

Yb充填スクッテルダイト化合物の高圧合成と熱電特 性

メタデータ	言語: eng					
	出版者:					
	公開日: 2016-11-18					
	キーワード (Ja):					
	キーワード (En):					
	作成者: 陳, 玉奇					
	メールアドレス:					
	所属:					
URL	https://doi.org/10.15118/00009028					

平成28年度

博士学位論文

題目

High-pressure synthesis and thermoelectric properties of Yb-filled skutterudite compounds (Yb 充填スクッテルダイト化合物の

高圧合成と熱電特性)

提出者

室蘭工業大学大学院

工学研究科 博士後期課程 創成機能工学専攻 強相関電子物性研究室

> 平成 25 年度入学 学籍番号 13094501

> > Chen Yu Qi

提出日 平成 28 年 6 月 28 日

Contents

Abstract

CHAPTER 1 Introduction

1.1	Overview of Thermoelectric Materials	- 1
1.1.1	Thermoelectric Effects	- 1
1.1.2	Application and performance characterization of thermoelectric materials	-3
1.2	Physical Parameters of Thermoelectric Materials	-6
1.2.1	Seebeck coefficient	-6
1.2.2	Electric conductivity	-7
1.2.3	Thermal conductivity	- 8
1.2.4	Hall effect	-9
1.3	Skutterudite-type Thermoelectric Material	11
1.3.1	Structure features of skutterudite	11
1.3.2	Thermoelectric properties of CoSb ₃ skutterudite	12
1.3.3	Voids filling and atoms substitution	13
1.4	Advantage of High Pressure and High Temperature Method	15
1.5	Motivation	16

CHAPTER2 Experimental Methods

2.1	High Pressure and High Temperature Synthesis	18
2.2	Thermal Transport Measurement	22

2.3	Resistivity Measurement	38
2.4	Hall Effect Measurement	39
2.5	Rietveld Analysis	41

CHAPTER3 Experimental Results of Yb_xCo₄Sb₁₂

3.1	Synthesize Condition and Sample Characterization	43
3.2	Crystal Structure Refinement	54
3.3	Electrical Transport Properties of Yb _x Co ₄ Sb ₁₂	57
3.4	Thermal Transport Properties of Yb _x Co ₄ Sb ₁₂	65
3.5	Dimensionless Figure of Merit ZT of Yb _x Co ₄ Sb ₁₂	70
3.6	Summary	- 71

CHAPTER4 Experimental Results of Yb_{0.6}Fe_yCo_{4-y}Sb₁₂

4.1	Synthesize Condition and Sample Characterization	72
4.2	Crystal Structure Refinement of Selected Yb _{0.6} Fe _y Co _{4-y} Sb ₁₂	78
4.3	Electrical Transport Properties of Yb _{0.6} Fe _y Co _{4-y} Sb ₁₂	83
4.4	Thermal Transport Properties of Yb _{0.6} Fe _y Co _{4-y} Sb ₁₂	86
4.5	Dimensionless Figure of Merit ZT of Yb _{0.6} Fe _y Co _{4-y} Sb ₁₂	89
4.6	Summary	90

CHAPTER5 Conclusion

Conclusion-----91

References

Acknowledgements

ABSTRACT

Thermoelectric (TE) materials are materials that can transfer heat into electricity or vice visa directly. The efficiency of TE materials are evaluated by a dimensionless figure of merit *ZT*, defined as $ZT=S^2T/\rho\kappa$, where *T* is the absolute temperature, *S* represents the Seebeck coefficient, ρ is electrical conductivity, and κ is the total thermal conductivity ($\kappa=\kappa_E+\kappa_L$, where κ_E and κ_L are the electrical and lattice contribution, respectively). Following with Slack's ideal TE material "Phonon Glass and Electron Crystal" concept, a binary skutterudites compound CoSb₃, which has a cubic unit cell ($Im\bar{3}$) with two fillable interstitial voids, has been intensely pursued as one of the most promising TE material owing to its flexibly tunable physical properties and excellent thermoelectric properties. However, its thermal conductivity κ is too large for a good TE material. It is believed that filling atoms, especially small and heavy atoms inside the interstitial voids, can remarkably decrease the lattice thermal conductivity κ_L . Yb has been proved as one of the most efficient filler for its low-vibration frequency which favors the maximum reduction of the κ_L . Unfortunately, the filling fraction of Yb is limited around 0.2 by conventional synthesis method at ambient pressure. High-pressure synthesis technique has an advantage to tune widely the composition of CoSb₃ based skutterudites.

In this study, we have tried to synthesize Yb_xCo₄Sb₁₂ with a high filling rate *x* by high-pressure synthesis technique. The electron probe micro-analysis results indicate that the actual Yb filling fraction *x* is improved to 0.29. The lowest κ_L of 2.02 W/m·K (28% of CoSb₃) is achieved in Yb_{0.29}Co₄Sb₁₂. On the other hand, the Seebeck coefficient *S* was decreased due to its high carrier concentration. To further optimize the figure of merit, the excess electrons in Yb_xCo₄Sb₁₂ need to be compensated. Therefore, the optimized Yb-filled Fe-substituted compounds Yb_xFe_yCo_{4-y}Sb₁₂ ($0 \le y \le 1$) were synthesized and the corresponding thermoelectric properties were also studied in detail. The optimized figure of merit *ZT* of 0.12 at 300 K was achieved in Yb_{0.3}Fe_{0.2}Co_{3.8}Sb_{11.8}, which is 12 times higher than that in CoSb₃.

In this study, using high-pressure synthesis method, we have succeeded in synthesizing filled skutterudite compounds with high filling ratio and improved their thermoelectric properties. This results contributes development of next-generation thermoelectric materials.

論文内容の要旨

熱電材料は、熱エネルギーを電気エネルギーに効率的に直接変換できる材料であり、温度 差発電等のモジュールに不可欠な電子材料である。熱電材料の性能は無次元性能指数 $ZT=S^2\sigma T/\kappa$ で評価される。ここで、T は絶対温度、S, σ , κ はそれぞれゼーベック係数、電気伝 導率,熱伝導率である。さらに, κ は電子による寄与 κ_E と格子による寄与 κ_L の和で表される。 非充填スクッテルダイト化合物 CoSb3 は、体心立方晶系(空間群: Im3)の結晶構造を持ち、12 個の Sb 原子が体心立方の体心位置を中心とした正 20 面体のカゴを形成しており、その中心は 空隙となっている。このカゴ内部の空隙は、一つの希土類イオンが充填できるほど大きく、 結晶構造内に大きな空隙を有する結晶構造となっている。CoSb3 は,その優れた熱電特性から 注目されているが, κ が高いことが欠点である。しかし,結晶構造中に存在する空隙に希土類 イオン等を充填することで、カゴ内部に充填されたイオンがまわりのイオンと弱く結合する ため、低エネルギーの局所的な振動(ラットリング)を行うことから、格子の基本振動を妨 げ, *κ*Lの大きな低減を引き起こすことが知られている。*κ*Lの大きな低減に寄与できる充填イ オンは、イオン半径が小さく、質量の大きなイオンが適しており、Yb は、最も効果的な充填 イオンの一つと考えられている。ラットリング効果を大きくするには、Yb イオンを高濃度に 充填する必要があるが、従来の常圧下における合成法では、Ybの充填率は 20% が限界であ る。しかし、高圧合成法を用いることで、化合物を構成するイオンの圧縮率の違い等により、 高圧下で高濃度に Yb イオンを充填した試料を合成できる可能性がある。

そこで、本研究では、高圧合成法により、高い Yb 充填率 x の Yb_xCo₄Sb₁₂の合成を試み、その熱電特性を評価した。その結果、充填率 x は 0.29 まで向上させることに成功した。 Yb_xCo₄Sb₁₂の κ_L は、2.02W/m·K まで低減した(CoSb₃の 28%)。また、ゼーベック係数は負の 値を示し、CoSb₃の p 型伝導体から、n 型伝導体へと変換することが確認できた。しかし、そ の絶対値は低下した。これは、高濃度に Yb を充填したことにより、キャリア濃度(電子濃度) が高くなり過ぎたためと考えられる。そこで、過剰な電子を補償するために、Co サイトを Fe で置換した Yb_xFe_yCo_{4-y}Sb₁₂ (0≤y≤1) の合成を行い、その熱電特性を評価した。 Yb_{0.3}Fe_{0.2}Co_{3.8}Sb_{11.8}の ZT は、300K においで、最大 0.12 まで向上した(CoSb₃の 12 倍)。

本研究では、高圧合成法を用いることで、高い充填率のスクッテルダイト化合物を合成で きることを示すとともに、熱電性能を向上させることに成功した。このことは、スクッテル ダイト型熱電材料の設計の幅を広げることにつながり、次世代熱電変換材料開発に新たな設 計指針を与えるものであると考えられる。

CHAPTER 1. Introduction

The global environment are under pressure due to the increasing demand for energy. Recently, there are lots of renewable energy flourishing. However, the lost heat reuse is still an important task for human being because the majority of the world's power is still generated by fossil fuel in which 60% energy lost as heat to the environment. Those lost heat is not only a big waste for energy but also a main reason for Greenhouse warming effect. Thermoelectric materials are among the most important potential candidates for convert heat energy into electrical directly or vice versa. In addition, the thermoelectric materials can work for smaller and faster devices, producing local energy from waste heat.

1.1 Overview of Thermoelectric Materials

1.1.1 Thermoelectric Effects

The thermoelectric effect refers to phenomena by which either a temperature difference creates an electric potential or an electric potential creates a temperature difference. Thermoelectric effect encompasses three separately identified effects, the Seebeck effect, Peltier effect and Thomason effect. In 1821, German physicist Thomas J. Seebeck discovered a phenomena that electricity produced directly from heat [1]. This production of electricity from heat is called the Seebeck effect. Seebeck effect occurs when there are two different metals or semiconductors, joined at both ends, to create a closed circuit. When one end has a different temperature applied to it than the other, a small current is created, which increases along with the variation in temperatures. In general, the Seebeck effect is described by the creation of an electromotive field: E = -S

 ΔT , where *E* is the amount of energy gained per unit charge that passes through a device in the opposite direction to the electric field produced by that device, *S* is the Seebeck coefficient (also known as thermo power), a property of the local material, and ΔT is the gradient in temperature *T*. In 1834, French physicist Jean Charles Athanase Peltier discovered that when a current is made to flow through a junction between two conductors A and B, heat may be generated (or removed) at the junction.[2] The presence of heating or cooling at an electrified junction of two different conductors is called Peltier effect. In 1851, William Thomson (later Lord Kelvin) was led by thermodynamic reasoning to conclude that sources of electron motive force exist in a thermoelectric circuit in addition to those located at the junctions. In particular, he predicted that an electromotive force would arise within a single conductor whenever a temperature gradient was present. The truth of this prediction were demonstrated by experiment and this phenomena is called Thomson effect.

Many process in industry produce huge quantities of waste heat and most of that heat goes unused. The discovery of thermoelectric effect greatly increased the interest of thermoelectric materials since the discover of Seebeck effect (for power generation) and the Peltier effect (for cooling and heat pumping).[3-5] (Often, more than one of the above effects is involved in the operation of a real thermoelectric device.) In a material that both heat and electricity, the heat energy could be converted into electric current or convert electric current into a heat source. This kind of materials can be used as refrigerators, power generators or temperature sensors without any moving parts (except electrons and holes).

2

In situation where moving parts or consumable flues are hard to work, bulk thermoelectric material have outstanding capability to serve those system. Solid state power generation and cooling based on thermoelectric effects is shown in fig. 1.1.1.



