%. If we can increase the vacancy concentration by finding another solid solution with higher solubility, we can improve the effect of phonon scattering and further reduce the thermal conductivity.



Figure 7 The band structure of InSb and GaSb

InSb has a narrow band gap which is only 0.17 eV at room temperature¹⁷. As is shown by figure 7, this narrow band gap allows for little control of its electronic properties near and above room temperature. With narrow band gap, the electrons in the valence band will be excited into the conduction band easily. So the temperature for intrinsic conduction is relatively low and that will decrease the temperature range for extrinsic conduction. Besides, when an electron is excited into conduction band, a hole will be left in the valence band. With the increasing of intrinsic carrier concentration, there will be two types of carrier, electron and hole, in this material. As is shown by equation 7, Seebeck coefficient will be decreased because of the compensation. The narrow band gap often leads to small effective mass²⁸ which results in low carrier concentration, as is shown by equation 8.

2.2 A new kind of vacancy compound: Ga2Te3 - GaSb

The structure and thermoelectric properties of Ga_2Te_3 -GaSb is similar to that of In_2Te_3 -InSb. Ga_2Te_3 also has a defect zinc-blende structure with one in every three sites on the gallium sub-lattice vacant²⁹. But compared with In_2Te_3 -InSb, the solid solution of Ga_2Te_3 -GaSb has several advantages.

Kurosaki²⁰ reports that, in the materials of Ga_2Te_3 prepared by hot pressing, regularly arranged two dimensional vacancy planes are detected throughout the whole area of the sample, which is shown in Figure 8²⁰. These vacancy planes exist along all four [111] directions with approximately 3.5 nm intervals. Kurosaki also reports that, compared with In₂Te₃, Ga₂Te₃ with the 2D vacancy planes can scatter phonons more effectively.





The molecular weight of In_2Te_3 (612.4) is heavier than that of Ga_2Te_3 (522.24), and the Debye temperature evaluated from the sound velocity of In_2Te_3 (159 K) is lower than that of Ga_2Te_3 (245 K)²⁰. So the thermal conductivity of In_2Te_3 should be lower than that of Ga_2Te_3 , but the result is opposite. As can be seen from figure 9²⁰, the thermal conductivity of Ga_2Te_3 is lower which indicates a highly effective phonon scattering mechanism related to ordering vacancies. The ordering state of the vacancy, such as regularly arranged vacancy planes, can also increase the mobility. With increased electric conductivity and reduced thermal conductivity, Ga_2Te_3 can achieve higher ZT value.



Figure 9²⁰ Temperature dependence of thermal conductivity of In_2Te_3 and Ga_2Te_3 . Balls and lines represent the measured and minimum κ values, respectively. Violet and orange symbols represent the results for Ga_2Te_3 and In_2Te_3 , respectively

Another advantage is that GaSb possesses a wider band gap, which is 0.72 eV at room temperature⁷. The wider band gap increases the temperature range for extrinsic conduction and

makes it easier to control the electronic properties by doping. With increasing band gap, there will be fewer intrinsic electrons excited into the conduction band, and the holes left in the valence band will also be fewer in number. This will prevent the Seebeck coefficient from decreasing at high temperatures due to mixed carrier conduction.

The electron effective mass of GaSb which is 0.042 m₀, is higher than that of InSb, which is only 0.014 m_0^7 . The electron kinetic energy can be expressed as:

$$E_k = \frac{\hbar^2 k^2}{2m^*} \tag{20}$$

So the carrier effective mass is inversely proportional to the second derivative of E_k , which is also the curvature of conduction band:

$$m^* = \hbar^2 \left(\frac{d^2 E_k}{dk^2}\right)^{-1}$$
(21)

As is shown by Figure 7, GaSb with large carrier effective mass has flat conduction band edge. From equation 10, we can see that Seebeck coefficient depends only on the location of Fermi level and electron scattering parameter. In the condition of same value of Fermi energy and Seebeck coefficient, GaSb with flat conduction band edge possesses larger gray area which indicates higher carrier concentration. This result agrees with equation 8 that large effective mass leads to high carrier concentration.

The solubility of Ga_2Te_3 -GaSb at 773K extends to 36mol% of $Ga_2Te_3^{19}$ which is greater than that of In_2Te_3 -InSb. The stoichiometric composition of this solid solution is $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$, so the vacancy concentration will be up to 12 mol%. The higher vacancy concentration can help to scatter phonons more effectively so as to achieve better TE performance.

There are also some disadvantages of the solid solution of Ga_2Te_3 -GaSb. Both GaSb and Ga_2Te_3 are initially p-type semiconductors³⁰. The effect of adding Ga_2Te_3 not only introduces vacancies into the solid solution, but also allows for some Te atoms to replace Sb atoms and thus dope the material n-type. So this solid solution, at least for some compositions, shows mixed carrier conduction¹⁹. Mixed n-type and p-type conduction leads to compensating effects which partially cancel out the induced Seebeck voltage⁸.

