Effects of single and double filling in skutterudites for thermoelectric applications

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NANYANG
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**EFFECTS OF SINGLE AND DOUBLE FILLING
IN SKUTTERUDITES FOR THERMOELECTRIC
APPLICATIONS**

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**SCHOOL OF MATERIALS SCIENCE AND
ENGINEERING**

2011

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APPLICATIONS**

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Table of Contents

Acknowledgements.....	I
Table of Contents	II
Abstract.....	V
Chapter 1 Introduction.....	1
1.1 Background	1
1.2 Objectives	2
1.3 Thesis Outline.....	3
Chapter 2 Literature Review.....	4
2.1 Thermoelectricity Background.....	4
2.1.1 Thermoelectric Effects	4
2.1.2 Thermoelectric Materials	8
2.1.3 Skutterudites	11
2.2 Theory of Electrical and Thermal Properties in TE Materials	17
2.2.1 Seebeck Coefficient	17
2.2.2 Electrical Resistivity	19
2.2.3 Thermal Conductivity	20
2.3 Single and Double Filling Effects in Skutterudites	24
2.3.1 Single Filling.....	24
2.3.2 Double Filling.....	30
Chapter 3 Experimental Procedures	34
3.1 Synthesis of Skutterudites	34
3.2 Characterizations	35

3.2.1	X-ray Diffraction, Surface and Compositional Analysis.....	35
3.2.2	High Temperature Electrical Resistivity and Seebeck Coefficient Measurement.....	36
3.2.3	High Temperature Thermal Conductivity Measurement.....	37
3.2.4	Low Temperature Measurements	40
Chapter 4	Electrical Properties of Single and Double Filled Skutterudites	41
4.1	Electrical Properties of La, Ca and Sr Single Filled Skutterudites	41
4.1.1	X-ray Diffraction Patterns and Rietveld Refinements	44
4.1.2	Seebeck Coefficient	51
4.1.3	Electrical Resistivity	53
4.1.4	Power Factor	56
4.1.5	Comparison of La, Ca and Sr Single Filling.....	58
4.2	Electrical Properties of Ca-La and Sr-La Double Filled Skutterudites	63
4.2.1	X-ray Diffraction Patterns, Rietveld Refinements and X-ray Photoelectron Spectroscopy Study	64
4.2.2	Seebeck Coefficient	70
4.2.3	Electrical Resistivity	73
4.2.4	Power Factor	75
4.2.5	Ca-La and Sr-La Comparison	76
Chapter 5	Thermal Properties of Single and Double Filled Skutterudites	80
5.1	Thermal Properties of La, Ca and Sr Single Filled Skutterudites	80
5.1.1	La Single Filled Skutterudites.....	80
5.1.2	Ca Single Filled Skutterudites	84

5.1.3	Sr Single Filled Skutterudites	87
5.1.4	Comparison of La, Ca and Sr Single Filling.....	91
5.2	Thermal Properties of Ca-La and Sr-La Double Filled Skutterudites	96
5.2.1	Ca-La Double Filled Skutterudites	96
5.2.2	Sr-La Double Filled Skutterudites	101
5.2.3	Ca-La and Sr-La Comparison	104
Chapter 6	Dimensionless Figure of Merit ZT in Single and Double Filled Skutterudites	107
6.1	ZT Values of Single Filled Skutterudites	108
6.1.1	La Single Filled Skutterudites.....	108
6.1.2	Ca Single Filled Skutterudites	109
6.1.3	Sr Single Filled Skutterudites	111
6.1.4	Comparison of La, Ca and Sr Single Filling.....	112
6.2	ZT Values of Ca-La and Sr-La Double Filled Skutterudites	114
6.2.1	Ca-La Double Filled Skutterudites	114
6.2.2	Sr-La Double Filled Skutterudites	115
6.2.3	Ca-La and Sr-La Comparison	116
Chapter 7	Conclusions and Future Work	118
7.1	Conclusions	118
7.2	Future Work	124
	Publication List	126
	References	127

Abstract

In recent years, skutterudites have attracted huge attention and are reckoned to be one of the most promising groups of thermoelectric (TE) materials due to their “phonon-glass electron-crystal” (PGEC) property facilitated by an open structure in which foreign filler atoms can fill in. In this thesis, we focus on the study of the single and double filling effects on both electrical and thermal properties of skutterudites for thermoelectric applications. La, Ca and Sr were chosen as the filler atoms for the single filled skutterudites, while Ca-La and Sr-La were selected as the dual filler atoms for the double filled skutterudites. In addition, Fe was doped in the Co sites to create holes and thus compensate the extra electrons due to the introduction of these filler atoms. The electrical properties such as the Seebeck coefficient and electrical resistivity were measured as a function of temperature from 5K to 800K, and the electrical power factor was calculated. The temperature dependence of the total, electronic and lattice thermal conductivity were evaluated. Based on these properties, the dimensionless figure of merit, ZT , which is the standard parameter to estimate the TE performance and efficiency, was determined.

The La, Ca and Sr single filling is noted to decrease the hole concentration due to the introduction of extra electrons. As a result, the Seebeck coefficient and electrical resistivity are observed to increase as the filling fraction increases. The hole concentrations of our samples were kept in the order of 10^{19}cm^{-3} , which is reckoned to be in the range of the optimal values for high electrical power factor in a TE material. When compared with unfilled skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ with similar Fe doping content, the electrical power factor is noted to

have improved by the La, Ca and Sr single filling. The effects of Ca and Sr single filling on the electrical properties were found to be comparable since they gave the same amount of electron to the lattice. With similar filling fraction and Fe doping content, the La single filling results in higher Seebeck coefficient and electrical resistivity than the Ca and Sr single filling since the La filling can provide more electrons to the lattice. The Ca-La and Sr-La double filling give intermediate electrical power factors between their parent single fillings due to the same reason. In general, the effects of both single and double filling on electrical properties depend largely on the amount and charge valence of the filler atoms.