Figure 1.1.1 Power generation (a) Electronic power generation, (b) thermoelectric cooler.

Figure 1.1.1 (a) sketches the thermoelectric power generation. The hot end has a higher temperature, so electrons and holes are driven to the cold end through diffusion and flow. Practical devices are made of many pairs of p-n legs, usually arranged such that current flows in series through all the legs and energy flows in parallel from the cold side to the hot side.

Thermoelectric cooler work in revise to thermoelectric coolers, as shown in fig. 1.1.1 (b). P-type and n-type conductor elements are interconnected on the cold and the hot sides, such that a current flows through all the elements in series, while the energy they carry (by electrons and holes) leaves the cold side in parallel.

1.1.2 Application and Performance Characterization of Thermoelectric Materials

The ability to produce heating/cooling or electricity given the proper configuration were summarized into Figure of Merit in 1910 by Altenkirch and grown into its modern format by Ioffe[5]:

$$ZT = S^2 T / \rho \cdot \kappa \tag{1.1}$$

, where *S* is the Seebeck coefficient (μ V/K), *T* is the absolute temperature (K), ρ is the electrical resistivity (Ω ·m), and κ is the total thermal conductivity (W·m⁻¹K⁻¹). ZT is defined as the dimensionless figure of merit which reflect the efficiency of a thermoelectric solid.

For power generation the efficiency is defined as heat in divided by work out and is given by:

Efficiency =
$$\frac{(T_h - T_{co})(\sqrt{(1 + ZT)} - 1)}{(T_{co} + \sqrt{(1 + ZT)}T_h)}$$
 (1.2)

, where T_{co} , T_h represent the temperature of the cold end and hot end, respectively. For refrigeration, efficiency is defined as the heat pumped out divided by the work in and is called the Coefficient of Performance (COP). The COP is defined as:

$$COP = \frac{(\sqrt{(1+ZT)}T_{co} - T_h)}{(T_h - T_{co})(1 + \sqrt{(1+ZT)})}$$
(1.3)

ZT value is a very convenient indicator for evaluating the potential efficiency of thermoelectric materials. Generally, the material is considered as suitable thermoelectric material for application with ZT values of close to unity. Therefore, high electrical conductivity (corresponding to low Joule heating), a large Seebeck coefficient (corresponding to large potential difference) and low thermal conductivity (corresponding to a large temperature difference) are needed in order to realize high-performance thermoelectric materials.

Figure 1.1.2 shows the figure of merit ZT as a function of temperature for some of recent high performance thermoelectric materials. The $Yb_xCo_4Sb_{12}$ shown in fig. 1.1.2 is the theoretical value and the actual value of $Yb_xCo_4Sb_{12}$ is relatively lower than this value. The p-type thermoelectric material for application around 800 K already achieved in CeFe₄Sb₁₂ compounds while that of n-type thermoelectric material is insufficient.



Figure 1.1.2. Dimensionless thermoelectric figure of merit (ZT) of recent highperformance bulk thermoelectric materials as a function of applied temperature. Adopt

from refer [6, 7].

1.2 Physical parameters of thermoelectric materials

1.2.1 Seebeck coefficient

Assuming that a non-degenerate semiconductor is in a steady state of electric field and temperature gradient, by relaxation-time approximation and Boltzmann equation, the <u>Seebeck</u> coefficient of this material can be expressed as:

$$S = \frac{\pm \kappa_B}{e} \left[\frac{E_F}{\kappa_B T} - \left(S + \frac{5}{2} \right) \right]$$
(1.4)

, where κ_B is the Boltzmann constant, $E_{F'} \kappa_B \cdot T$ is the simple Fermi level and *s* the scattering factor.

The sign of *S* indicate the type of condition. Positive represent hole conduction type (p-type) while negative means electric conduction type (n-type). For mostly thermoelectric materials, the value of $E_F / \kappa_B T$ is around -2.0 ~ 5.0. This value change with scattering mechanism of materials. Acoustic phonon scattering act as -1/2, optical scattering shows 1/2 and ionized impurity scattering is -3/2. When doping elements in the semiconductive thermoelectric materials, the ionized impurity concentration increases, hence the corresponding ionized impurity scattering factor also will increase which would decrease the mobility of charge carrier. This would lead an improved Seebeck coefficient for a material with certain carrier concentration. In addition, for two or more alloy solid solution or compounds, alloy scattering factor act as -1/2) should also be considered in the carrier scattering mechanism. In this condition, neutral impurity scattering factor is treated as zero.

If the material is single band non-degenerate semiconductor, the Seebeck coefficient could be expressed as:

$$S = \frac{\pm \kappa_B}{e} \left[\frac{E_F}{\kappa_B T} + \ln \frac{N}{n} \right]$$
(1.5)

, where N is the density of state, n the carrier concentration.

If the material is single with degenerate semiconductor, the corresponding Seebeck coefficient could be expressed as:

$$S = \pm \frac{8\pi^2}{3} \frac{\kappa_B^2 T}{eh^2} m^* \frac{\pi^{2/3}}{3n}$$
(1.6)

, where h is the Planck constant ($h=6.63 \times 10^{-34}$ Js), m^* the carrier effective mass; n the carrier concentration.

Above all, Seebeck coefficient is the voltage built up when a small temperature gradient is applied to a material. Seebeck coefficient is related to Fermi level, scattering factor, carrier concentration, density of state and so on. It elaborate interaction between electric transport and carriers. Seebeck coefficient is proportional to carrier effective mass while inversely proportional with carrier concentration of material.

1.2.2 Electric Conductivity

According to the thermal equilibrium model, the electric conductivity of semiconductor materials could be expressed as:

$$\sigma = n e \mu \tag{1.7}$$

, where *n* is the carrier concentration (cm⁻³), *e* is elementary charge (e= 1.6×10^{-19} C), μ is the carrier mobility (cm²/Vs).

Therefore, the electric conductivity of materials is correlated with scattering factor, relaxation time, effective mass of charge carrier and Fermi energy. The effective mass is in direct proportion to carrier concentration while in reversed proportion to carrier mobility.

1.2.3 Thermal Conductivity

For semiconductor, the total thermal conductivity is mainly composed two attributes, lattice (phonon) thermal conductivity and electric thermal conductivity.

In crystalline solids, atoms or molecules are elastic arranged in crystal lattice and they can vibrate around their equilibrium position. This vibration format a lattice wave which is one way of energy transfer. The quantized energy of lattice vibration wave is called 'phonon', which is a quasi-particle. Lattice thermal conductivity comes from phonon transmission.

From the molecular dynamics theory, thermal conductivity in crystals can approximately expressed as:

$$\kappa_{ph} = \frac{1}{3}Cvl \tag{1.8}$$

, where C is the heat capacity per unit volume, *v* is the average particle velocity, and *l* is the mean free path of a particle between collisions. The transfer of lattice vibration wave could be regarded as the spread of phonons. Lattice thermal conductivity can be decreased by introducing scattering source, such as lattice defect, grain boundary and so on[8]. When charge carriers directional moving, they do not only transfer electrons but also thermal energy. For semiconductors with high carrier concentration or intrinsic excitation, the contribution of electric can be expressed by Wiedemann-Franz law:

$$\kappa_e = L\sigma T \tag{1.9}$$

, where *L* is the Lorentz constant, σ is the electric conductivity and *T* the absolute temperature. For mostly thermoelectric materials, Lorentz constant can be treated as $2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$.

1.2.4 Hall coefficient

The Hall effect describes what happens to current flowing through a conducting material (a metal, a semiconductor) if it is exposed to a magnetic field *B*. The Hall coefficient R_H (cm³/C) is defined as:

$$R_H = \frac{V_{Hall}d}{IB} \times 10^8 \tag{1.10}$$

, where V_H (V) is the Hall voltage, d (cm) is the depth of plate which perpendicular to the magnetic field, I (A) is the corresponding current, and B (Oe) is the magnetic field. Without considering the case of amendments, the carrier concentration n (cm⁻³) can be calculated from the relationship:

$$n = \frac{1}{R_H e} \tag{1.11}$$

, where e is the elementary charge ($e=1.6\times10^{-19}$ C). Combining with the electronic resistivity ρ , the carrier mobility μ (cm²/Vs) can be obtained as:

$$\mu = |R_H|/\rho \tag{1.12}$$

Thermoelectric figure of merit can be optimized by optimizing one of the parameters, Seebeck coefficient, thermal conductivity and electric conductivity. However, these three parameters are not separated. When one of them changed, the remaining two will also be changed accordingly. In fact, there has another important parameter, carrier concentration, which does not directly occur in the figure of merit formula. Carrier concentration is closed linked Seebeck coefficient, thermal conductivity and electric conductivity, as shown in fig. 1.2.1. Thermoelectric research is concentrated in semiconductors instead of metals or insulators although thermoelectric properties were firstly put to use with metal system. As the carrier concentration increases from insulator through semiconductor to metal, the Seebeck coefficient drops linearly while the electric conductivity increases. The electronic component of thermal conductivity increase with carrier concentration.



Fig. 1.2.1 The schematic diagram showing the dependence of basic thermoelectric parameters *vs.* carrier concentration in CoSb₃ based skutterudite.[9]

1.3 Skutterudite-type Thermoelectric Material



1.3.1 Structural Features of Skutterudite

Fig. 1.3.1 Schematic illustration of skutterudite crystal (a) Binary skutterudite structure; (b) Filled skutterudite structure

In 1996 it was found that some of the lanthanide skutterudites had excellent thermoelectric properties above room temperature [10, 11] and this greatly increased the interest in these material for thermoelectric application. As one of the most promising thermoelectric materials, skutterudites has attracted a lot of study for its amenably tunable physical properties [12-15] and the open structure.

A concept of a phonon-glass electron-single-crystal (PGEC), first introduced by Slack [16]. Slack *et al.* proposed that in order to optimize the figure of merit, phonons, which are responsible for thermal conductivity, must pass the material as they would in a glass (experiencing a high degree of phonon scattering, i.e., lowering thermal conductivity) while electrons must experience it as a crystal (experiencing very little scattering, i.e., maintaining electrical conductivity).

The skutterudite compounds, identical in structure to CoAs₃ - the structure first identified by Oftedal in 1928 - are known as sutterudites. Binary skutterudites (prototype CoAs₃, space group $Im\overline{3}$ are structures with the general formula MX₃ where M is one of transition metals cobalt, rhodium or iridium and X stands for phosphorus, arsenic or antimony). The structure is body-centred cubic crystal with the space group Im $\overline{3}$ (T_h^5 , No. 204) as shown in as shown in fig. 1.3.1 (a). The large voids in skutterudite form cages into which atoms may be inserted. Taking into account of the two voids in unit cell, one can represent the skutterudite formula as $\Box_x M_4 X_{12}$, where \Box illustrating the empty octant. The large voids in unit cells is able to accept foreign ions which would resulting in the formation of filled skutterudites (Fig. 1.3.1 (b)). One of the remarkable features of this material is that the cage-like open structure can be filled with foreign atoms acting as phonon rattlers. The "rattling" of the filled atoms scatters phonons strongly and drastically reduces the thermal conductivity of the skutterudite compounds. Lanthanide was firstly filled into the FeP₃ based skutterudite by Jeitschko et. al. in 1977[17]. A large number of these filled skutterudite compounds have been synthesized until now, where the filling atom is typically rare earth elements lanthanide, actinide, alkaline-earth, alkali, thallium, and so on [18, 19].