Although Ga₂Te₃ contains regularly arranged 2D vacancy planes, the doping with GaSb might affect the formation of the vacancy plane and the crystal symmetry^{31,32}. The effect of Ga₂Te₃ concentration on the formation of ordering state of vacancy needs further investigation.

2.3 Thermoelectric properties of Ga2Te3 - GaSb

The solid solution of $Ga_2Te_3 - GaSb$ with a composition of $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$ were prepared by the vacuum melting method. The melting temperatures of these pure elements and compound are displayed in Table 1. As can be seen from Table 1, the melting point for pure gallium is only 303 K which is much lower than others. The stoichiometric quantities of the three pure elements of gallium, antimony and tellurium were put into a quartz ampoule and then the ampoule was sealed under vacuum. The ampoule was vertically hung into a tube furnace. The sample was heated to 1173 K with the heating rate of 1 K/min and soaked at that temperature for about 20 hours to mix all the elements homogeneously in the liquid phase. The slow heating rate of 1 K/min is adopted to prevent volatilization of the elements. Then the sample is slow cooled to 873 K in the furnace with the cooling rate of 0.2 K/min and held at that temperature to anneal for 3 days. After 3 days annealing the sample is cooled down to room temperature with the rate of 0.5 K/min in the furnace. Because of the poor mechanical properties of gallium, the sample prepared by vacuum melting method often contains tiny cracks throughout the body. So the slow cooling rate is applied to minimized the cracks in the sample and prevent the ampoule from explosion due to fast cooling. Another reason for the slow cooling rate is to increase the grain boundary size so as to decrease the effect of grain boundary scattering of phonons. The fast cooling process, such as quenching, will decrease the grain boundary size. Because the objective of the research is to study the effect of vacancy structure on the reduction of lattice thermal conductivity, we want to minimize the contribution of grain boundary scattering of phonons. All the samples, including the zinc and indium doped samples described in chapter 3, are prepared in the same way.

Table 1 Melting temperature of these pure elements and compounds

Materials	Gallium	Antimony	Tellurium	GaSb	Ga ₂ Te ₃
Melting temperature (K)	303	903	723	985	1065

The resulting ingot was cut by low diamond saw into rectangular parallelepiped with dimensions of $3 \times 3 \times 8 \text{ mm}^3$ for thermoelectric property measurement. Additionally, a small piece of the sample was pulverized to prepare a powder for structural characterization. The crystal structure of the sample is measured by powder X-ray diffraction analysis using Miniflex II Desktop X-ray Diffractometer produced by Rigaku Corporation. The electrical and thermal

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properties were measured by bath-type cryostat. The sample was tested under vacuum and measured from 80 K to 300 K using liquid nitrogen as refrigerant. Two thermocouples of copper – constantan were soldered to the sample at two points along its length; these thermocouples are used to measure the temperature difference long the sample. One end of the sample is attached to an 800 Ω resistor which acts as a heater, the other is soldered directly to the copper cold tip of the cryostat. The electrical conductivity is measured by passing current through the sample and recording the voltage between the two copper legs of the thermocouples. When energizing the resistor with current, heat is developed and flows down the sample length. After a steady state is reached, the thermocouples detect the temperature difference which is used to calculate the Seebeck coefficient. The thermal conductivity is calculated by the resistor power, temperature difference and sample dimensions. The carrier concentration and carrier mobility are measured on small Hall bars cut from the same ingot from -3T to +3T using a VersaLabTM produced by Quantum Design, Inc.



Figure 10 XRD patterns for $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$ with different content of Ga_2Te_3 As reported by Woolley¹⁹, the solubility of Ga_2Te_3 in GaSb can reach up to 36 mol%.

Therefore, solid solutions in the composition of $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$ with x varying from 0 to 0.36 are prepared by vacuum melting method. Figure 10 shows that, the samples with the content of Ga_2Te_3 up to 25 mol% possess the single phase of zinc-blende structure. For the samples with 30 mol% and 36 mol% of Ga_2Te_3 , impurity phases are detected around the (111) peak, as is indicated by black dots. Woolley reported that the single phase of the solid solution with 36 mol% of Ga_2Te_3 is achieved after 12 month of annealing at 773 K. So the occurrence of

impurity phase for the present samples with high Ga₂Te₃ content might be due to the insufficient annealing time which in the present case is only 3 days.



Figure 11 Dependence of lattice constant of $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$ on content of Ga_2Te_3