In terms of thermal conductivity, effective reduction was found in all La, Ca and Sr single filling, as these filler atoms can “rattle” in the oversized voids to scatter the phonons. This thermal conductivity reduction was observed to improve further as the filling fraction increased. Among the three kinds of filler atoms, La induced the most reduction in the thermal conductivity, and the reduction of thermal conductivity by Ca single filling was the lowest. This is attributed to their different point defect phonon scattering, which is caused by the mass fluctuation between the filler atoms and the remaining unfilled voids. The heavier the filler atom, the stronger the point defect phonon scattering can be induced. Hence, the La single filled skutterudites, which have the largest mass fluctuation, give the strongest point defect phonon scattering while the Ca single filled ones, which possess the smallest mass fluctuation, provide the weakest point defect phonon scattering. Sr filling gave the intermediate point defect phonon scattering effect due to its intermediate atomic weight. Further reduction of the thermal conductivity was

achieved by Ca-La and Sr-La double filling. The enhancement in the thermal conductivity reduction mainly comes from the broadening of the resonant rattling frequency range when two filler atoms of different elemental groups (alkaline-earth and rare-earth respectively) are employed. As a result, in the present work, Ca-La and Sr-La double filling are found to be more effective on thermal conductivity reduction than the reported Ce-La and Ba-Sr double filling whose filler atoms are from the same elemental group. With similar compositions, Sr-La double filling was noted to perform better than Ca-La double filling for reducing the lattice thermal conductivity. This is due to the heavier mass and larger size of Sr that has created more mass fluctuation and strain field difference in the lattice than that of Ca. Hence, the point defect phonon scattering by Sr-La double filling is stronger than that by Ca-La double filling.

The dimensionless figures of merit, ZT , in our single and double filled skutterudites were calculated based on their electrical and thermal properties. The La, Ca and Sr single filling has improved the ZT values up to nearly twice as high as that of the unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. This is mainly attributed to the dramatic reduction of the thermal conductivity due to the single filling. It is also observed that the Ca-La and Sr-La double filling can further enhance the ZT values due to their further reduction in the thermal conductivity. In general, it is found that filling into skutterudites results in overall ZT enhancement, where the contribution mainly comes from the significant reduction of thermal conductivity.

Chapter 1 Introduction

1.1 Background

Over the past decade, thermoelectricity (TE) has emerged to be a subject of interest due to the need of more green and efficient refrigeration and power generation. Thermoelectric refrigerators are friendly to the environment since they do not need CFC gas or any other refrigerants. Furthermore, thermoelectric refrigeration can also be applied for small-scale, localized cooling such as that in computers, infrared detectors, electronics, and optoelectronics, as well as many other applications. Thermoelectric power generation, on the other hand, has the potential to become part of the alternative energy technologies to reduce our dependence on fossil fuels and reduce greenhouse gas emissions. In addition, they have many advantages compared to conventional power generators, such as small size, no noise or vibration, and light weight [1].

A good thermoelectric material follows the model of “phonon-glass electron-crystal (PGEC)”, which means the material should possess thermal conductivity as low as a glass, and electrical conductivity as high as a perfect single crystal. The promising “PGEC” bulk thermoelectric materials include skutterudites, clathrates, half-Heusler alloys, β -Zn₄Sb₃ alloys, Chalcogenides, etc. Among these materials, skutterudites lead in performance at high temperature range [2]. Skutterudites are members of a family of compounds which have open structure or cage-like

structure. Certain atoms, such as that from rare-earth, alkaline-earth and Group IV, can be inserted into the interstitial voids or cages of these materials. The inserted or filled atoms can then “rattle” in the over-sized voids and result in the scattering of the phonons that leads to the dramatic reduction of thermal conductivity. By filling and doping, the compositions of skutterudites can be adjusted to optimize their thermoelectric properties, such as charge carrier concentration, Seebeck coefficient, electrical resistivity and thermal conductivity. The diversity of potential compositional variations is one of the key reasons that this material is considered in this PhD research project.

1.2 Objectives

In this work, we aim to study the effects of single and double filling on the electrical and thermal properties of skutterudites for thermoelectric applications. The rare-earth atom (La) and the alkaline-earth atoms (Ca and Sr) are chosen as the filler atoms due to their difference in atomic weight, radius and ionic charge.

In order to achieve further enhancement on the TE properties, Ca-La and Sr-La double filling are explored. The effect of dual filling of atoms that comes from different elemental groups is studied. Finally, based on the findings in both electrical and thermal properties, the effects of the single and double filled skutterudites on the figure of merit, ZT , are evaluated.

1.3 Thesis Outline

There are **seven chapters** in this thesis. **Chapter 1** gives the background of thermoelectric material research and the objectives of our research on skutterudite materials for the thermoelectric applications. **Chapter 2** provides a detailed review of literature including the introduction of thermoelectric materials especially on skutterudites, and followed by the theory of electrical and thermal properties in thermoelectric materials. **Chapter 3** presents our experimental procedures of skutterudite synthesis and characterizations. **Chapter 4 and 5** discuss the results of electrical and thermal properties of single and double filled skutterudites. **Chapter 6** shows the dimensionless figure of merit ZT values of these skutterudites based on their electrical and thermal properties. Finally, conclusions and recommendation of future work are presented in **Chapter 7**.

Chapter 2 Literature Review

2.1 Thermoelectricity Background

2.1.1 Thermoelectric Effects

Thermoelectric effect is the direct conversion of heat differences to electric voltage and vice versa. It contains three reversible effects, namely, the Seebeck effect, Peltier effect and Thomson effect.

In 1821, the Seebeck effect was discovered by the Estonian physicist Thomas Johann Seebeck where the joining of two dissimilar metals or semiconductors (n-type and p-type) with a temperature difference at the two junctions will result in the generation of a voltage that is proportional to the temperature difference, as shown

in Figure 2-1. The Seebeck coefficient or thermopower is defined as $S = \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T}$.

Figure 2-1 Seebeck effect in two dissimilar semiconductors (n-type and p-type).

The Peltier effect is the reverse of the Seebeck effect, and was reported by Jean Peltier in 1834. It occurs when a current is passed through two dissimilar metals or semiconductors (n-type and p-type) joined together with two junctions. A temperature gradient will develop between the two junctions since the heat is carried by the charge carriers (electrons or holes) from a junction to the other, as shown in Figure 2-2. The heat Q is proportional to the charge current I : $Q = \Pi \times I$, where Π is called the Peltier coefficient.