1.3.2 Thermoelectric properties of CoSb₃ skutterudites

Binary skutterudites CoSb₃, which has received the most interest because of its excellent electric transport properties [1]. However, its high thermal conductivity restricted its application. It is believed that filling atoms such as rare-earth or other metallic inside the Sb-icosahedron can remarkably decrease the thermal conductivity [2-4].

1.3.3 Void Filling and Atoms Substitution

The open structure of skutterudites make it possible to tailor the interconnected thermoelectric physical parameters *S*, σ , κ by doping or substitution. The figure of merit can be improved through the independent adjustment of these properties. The challenge to develop thermoelectric materials with superior performance is to tailor the interconnected physical parameters *S*, σ , κ for a crystalline system.

Filling foreign atoms in the host voids can greatly suppress the lattice thermal conductivity. The voids have a parameter varies from 1.763 to 2.037 Å. The filler ions weakly bound with border atoms and exhibit random motion (rattling) inside the host voids. Thus, they produce Einstein-like vibrations. Those vibrations interact with a broader spectrum of lattice phonons, reducing their mean free paths, and are responsible for a substantial decrease in the lattice thermal conductivity. The low frequency heat-carrying phonons will be largely scattered. The lattice thermal conductivity will be decreased subsequently while the electric transport properties do not impacted.

The rare earth elements act as electrons donors in the system. A proper doping ratio could observably decrease the lattice thermal conductivity and increase ZT value. When doping ratio too high, the effect will be reversed because of the partly doping compounds has a wider scattering range compared with filled skutterudites.

In most instances, we also need a hole donors to assist adjusting the properties of material. Fe and Mn have fewer electrons than Co, so they could effectively tune the carrier concentrations. For both binary and filled skutterudites, substitute Co for Fe (or Mn) would introduce holes into the original system and drive material from n-type to p-type. (But material will keep n-type when the content of Fe or Mn is too low.) Many of

rare earth doping skutterudite compounds could get improved thermoelectric performance by partly Fe substituting Co.

1.4. Advantage of high pressure and high temperature method

The most conventional method to synthesize skutterudites compounds is melting, quenching, annealing, and sintering by hot press or spark plasma sintering (SPS) method. However, this method is not suitable for the heavier rare earths filled skutterudite compounds. With the development of high-pressure technology, it has been demonstrated that the skutterudites with smaller/heavier rare earths filled skutterudites, which cannot be synthesized under ambient pressure, might be synthesized with the aid of high pressure [20-23].

High pressure benefits the entrance of heavier rare earths into the voids of the skutterudite structure than ambient pressure. $GdRu_4P_{12}$ and $TbRu_4P_{12}$ have been succeeded synthesized by using high pressure and high temperature method [21]. Those compounds show various interesting physical properties. Furthermore, we can fill foreign atoms to unfilled skutterudite compounds with high filling ratio. For example, $La_xRh_4P_{12}$ (x≤0.9) were prepared under high pressure and the compounds show superconducting transition at around 17 K [24].

Besides, the synthesize time was reduced from few days (for conventional melting, quenching, annealing, and fabricate by spark plasma sintering method) to few hours (high pressure and high temperature method).

1.5. Motivation

Among the skutterudite family, $CoSb_3$ based skutterudite compound is narrow band semiconductor with many unique advantages such as rich raw material, low cost, nontoxic, excellent electric properties. Besides, $CoSb_3$ has excellent thermoelectric properties: room temperature resistivity $1.89 \times 10^{-5} \Omega$ ·m, Seebeck coefficient 220 V/K. CoSb₃ has received the most interest because of its excellent electric transport properties. However, its relatively high thermal conductivity restricted its application for ideal thermoelectric crystal [25]. Filling foreign atoms inside the voids of the skutterudite structure are proved to be an effective way to decrease lattice thermal conductivity of CoSb₃.

Considering the high lattice thermal conductivity of CoSb₃ are mainly caused by longwavelength longitudinal acoustic phonons, Yb should be an effective filler for its low vibrational frequency[26]. Therefore, this study focus on the thermoelectric properties of Yb filled CoSb₃ based skutterudite.

The most conventional method to synthesizing $Yb_xCo_4Sb_{12}$ compounds is by the hotpress or spark plasma sintering after melting, quenching, annealing, and sintering. However, the filling fraction of Yb in CoSb₃ based skutterudite is reported to limit below 20% by those conventional methods under ambient pressure. On the basis of theoretical calculations, Shi *et al.* [27]estimated the filling fraction limit (FFL) of Yb for CoSb₃ to be about 0.21 using a thermal-dynamic analysis. On the other hand, Mei *et al.* [28] reported an FFL value of 0.3 for Yb in Sb₁₂ voids on the basis of an *ab* initio density functional calculations. Recently, CoSb₃ compounds with a high level of Yb doping have been reported; however, the actual Yb doping ratio were not determined. [29, 30] It should be interesting and meaningful to study actual FFL of Yb in CoSb₃-based skutterudite and corresponding physical properties. High pressure benefits the entrance of heavier rare earths into the voids of the skutterudite structure than ambient pressure.

In this work, all the compounds were synthesized by the high pressure and high temperature method. However, higher Yb filling fraction also results high electron carrier concentration which is harmful for higher Seebeck coefficient. To optimize the dimensionless figure of merit ZT, the excess electrons in Yb_{0.6}Co₄Sb₁₂ system need to be compensated. On the basis of optimizing the Yb filling fraction in CoSb₃ skutterudites, the carrier concentration of optimized Yb filled skutterudites Yb_{0.6}Co₄Sb₁₂ was further tuned to improve and the thermoelectric properties of Yb_xCo₄Sb₁₂ compounds. Fe is considered as hole doping element for Co-site substitution because Fe has one less 3d electron than Co while keep similar atomic radius with Co. It is expected that proper substituting content of Fe on Co would improve the thermoelectric behavior of ternary skutterudite Yb_xCo₄Sb₁₂ by compensating the excess electrons in Yb_xCo₄Sb₁₂ system.

CHAPTER 2 Experimental methods

2.1 High Temperature and High Pressure Synthesis

Although skutterudites could be synthesized without high pressure, high filling fractions targeted in this project required high pressure. All the samples reported in this work were synthesized by using the high pressure and high temperature apparatus (UHP-500, Sumitomo Heavy Industries), as shown in Fig. 2.1.

The right partial enlarged figure illustrates the assembled cubic-anvil module. The cubicanvil module is comprised of six anvil stage (made by tungsten carbide) and four guide block which have 45 inclined plane. The upper and the lower anvil stages are fixed while the other four anvil holder are settled on the four guide block so that the anvil can slide on the wedge. The movement of the four side anvil is synchronized by the wedge system. Each anvil stage have a top 12×12 mm² square face. The sample container made by pyrophyllite is formed into a cube of 16 mm edge length.

Oil press is achieved by pressing up bottom frame. Because the guide block are 45° inclined plane. The up-move of the bottom frame will press the four anvils in horizontal direction and the hydrostatic press can be generated on six faces of the pyrophyllite cube. Oil pressure system is control based on a pre-press, keep pressure, and decrease pressure pattern. The highest pressure is 70 MPa.

The heat system is achieved by current heating method. The AC current is passed from the anvil, stainless ring and Mo disk high temperature can be carried out between the graphite. The temperature inside the graphite tube will be increased. A hole were punched in the place which tangency to the graphite. The temperature is detected by putting a K-type thermocouple in the hole.



Fig 2.1.1 DIA-type high pressure apparatus UHP-500 and the assembled anvil module configuration.



Fig. 2.1.2 The current route in the compressible pyrophyllite cube.

High-purity ytterbium (Yb, 99.9%) powders were mixed and milled in stoichiometric ratio using the agate mortar and then sealed in the BN capsule. Assembled the parts (Fig. 2.3) as shown in Fig. 2. 2 The pyrophyllite cube in Fig. 2.2 was heated at 1000C for 10 hr to remove the moisture. The sample container was assembled and placed in the anvil cavity and set the press system. After arrive the 2GPa stably, the heat procedure can be started. The heating rate was 50°C/min and the target temperature 900°C. Keep the temperature at 900°C for 3 minute and then decrease to 590°C and keep at 590°C for 120 minute. The displayed temperature depend on the precious of the parts, especially the place of the thermocouple. Therefore, the temperature cannot be controlled only depend on the temperature, but also need pay attention on the current power.



Fig. 2.1.3 The sample container assembly for UHP-500 synthesis [1].

Initial survey experiment were conducted using in-situ observation in the KEK (Tokyo, Japan) by previous researchers. However, the actual synthesized temperature is hard control preciously. Unsuccessful control of synthesis temperature or the starting elements ratio always results in further segregation of low filling fraction and metal diantimonide impurities. In this project, the impurity phases under 4 % were considered as success synthesized. If the impurity higher than 4 %, the sample would be synthesized again until the impurity phases keep within 4 %.

2.2 Thermal Transport Measurement (TTO option of PPMS)

The TTO option is used to measure the thermal transport properties: thermal conductivity κ , Seebeck coefficient *S* and electrical resistivity ρ . However, the epoxy bond paste which used to fix sample influenced the precious of resistivity, therefore, we will measure resistivity using 4 terminal method individual. That is, only thermal conductivity κ and Seebeck coefficient *S* value were believed from TTO option.

The TTO system determines the thermal conductivity κ and Seebeck coefficient *S* by creating a specified temperature drop between the two ends of sample. The sketch map of sample assembled for TTO measurement is shown in Fig. 2.2.1. The sample end is adhere to the leads by epoxy bonds. Heat is applied to one end of the sample by running current through the heater (Q_{+/-}). The thermal conductivity and the Seebeck coefficient are calculated as follows:

$$\kappa = \mathbf{Q} \cdot \frac{d}{T_{hot} - T_{cold}} \tag{2.1}$$

$$S = \frac{V_+ - V_-}{T_{hot} - T_{cold}}$$
(2.2)

where T_{hot} , T_{cold} is the temperature measured at the thermometer shoes(copper lead); V+, Vis the voltage responded at the sample two ends during the heat pulse; Q is the heat energy and d is the height of the sample.



Fig. 2.2.1 Sketch map of sample connect for TTO measurement

For TTO measurement, the sample should be modified to rectangular bulk (2.0mm×1.0mm×0.5mm). The surface should be polished with abrasive paper (#3000 and #8000) and cleaned. After measured the size of sample, the sectional area and the total surface area of the other 4 surface need calculated by self. The mounting sequence proceed as below with the help of a puck-mounting station.

- Prepare adhesive agent(Silver-filled H20E epoxy). Take out equivalent part A and part B of expxy bond (made by EPO-TEX. Co.) on the clean paper by using toothpick. (The toothpick for taking Part A and Part B should be separated.) Mixed the part A and Part B throughly using another new toothpick.
- (2) Prepare copper lead. As shown in Fig. 2.2.2, there are two kinds of copper lead. Shape a can be used for small sample while shape B can be used for big sample. Besides, the shape b need to be cut to shape c for the convenient of assembling. Those copper lead can be used again after measurement.
- (3) Adhere copper leads to the ends of sample. Adhere sample to copper lead as shown in Fig. 2.2.3 and heat it at 150°C for 5 min. A few of epoxy bond would be enough because too much epoxy will influenced the measurement result.



Fig. 2.2.2 Shape of copper lead.



Fig. 2.2.3 Adhere lead to bottom end of sample.

After the bottom of the sample is fixed to the lead, adhere the other lead to the top of sample the same as (3). Before adhere the lead to the top end of sample, the lead should be bended to the following shape.



Fig. 2.2.4 Adhere lead to the top end of sample.