Figure 11 shows that lattice constant of this solid solution with different content of Ga_2Te_3 . The lattice constant of pure GaSb is 6.093 Å and that of pure Ga_2Te_3 is 5.898 Å³³. According to the Vegard's Law, the lattice constant should decrease with increasing amount of Ga_2Te_3 . From Figure 11, the lattice constant decreases linearly with the content of Ga_2Te_3 increasing to 0.15, which indicates that all the Ga_2Te_3 goes into the lattice of GaSb in this composition range. When the content of Ga_2Te_3 is higher than 0.15, the lattice constant saturates, suggesting that a solubility limit has been exceeded in this range. These results are consistent with the onset of impurity phase that we see at high Ga_2Te_3 concentration. Both GaSb and Ga₂Te₃ are initially p-type semiconductors. Because the Te atom has one more valence electron than the Sb atom, we expect that adding Ga₂Te₃ into GaSb will dope the semiconductor to n-type as Te atoms replace some Sb atoms. The hole concentration of pure GaSb sample at 300 K is 3.3×10^{17} cm⁻³, while the sample with 4 mol% of Ga₂Te₃ is n-type with an electron concentration at 300 K of 3.7×10^{18} cm⁻³. Table 2 shows the type of semiconductor with different content of Ga₂Te₃. With increasing Ga₂Te₃ concentration, the electron concentration decreases. When x=0.07, the electron concentration decreases to 1.23×10^{18} cm⁻³ at 300 K. With further increasing amount of Te, the solid solution turns back to p-type at 20 mol% of Ga₂Te₃.

Table 2 Type of semiconductor of $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$ with different content of Ga_2Te_3

Content of Ga ₂ Te ₃	x=0	x=5%	x=10%	x=15%	x=20%	x=25%
Type of semiconductor	Р	Ν	Ν	Ν	Р	Р

For the sample with 10 mol% and 15 mol% of Ga_2Te_3 , the electron concentration is only about 1×10^{17} cm⁻³. As is shown by equation 22, the product of electron and hole concentration is constant. So the hole concentration is not negligible and mixed conduction will occur which will decrease the Seebeck coefficient.

$$n_n n_p = 4 \left(\frac{2\pi m kT}{h^2}\right)^3 \left(\frac{m_n^* m_p^*}{m^2}\right)^{3/2} \exp\left(-\frac{\varepsilon_g}{kT}\right)$$
(22)

Additionally, with large amounts of Ga_2Te_3 , we find that there are more cracks throughout the sample which makes the transport property measurement problematic. For these reasons we focus only on the samples with content of Ga_2Te_3 up to 7 mol% for thermoelectric measurement.

The lattice thermal conductivity of $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$ is shown in Figure 12. Pure GaSb with zinc-blende structure possesses a moderately large thermal conductivity both at high and low temperature. With increasing amount of Ga_2Te_3, the lattice thermal conductivity monotonically decreases. Abdurakh³⁴ reported that, for the solid solution with 5 mol% Ga_2Te_3, a thermal conductivity of 0.08 W/cmK at room temperature. For our sample of this composition, we find a value of 0.075 W/cmK, quite consistent with the reference data.



Figure 12 Dependence of lattice thermal conductivity of $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$ on temperature

As can be seen from Figure 13, the lattice thermal conductivity both at 80 K and 300 K is suppressed by more than one order of magnitude. Because the mass and atomic size difference between Te and Sb is small, the phonon scattering effect caused by replacing an Sb atom by a Te atom should be negligible. So the pronounced decrease in κ_L is evidently due to the occurrence of vacancies on the gallium sub-lattice. At high temperature (300 K), because more phonons are generated in the lattice, the phonon-phonon scattering is predominant. At low temperature (80 K), there are fewer phonons generated, so the grain boundary and point defect scattering are predominant. Because all the samples are prepared in the same method with same cooling rate, the grain size should not differ significantly from sample to sample. Thus the large reduction of κ_L at low temperature is predominantly due to the phonon scattering by point defects. From Figure 13, we can see that the reduction at 80 K is even stronger than that at 300 K, which indicate that the vacancy structure can scatter phonons effectively and reduce the lattice thermal conductivity very strongly.



Figure 13 Dependence of lattice thermal conductivity on content of Ga₂Te₃ at 80 K and 300 K
GaSb is initially p-type semiconductor, but it transitions to n-type when Ga_2Te_3 is added. The reason for this is that some Te atoms replace Sb atoms and provide one valence electron. The electron concentration goes up to 4×10^{18} cm⁻³ when 5 mol% of Ga_2Te_3 is added and the resistivity of the solid solution decreases strongly compared to pure GaSb, which is shown in Figure 14.



Figure 14 Temperature dependence of resistivity of (Ga₂Te₃)_x(Ga₃Sb₃)_{1-x}

With increasing electron concentration, the resistivity decreases when x varied from 0 to 0.04 and the lowest resistivity is reached when the content of Ga_2Te_3 is 4 mol%. With further increase of tellurium, the resistivity of the solid solution rises. Because Ga_2Te_3 possesses large resistivity which is about 500 Ω cm at room temperature, the samples with large amount of Ga_2Te_3 possess high resistivity. The resistivity of the solid solution goes up when x varies from 0.04 to 0.07 which is due to the increasing amount of Ga_2Te_3 . Especially, when x=0.07, the

resistivity increases greatly to about 0.015 Ω cm which is consistent with reference data³⁵. These changes in resistivity may reflect a combination of increased electron scattering³⁶ (see below) and an alteration of the band structure for increasing Ga₂Te₃ content. The sample with 7 mol% of Ga₂Te₃ also possesses the lowest thermal conductivity due to strong phonon scattering by the vacancy structure. So the vacancy on gallium sub-lattice might also affect the electrical property of this solid solution.