Figure 2-2 Peltier effect in two dissimilar semiconductors (n-type and p-type).

Thomson effect was predicted and subsequently experimentally proved by William Thomson (Lord Kelvin) in 1851. When a current I passes through a single metal or semiconductor which has a temperature difference ΔT between both ends, heat Q will be generated or absorbed as described by $Q = \beta I \Delta T$, where β is the Thomson coefficient. It is noted that the Seebeck coefficient S depends on temperature T and thus different at different places, this material can hence be thought of as a series of many Peltier junctions, each of which is generating or absorbing heats.

The three thermoelectric coefficients can be expressed by Thomson or Kelvin relationships: $\Pi=ST$ and $\beta=TdS/dT$. These relationships can be derived using irreversible thermodynamics and are believed to hold for all thermoelectric materials.

The potential of a material for Thermoelectric (TE) applications is determined by the dimensionless thermoelectric figure of merit, $ZT=S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, $S^2\sigma$ is referred to as the electrical power factor, T is the temperature in Kelvin and κ is the total thermal conductivity ($\kappa_T=\kappa_L+\kappa_E$, the lattice and electronic contribution, respectively) [3].

For a TE couple with p-type and n-type materials, its figure of

merit, $Z_c = \frac{(S_p - S_n)^2}{[(\frac{\kappa_p}{\sigma_p})^{1/2} + (\frac{\kappa_n}{\sigma_n})^{1/2}]^2}$. As a TE power generator, the maximum efficiency,

$$\phi_{\max} = \frac{T_H - T_C}{T_H} \times \frac{\sqrt{1 + Z_c \bar{T}} - 1}{\sqrt{1 + Z_c \bar{T}} + \frac{T_C}{T_H}} [4], \text{ where } T_H \text{ is the hot-side absolute temperature,}$$

T_C is the cold-side absolute temperature, $\frac{T_H - T_C}{T_H}$ is the Carnot efficiency,

$\bar{T} = \frac{T_H + T_C}{2}$. As a result, increasing the figure of merit Z_c will increase the

efficiency of power generation and push it to the limit of the Carnot efficiency. For

TE refrigeration, the energy efficiency is measured by its coefficient of performance (COP), which has the maximum

value $\phi_{\max} = \frac{T_c}{T_H - T_c} \times \frac{\sqrt{1 + Z_c \bar{T}} - \frac{T_H}{T_c}}{\sqrt{1 + Z_c \bar{T}} + 1}$ [4]. When Z_c tends towards infinity, COP

will approach $\frac{T_c}{T_H - T_c}$, which is the efficiency of an inverted Carnot refrigerator.

From 1940s to the early 1990s, the highest ZT value that has been achieved was quite low ($Z \leq 1$). After that, resurgence of interest in TE applications has resulted in significant ZT improvement in the recent years [5-10]. Figure 2-3 shows the trend of the ratio of maximum TE power generation efficiency $\phi_{\max}$ and the Carnot efficiency ϕ_{Carnot} versus ZT for TE waste-heat recovery operating between 100°C to 400°C (typical temperature gradient between the cold-side and hot-side of a TE generator in a vehicle). When ZT approaches to the value of 3, the efficiency of a TE generator can reach nearly 40% of the Carnot efficiency, which is comparable to the conventional engines.

Figure 2-3 The ratio of maximum TE power generation efficiency ϕ_{max} and the Carnot efficiency ϕ_{Carnot} versus ZT for TE waste-heat recovery operating between 400°C to 100°C.

2.1.2 Thermoelectric Materials

As a good thermoelectric material, it should possess high electrical power factor $S^2\sigma$ as well as low thermal conductivity κ . It is noted that, all the three parameters, the Seebeck coefficient S , electrical conductivity σ and electronic thermal conductivity κ_E , are functions of carrier concentration. As shown in Figure 2-4, the electrical conductivity and electronic thermal conductivity increase with the increase of carrier concentration while the Seebeck coefficient decreases. The electrical power factor gets the maximum at a carrier concentration of around $10^{19}/\text{cm}^3$, which corresponds to semiconductor materials. Hence, semiconductors are the most researched materials for thermoelectric applications, while metals and insulators are usually unsuitable due to their low electrical power factor.

Figure 2-4 Schematic dependence of electrical conductivity, Seebeck coefficient, power factor, and thermal conductivity on concentration of free carriers [4].

Thermoelectric materials, which are employed in commercial applications, can be divided into three groups with different temperature ranges of operation (Figure 2-5). One group is the alloy based on bismuth in combinations with antimony, tellurium, and selenium, used at low temperature below 450K. They are usually employed in thermoelectric refrigeration. Another group, which is found their applications in the intermediate temperature range (up to around 850K), is the lead telluride based materials. The last group is silicon germanium alloys applied in the high temperature range (up to 1300K).

Figure 2-5 Performance of the established thermoelectric materials [4].

Although the aforementioned materials still remain as the cornerstones for commercial applications in thermoelectric generation and refrigeration, significant advancements have been made in the synthesis of new materials and the fabrication of new material structures to improve the thermoelectric performance significantly. Efforts have been focused on the improving of the figure-of-merit by reducing the lattice thermal conductivity. Two research directions are currently being pursued, namely, the search for so-called ‘phonon-glass electronic-crystals’ (PGEC), as it is proposed that crystal structures containing weakly bound atoms or molecules that “rattle” within an atomic cage could conduct heat like a glass, but conduct

electricity like a crystal. Candidate materials receiving considerable attention for this mechanism are the filled skutterudites and the clathrates. The other approach is to fabricate low-dimensional structures such as quantum wells, quantum wires and quantum dots, so as to enhance phonon interface scattering and thus achieve low lattice thermal conductivity.

2.1.3 Skutterudites

Skutterudites get their name from a naturally occurring mineral CoAs_3 , which was found in a small mining town Skutterud in Norway. The family of skutterudites encompasses binary compounds, which can be depicted as MX_3 , where M is a metal atom such as Co, Rh, or Ir, while X represents a pnictogen atom such as P, As, or Sb. Among these compounds, CoSb_3 based skutterudites are most studied as thermoelectric materials. One of their advantages as thermoelectric candidates is their high electrical power factor.