- (4) Install shoes for sample. Because the shoe is very easy soft, so excessive force or misthreading of the piece can easily damage the threads. The corresponding sample lead need inserted and held in the shoe by hands and a small stainless steel metric M1 screw carefully. The metal tweezers cannot touch the shoes at any time. The sequence of assembling shoes is: Hot-Heat-Cold.
- (5) Install sample on TTO puck. Place the puck in the TTO puck-mounting station and clamp the cold-foot lead to the cold-foot on the puck with the help of the small Phillips screwdriver. Then, the other end of each shoe should also inserted to corresponding five-pin electrical plug using the tweezers, as illustrated in Fig. 2.2.5. In addition, all of the line should neither touch each other nor any part of the puck.

- (6) Place the shield on the puck. Remove the shield cap and screw the shield carefully into the base of the puck. Be care to verify that no wires, shoes, or the sample do not touch the shield. Replace the shield cap after fixed the shield well.
- (7) Checking the sample contact. In order to ensure the condition of sample contact is well or not, the electrical contact to the sample must be checked after mounting it on the puck. Plug the puck into the test box and check resistivity between V+/- and I+/with an ohmmeter. The corresponding resistivity value should be:
 - 3-4: around 200 Ω ;
 - 5-6: around 2 k Ω ;
 - 7-8: around 100Ω ;
 - 9-10: around 100Ω;
 - 11-12: show different resistivity value according to sample property;
 - 13-14: show different resistivity value according to sample property.



Fig. 2.2.5 Illustrating sockets for each shoe assembly.



Fig. 2.2.6 Sample holder with the shield.



Fig. 2.2.7 Test box

After assembled sample on the parts, the measurement sequence need to be prepared as following.

PPMS can measure lots of physical properties by using different option. For TTO measurement, the thermal transport option need to be active if not currently active. Do the following at the PPMS Multivu window: select Utilities – Activate Option, click on Thermal Transport under the Available Options heading, and then select Connection Diagram.

PPMS MultiVu lis View Sample Sequ	uence Measure Graph Instru	ment Utilities Help				_16
elected Sequence: 20110126_Magnet.sec						
equence Status						
requence rae						
Bun Pause						
LUCK						
	Opt	ion Manager				×
					Asting Ostions	
		valiable uptions :		-	Active Options :	
	A	C Transport		Astiusta >>	Thermal Transport	
	H	leat Capacity		Activate		
		teat Capacity for Hit felium?	30		1	
	E	lesistivitu		<< Deactivate		
		realouting				
				Connection		
				Diagrams		
				Close		
					I	
Sequence Idle	300.01 K, Stable	-0.06 De, Persistent	2.63 Torr	Log File Hecolding		
Sequence Idle Seq: (none)	300.01 K, Stable Set: 300.00 K	-0.06 De, Persistent Set: 0.0 De	2.63 Torr Purged	Log File		

Fig. 2.2.8 PPMS Option manager

- (2) Change cable according to the Connection Diagram.
- (3) Check the Power. TTO measurement use the MODEL6000, MODEL6500 and MODEL7100 (Fig.2.4.10). Sometimes only MODEL6000 is active, if so, the power of MODEL6500 and MODEL7100 need to be turn on and then restart the PC.



Fig. 2.2.9 TTO connection diagram.



Fig.2.2.10 MODEL6000, MODEL6500, and MODEL7100.

(4) Ensure Temperature at 300 K. Before open the chamber, first ensure the temperature is 300 K. If the temperature of the chamber is low, open the chamber will result frost in the chamber and cannot vcuumize.

(5) Insert sample in the chamber. Do the following: click **Vent Cont.** button at the **Chamber** windows; After the state became Flooding at the bottom of the status bar. Insert the sample puck inside the chamber using the sample insert tool as shown in the Fig. 2.2.12.

(6) Assembled Charcoal (4038-010) in the bottom of the Contact Baffle (as illustrated in Fig. 2.2.13) and insert it inside the chamber and then close the chamber. The Charcoal will help to create a more uniform thermal environment for the puck when high vacuum is enabled in the chamber.

(7) Click **Purge/Seal** button to vaccumize the chamber. Wait until the status become purge, then click the **HiVac** button. The status will show AtHiVac when the chamber became high vaccum.



Fig. 2.2.11 Chamber control window



Fig. 2.2.12 Sample insert tool.


Fig. 2.2.13 Charcoal and Contact Baffle Assembly.

(8) Active TTO option. Choose the **Thermal Transport** and the click the **Activate** button. Because only one measurement option may be active at a time, first click Deactivate if the another option is activate and then activate Thermal Transport option.

Option Manager		×
Available Options : AC Transport Heat Capacity Heat Capacity for He3 Helium3 Thermal Transport	Activate ->>> << Deactivate	e Options :
	Close	

Fig. 2.2.14 Option manager

(9) Ensure the Config. File. After activate the Thermal Transport option, the windows in Fig.2.2.16 will be shown. Thermal transport Log window signify the Config File of the Hot, Cold and heat, respectively. The number indicated in Thermal Transport Log should be same with the Hot, Cold and Heat shoe number which used in sample puck. If the number shown in the Thermal Transport Log is different, we need change the Config File by do the following: Minimize the Multivn windows – Open C/Qdppms/Thermal Transport/System/TTO.ini search the corresponding Config File from the C/Qdppms/Thermal Transport/System/ Calibration folder - change the cgf file in TTO.ini to the corresponding Config File, as shown in Fig. 2.2.16.



Fig. 2.2.15 Windows after activate the Thermal Transport option.



Fig. 2.2.16 Change the Config File in Thermal Transport Log

(10) Click the data file in the Thermal transport windows as shown in Fig.2.2.17. Click the Browse button to make a data file. Fig.2.4.18 shows the input windows of sample information. Input the sample length, cross section ans Surface Area calculated in beginning of 2.2.2. Emissivity value is 0.9.

A Thermal Transport [No Data	file]	⊐×
Install Data File Sample Wav	eform Advanced Debug	
Path		_
C:\QdPpms\Data		_
File Name		_ 11
J		- 11
Title		-
Capture Raw Data	Browse View	
Status Thermal Transport Beady	Measure Help	

Fig. 2.2.17 Data file

Thermal T	ransport Sample Properties
2	Enter Sample Properties
Material	Yb0.6Co4Sb12
Comment	
Length	1.995 mm Surface 6.53961 mm ²
Cross Section	0.661878 mm ² Emissivity 0.9
	OK Cancel Help

Fig. 2.2.18 Input sample information

(11) Click the **Measure** in the bottom of the Thermal transport window. The Thermal Transport Measurement windows shown in Fig. 2.2.19 will be shown. Change the parameter shown in the red circle of Fig.2.2.19 and click Start button. Wait few minutes to check the waveform. The corrected waveform is shown in Fig. 2.2.20.

👠 Thermal Transport Measurement 📃 🗖 🔀						
Settings Thermal Resistivity	Settings Thermal Resistivity Last Measurement					
Measure Type	Temp.	К				
Market Thermal Conductivity	Field	0e				
Seebeck Coefficient	Conduct.	W/K-m				
Electrical Resistivity	Seebeck	μV/K				
General	Resist.	Ohm-m				
Save Marginal Results	ZT					
Discard First N Results = 3	Period	sec				
Next Measurement	Power	mW				
Period 400 sec	Current Measurement					
Power 13.5 mW	Period	sec				
Set Clear	Power	m₩				
	Progress					
Start Pause Close Help						

🚺 Thermal Transport Measurement 📃 🗔 🗙						
Settings	Thermal	Resistivity		-Last Mea	surement	
Settings	and Limits		·	Temp.		К
	Min	Max		Field		0e
Period	30	1430	sec	Conduct.		W/K-m
Power	0.001	(51)	mW	Seebeck		μV7K
Temp Ri	se	3	(%)	Resist.		Ohm-m
Seebeck	< 1	1000	υV	ZT		
Period				Period		sec
Ratio	8			Power		m₩
				Current Measurement		
				Period		sec
9	Set	Clear		Power		mW
				Progress		
Start	Pause	Close	Help			

🚹 Thermal Transport Measurement					
Settings Thermal Resistivity 🔳 🕨	Last Measurement				
Limits and Settings	Temp K				
Min Max	Field Oe				
Excitation 0.01 1 mA	Conduct W/K-m				
Frequency 17 17 Hz	Seebeck µV/K				
Duration 1 sec	Resist Ohm-m				
Constant Current Mode	ZT				
Low Resistance Mode	Period sec				
C Always Autorange	Power mW				
Sticky Autorange	Current Measurement				
O Fixed Range 5V	Period sec				
Set Clear	Power mW				
	Progress				
Start Pause Close Help					

Fig. 2.2.19 Thermal Transport Measurement.



Fig. 2.2.20 Thermal Transport Waveform.

(12) Write Sequence. As shown in Fig. 2.2.21. To get stable data at 300K, the temperature was keep at 300 K for 1 hour and then decrease to 5 K with 0.3 K/min.

🔆 TTO-300-5K-0.3Kmin.seq	
Selected Line: 8	
Set Temperature 300K at 12K/min. Fast Settle	
Wait For Temperature, Delay 3600 secs, No Action	
Set Temperature 5K at 0.3K/min. Fast Settle	
Wait For Temperature, Delay 1200 secs, No Action	
TTO Stop	
Chamber Seal Immediate	
Set Temperature 300K at 15K/min. Fast Settle	
End Sequence	

Fig. 2.2.21 Example of TTO Sequence.

(13) Run sequence and clicking the **View** in the **Data File** panel of the Thermal Transport Windows to open the result figure.



Fig. 2.2.22 Status of Heater (on, off) and normal temperature decrease behavior. (b) Status of Heater (on, off) and abnormal temperature decrease behavior.

Fig. 2.2.22 shows the status of (a) normal waveform and (b) abnormal waveform. The normal status indicate that the period of Heater (on/off) is consistent with the period of temperature (increasing/decreasing). Waveform behavior shown in Fig. 2.4.22 (b) indicate that the sample cannot cool down in the Heater period. At this time, the cooling speed in the sequence need to more slowly.

In addition, the Log need to be taken for any measurement. Do the following: Utilities/Log PPMS Data/General-Browse, make a new folder and click open, Select all

the Standard Item and Diagnostic Items/Click **Start** button to take the Log data/Click the **View Data** to show the Log Data.

Log Data	×
General Standard Items Diagnostic Items Advanced	
Data File Parameters	
Data File: 20131209 dat	
Repeat Every 120 Second(s) [0.250 min - 99999 max]	
View Data	
Start Stop Acquire Once	Close

Fig. 2.2.23 Log Data.

(14) After the measurement finish, the status in left will became **Sequence Idle**. Ensure the chamber temperature is 300K. Then, open the chamber by click **Vent Cont**. Button. Then open the Dewar and take off the sample. Close the Dewar and click **Purge/Seal** button to seal the chamber.

2.3 Resistivity

By using four-wire resistance measurement method, the sample resistivity can be precious measured with greatly reduction of the contribution of the leads and the joints to the resistance. Fig. 2.3.1 shows the attach way of wires on the sample. After attached the wire on sample one by one, the sample with four –wire is mounted on Resistivity puck and wired to the four contact. The outer wire contact applied current on sample and the inside two wire detect the voltage between the inside wires. The resistance then can be calculated with Ohm's law. Fig. 2.3.1 shows the schematically and actual four-wire resistivity sample. The magnetroresistance can also be measured by using this attach way with applied.



Fig. 2.3.1 Four-wire resistivity measurement.