Figure 15 Temperature dependence of carrier concentration of $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$

The resistivity of the solid solution could be explained by the variation of carrier concentration and mobility with increasing amount of Ga₂Te₃. Figure 15 shows the temperature dependence of electron concentration. GaSb is p-type semiconductor, the hole concentration is 3.3×10^{17} cm⁻³ at room temperature. After adding Ga₂Te₃ into GaSb, the solid solution changes to n-type and the electron concentration is about 1×10^{18} cm⁻³ for 1 mol% sample. With

increasing amount of Ga₂Te₃, the electron concentration increases and reaches the maximum value when x=0.05. The electron concentration for the 5 mol% sample is about 4×10^{18} cm⁻³ which indicates a strongly degenerate conductor. When the value of x is higher than 0.05, the electron concentration decreases and reaches the minimum value of 1×10^{18} cm⁻³ when x equals 0.07. With increasing amount of Ga₂Te₃, higher vacancy concentration is also achieved in the solid solution. The vacancy can not only scatter phonons to decrease lattice thermal conductivity, but also scatter electrons effectively which reduces the mobility. We will discuss this in the following paragraph. From Figure 15, we can see that the electron concentration is not changing significantly over the temperature range and almost remains constant for all the samples. The reason for this is the large band gap of GaSb which is about 0.72 eV at room temperature. With large band gap, the electron in valence band requires higher energy to be excited into the conduction band. This increases the temperature range for extrinsic conduction and makes it easier to control the electronic properties near and above room temperature by doping.



Figure 16 Temperature dependence of mobility of $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$

For our sample, the hole mobility of GaSb is about 700 cm²/Vs at room temperature which is consistent with the reference data³⁷. As is shown in Figure 16, when the amount of Ga₂Te₃ is 1 mol%, the electron mobility is about 1200 cm²/Vs at room temperature, which is the highest among all the samples. With increasing amount of Ga₂Te₃ and thus more vacancies, the mobility decreases. When the value of x equals 0.07, the mobility decreases greatly to approximately 400 cm²/V×s; in this regime, electrons are scattered by lattice vibration as well as vacancies, and as expected the sample with highest vacancy concentration possesses the smallest mobility. The combination of reduced carrier concentration and mobility is the reason why the sample with 7 mol% of Ga₂Te₃ has very large electrical resistivity. Since the electron scattering process includes phonon-electron scattering, point defect scattering and ionized impurity scattering, such as Te ions placed in Sb sub-lattice, it is difficult to determine the scattering parameter λ . For our sample, the mobility always decreases with temperature, which indicates lattice scattering and point defect scattering are predominant. It is reported that¹¹, for the solid solution of In₂Te₃-InSb with 7 mol% of In₂Te₃, the electron mobility is 1000 cm²/Vs which much higher than our samples. This is because of the small effective mass of InSb which is only 0.014m₀ at room temperature. The vacancy structure can scatter phonons effectively to reduce the lattice thermal conductivity (κ_L). At the same time, vacancies can also scatter electrons to decrease the mobility (μ) and electrical conductivity, so it is useful to calculate the value of μ/κ_L as function of x to determine the optimized content of Ga₂Te₃. The result of this procedure is shown in Figure 17. The maximum value of μ/κ_L is achieved at x=0.04. When x is less than 0.04, the lower value is caused by high lattice thermal conductivity which is due to the low vacancy concentration; when x is larger than 0.04, μ/κ_L is reduced because of the point defect scattering of electrons. Samples with 4 mol% of Ga₂Te₃ should achieve optimized thermoelectric performance.



Figure 17 Dependence of the value of μ/κ_L on content of Ga₂Te₃

GaSb and Ga₂Te₃ are both p-type semiconductors. Nominally undoped GaSb possesses large Seebeck coefficient which is about 600 μ V/K at room temperature. Ga₂Te₃ has even higher Seebeck coefficient of 800 μ V/K²⁰ at room temperature. With the addition of Ga₂Te₃ into GaSb, this solid solution converts to n-type and the Seebeck coefficient decreases as is shown in Figure 18. The absolute value of S first decreases when x changes from 0 to 0.03, and then increases as x increases from 0.04 to 0.07, reflecting the trend in electron concentration.



Figure 18 Temperature dependence of Seebeck coefficient of $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$

As is shown by equation 10, in partial degenerate semiconductor, the Seebeck coefficient is only related to electron scattering parameter (λ) and Fermi level. Because the variance of λ is small, the changing of S is controlled by Fermi energy. Assuming λ =-1/2 which indicates the lattice scattering of electrons is predominant, we calculate the reduced Fermi energy (η) at room temperature from equation 10 and plot it in Figure 19.



Figure 19 Dependence of reduced Fermi energy (η) on Ga₂Te₃ content



Figure 20 Dependence of effective mass on Ga₂Te₃ content

Doping of Ga_2Te_3 increases the Fermi level, which reaches the maximum of 0.23 at x=0.04. With further adding of Ga_2Te_3 , the Fermi level decreases. All the reduced Fermi energy is greater than -2, which indicates that all the Ga_2Te_3 doped samples are partial degenerated semiconductors⁵. From the theory of Fermi-Dirac distribution, the optimized Fermi level should slightly shift into the conduction band. For our sample, when x varies from 0.02 to 0.05, the Fermi level is in the conduction band which is close to the optimized value.