In 1928, Oftedal [11] identified skutterudites as the body-centered-cubic structure, belonging to the space group $Im\bar{3}$. The structure of skutterudite is illustrated in Figure 2-6, where the unit cell is displaced by a one-quarter distance along the body diagonal. There are two voids lying in the unit cell since only six of the eight small cubes contain rectangular rings of pnictogen atoms. Relatively large metal atoms, such as rare earth atoms and alkaline earth atoms, can be filled into the voids to form filled skutterudites, which possess both optimum electronic and lattice properties.

Figure 2-6 The skutterudite structure with the metal atoms M (open circles) forming a simple cubic sublattice, and the pnictogen atoms X (solid circles) arranged in planar, near-square four-membered rings [12].

Figure 2-7 The unit cell of the skutterudite structure centered at the position (000). Metal atoms (Co in this case) are octahedrally coordinated by the pnictogen atoms and one of the octahedrons is highlighted. Dashed circles represent the filler ions [12].

The more convenient view for understanding the detailed atomic arrangement and atomic bonding is depicted in Figure 2-7, which shows the actual unit cell centered at the 2a position (the site of the filler atom) at (000). Each metal atom is bonded with six pnictogen atoms to form a tilted octahedron and each octahedron shares corners with the six neighboring octahedra. It is the tilted octahedra that give rise to the planar, rectangular rings of pnictogen atoms shown in Figure 2-6. It should be pointed out that the metal-metal distance is too large to form a bond, and each pnictogen atom X has two bonds with its two nearest neighboring pnictogen atoms to form the X_4 ring, and two bonds with two nearest metal atoms to form the tilted octahedron. It is believed that the pnictogen atoms apply σ bonds to form the X_4 ring. Each pentavalent pnictogen atom (ns^2np^3) donates two valence electrons to bond with its two nearest neighboring pnictogen atoms and the other three valence electrons to bond with the two nearest metal atoms. In a tilted octahedron with six pnictogen atoms around a metal atom, the pnictogen atoms contribute $3 \times 1/2 \times 6 = 9$ electrons to the MX_6 octahedron, which is just the right number to engage nine valence electrons of the Co-like metal (d^7s^2) to form the 18-electron rare-gas configuration that favors the two notable attributes of binary skutterudites—diamagnetism and semiconducting behavior. From the perspective of the metal atom M, it contributes $6 \times 2 - 9 = 3$ electrons to bond with six neighboring pnictogen atoms resulting in the octahedral d^2sp^3 hybrid orbitals representative of the M-X bonding. So the metal is left in the +3 state with six nonbonding electrons adopting the maximum spin-pairing configuration consistent with the low-spin d^6 state [13]. Experimental values of the lattice constants and average void radii in binary

skutterudites are given in Table 2-1. From the perspective of filling, the lattice constant and the void radius increase from phosphite skutterudites to arsenide skutterudites and then to antimony skutterudites. Moreover, the lattice constant increases as the mass of the metal atom increases for each skutterudite family.

Table 2-1 Structural Parameters of Binary Skutterudites [14, 15]

Binary Skutterudites Lattice	Lattice Constant (Å)	Void Radius R (Å)
CoP ₃	7.7073	1.763
RhP ₃	7.9951	1.909
IrP ₃	8.0151	1.906
NiP ₃	7.8192	-
CoAs ₃	8.2055	1.825
RhAs ₃	8.4507	1.934
IrAs ₃	8.4673	1.931
CoSb ₃	9.0385	1.892
RhSb ₃	9.2322	2.024
IrSb ₃	9.2503	2.040

It should be noted that this bonding scheme represents a rather rigid constraint on the binary skutterudites. For example, Fe or Ni cannot fully replace Co-like metal to form the binary skutterudites. However, a partial substitution for Co-group metal is possible and actually the solubility limits are quite large [14, 15]. Moreover, according to the formula $2Co^{3+}(d^6) \leftrightarrow Fe^{2+}(d^6) + Ni^{4+}(d^6)$, Co can be symmetrically substituted by Fe and Ni to preserve the total number of electrons, for example, $Fe_2Ni_2Sb_{12} \equiv Fe_{0.5}Ni_{0.5}Sb_3$. The pnictogen atom such as Sb can also be replaced by a combination of a tetravalent (e.g., Ge) and hexavalent (e.g., Se) to form the isoelectronic phase with the binary skutterudites, for example, $Co_4Ge_6Se_6$

$\equiv \text{CoGe}_{1.5}\text{Se}_{1.5}$. Ultimately, the skutterudite-related ternaries can be formed by a symmetrical replacement on both the metal and pnictogen sites, such as $\text{Fe}_4\text{Sb}_8\text{Te}_4 \equiv \text{FeSb}_2\text{Te}$. Ternary skutterudites usually have much lower thermal conductivity than binary skutterudites. However, the strong lattice disorder, which causes the low lattice thermal conductivity, also suppresses the carrier mobility and thus causes the low electrical conductivity. Ternary skutterudites often have poor Seebeck coefficients, hence they are not good candidates for promising thermoelectric materials.

The figure of merit is related to the Seebeck coefficient S , electrical conductivity σ and thermal conductivity κ , and within the classical approximation, it is proportional to $\mu(m^*/m)^{3/2}/\kappa_L$, where μ stands for the carrier mobility, m^* refers to the effective mass, and κ_L is the lattice thermal conductivity [16]. It can be derived that either a large carrier mobility or a large effective mass can result in a high power factor, which depends on $\mu(m^*/m)^{3/2}$.