2.4 Hall effect

The carrier concentration is not a necessary parameter to estimate the figure of merit ZT. However, it is an important parameter to analysis the carrier transport property in metal or semiconductor. The information of carrier concentration can be estimated by measuring the Hall Effect. In 1879, Hall observed that when an electrical current passes through a sample placed in a magnetic field, a potential proportional to the current and to the magnetic field is developed across the material in direction perpendicular to both the current and to the magnetic field [2], as shown in Fig. 2.4.1.



Fig.2.4.1 Hall effect.

There are lots of methods that can be used for measuring Hall effect. Here, we measure Hall effect by using van der Pauw technique, that is, a combination of a resistivity measurement and a Hall measurement. The sample shape for Hall effect measurement is a thin square plate, as shown in Fig. 2.4.2. As shown in Fig.2.4.2, a current I is forced through the contacts 1 and 3 and the Hall voltage V_H (= V_{24}) is measured across the remaining contacts 2 and 4. The hall coefficient can be expressed as:

$$R_{H} = \frac{V_{H}d}{IB} \times 10^{8} \ (cm^{3}/C)$$
(2.3)

, where d is the thickness of sample (cm) and B is the applied magnetic field (Oe), I is the applied current (A), and V_H is the corresponding voltage. According the value of Hall coefficient, the information of main carrier type can be obtained.

The corresponding carrier concentration can be calculated by using:

$$n = \frac{1}{|R_H|e} \tag{2.4}$$

, where e is the unit charge with $e = 1.6 \times 10^{-19}$ C. When considering correction, a parameter of $3\pi/8$ need to be multiplied.

Combining with the results of resistivity measurement, the carrier mobility can be estimated by:



$$\mu = \frac{|R_H|}{\rho} \quad (cm^2/\nu \cdot s) \tag{2.5}$$

Fig. 2.4.2 Four-wire Van der Pauw Hall effect measurement.

Here, we use the 4 wire resistivity measurement with applied field. Considering the Hall voltage is very weak, the number of Reading Count should be very high to reduce error. The reading count is range from 5000 to 10000 according to sample.

2.5 Rietveld refinement

The crystal structure of synthesized skutterudites were refined by using Rietveld refinement with RIETAN-FP. The software needed for Rietveld analysis are listed in Table 2.6.1.

Table 2.6.1	Software	used in	Rietveld	analy	ysis
-------------	----------	---------	----------	-------	------

Software	Usage			
IPAnalyzer	Parameter calibration			
PDIndexer	Lattice constant			
Mama Editor	Edit and run *.ins file;			
Maruo Editor	Display output file;			
RIETAN-FP	Rietveld analysis;			
Igor Pro	Output *.int and *.bkg files;			
Igor 110	Display Rietveld analysis pattern;			
VESTA	Display crystal structure			

The X-ray diffraction pattern for Rietveld analysis need used x-ray diffraction patterns with synchrotron radiation at ambient pressure and room temperature. The synchrotron radiation experiments with λ =0.62 Å were performed at the BL10XU in the Spring-8. The Rietveld refinement were carried out with the program (RIETAN_FP) developed by Izumi [3]. The detail of analysis steps were listed below.

I. Parameters calibration

With the aid of IPAnalyzer, the parameters such as the wave length, camera pixel size, pixel distortion, and IP tilt, can be calibrated by analysis standard compound CeO₂. The length should be first calculated first from the difference of ImagePlate length. Then, the parameters of pixel can be calibrated. After got those parameters, the analysis for sample profile can be started with those parameters.

II. Rietveld analysis

After get the X-ray profile from IPAnalyzer, this profile need to manage further with Igor Pro to get the background file. From Igor Pro, we can get two file: *.int and *.bkg.

Both of them are needed for Rietveld analysis. The input file *.ins can be get from the install package of RIETVELD-FP and also can be output by VESTA. Put those three file (:*.ins, *.int, and *.bkg) in the same folder and the Rietveld analysis can be started by running Rietveld-FP by Maruo. Several output file (*.lst, *.itx ...) which concluded analysis results will be made in the same folder after the analysis process finished. This analysis need repeated dozens of times so that the calculated profile can be fitted well with experimental profile.

III. Goodness factor of Rietveld analysis

The goodness of Rietveld analysis is judged by several factors R_{wp} , S, R_e , et al. All those factors are outputted in *.lst file. In those factors, the most important factor is R_{wp} and S. The lower value Rwp means high fit degree. The S=1 indicated almost a perfect coincide between calculated profile and the experimental profile.

CHAPTER 3 Experimental Results of Yb_xCo₄Sb₁₂

3.1 Synthesize Condition and Sample Characterization

Partially Yb filled CoSb₃ based skutterudites were synthesized by using high pressure and high temperature method. However, Co, Sb, and Yb have very difference physical properties (Tab. 3.1.1). Besides, the formation of CoSb₂ impurity is close to CoSb₃. Therefore, synthesize for high pure CoSb₃ ask for precious synthesize condition.

The phase diagram of $CoSb_3$ were shown in Fig. 3.1.1. To obtain high pure Yb filled $CoSb_3$, the Yb should be melted so that the Yb atoms can be inserted into the $CoSb_3$ voids. That is, the mixed stoichiometric elements needs first increased above 900 °C and then decreases to 600 °C. The synthesize condition under high pressure were different from that of ordinary pressure. The melting point of elements decreases with increasing pressure. The synthesize temperature under 2 GPa were decided from in-situ XRD experiment.

The detected temperature by UHP-500 is sensitive to the position of thermocouple hole in the cubic pyrophyllite. In addition, the thermocouple line is easy to break at high temperature. Therefore, the synthesize condition is controlled by power with temperature as assistant. Every synthesize process might have different power-temperature due to the match up condition BN, graphite, and pyrophyllite. To get one pure sample (with impurity phases content lower than 4%), it always need several times synthesize. Table 3.1.2 only lists the synthesize condition of pure samples.

For those synthesized compounds, X-ray diffraction indicated that some place are highpure skutterudites (impurity almost equal to zero) while some places have secondary phase (impurity content are high). If all the points on a certain phase show lower impurity ratio (\leq 4%), it was believed that this phase is pure. If one or more points shows high impurity content while others shows low impurity content, this kind of phase was treated as impurity.

Element	Melting Point	Boiling Point	Atomic Radius	Atomic	Crevetal Streveture
Element	(°C)	(°C)	(Å)	Weight	Crystal Structure
Со	1495	2927	1.248	58.93	rhombohedra
Sh	631	1635	1 40	121 75	Hexagonal close-
50	031	1055	1.40	121.75	packed
Yb	824	1196	1.76	173.05	Face-centered cubic

Table 3.1.1 The physical properties parameters of Cobalt, Antimony, and Ytterbium.



Fig. 3.1.1 The phase diagram for CoSb₃ under ordinary pressure.[35]

Sample No.	compound	Synthesize condition	Power	Secondary phases (≤4%)	Results
c_13120 3_chen	CoSb ₃	2 GPa, 600°C, 120 min	388W; 256W	-	\bigcirc
c_14011 0_chen	Yb _{0.1} Co ₄ Sb ₁₂	2 GPa, 600°C, 120 min	385W; 260W	CoSb2, Yb	∇
c_14011 9_chen	Yb _{0.2} Co ₄ Sb ₁₂	2 GPa, 600°C, 120 min	383W; 265W	Sb	0
c_14012 1_chen	Yb _{0.3} Co4 Sb ₁₂	2 GPa, 600°C, 120 min	385W; 256W	Sb, Yb	∇
c_14020 2_chen	Yb _{0.4} Co ₄ Sb ₁₂	2 GPa, 600°C, 120 min	355W; 245W	Sb, Yb	∇
c_14012 6_chen	Yb _{0.5} Co ₄ Sb ₁₂	2 GPa, 600°C, 120 min	380W; 242W	Sb, Yb	∇
c_14043 0_chen	Yb _{0.6} Co ₄ Sb ₁₂	2 GPa, 600°C, 120 min	367W; 260W	YbSb2, CoSb2	∇
c_14042 4_chen	Yb _{0.7} Co4 Sb ₁₂	2 GPa, 600°C, 120 min	377W; 243W	YbSb2, Sb	∇
c_14051 6_chen	Yb _{0.8} Co ₄ Sb ₁₂	2 GPa, 600°C, 120 min	390W; 245W	YbSb2, CoSb2	×

Table 3.1.2 Synthesize condition of pure compounds.









Fig. 3.1.2 X-ray pattern for $Yb_xCo_4Sb_{12}$ ($0 \le x \le 0.7$).

All the synthesized samples were characterized by powder X-ray diffraction with Co K α_1 radiation and Si as a standard. The lattice constant *a* for the samples was calculated using the least-squares fitting method. The point analysis of EPMA (beam size 50m) were used to determine the actual compound composition. Fig. 3.1.2 shows X-ray diffraction pattern of Yb_xCo₄Sb₁₂ ($0 \le x \le 0.8$). As shown in Fig. 3.1.2, high-purity partially Yb filled CoSb₃-based skutterudites were synthesized by high pressure method. Small peaks associated with secondary phases (Sb, Yb, CoSb₂, YbSb₂, and Yb₅Sb₄) were detected (impurity ratio ≤ 4 %). For *x* higher than 0.6, the intensity of YbSb₂ peaks were increased, likely because the filling fraction limit (FFL) of Yb is excessed.



Fig. 3.1.3 Dependence of nominal Yb doping content of calculated lattice constant.



Fig. 3.1.4. Nominal doping ratio x dependence of actual Yb doping ratio (EPMA).

Figure 3.1.3 plots the nominal Yb doping content dependence of calculated lattice constant. As the nominal Yb filling fraction increasing, the lattice constant of $Yb_xCo_4Sb_{12}$ also increases, the maximum lattice constant of 9.065 were observed for $Yb_{0.6}Co_4Sb_{12}$.

Figure 3.1.4 shows the nominal doping ratio x dependence of actual Yb doping ratio (determined by EPMA). The theoretical Yb filling fraction is found to be 0.3[36], however, the reported highest Yb filling fraction is only around 0.2[37]. By using high pressure and high temperature method, the actual Yb filling fraction was achieved to be 0.29, the highest value reported until now. This results confirmed that the high-pressure synthesis technology has an advantage to tune widely the composition of CoSb₃ based skutterudites.



Fig. 3.1.5 Elemental distribution mapping and secondary electron image of (a) $Yb_{0.2}Co_4Sb_{12}$ [38] and (b) $Yb_{0.3}Co_4Sb_{12}$.

The electron probe micro-analysis were conducted on selected samples to get the information of the elemental distribution in samples. Figure 3.1.5 shows the Elemental distribution mapping and secondary electron image of $Yb_{0.2}Co_4Sb_{12}$ and $Yb_{0.3}Co_4Sb_{12}$, respectively. As shown in Fig.3.1.5, the matrix is skutterudite but some local elemental rich place can be observed and distributed randomly on the samples. Those local rich elemental cannot detected by XRD. Those local rich elements might attributed to the decreases of thermal conductivity on the one hand, however, one the other hand, it might also lead to an decreased the electronic conductivity.

From the point view of enthalpy of phase formation, the reaction route can be described as below[37]:

$$nM + 4CoSb_3 = \frac{2-n}{2-y} M_y Co_4 Sb_{12} + \frac{2(n-y)}{2-y} MSb_2 + \frac{4(n-y)}{2-y} CoSb_2$$
(3.1)

, where M is the rare earth element Yb, *n* is the nominal Yb doping ratio, and *y* is the actual filling fraction of Yb. This reaction can explains why impurities are hard to avoid. High pressure benefits the entrance of heavier rare earths into the voids of the skutterudites and thus can decreases the ratio of impurities and synthesized higher filling fraction compounds with high purity.