From equation 8, for the partial degenerate semiconductor, the electron concentration is controlled by Fermi energy and effective mass. The room temperature effective mass as a function of x is shown in Figure 20. The effective mass increases with increasing x and reaches the maximum of $0.4m_0$ at x=0.06. The effective mass is quite large compared to that of InSb which is only $0.014m_0$. The large effective mass can help to achieve higher carrier concentration at given Seebeck coefficient.



Figure 21 Dependence of weighted mobility (μ^*) on content of Ga₂Te₃



Figure 22 Dependence of F factor on content of Ga₂Te₃

As is shown by equation 11, the electrical conductivity is controlled by carrier concentration and mobility. Higher effective mass can increase the electron concentration, but can also decrease the mobility, because heavier carriers will move at lower speed. So we calculate the weighted mobility as is shown by equation 12 and plot it in Figure 21. The sample with highest weighted mobility will have the largest electrical conductivity. From Figure 21, the weighted mobility increases first till x=0.04 and then decreases which is consistent well with the result that the sample of x=0.04 has the smallest resistivity (0.0017 Ω cm at room temperature) among all the samples. The F factor which is expressed by equation 17 is shown in Figure 22. F factor is the criterion of materials to determine their suitability for thermoelectric application. The samples of x=0.04 and 0.05 with higher value of factor F will have better thermoelectric performance.

From Figure 23, the highest power factor is achieved when x=0.04, which is mainly due to the largest electrical conductivity of this sample. With additional Ga₂Te₃, the power factor decreases which is caused by the increased resistivity.

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Figure 23 Temperature dependence of power factor of $(Ga_2Te_3)_x(Ga_3Sb_3)_{1-x}$

The figure of merit as a function of temperature is shown in Figure 24. The p-type GaSb has small figure of merit of 0.01 at room temperature, mainly due to the large thermal conductivity. Doping with Ga_2Te_3 increases the figure of merit of this solid solution and achieves the highest value of 0.07 at room temperature when x=0.04. The addition of Ga_2Te_3 improves the electronic properties and the power factor and also introduces vacancy structure to scatter phonons effectively.



Figure 24 Temperature dependence of figure of merit of (Ga₂Te₃)_x(Ga₃Sb₃)_{1-x}

The 4 mol% sample with large value of weighted mobility and Factor F has the highest figure of merit. The decrease of ZT with further increasing amount of Ga_2Te_3 is caused by the reduced electrical conductivity. When more Ga_2Te_3 is added, the carrier concentration is decreased due to the reduction of Fermi energy. And the increased amount of vacancy will scatter electrons that results in lower mobility. From Figure 24, the figure of merit increases exponentially with temperature, and it is reasonable to expect the solid solution of $Ga_2Te_3 - GaSb$ will have better thermoelectric performance at high temperature.

The effective phonon scattering by vacancy structure in the solid solution of Ga_2Te_3 – GaSb strongly deceases the lattice thermal conductivity in this system. The reduction is more than one order of magnitude both at low and high temperature. Introduction of Ga_2Te_3 into GaSb also affects the type and concentration of carriers, and the electrical properties can be optimized

as a function of Ga_2Te_3 content. However, with increasing amount of Ga_2Te_3 , the addition of vacancies also leads to additional carrier scattering and lowers the mobility and electrical conductivity. Therefore in order to obtain higher figure of merit, the amount of Ga_2Te_3 should be controlled to the value where good electrical conductivity and poor thermal conductivity can be achieved simultaneously.

2.4 Effect of preparation method on thermoelectric properties of Ga2Te3 - GaSb

All the above samples with the composition of $(Ga_2Te_3)_X(Ga_3Sb_3)_{1-x}$ are prepared by melting the pure elements of stoichiometric quantities in the sealed ampoule and then followed by slow cooling in the furnace to anneal. Because of the poor mechanical properties of these samples, the slow cooling rate of 0.2 K/min is used to prevent the cracks in the sample which make the transport property measurement problematic. But the slow cooling may cause segregation or some impurity phase during the solidification process which results in the inhomogeneous composition. Small amounts of impurity may be difficult to detect using X-ray diffraction. Besides, the slow cooling rate may also increase the grain size of the crystal which weakens the effect of grain boundary scattering of phonons. In order to test for the occurrence of these proposed effects, a modified sample synthesis procedure was instituted. One sample with 5 mol% of Ga₂Te₃ was quenched from molten state to prevent the segregation and impurity phase in solidification process and decrease the grain size to further reduce the thermal conductivity.