Binary skutterudites have exceptionally large carrier mobilities, up to values of several thousands $\text{cm}^2/\text{V}\cdot\text{sec}$ in their single crystal form, and more than $1000\text{cm}^2/\text{V}\cdot\text{sec}$ even in polycrystalline samples [17]. In general, for a given carrier density, hole mobilities are an order of magnitude larger than electron mobilities. The mobility can be limited either by phonon or impurity scattering due to sample purity and grain size. Seebeck coefficients of binary skutterudites are remarkably large, typically $200\text{-}500\mu\text{V/K}$ for pure samples at 300K , and more than $-100\mu\text{V/K}$ even at the near metallic carrier densities $\sim 10^{21}\text{cm}^{-3}$. The reason for large Seebeck coefficients in binary skutterudites, even in high carrier density samples, is the

large effective mass of carriers, especially of electrons. Due to the remarkably large mobility and high carrier effective mass, binary skutterudites have exceptionally high power factors of more than $3 \times 10^{-3} \text{ W/m-K}^2$ for both n- and p-type samples.

2.2 Theory of Electrical and Thermal Properties in TE Materials

2.2.1 Seebeck Coefficient

Seebeck coefficient or thermopower is the electric potential across a material which has an applied thermal gradient in the same direction. It can be alternatively thought of as the heat per carrier divided by the charge per carrier, or the ratio of the entropy per carrier to the charge per carrier [18].

For a metal, the electronic specific heat (C_{el}) is given by

$$C_{el} = \frac{1}{3} \pi^2 k_B^2 T D(E_F), \quad \text{Equation 2-1 [19]}$$

where $D(E)$ is the density of states at energy E , k_B is Boltzmann constant and E_F is the Fermi energy. So the electronic specific heat per carrier (c_{el}) can be expressed by C_{el}/n , where n is the number of carriers. As we know, the carrier distribution of a metal is highly degenerate. As a result, $k_B \ll E_F$, c_{el} can be simplified as follows:

$$c_{el} = \frac{C_{el}}{n} = \frac{\pi^2 k_B^2 T D(E_F)}{3n} \sim \frac{k_B^2 T}{E_F}. \quad \text{Equation 2-2 [19]}$$

The Seebeck coefficient of a metal can then be given by

$$S \sim \frac{c_{el}}{e} \sim \left(\frac{k_B}{e} \right) \frac{k_B T}{E_F}. \quad \text{Equation 2-3}$$

The quantity $k_B/e \approx 87 \mu\text{V/K}$ is the Seebeck coefficient of a classical electron gas. Metals usually have the Seebeck coefficient much lower than this value (in the order of 1-10 $\mu\text{V/K}$) and it will linearly increase with the increase of temperature.

The character of the Seebeck coefficient in semiconductors is quite different from metals. The heat per carrier is equal to the difference of its energy and the Fermi energy. Its energy is almost the same as the band gap (E_g). Generally, the Fermi level is at the center of the band gap for a typical semiconductor. So the heat per carrier can be calculated as $E_g/2$. The Seebeck coefficient of a semiconductor can hence be written as:

$$S \sim \frac{E_g / 2}{eT} \sim \left(\frac{k_B}{e}\right) \frac{E_g}{2k_B T}. \quad \text{Equation 2-4 [19]}$$

For semiconductors, the Seebeck coefficient is usually greater than the value 87 μ V/K, and increases further with decreasing temperature. If it is an n-type semiconductor with electron conduction, the Seebeck coefficient is negative; on the other hand, for a p-type semiconductor with hole conduction, the Seebeck coefficient is positive.

The above discussion is based on a single carrier system. For a two-carrier system, the Seebeck coefficient can be described as a weighted average of their electrical conductivity (σ_n and σ_p):

$$S = \frac{S_n \sigma_n + S_p \sigma_p}{\sigma_n + \sigma_p}. \quad \text{Equation 2-5}$$

From Equation 2-5, the absolute Seebeck coefficient is reduced in a two-carrier system as compared to a single carrier system due to the opposite sign of S_n and S_p . Hence the semiconductor should be doped with either donor or acceptor states to make extrinsic conduction of a single carrier in order to maintain high Seebeck coefficient at high temperature. If the direct band gap is increased to more than

$10k_B T$, the minority carrier contribution on the Seebeck coefficient can also be minimized.

There is relationship between carrier concentration and Seebeck coefficient using parabolic band and energy-independent scattering approximation for metals or degenerate semiconductors [20]. The coefficient can be written as:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}, \quad \text{Equation 2-6}$$

where n is the carrier concentration and m^* is the effective mass of the carrier. It can be seen that the Seebeck coefficient increases with the decreasing carrier concentration and the increase of carrier effective mass. For a good TE material, the Seebeck coefficient should be in the order of 150-250 μ V/K or greater.

2.2.2 Electrical Resistivity

The electrical resistivity (ρ) and electrical conductivity (σ) can be given by

$$1/\rho = \sigma = ne\mu, \quad \text{Equation 2-7}$$

where n is the carrier concentration, e is the charge of electron and μ is the carrier mobility. For metals, they usually have high carrier concentration, typically $n \approx 10^{22}$ carriers/cm³. Thus the electrical resistivity is very low in metals, on the order of 10^{-6} Ω .cm. The electrical resistivity of metals will increase with the increase of temperature due to the enhancement in the scattering effect of the charge carriers on crystal lattice. For semiconductors, the carriers must be thermally excited from the valence band to the conduction band across a bandgap for conduction. This activating behavior can be expressed by the following formula:

$$1/\rho = \sigma = \sigma_0 \exp(-E_g / k_B T), \quad \text{Equation 2-8}$$

where E_g is the bandgap between the valence band and the conduction band, σ_0 is a constant and k_B is the Boltzmann constant. According to this relationship, the electrical resistivity will decrease with the increase of temperature, and there are two ways to enhance the electrical conduction in semiconductors. One is to make a narrow bandgap E_g ($E_g \approx 10k_B T$, or 0.25eV at 300K), and the other is to have a high carrier mobility μ ($\mu \approx 2000 \text{cm}^2/(\text{V}\cdot\text{s})$). For a good TE material, the typical value of the electrical resistivity is on the order of $10^{-3} \Omega\cdot\text{cm}$.

2.2.3 Thermal Conductivity

Thermal conductivity κ is the ability of heat conduction in a material. The heat flow under a temperature gradient in a solid material can be defined by

$$Q = -\kappa A \frac{\Delta T}{\Delta x}, \quad \text{Equation 2-9}$$

where Q is the flux of heat flow, κ is the thermal conductivity, A is the cross sectional area of this solid material, $\Delta T/\Delta x$ is the temperature gradient.