3.2 Crystal structure refinement







Fig. 3.2.1 Rietveld refinement of synchrotron X-ray powder diffraction for Yb_{0.2}Co₄Sb₁₂, Yb_{0.4}Co₄Sb₁₂, and Yb_{0.6}Co₄Sb₁₂.

The observed data are expressed as red points, the calculated profile are shown as green line, and the difference curve for the observed data and the calculated data is presented at the bottom along with the tag marks. The position peak of impurities is ignored to reduce error.

The crystal structure of Yb_{0.2}Co₄Sb₁₂, Yb_{0.4}Co₄Sb₁₂, and Yb_{0.6}Co₄Sb₁₂ was refined by the Rietveld method by using RIETAN_FP. The entire profile of X-ray diffraction data is fitted to the calculated pattern, as shown in Fig. 3.2.1. The fitted fata of all samples fitted very well with the observation data. The goodness of fit parameter *S* range from 1.16 to 1.63 and the weighted pattern indicator R_{wp} is around 3.2% to 4.5%. The calculated crystal bond distances and bond angles of Yb_{0.2}Co₄Sb₁₂, Yb_{0.4}Co₄Sb₁₂, and Yb_{0.6}Co₄Sb₁₂ is listed in Table 3.2.1.

From Table 3.2.1, it can be observed that Yb doping ratio can influence both the interatomic distances and the bond angles. Therefore, it might be speculated that the band structure of Yb doped CoSb₃ skutterudite might also related with the Yb doping ratio. In addition, the Sb - Sb distance along the shorter edge and the longer edge gradually decreased as Yb doping ratio increasing, indicative that the increased Yb content can promote the Sb₄ clusters change from rectangular to square.

Interatomic distances (Å)													
Sample	Yb-Sb	Yb-Co			Co-Sb	Sb-Sb'	Sb-Sb''						
Yb _{0.2} Co ₄ Sb ₁₂	3.3543	3.9113			2.5299	2.9593	2.8491						
Yb _{0.4} Co ₄ Sb ₁₂	3.3601	3.9023		,	2.5225	2.9441	2.8501						
Yb _{0.6} Co ₄ Sb ₁₂	3.3795	3.9274		,	2.5421	2.9506	2.8705						
Bond angles(deg)													
Sample	Yb-Sb-	Yb-Sb-	Yb-S	b-	Co-Sb-	Co-Sb	- Co-Sb-						
	Co	Sb'	Sb''		Sb'	Sb''	Со						
Yb _{0.2} Co ₄ Sb ₁₂	82.03	154.87	64.87		107.92	109.24	4 126.40						
Yb _{0.4} Co ₄ Sb ₁₂	81.78	154.85	64.84		108.15	108.95	5 126.56						
Yb _{0.6} Co ₄ Sb ₁₂	81.77	154.87	64.87		108.16	109.11	1 126.26						

Table 3.2.1 Crystal structure parameters for $Yb_{0.6}Co_4Sb_{12}$.

3.3 Electrical transport properties of Yb_xCo₄Sb₁₂ (0≤x≤0.7)

The temperature dependence of seebeck coefficient S for Yb_xCo₄Sb₁₂ ($0 \le x \le 0.7$) is plotted in Fig. 3.3.1. The seebeck coefficient for CoSb₃ and Yb_{0.1}Co₄Sb₁₂ is positive, whereas that for higher Yb doped samples ($x \ge 0.2$) is negative, indicative a dominant carriers transition from hole to electron, that is, the sample transferred from p-type to n-type semiconductor. The maximum value of *S* was observed in Yb_{0.2}Co₄Sb₁₂ with the value of 86.3 μ V/K at 300 K.

Figure 3.3.2 shows the electrical resistivity ρ as a function of temperature T for $Yb_xCo_4Sb_{12}$ ($0 \le x \le 0.7$) compounds. While $CoSb_3$ and $Yb_{0.1}Co_4Sb_{12}$ exhibits an decreased resistivity as temperature increasing, the higher Yb doped samples ($x \ge 0.2$) shows an increased resistivity as temperature increasing. This results indicated that $CoSb_3$ and $Yb_{0.1}Co_4Sb_{12}$ is semiconductor while the higher Yb doped sample is semimetal. In addition, the resistivity for $Yb_xCo_4Sb_{12}$ ($x \ge 0.2$) is much smaller than that of $CoSb_3$. For example, the resistivity of $CoSb_3$ is $0.44 \times 10^{-4} \ \Omega \cdot m$ at 300 K and that of $Yb_{0.2}Co_4Sb_{12}$ is $5.8 \times 10^{-5} \ \Omega \cdot m$.

In addition, the resistivity of Yb_{0.2}Co₄Sb₁₂ is lower than that of Yb_{0.2}Co₄Sb₁₂ (6.3×10^{-5} Ω ·m) prepared by the melting and hot pressing methods[38]. It is also even lower than that of nanostructured Yb_{0.2}Co₄Sb₁₂ ($0.11 \times 10^{-4} \Omega$ ·m) at 300 K. The room temperature is decreased with increasing Yb content; e.g. ρ of Yb_{0.4}Co₄Sb₁₂ was decreased to $4.6 \times 10^{-5} \Omega$ ·m.



Fig. 3.3.1 Temperature dependence of seebeck coefficient S for $Yb_xCo_4Sb_{12}$ ($0 \le x \le 0.7$).



Fig. 3.3.2 Temperature dependence of electrical resistivity for $Yb_xCo_4Sb_{12}$ ($0 \le x \le 0.7$).

Fig.3.3.3 shows the temperature dependence of carrier concentration for $Yb_xCo_4Sb_{12}$ ($0 \le x \le 0.7$). The carrier concentration for CoSb₃ and Yb_xCo₄Sb₁₂ almost keep a value of constant above 150 K. However, the carrier concentration for $Yb_{0.1}Co_4Sb_{12}$ ($0.2 \le x \le 0.7$) exhibit a linearly increased carrier concentration with increasing temperature. The Yb occupancy increases with increasing Yb content x, which results in a high carrier concentration ranging from 3.59×10^{18} cm⁻³ to 1.08×10^{21} cm⁻³ (x=0.7).



Fig. 3.3.3 Temperature dependence of carrier concentration *n* for Yb_xCo₄Sb₁₂ ($0 \le x \le 0.7$) [38].

Fig. 3.3.4 shows the temperature dependence of carrier mobility μ_H for Yb_xCo₄Sb₁₂ (0≤x≤0.7). With increasing temperature, the mobility for CoSb₃ and Yb_{0.1}Co₄Sb₁₂ increases while carrier mobility μ_H for decreases Yb_xCo₄Sb₁₂ (0.2≤x≤0.7). All the compounds shows saturate carrier mobility at low temperature. The room temperature μ_H decreases from the value of 157 cm²V⁻¹s⁻¹ for Yb_{0.2}Co₄Sb₁₂ to 12 cm²V⁻¹s⁻¹ for Yb_{0.6}Co₄Sb₁₂.



Fig. 3.3.4 Temperature dependence of carrier mobility μ_H for Yb_xCo₄Sb₁₂ (0 \leq x \leq 0.7). Figure 3.3.5 shows the room temperature Yb content x dependent of carrier concentration n. Figure 3.3.6 shows the room temperature Yb content x dependent of carrier mobility μ_H .





Fig. 3.3.5 Room temperature Yb content x dependent of carrier concentration n.



Fig. 3.3.6 Room temperature Yb content x dependent of carrier mobility μ_{H} .

The room temperature transport properties of selected Yb_xCo₄Sb₁₂ (x=0, 0.2, 0.4, and 0.6) are listed in Table 3.3.1. The thermal conductivity were reduced from 6.44 Wm⁻¹K⁻¹ (x=0) to 3.59 Wm⁻¹K⁻¹ (x=0.6) with increasing x due to the enhancement of the rattling effect of Yb fillers. Moreover, a high Yb filling fraction increases the charge carrier concentration and decreases the electrical resistivity. Unfortunately, the Seebeck coefficient is also decreased due to the excess carriers. Therefore, a maximum power factor of 1290 μ Wm⁻¹K⁻² was achieved in Yb_{0.2}Co₄Sb₁₂ other than Yb_{0.6}Co₄Sb₁₂.

EPMA	Nominal	κ	κ _L	ρ	S	n	PF
	Yb ratio	Wm ⁻¹ K ⁻¹	Wm ⁻¹ K ⁻¹	mΩ·cm	μV/K	10^{20} cm^{-3}	$\mu Wm^{-1}K^{-2}$
CoSb _{2.93}	0	6.44	6.27	4.4	99.3	0.036	210
Yb _{0.164} Co ₄ Sb _{11.57}	0.2	3.76	2.53	0.58	-86.3	0.669	1290
Yb _{0.2} Co ₄ Sb _{11.32}	0.4	3.74	2.42	0.46	-73.2	6.38	970
Yb _{0.29} Co ₄ Sb _{11.71}	0.6	3.59	2.02	0.47	-64.1	6.02	1010

Table 3.3.1 Summary of compositions and transport properties of CoSb₃ skutterudites partially filled with Yb at room temperature.

3.4 Thermal transport properties of $Yb_xCo_4Sb_{12}$ ($0 \le x \le 0.7$)

Fig. 3.4.1 shows the temperature dependence of total thermal conductivity κ , electric thermal conductivity κ_e , and lattice thermal conductivity κ_L for Yb_xCo₄Sb₁₂ (0≤x≤0.7), respectively. The lattice thermal conductivity component κ_L were obtained by subtracting the electronic thermal conductivity component κ_e from the total thermal conductivity κ . According to Wiedemann-Franz law, the electronic thermal conductivity can be expressed as:

$$\kappa_e = L_0 T / \rho \tag{3.2}$$

, where the L₀ is the Lorenz number (L₀= $2.44 \times 10^{-8} W\Omega^{-1} K^{-2}$), T is the absolute temperature, and ρ is the electrical resistivity.

From Fig. 3.4.1, it can be observed that κ and κ_L decreases with increasing Yb filling fraction. The minimum value of κ_L were observed in Yb_{0.6}Co₄Sb₁₂ with the value of 2.02 Wm⁻¹K⁻¹ at 300 K. The decrease of κ_L indicate an stronger resonant scattering for phonons, presumably owing to rattling of Yb atoms.

Compared with Yb doped compounds synthesized by conventional approaches, $Yb_{0.6}Co_4Sb_{12}$ synthesized by high pressure exhibits a lower lattice thermal conductivity. This low lattice thermal conductivity is even comparable to the double rare earth elements doped CoSb₃ skutterudites. Lower value of thermal conductivity is expected by filling two kinds of rare earth elements and substitution the Co site with other transition metals, such as Fe and so on.












Fig.3.4.1 Temperature dependence of total thermal conductivity and κ and lattice thermal conductivity, respectively κ_L for Yb_xCo₄Sb₁₂ (0 \leq x \leq 0.7).

3.5 Figure of merit ZT of Yb_xCo₄Sb₁₂ (0≤x≤0.7)

Fig. 3.5.1 shows the dimensionless figure of merit ZT for $Yb_xCo_4Sb_{12}$ ($0 \le x \le 0.7$) from 2 to 300 K. All the Yb doped samples exhibits improved ZT values compared with unfilled CoSb₃. The maximum ZT value of 0.1 was obtained in Yb_{0.2}Co₄Sb₁₂ at room temperature. Higher Yb filling fraction do not improve the figure of merit ZT but decreased it. This should be related with the relative high carrier concentration in high Yb filling system. Considering higher Yb filling fraction can results lower thermal conductivity, the higher figure of merit should be achieved if the excess carrier can be compensated.