The sample with 5 mol% of Ga_2Te_3 possesses the highest electron concentration which is 4.23×10^{18} cm⁻³ at room temperature. The reason for this is that some Te atoms replace Sb atoms

and provide one electron. When three Te atoms replace Sb atoms on the lattice site instead of forming Ga_2Te_3 , a small amount of antimony is precipitated; the vacancy concentration is also reduced. So I prepared the compounds of Ga_2Te_3 and Ga_3Sb_3 in the first step. After that, I melted these two compounds in the ratio of 5% - 95% together at 1173 K and then slowly cooled in the furnace and annealed for 3 days instead of melting the pure elements. Samples of the same composition of 5 mol% of Ga_2Te_3 were prepared using these two new methods and the data is compared with that of the original sample.



Figure 25 XRD patterns for (Ga₂Te₃)_{0.05}(Ga₃Sb₃)_{0.95} with different synthesis methods

From Figure 25, all the three samples with different synthesis methods possess the zincblende structure with same lattice constant. The data of lattice thermal conductivity is plotted in Figure 26. The two samples with new synthesis methods possess lower κ_L . The reduction of κ_L of the quenched sample is due to the decreased grain size and increased effect of grain boundary scattering of phonons. The quenching process can help to prevent the impurity phase during solidification which leads to higher Ga₂Te₃ and vacancy concentration that decrease the lattice thermal conductivity. Additionally, it is possible that an ordered vacancy state could be formed by quenching, as is reported by Chang-eun Kim³², which can scatter phonons more effectively. The sample prepared by melting 5 mol% Ga₂Te₃ and 95 mol% Ga₃Sb₃ possesses even lower lattice thermal conductivity which is caused by the reduced number of Te atoms replacing Sb atoms and increased vacancy concentration. But the resistivity for the new samples increase compared to the original one. Especially for the sample of 5% - 95%, the resistivity is increased by ten times as is shown in Figure 27.



Figure 26 Temperature dependence of lattice thermal conductivity of $(Ga_2Te_3)_{0.05}(Ga_3Sb_3)_{0.95}$ with different synthesis methods



Figure 27 Temperature dependence of resistivity of (Ga₂Te₃)_{0.05}(Ga₃Sb₃)_{0.95} with different synthesis methods

The reason for the increased resistivity for new samples is the reduced carrier concentration and mobility as is shown by Figure 28 and 29. The electron concentration of the quenched sample is half of the original one which indicates less replacing Te atoms and more vacancies. Vacancy can scatter phonons as well as electrons which leads to low mobility. But the mobility of quenched sample is close to the original one which might be due to the occurrence of an ordered state of vacancy. The ordered state will decrease the number of scattering centers in the lattice thus to increase the mobility. The sample of 5% - 95% has even lower electron concentration. With increased concentration, vacancies scatter phonons greatly that leads to the very small mobility compared to the original sample. There is not much difference of Seebeck coefficient between the quenched sample and the original one, but the sample of 5% - 95% has a fairly large value of S as can be seen from Figure 30. From equation 10, the reduced Fermi energy is -1.06 for the 5% - 95% sample, which is much smaller than that of the original sample (0.14). The new synthesis method of melting the compounds of Ga₂Te₃ and GaSb reduces the Fermi level which is consistent with decreased carrier concentration.



Figure 28 Temperature dependence of carrier concentration



Figure 29 Temperature dependence of mobility



Figure 30 Temperature dependence of Seebeck coefficient of (Ga₂Te₃)_{0.05}(Ga₃Sb₃)_{0.95} with different synthesis methods

From Figure 31, the power factor of the new samples is reduced because of the increased resistivity. Although the new methods reduce the number of Te atoms replacing Sb and increase the vacancy concentration thus to further decrease the thermal conductivity, the lower carrier

concentration and mobility strongly suppresses the figure of merit, as is shown in Figure 32. Increasing the amount of vacancy can reduce the thermal conductivity, but taking into account of the carrier concentration and mobility, we need to control the vacancy concentration in a reasonable range to achieve higher ZT value.



Figure 31 Temperature dependence of power factor of (Ga₂Te₃)_{0.05}(Ga₃Sb₃)_{0.95} with different synthesis methods



Figure 32 Temperature dependence of figure of merit of $(Ga_2Te_3)_{0.05}(Ga_3Sb_3)_{0.95}$ with different synthesis methods

CHAPTER 3 Effect of doping on thermoelectric properties of Ga₂Te₃ – GaSb

In order to optimize the electronic property of this solid solution, the effect of p-type doping and isoelectronic substitution of $Ga_2Te_3 - GaSb$ is studied.

3.1 Thermoelectric property of Zinc-doped sample

Both of the compounds of GaSb and Ga₂Te₃ are p-type semiconductors, but the solid solution with content of Ga₂Te₃ varying from 1% to 15% is n-type. The addition of Ga₂Te₃ greatly decreases thermal conductivity, and the Seebeck coefficient of this solid solution is quite large which is around -200 μ V/K at room temperature, but the large resistivity caused by low carrier concentration reduces the figure of merit. When the content of Ga₂Te₃ is 7%, the room temperature data of resistivity and carrier concentration is 0.015 Ω cm and 1.2×10¹⁸ cm⁻³. Because Zn has one less valence electron then Ga, the replacing of Ga by Zn will increase the hole concentration. So we tried p-type doping of zinc on Ga site to change the electronic properties so as to achieve better thermoelectric performance.