The thermal conductivity κ is the sum of two main components:

$$\kappa = \kappa_L + \kappa_E, \quad \text{Equation 2-10}$$

Where κ_L is the lattice thermal conductivity and κ_E is the electronic thermal conductivity. The electronic thermal conductivity is related to the transfer of heat by the carriers. It can be expressed by Wiedmann-Franz law as:

$$\kappa_E = L_0 T \sigma, \quad \text{Equation 2-11}$$

where L_0 is the Lorenz number $2.0 \times 10^{-8} \text{V}^2 \text{K}^{-2}$. The lattice thermal conductivity κ_L is related to the transfer of heat by quantized vibrations of the lattice, and can be determined by subtracting electric thermal conductivity κ_E from the total thermal conductivity κ . Since a good TE material needs to possess high electrical conductivity, the objective should be reducing the lattice thermal conductivity κ_L , lowering total thermal conductivity κ . From kinetic theory, κ_L can be expressed by

$$\kappa_L = \frac{1}{3} C_V v l, \quad \text{Equation 2-12 [3]}$$

where C_V is the heat capacity, v is the velocity of sound, and l is the mean free path of the phonons. When the temperature is above room temperature, the velocity of sound v and the heat capacity C_V are essentially independent on temperature. So the lattice thermal conductivity κ_L is determined by the mean free path of the phonons l . The minimum thermal conductivity (κ_{min}) defined by Slack [21] as the thermal conductivity when the mean free path of phonons is about the inter-atomic distance between the atoms within the crystal, is reckoned to be between 0.25 to 0.5 W/(m.K) [21, 22].

Lattice thermal conductivity is dependent on three main phonon scattering mechanisms; namely, phonon scattering by the crystal lattice, phonon-phonon scattering, and phonon-electron scattering. Phonon scattering by the crystal lattice usually results from grain boundaries, point defects or dislocations. Phonon-phonon scattering has two types: normal scattering or “N-process”, and Umklapp scattering or “U-process”. N-process results in an outgoing phonon, which still lies in the first Brillouin zone after the collision of two incoming phonons, as shown in

Figure 2-8 (a). As a result, the net phonon momentum does not change after the collision, and consequently the lattice thermal conductivity is not affected. On the contrary, U-process creates an outgoing phonon whose wavevector is outside the first Brillouin zone, as shown in Figure 2-8 (b). This wavevector is physically equivalent to a vector inside the first Brillouin zone by the addition of a reciprocal lattice vector $\mathbf{G}$. So U-process can change the net phonon momentum and affect the lattice thermal conductivity.

Figure 2-8 (a) N-process, (b) U-process

At moderately high temperature (room temperature and above), it is noted that U-process is the main phonon scattering mechanism. In this regime, the lattice thermal conductivity can be expressed by

$$\kappa_L \propto 1/T . \quad \text{Equation 2-13 [23]}$$

At low temperature, on the other hand, the number of phonons is relatively small. As a result, the phonon-phonon scattering is not the primary mechanism and the grain boundary scattering plays a key role. The lattice thermal conductivity can be written as

$$\kappa_L \propto T^3. \quad \text{Equation 2-14 [24]}$$

In the intermediate temperature regime, the mechanism is the combination of grain boundary scattering and point defect scattering [24]. The typical curve of κ_L vs. T due to the interrelation of these three scattering processes is shown in Figure 2-9. The high peak indicates a highly ordered crystal structure, whereas a flattening of this peak indicates the increase disorder in the crystal structure.

Figure 2-9 Typical κ_L vs. T curve, showing the influence of various scattering mechanisms [24].

2.3 Single and Double Filling Effects in Skutterudites

2.3.1 Single Filling

Although unfilled binary CoSb_3 has reported to have a high power factor, the remaining important transport parameter, thermal conductivity κ , is still too large to make it a promising thermoelectric material.

As mentioned earlier in Section 2.1.3, there are two empty voids in the skutterudite structure. Foreign atoms, such as rare-earth, actinide or alkaline earth atoms, can be introduced into the voids to form a filled skutterudite $\text{R}_y\text{Co}_4\text{Sb}_{12}$ (R is the filler atom; y is the filling fraction, which is less than 1) structure.

The ultimate benefit of forming filled skutterudites is the promotion of significantly low lattice thermal conductivity as compared to unfilled binary CoSb_3 (nearly a tenfold reduction can be achieved). The filler atoms are loosely bonded in the voids and thus have very large atomic displacement parameters. They can “rattle” as local Einstein oscillators and effectively scatter the phonons.

The filler ions donate electrons when they enter the voids of the binary skutterudites. So the electron density increases with the increase of filling fractions, often enhanced by 2-3 orders of magnitude. With such high electron concentrations, the usual semiconductors would have small Seebeck coefficients. However, filled skutterudites possess impressive high Seebeck coefficient ($\sim 150\mu\text{V/K}$) even at these high carrier densities. The reason is that filled skutterudites have exceptionally large effective mass of carriers due to the hybridization of the filler

ion states with the states of the metal atom, which gives rise to the formation of a manifold of rather flat bands [25]. In spite of the degraded carrier mobility, the enhancement in the effective mass of carriers preserves the high power factor property of filled skutterudites.

Combining the high power factors with low lattice thermal conductivity, filled skutterudites have shown much better thermoelectric properties than the unfilled binary CoSb_3 , and have emerged to be excellent intermediate-to-high-temperature thermoelectric material candidates.

The filling fraction is dependent on the filler ion type in CoSb_3 -based skutterudites. The study on maximum void occupancy for the various filler species in cobalt triantimonide has been reported by other researchers and is summarized in Table 2-2.