Fig. 3.5.1 Temperature dependent of figure of merit ZT for Yb_xCo₄Sb₁₂ (0≤x≤0.7).

3.6 Summary

High pure Yb_xCo₄Sb₁₂ ($0 \le x \le 0.8$) compounds were synthesized under high pressure. The actual filling fraction limit of Yb was found to be 0.29 by high pressure and high temperature synthesize technology. The lattice constant increases with increasing actual Yb filling fraction. The lattice thermal conductivity were decreased with increasing Yb filling fraction. The lowest room temperature lattice thermal conductivity of 2.02 Wm⁻¹K⁻¹ was observed in Yb_{0.6}Co₄Sb₁₂. Although high Yb content can enhance the electrical conductivity and thermal conductivity, it also decreased the Seebeck coefficient due to the relative high carrier concentration. The optimized ZT value of 0.1 for Yb_{0.2}Co₄Sb₁₂ was achieved at room temperature. Higher figure of merit is expected in high Yb filling fraction compounds with the introduction of holes donor elements.

CHAPTER 4 Experimental results for Yb_{0.6}Fe_yCo_{4-y}Sb₁₂

4.1 Synthesize condition and sample characterization

Fe substitute $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0 \le y \le 1$) samples were prepared at high temperature and a high pressure using a cubic-anvil high-pressure apparatus. Due to the secondary phases of FeSb₂ is easy formed above 600 °C, the synthesize temperature were carefully controlled to between 590 °C to 600 °C. All the compounds were prepared by reaction of stoichiometric amounts of components at around 590 °C and 2 GPa. The reaction time was 120 minutes.

Fe substitution would affect not only transport properties of the ternary skutterudite $Yb_{0.6}Co_4Sb_{12}$ but also the actual Yb filling ratio in $Yb_{0.6}Co_4Sb_{12}$. Various attempts have been made referring to Yb-filled or/and Fe-substitute $CoSb_3$ skutterudite compounds [40-46]. However, most of them paid attention on the influence of different element or rare earth filling fraction. There is barely information about Yb-ratio fixed and Fe ratio varied compounds which are necessary for study the influence of Fe substitution on the TE properties of Yb-filled skutterudites. We hope that this work will provide a link to previous works and allow for a direct compare of the Fe doping on the influence of the thermoelectric properties of Yb-filled CoSb_3 skutterudites.

The crystalline phases of synthesized samples were characterized by powder X-ray diffraction with $CoK\alpha_1$ radiation and silicon as a standard. Electron probe micro analysis was employed to detect the actual components and elements distribution.

Figure 4.1.1 shows the X-ray diffraction patterns of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0 \le y \le 1$). The relative intensities of the impurity phases with respect to the main peak reflection are below 4 %. The secondary phases located in the sample randomly as micro-size particles and can be treated as static point defect which only provide additional carrier and phonon scattering source.









Figure 4.1.1 X-ray patterns of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0 \le y \le 1$).

Figure 4.1.2 shows elemental mapping and secondary electron image of $Yb_{0.6}Fe_{0.3}Co_{3.7}Sb_{12}$. Elemental mapping of $Yb_{0.6}Fe_{0.3}Co_{3.7}Sb_{12}$ shows a homogeneous Yb/Fe chemical distribution in the skutterudite matrix. Some local rich segments (indicative of Yb and FeSb₂) are also observed.



Figure 4.1.2 Electro probe micro-analysis (EPMA) of Yb_{0.6}Fe_{0.3}Co_{3.7}Sb₁₂ [47]

4.2 Crystal structure refinement of selected $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$



Figure 4.2.1 Rietveld refinement of synchrotron X-ray powder diffraction for $Yb_{0.6}Fe_{0.3}Co_{3.7}Sb_{12}$.



Figure 4.2.2 Rietveld refinement of synchrotron X-ray powder diffraction for $Yb_{0.6}Fe_{0.9}Co_{3.1}Sb_{12}$. The observed data are shown as points, the calculated profile are shown as red line, and the difference curve is presented at the bottom along with the tag marks indicating the Bragg positions.



Figure 4.2.3 MEM charged density of Yb_{0.6}Fe_{0.9}Co_{3.1}Sb₁₂.



Figure 4.2.4 MEM charged density of (010) face of Yb_{0.6}Fe_{0.9}Co_{3.1}Sb₁₂.

The influence of Fe substitution on the crystal structure of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ was studied with Rietveld refinement for synchrotron powder X-ray diffraction data with $Yb_{0.6}Co_{2.5}Fe_{1.5}Sb_{12}$ as starting model [41]. Figure 4.2.1 and figure 4.2.2 shows the observed X-ray diffraction pattern and calculated profile and their difference for $Yb_{0.6}Fe_{0.3}Co_{3.7}Sb_{12}$ and $Yb_{0.6}Fe_{0.9}Co_{3.1}Sb_{12}$, respectively. The inset shows the calculated skutterudite structure. Figure 4.2.3 shows the MEM charged density of $Yb_{0.6}Fe_{0.9}Co_{3.1}Sb_{12}$. Figure 4.2.4 shows the MEM charged desity distribution of (010) face of unit skutterudite of $Yb_{0.6}Fe_{0.9}Co_{3.1}Sb_{12}$. The refined crystal and structure parameters obtained from the Rietveld analysis are listed in Table 1. The lattice constants estimated from Rietveld analyses were consistent with that obtained from XRD and were confirmed from the atom bond distances listed in Table 4.2.1.

Parameter/compound	Yb ₀₆ Fe _{0.3} Co _{3.7} Sb ₁₂	Yb ₀₆ Fe _{0.5} Co _{3.5} Sb ₁₂	Yb ₀₆ Fe _{0.9} Co _{3.1} Sb ₁₂
EPMA	Yb _{0.3} Fe _{0.2} Co _{3.8} Sb ₁₂	Yb _{0.47} Fe _{0.38} Co _{3.62} Sb ₁₂	Yb04Fe0.6Co3.4Sb12
R _{wp}	6.68	7.25	3.24
S	1.96	1.89	1.32
B (Å ²) for Yb	2.169	2.218	2.299
Y	0.15857	0.15862	0.15885
Z	0.33696	0.33690	0.33707
Interatomic distances (Å) and bond angles (deg)			
Yb-Sb	3.3721(8)	3.36499	3.37769
Yb-Co/Fe	3.9209(8)	3.92282	3.92497
Co/Fe-Sb	2.5357(8)	2.53629	2.53789
Sb-Sb(Long)	2.9526(9)	2.969113	2.953713
Sb-Sb(Short)	2.8717(4)	2.86349(4)	2.879732
R _{Sb}	1.0281	1.0369	1.0257
Yb-Sb-Co/Fe	81.83(9)	82.03(5)	81.81(5)
Yb-Sb-Sb'	154.78(0)	154.818	154.767(13)
Yb-Sb-Sb''	64.78(5)	78.785	78.865
Co/Fe-Sb-Sb'	108.09(3)	107.927	108.127
Co/Fe-Sb-Sb''	109.03(6)	109.186	109.006
Co/Fe-Sb-Co/Fe	126.46(4)	126.4777	126.485

Table 4.2.1 EPMA and crystal structure parameters for $Yb_{06}Fe_yCo_{4-y}Sb_{12}$ refined by the Rietveld analysis at room temperature.

4.3 Electrical transport properties of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0 \le y \le 1$).



Figure 4.3.1 Seebeck coefficient S of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0 \le y \le 1$) at 280 K.

Figure 4.3.1 shows that the temperature dependence of Seebeck coefficient S of Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ ($0 \le y \le 1$). The absolute value of all the Seebeck coefficient increases with increased temperature. Small content of Fe substitution keep the compounds Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ ($0 \le y \le 0.8$) in the n-type semiconductor while the Fe content increased to 0.9, the compounds transferred from n-type semiconductor to p-type semiconductor. Seebeck coefficient first increases with Fe content increasing, then slightly decreased after reaching its maximum absolute value, finally transferred from negative to positive value abruptly as Fe content increased to 0.9.



Figure 4.3.2 Temperature dependence of electrical conductivity σ of Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ (0 \leq y \leq 1).

Figure 4.3.2 shows that the temperature dependence of electrical conductivity σ of Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ (0≤y≤1). The σ of Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ with low Fe content (y=0, 0.2) depends stronger on temperature. The similar behavior of ρ is also observed in higher Fe content (x=0.9, 1). The σ for Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ (0.3≤y≤0.8) is almost temperature independence.



Figure 4.3.3 Power factor of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0 \le y \le 1$).

Figure 4.3.3 shows the power factor PF of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0 \le y \le 1$). The maximum of PF was observed in $Yb_{0.6}Fe_{0.2}Co_{3.8}Sb_{12}$ with the value of 1.38 mW/m·K² at 300 K.



4.4 Thermal transport properties of Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ (0≤y≤1).



Figure 4.4.1 Temperature dependence of (a) total thermal conductivity κ , (b) electric thermal conductivity κ_e , and (c) lattice thermal conductivity κ_L in Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ at 300 K.

Figure 4.4.1 (a) shows the temperature dependence of total thermal conductivity. As Fe content increasing, an additional reduction of thermal conductivity in Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ (except y=0.2) are observed above 50 K. This behavior was also observed in other Fe substituted CoSb₃-based compounds. To investigate the origin of this behavior, the electronic contributed thermal conductivity is isolated by using the Wiedemann-Franz law: $\kappa_e = L_0 T/\rho$, where L_0 denotes the Lorenz number with a numerical value of $L_0 = 2.0 \times 10^{-8} \text{ V}^2/\text{deg}^2$, which is an experimental value estimated by Dyck *et al.* for skutterudites. The electric thermal conductivity κ_e is plotted in Fig. 4.4.1 (b).

The lattice thermal conductivity κ_L is obtained by subtracting κ_e from k and is plotted in Fig. 4.4.1 (c). From Figure 4.4.1 (c), it is clear that boundary scattering is dominant phononscattering mechanism below 20 K with point defect and resonance scattering being dominant at 20 - 100 K. Considering all the compounds were synthesized under same condition and all have similar lattice constants, the reduced thermal conductivity between 50 and 100 K should mainly originate from the enhanced point defect and resonance scattering effect (rattling effect). The κ_L of Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ follows well with the $\sim T^{-1}$ dependence above 100 K, implying the main phonon scattering mechanism is umklapp process (phonon-phonon scattering). As a consequence, the room temperature κ_L of Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ slightly increased although Yb filling content increased. That is, higher Yb filling fraction does not decrease κ_L further. Similar behavior were also observed in La, Ce, and Nd filled CoSb₃ skutterudites with the explain that the partially voids filling led a relative structure disorder which acted as one static scattering mechanism in addition to the 'rattling' of voids filling atoms. On the other hand, this result might also suggest a suppressed 'rattling' effect in Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ compared with their parent compound Yb_{0.6}Fe_yCo_{4-y}Sb₁₂.

The lessened κ originated from the dwindled electronic thermal conductivity. This is strange because the mass and volume differences between Fe and Co were only 5 % and 6 % respectively, which can causes only small structure disorder and thus little additional carrier scattering. The ingredient fluctuation between the high Fe and low Fe segment might play a dominant role in reducing the electric thermal conductivity.

4.5 Figure of merit ZT of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0 \le y \le 1$).



Figure 4.5.1 Temperature dependent of figure of merit ZT for Yb_{0.6}Fe_yCo_{4-y}Sb₁₂ (0≤y≤1).