We studied the effect of doping of the solid solution with 4 mol% of Ga_2Te_3 which possesses the highest figure of merit. The samples in the composition of $(Zn_xGa_{1-x})_{2.96}Sb_{2.88}Te_{0.12}$ (x=0, 1%, 2%, 5%, 10%) are prepared by the same vacuum melting method as is stated above. From Figure 33, we can see that all the samples possess zinc-blende structure. For the sample with 10% Zn, the second phase of Sb is detected as is pointed out by the black arrow. Figure 34 shows the lattice constant of samples with different content of Zn. The bending of the line at 5% and 10% of Zn indicates the limit solubility and that not all the Zn atoms replace Ga atoms in the lattice. For the samples with 5% and 10% of Zn, some impurity phases might be formed. Because the compound of ZnTe also crystallizes in zinc-blende structure, it is hard detect in the XRD pattern. The thermal conductivity of these samples increases with increasing amount of Zn which will be discussed in detail later. It is consistent with the fact that ZnTe has large thermal conductivity (about 0.18 W/cmK at room temperature³⁸). Because it takes one more Zn atom to form the compound of Zn₃Te₃ than Zn₂Te₃, when more ZnTe is formed, there will be not enough Zn atoms to balance the Sb atoms which results in the precipitated Sb. This agrees with the second phase of Sb in 10% Zn sample shown by Figure 33. So it is possible that ZnTe is formed in the samples.



Figure 33 XRD patterns of the zinc-doped samples



Figure 34 Dependence of lattice constant of zinc-doped samples on content of Zn As is shown by Figure 35, the lattice thermal conductivity is always increasing with increasing amount of Zn. This might be due to the formation of ZnTe which possesses large thermal conductivity. With increasing amount of ZnTe, less Ga₂Te₃ and Zn₂Te₃ is formed which results in the lower vacancy concentration. The reduced effect of phonon scattering by vacancy will also cause the lattice thermal conductivity to increase.



Figure 35 Temperature dependence of lattice thermal conductivity of zinc-doped samples

The solid solution without Zn is n-type semiconductor. After doping, it turns to be p-type. As is shown in Figure 36, for the sample with 1% Zn, the Seebeck coefficient changes its sign at certain temperature. For the samples with 5% and 10% of Zn, the Seebeck coefficient is relatively low which is due to the increased carrier concentration.



Figure 36 Temperature dependence of Seebeck coefficient of zinc-doped samples The doping of Zn increases the hole concentration greatly, as is shown in Figure 37. But from Figure 38, we can see that the doping of Zn also decreases the mobility by more than one order of magnitude. As mentioned earlier, it is quite typical for the hole mobility to be smaller than that of electron. Additionally, it is expected that there will by strong ionized impurity scattering by Zn ions.



Figure 37 Temperature dependence of carrier concentration of zinc-doped samples



Figure 38 Temperature dependence of mobility of zinc-doped samples

The temperature dependence of resistivity is shown in Figure 39. Because of the greatly reduced mobility, the resistivity of 1% and 2% Zn sample is increased. Especially for the sample with 1% Zn, the resistivity is huge. The samples with 5% and 10% Zn have very small resistivity which is due to the large carrier concentration.



Figure 39 Temperature dependence of resistivity of zinc-doped samples



Figure 40 Temperature dependence of figure of merit of zinc-doped samples

Figure of merit for the samples with different content of Zn is plotted in Figure 40. The ZT value of the zinc-doped sample is decreased compared to the sample without doping. The doping of zinc changes the solid solution to p-type semiconductor. At small amount of Zn, the resistivity is increased greatly which is due to the reduced mobility by ionized impurity scattering of electrons. At higher amount of Zn (5% and 10%), the resistivity is reduced, but the doping of Zn alters the band structure and Fermi level which affects Seebeck coefficient. The addition of Zn

also helps to form second phase, such as ZnTe, which affects the formation of vacancy structure. The doping of Zn altered the carrier type and electronic properties, but the negative effect on mobility, Seebeck coefficient and thermal conductivity limits its thermoelectric performance.

3.2 Effect of isoelectronic substitution on thermoelectric properties

The doping of Zinc introduces ionized impurity into the solid solution and reduces the mobility greatly which results in increased resistivity. Because of the small mass and atomic size difference between Zn and Ga, the replacing of Ga by Zn cannot help to scatter phonons effectively to reduce thermal conductivity. So we studied the effect of isoelectronic substitution of indium on Ga site. Because Ga and In are in the same column of the periodic table and have equal valence electrons, the replacing of Ga by In will not reduce mobility due to ionized impurity scattering, and the mass and atomic size difference between Ga and In will increase the phonon scattering effect to decrease thermal conductivity.