Table 2-2 Maximum Void Occupancy in Pure CoSb_3

Filler Ion	Maximum Void Occupancy (%)	Reference
Ce	10	[26]
Tl	22	[27]
La	23	[28]
Yb	25	[29]
Eu	44	[30]
Ba	45	[31]

The filling ions bring in the extra electrons to the structure and make the filled skutterudites paramagnetic and metallic. So the thermopower is depressed as compared to unfilled CoSb_3 . The filling fraction is usually much less than 1 in

cobalt triantimonide. It can be increased if the amount of Fe substitution for Co sites increases. When Fe ions are substituted for all the Co ions, complete filling can be done. Since Fe has one electron less than Co, Fe doping can compensate the extra electrons which arise from the filler ions. With suitable doping and filling fraction, filled skutterudites can be forced back into the semiconducting domain and the thermopower can be comparable to the unfilled CoSb_3 . Filled CoSb_3 -based skutterudites with Fe doping are usually depicted as $\text{R}_y\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$.

Partial filling is thought to be more effective in reducing the lattice thermal conductivity than complete filling [28], where the largest decrease in the lattice thermal conductivity, compared to unfilled CoSb_3 , is found in partial filling. This suggests a point-defect-type phonon scattering effect due to the partial, random distribution of filler ions in the voids as well as the “rattling” effect of the filler ions, resulting in the scattering of a larger spectrum of phonons than in the case of complete filling. Furthermore, partially filled skutterudites can be thought of as solid solutions of fully filled skutterudites $\text{RFe}_4\text{Sb}_{12}$ and unfilled CoSb_3 [32]. This makes easy understanding of the point-defect-type phonon scattering effect in the partially filled skutterudites since the mass difference of filler ion R and the void is 100%. An additional benefit of partial filling is that it can be used to adjust the electronic properties like carrier concentration, electrical conductivity and Seebeck coefficient.

2.3.1.1 La Single Filling

La single filled skutterudites were reported as a kind of potential thermoelectric materials as early as 1996 by Sales *et al.* [33]. The ZT value of 0.9 ± 0.2 was obtained at 800K in $\text{LaFe}_3\text{CoSb}_{12}$ due to its low thermal conductivity ($1.6\text{W}/(\text{m.K})$) and high Seebeck coefficient ($200\mu\text{V}/\text{K}$). In 1998, Nolas *et al.* found that partial La filling can reduce the lattice thermal conductivity optimally as compared with fully La filled skutterudites [28]. The minimal lattice thermal conductivity of $2\text{W}/(\text{m.K})$ at room temperature was obtained in $\text{La}_{0.31}\text{Co}_4\text{Sn}_{1.48}\text{Sb}_{11.2}$. This partial La filling was thought to give a point defect phonon scattering effect due to the partial, random distribution of La in the voids as well as the “rattling” effect of the La ions. Later, the high temperature electrical properties of $\text{LaFe}_4\text{Sb}_{12}$, as well as other rare-earth (Ce, Sm, Eu, Er, Yb) fully filling skutterudites, were published by Rowe *et al.* [34]. $\text{LaFe}_4\text{Sb}_{12}$ has the lowest electrical resistivity among all the rare-earth fully filling skutterudites studied due to its highest carrier mobility. Its power factor, which reached $2.2\text{mW}/(\text{m.K}^2)$ at 800K, is the second highest. In 1999, the large mean-square displacement of the La atom in $\text{LaFe}_3\text{CoSb}_{12}$ was confirmed using single-crystal neutron diffraction, which proved the large-amplitude rattling of La in the lattice. The effect of porosity of $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ was studied by Yang *et al.* [35]. Seebeck coefficient was independent of porosity, while the increase of electrical resistivity was consistent with the reduction of thermal conductivity. Hence, porosity does not affect the ZT significantly. The synthesis method of mechanical alloying and hot pressing was used in order to shorten the long annealing duration in the traditional solid state synthesis [36-41]. In 2005,

Takabatake *et al.* compared the lattice thermal conductivity of $\text{LaT}_4\text{Sb}_{12}$ with $\text{SrT}_4\text{Sb}_{12}$ and $\text{BaT}_4\text{Sb}_{12}$ ($T=\text{Fe}$ or Ru), and found that $\text{LaT}_4\text{Sb}_{12}$ has the strongest acoustic resonance scattering due to the smallest ion radius and largest atomic displacement parameter of La among these three kinds of filler atoms [42].

2.3.1.2 Ca and Sr Single Filling

Ca single filled n-type skutterudites $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ ($0 < x \leq 0.2$) were first synthesized and characterized for high temperature thermoelectric applications by Puyet *et al.* in 2004 [43, 44]. The large atomic displacement parameter of Ca relative to Co or Sb, determined from neutron diffraction refinement, indicated the induced rattling effect of Ca. However, the lattice thermal conductivity of Ca filled skutterudites was still considered high (4-6W/(m.K) at room temperature) in comparison to Ce [32, 45-49], La [28, 33], Yb [50-57] and Tl [58] single filled skutterudites, which shows the influence of filler atoms from different elemental groups.

The maximal ZT value of 0.45 at 800K was found in $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$ among $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ ($0 < x \leq 0.2$). Later Puyet doped Ni at the Co site and found that Ni doping substantially decreased the electrical resistivity without any detrimental effect on the Seebeck coefficient and thus improve the ZT value to 1 at 800K [59, 60]. In 2006, He theoretically modeled the lattice thermal conductivity of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ using the Debye model and made the conclusion that increasing Ca filling fraction can decrease the lattice thermal conductivity due to the enhance of phonon-point defect scattering and phonon resonance scattering [61].

Also In 2006, Sr single filled n-type skutterudites $\text{Sr}_y\text{Co}_4\text{Sb}_{12}$ ($0 < y \leq 0.4$) were reported and characterized by Zhao *et al.* [62]. Compared with $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ [44], Sr can achieve higher filling fraction, and hence resulted in lower electrical resistivity and lattice thermal conductivity than $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ at similar filling fraction. Sr is therefore an interesting element to look at as filler.

As shown in the literature, the studies of single filling effects on thermoelectric properties of skutterudites mainly focus on the performance enhancement by single filling as compared with unfilled skutterudites, and also the effect of filling fraction variation. There are few comparisons between each single filled skutterudite system due to the difference in the sample compositions, synthesis methods and the temperature range of characterizations in each work. In the present work, Fe-doped La, Ca and Sr p-type single filled skutterudite systems are prepared under the similar experimental procedures and characterized in the same temperature range from 5K up to 800K. The performance improvements of single filling are shown by comparing with the Fe-doped unfilled skutterudite system. The effects of filling fraction variation on thermoelectric properties are also studied. Moreover, among these systems, similar compositions are chosen for comparison in order to study the characteristics of each filler atom on thermoelectric properties of single filled skutterudites, such as the different charge valences, atomic mass and radii in these three kinds of filler atoms.