Figure 4.5.1 shows the temperature dependent of figure of merit ZT for $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0 \le y \le 1$). Compared with the parent compound $Yb_{0.6}Co_4Sb_{12}$, the ZT of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ (y=0.2, 0.3, 0.4, 0.5, 0.6) are clearly improved. The highest ZT (0.12) was achieved in the Fe content of 0.3 at 300 K. A higher ZT in $Yb_{0.6}Fe_{0.3}Co_{3.8}Sb_{12}$ can be achievable in the hightemperature range.

4.6 Summary

In this work, we aim to enhance the figure of merit ZT of n-type $Yb_xFe_yCo_{4-y}Sb_{12}$ system by varying the Fe substitution ratio. A serious of Yb fixed Fe various compounds $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0 \le y \le 1$) were studied in detail.

The Fe-substitution ratio effect on the thermoelectric performance of $Yb_xFe_yCo_{4-y}Sb_{12}$ were studied from the view of both electrical and thermal transport properties. Powder XRD data indicated that all the compounds are high-purity skutterudites. EPMA analysis reveals that $Yb_xFe_yCo_{4-y}Sb_{12}$ have net-like composition fluctuate in addition to the mass and volume fluctuate caused by Fe substitution for Co. The resistivity were increased by Fe substitution. $Yb_xFe_yCo_{4-y}Sb_{12}$ exhibits enhanced Seebeck coefficient. Fe substitution lead to a further decreased thermal conductivity which mainly origin from the reduced electric thermal conductivity. As a consequence, an optimized figure of merit was achieved in $Yb_{0.6}Fe_{0.3}Co_{3.7}Sb_{12}$. Heat capacity measurement indicate that Fe substitution for Co do not affect θ_E although the actual Yb filling ratio increased in $Co_{4-y}Fe_ySb_{12}$ polyanion.

CHAPTER 5 Conclusion

Thermoelectric materials have received considerable attention for use as an alternative energy conversion technology. $CoSb_3$ -based skutterudite compounds have been believed to be one of the best candidates of thermoelectric materials due to their excellent thermoelectric properties. Filling atoms inside the voids of the skutterudite structure would lead to a rattling behavior that can remarkably decrease the lattice thermal conductivity. Furthermore, the small and heavy atoms should be more effective in rattling. Therefore, the heavy rare-earth atoms are suitable for rattlers for $CoSb_3$. However, for only Yb, a small amount (x<0.2) of partial doping to $CoSb_3$ has been succeeded by standard synthesis at ambient pressure.

We have tried to synthesize $Yb_xCo_4Sb_{12}$ with a high filling rate (x \leq 0.7) by a high-pressure synthesis technique and have investigated rattling effect of Yb atoms on thermoelectric properties by measuring Seebeck coefficient and thermal conductivity. The highest Yb doping ratio was found to be 0.29 which is highest value reported until now. The thermal conductivity at room temperature showed a minimum for x=0.6. However, the high filling fraction of Yb was also accompanied with high carrier concentration which led to a reduced Seebeck coefficient and thus low figure of merit ZT. To further optimize the thermoelectric performance, the excess electrons in Yb_{0.6}Co₄Sb₁₂ needs to be compensated by introducing a hole donor element, such as Fe, in Co site.

Then, we focus on the characterization of skutterudite $Yb_xFe_yCo_{4-y}Sb_{12}$ (x=0.6; $0 \le y \le 1$) which were synthesized under high pressure. The effect of Fe substitution was studied by measuring the crystal structure, thermoelectric, magnetic and specific heat properties. Rietveld refinement based on the synchrotron radiation X-ray data indicates that the rectangular Sb₄ ring is transformed into quasi-square with increasing Yb content and/or Fe substitution content. The carrier concentration dependent of effective mass suggests that the conduction band of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ do not affected by filler but by Fe substitution. The reduction of total thermal conductivity κ mainly originate from the decreases of electron contribution. The lattice contributed thermal conductivity were slightly increased owing to the decreased resonant vibration phonon scattering. Reasonable Fe substitution for Co site leads to a ~ 38% increase in maximum ZT (0.12). According to the specific heat analysis, higher Yb doping benefits lower Debye temperature due to decreased covalent bonding within the Co₄Sb₁₂ polyanion structure while the Fe substitution lead to an increased Debye temperature. The Einstein temperature decreased with increasing Yb filling fraction but Fe substitution for Co site do not change the Einstein temperature further.

References

- [1] T. J. Seebeck, Akad. Wiss. Berlin, 289 (1821).
- [2] A. d. C. J. C. Peltier, *Physique*, **56** (1834).
- [3] A. F. Ioffe, S. V. Airepetyants, A. V. Ioffe, N. V. Kolomoets, and L. S. Stil'bans, Dokl. Akad. Nauk. SSSR 106, 981 (1956).
- [4] A. F. Ioffe, Semiconductor thermoelements and thermoelectric cooling, Infosearch, London (1957).
- [5] A. F. Ioffe: Soviet Phys. Tech. Phys. 1, 462 (1956)
- [6] J.-F. Li, W.-S. Liu, L.-D. Zhao, and M. Zhou, NPG Asia Materials, 2 (2010) 152.
- [7] Pryts, PhD thesis, University of Oslo "Electronic structure and bonding in thermoelectric skutterudite," 2007.
- [8] A. M. M. thesis, "Modeling of the thermoelectric properties of bulk and nanocomposite thermoelectric materials," 2008.
- [9] K. T. Wojciechowski, MATERIAIY CERAMICZNE, 62 (2010) 461.
- [10] B. C. Sales, D. Mandrus, R. K. Williams, Science, 272 (1996) 1325.
- [11] A. Borshchevsky, T. Caillat, and J.-P. Fleurial, "Solid solution formation: improving the thermoelectric properties of skutterudites," in *Thermoelectrics*, 1996., *Fifteenth International Conference*, pp. 112-116.
- [12] G. Nolas and C. Kendziora, *Phys. Rev. B*, **59** (1999) 6189.
- [13] J. W. Sharp, E. C. Jones, R. K. Williams, P. M. Martin and B. C. Sales, J. Appl. Phys. 78 (1995) 1013.

- B. C. Sales, D. Mandrus, B. Chakoumakos, V. Keppens, and J. Thompson, Phys. Rev. B, 56 (1997) 15081.
- [15] I. K. Dimitrov, M. E. Manley, S. M. Shapiro, J. Yang, W. Zhang, L. Chen, Phys. Rev. B, 82 (2010) 174301.
- [16] G. A. Slack, "CRC Handbook of Thermoelectrics.," *ed.* Boca Raton, FL: CRC Press, 1995, pp. 407–440.
- [17] W. Jeitschko and D. Braun, Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, **33** (1977) 3401.
- [18] B.C. Sales, "Filled skutterudites," *Handbook on the Physics and Chemistry of rare earths*, vol. 33, 2003.
- [19] C. Uher, "Skutterudites: prospective novel thermoelectrics," *Semiconductors and semimetals*, **69** (2001) 139.
- [20] C. Yuqi, Y. Kawamura, J. Hayashi, and C. Sekine, Jpn. J. Appl. Phys., 55 (2016) 04EJ02.
- [21] C. Sekine, T. Uchiumi, I. Shirotani, K. Matsuhira, T. Sakakibara, T. Goto, *et al.*, Phys. Rev. B, **62** (2000) 11581.
- [22] C. Sekine, T. Uchiumi, I. Shirotani, and T. Yagi, Phys. Rev. Lett. 79 (1997) 3218.
- [23] H. Takizawa, K. Miura, M. Ito, T. Suzuki, and T. Endo, J. Ally.Compd., 282 (1999)
 79.
- [24] I. Shirotani, S. Sato, C. Sekine, K. Takeda, I. Inagawa, and T. Yagi, J. Phys. Condens. Matter, 17 (2005) 7353.
- [25] T. Caillat, A. Borshchevsky, and J. P. Fleurial, J. Appl. Phys, 80 (1996) 4442.
- [26] J. Y., L.L. Xi, X. Shi, W. Zhang, L.D. Chen and J.H. Yang, Scientia Sinica Physica, 41 (2011) 706.

- [27] X. Shi, W. Zhang, L. D. Chen, and J. Yang, Phys. Rev. Lett., 95 (2005) 185503.
- [28] Z. Mei, W. Zhang, L. Chen, and J. Yang, Phys. Rev. B, 74 (2006) 153202.
- [29] K.-H. Park, W.-S. Seo, D.-K. Shin, and I.-H. Kim, J. Korean Phys. Soc., 65 (2014)
 491.
- [30] J. Yang, Q. Hao, H. Wang, Y. C. Lan, Q. Y. He, A. Minnich, *et al.*, Phys. Rev. *B*, 80 (2009) 115329.
- [31] I. Shirotani, K. Takeda, C. Sekine, J. Hayashi, R. Nakada, K. Kihou, Y. Ohishi, T. Yagic, Zeitschrift f
 ür Naturforschung B, 61 (2006) 1471.
- [32] E.H. Hall, On a new action of the magnet on electric currents, American Journal of Mathematics, 2 (1879) 287.
- [33] PPMS, PPMS Heat Capacity manual.
- [34] F. Izumi, K. Momma, Solid State Phenom., **130** (2007) 15.
- [35] 古河機械金属株式会社, n-型スクッテルダイト系Yb-Co-Sb熱電変換 材料の製造方法, in, Japan, 2012.
- [36] Z. Mei, W. Zhang, L. Chen, and J. Yang, Phys. Rev. B, 74 (2006) 153202.
- [37] X. Shi, W. Zhang, L.D. Chen, and J. Yang, Phys. Rev. Lett., 95 (2005) 185503.
- [38] Y. Chen. Y. Kawamura, J. Hayashi, and C. Sekine, Jpn. J. Appl. Phys. 54 (2015) 055501.
- [39] G. S. Nolas, M. Kaeser, and T. M. Appl. Phys. Lett., 77 (2000) 1855.
- [40] K.-H. Park, S. Lee, W.-S. Seo, et al., J. Korean Phys. Soc., **64** (2014) 863.
- [41] D. Yongkwan, P. Pooja, T.M. Tritt, et al., J. Solid State Chem., **209** (2014) 1.
- [42] S. Ballikaya, C. Uher, et al., J. Alloys Compd., **585** (2014) 168.
- [43] Y. Dong, P. Puneet, T.M. Tritt, et al., Phys. Stat. Solidi (RRL), 7 (2013) 418.

- [44] C. Zhou, D. Morelli, X. Zhou, G. Wang, and C. Uher, Intermetallics, 19 (2011) 1390.
- [45] R. Liu, J. Yang, X. Chen, X. Shi, et al., Intermetallics, **19** (2011) 1747.
- [46] L. Zhang, A. Grytsiv, M. Kerber, et al., J. Alloy. Compd., **490** (2010) 19.

Acknowledgments

I would like first to thanks my supervisor Prof. Sekine Chihiro. Thank you for accepting me as your doctoral students and teach me how to be a researcher.

My sincere thanks also go to Prof. Kawamura Yukihiro who kindly teach me the experiment detail and explain with English patiently.

Thank you for the technical staff Junichi Hayashi who help me in EPMA and Rietveld analysis experiment.

Thank you for Prof. Takeda, Prof. Hirai and Prof. Sakai for supporting in experiment and study kindly.

Thank you for doctoral student Kanazawa san and the graduated students Kawai san, Kato san, Deminami san, Tanikawa san, Uchimura san and Mikake san who hive give me lots of support in my experiment.

Thank you for all students now in Sekine Lab members for all happy days.

A special thanks to my beloved husband Liang. Thank you for your encouraging and support in everything. My deepest thanks and love is given to my parents for everything they give to me.

Thanks to God, my good Father, who lead my life and teach me how to live day by day.