Figure 41 XRD patterns of samples with indium substitution

We substituted In into the solid solution with 4 mol% Ga_2Te_3 which possesses the highest figure of merit. The samples in the composition of $(In_xGa_{1-x})_{2.96}Sb_{2.88}Te_{0.12}$ (x=0, 5%, 10%, 15%) are prepared by vacuum melting method and XRD patterns are plotted in Figure 41. As is reported by Garandet³⁹, InSb and GaSb can form complete solid solution. From Figure 41, the sample with 5% In possesses the single phase of zinc-blende structure. But for the samples with 10% and 15% In, a second phase, as is indicated by black arrows, is detected to be in the composition of $(In_{0.2}Ga_{0.8})Sb$. The stoichiometric deviation of the second phase from the main phase is caused by segregation during cooling process. As is seen from Figure 42, the lattice constant of 10% and 15% In sample is smaller than expected value (dashed line) calculated from Vegard's Law. The smaller lattice constant indicates the lower In concentration than the stoichiometric composition which is caused by the formation of the In-rich second phase.



Figure 42 Dependence of lattice constant on content of indium

In has heavier mass and larger atomic size than Ga, so we should expect the reduced thermal conductivity due to point defect phonon scattering. From Figure 43, the lattice thermal conductivity is decreased with increasing In, especially at high temperature.



Figure 43 Temperature dependence of lattice thermal conductivity of samples with indium substitution

InSb and In_2Te_3 are both n-type semiconductors, so the doping of In will not change the carrier type of the solid solution. As is shown in Figure 44, the Seebeck coefficient for the samples with different In content are almost the same. And from equation 10, the Seebeck coefficient for partial degenerate semiconductor is only controlled by scattering parameter and Fermi energy which means that the position of Fermi level for all the samples are the same.



Figure 44 Temperature dependence of Seebeck coefficient of samples with indium substitution

Since InSb has small effective mass which is about 0.014 m_0 , the substitution of In will decrease the effective mass of the solid solution. From equation 8, the carrier concentration for partial degenerate semiconductor is related to Fermi level and effective mass. Although the Fermi energy for all the samples are the same, the reduced effective mass will decrease the carrier concentration of In-substituted sample which is consistent with the data of carrier concentration as is shown in Figure 45.



Figure 45 Temperature dependence of carrier concentration of samples with indium substitution

Because doping of In will not introduce ionized impurities, the mobility is not decreased significantly. So, unlike the Zn-doped sample, the resistivity, as is shown in Figure 46, is increased but still of the same order of magnitude as the sample without indium.



Figure 46 Temperature dependence of resistivity of samples with indium substitution From Figure 47, the power factor of the In-substituted sample is decreased which is mainly due to the lowered carrier concentration. The figure of merit is plotted in Figure 48. The thermal conductivity of the In-doped sample is slightly decreased, but the small effective mass which results in the reduced carrier concentration and electrical conductivity decreases the ZT value.



Figure 47 Temperature dependence of power factor of samples with indium substitution



Figure 48 Temperature dependence of figure of merit of samples with indium substitution

The sample with 10% and 15% of In contains second phase which is formed by segregation in the slow cooling process. An attempt was made to quench the sample from the liquid state, but this did not remove the impurity phase. The In-rich second phase is difficult to remove which might be due to the flat liquidus line in phase diagram of InSb-GaSb. The addition of In lowers thermal conductivity because of increased phonon scattering by point defect, but the small effective mass of InSb which results in the reduced power factor cannot help to improve its thermoelectric properties.

CHAPTER 4 Conclusion

The vacancy structure on Ga sub-lattice greatly decreases lattice thermal conductivity of $Ga_2Te_3 - GaSb$. The reduction at both 80K and 300K is over one order of magnitude. Addition of Ga_2Te_3 changes carrier type, increases electron concentration and lifts Fermi level of these solid solutions. And wider band gap of GaSb makes it easier to control electronic properties by doping. But with large amount of Ga_2Te_3 and high vacancy concentration, the reduction of lattice thermal conductivity is limited and mobility is reduced due to point defect scattering of phonons. So the value of μ/κ_L is lowered. Large amount of Ga_2Te_3 also reduces Fermi level resulting in decreased carrier concentration. So we need to control the amount of Ga_2Te_3 to achieve higher figure of merit. The optimized content of Ga_2Te_3 is 4 mol%.

Extrinsic doping of zinc introduces ionized impurity which reduces the mobility significantly. In Zn-doped samples, a second phase of ZnTe is formed which lowers vacancy concentration and increases lattice thermal conductivity. The vacancy structure is very sensitive to composition and the formation of impurity phase will affects the vacancy concentration. In indium substituted samples, the reduction of lattice thermal conductivity is smaller than that of $Ga_2Te_3 - GaSb$, which indicates that vacancy structure can scatter phonons more effectively than In substitution. Because of the large effective mass of GaSb, the sample without In substitution which possesses larger effective mass has higher carrier concentration and power factor.

Prospective research will involve measurement of high temperature thermoelectric properties of $Ga_2Te_3 - GaSb$. The thermoelectric performance of other vacancy compounds, for example $Ga_2Te_3 - ZnTe$, will also be investigated in the future.

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