2.3.2 Double Filling

Double filling is subsequently reported as an effective approach to further improve the thermoelectric properties of skutterudites. Since each type of filler ions has its own characteristic (Einstein) frequency of “rattling” that reflects its mass, size, and the strength of coupling with the atoms forming the cage. Two different filler ions could have two different “spring constants” and thus different frequencies. Hence, filling two different filler ions into the voids of skutterudites could scatter a broader spectrum of phonon and reduce the lattice thermal conductivity more effectively than single filled skutterudites. It is believed that the larger difference in size and mass of the two filler ions, the better the phonon scattering effect could be achieved by the double filled skutterudites possess.

In 1998, Rowe *et al.* synthesized p-type double filled skutterudites $\text{Ce}_{0.8}\text{Ln}_{0.2}\text{Fe}_4\text{Sb}_{12}$ (Ln=La, Sm, Eu, Er and Yb) and measured their high temperature electrical properties [34]. He found that $\text{Ce}_{0.8}\text{Yb}_{0.2}\text{Fe}_4\text{Sb}_{12}$ has the maximum power factor of $3.2\text{mW}/(\text{m}\cdot\text{K}^2)$, which was 1.5 times higher than that of $\text{CeFe}_4\text{Sb}_{12}$ at the same temperature. In 2003, Bérardan *et al.* prepared p-type $\text{Ce}_{1-p}\text{Yb}_p\text{Fe}_4\text{Sb}_{12}$ and found that double filling can enhance more than 20% Seebeck coefficient at room temperature as compared to $\text{CeFe}_4\text{Sb}_{12}$ or $\text{YbFe}_4\text{Sb}_{12}$ [63]. Later, they synthesized $\text{Ce}_{y/2}\text{Yb}_{y/2}\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$ and $\text{Ce}_{y/2}\text{Yb}_{y/2}\text{Fe}_{4-x}\text{Ni}_x\text{Sb}_{12}$ samples and reported that Yb, which has intermediate valence between +2 to +3, has its valence state decreases as Yb filling fraction increases [64]. It is a different effect on hole concentration as compared to Ce [65, 66].

The reduction of the thermal conductivity and the improvement of the power factor in double filled $\text{Ce}_{0.40}\text{Yb}_{0.53}\text{Fe}_4\text{Sb}_{12}$ led to its improved ZT value as compared to single filled $\text{Ce}_{0.85}\text{Fe}_4\text{Sb}_{12}$ and $\text{Yb}_{0.92}\text{Fe}_4\text{Sb}_{12}$ [65, 66]. The enhancement of ZT values in $\text{Ce}_y\text{Yb}_{0.5-y}\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ as compared to $\text{Yb}_{0.5}\text{Fe}_{1.5}\text{Co}_{2.5}\text{Sb}_{12}$ was also observed by Yang *et al.* [67]. Based on the measured ZT value of 0.5 at 500K, the highest ZT value of 0.95 at 800K was expected in $\text{Ce}_{0.44}\text{Yb}_{0.32}\text{Fe}_{3.02}\text{Co}_{0.98}\text{Sb}_{12}$ among all the Ce-Yb double filled skutterudites prepared by Bérardan *et al.* [57].

For other elemental groups, the lattice thermal conductivity of Ba-La and Ba-Ce n-type double filled skutterudites was compared with Ba-Sr n-type double filled ones at both the high and low temperatures by Chen *et al.* [68, 69] and Yang *et al.* [70] respectively. It was found that Ba-La and Ba-Ce were more effective in scattering phonons than Ba-Sr. They proposed that using filler atoms of different chemical natures, such as the rare earths, the alkaline earths, or the alkalines, can provide a broader range of resonant phonon scattering and thus suppress the lattice thermal conductivity effectively.

Following that, many groups have studied various systems of double filled skutterudites. Ce-La p-type double filled skutterudites $\text{Ce}_m\text{La}_n\text{Fe}_{1.0}\text{Co}_{3.0}\text{Sb}_{12}$ ($m+n=0.2-0.4$) have been synthesized using spark plasma sintering and studied by Lu *et al.* [71, 72]. The double filled skutterudites showed lower thermal conductivity and higher Seebeck coefficient than single filled skutterudites. A low thermal conductivity of $1.81\text{W}/(\text{m.K})$ at 673K and then a high ZT value of 0.60 at 773K were observed in $\text{Ce}_{0.1}\text{La}_{0.2}\text{FeCo}_3\text{Sb}_{12}$.

Sr-Yb n-type double filled skutterudites $\text{Sr}_{0.3}\text{Yb}_y\text{Co}_4\text{Sb}_{12}$ ($y=0.1, 0.2$ and 0.3) were prepared and characterized by Bai *et al.* in 2006 [73]. The reduced lattice thermal conductivity of $\text{Sr}_{0.3}\text{Yb}_y\text{Co}_4\text{Sb}_{12}$ was observed as compared to $\text{Sr}_{0.3}\text{Co}_4\text{Sb}_{12}$ [62]. $\text{Sr}_{0.3}\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ has the maximal ZT value of 1.09 at 850K, which is 21% higher than the highest value of Sr single filled CoSb_3 with nominal composition of $\text{Sr}_{0.4}\text{Co}_4\text{Sb}_{12}$.

In 2006, Tang *et al.* studied Ca-Ce p-type double filled skutterudites $\text{Ca}_m\text{Ce}_n\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ by x-ray photoelectron spectroscopy quantitative analysis and found that Sb has five chemical states whose contents are correlative with the total filling fraction; the filling atoms have three filling positions and tend to fill the center position of the Sb-icosahedron voids [74]. The lowest lattice thermal conductivity was found when the total filling fraction was about 0.3 rather than higher values. As a result, the largest ZT value of 1.2 at 750K was obtained in $\text{Ca}_{0.18}\text{Ce}_{0.12}\text{Fe}_{1.45}\text{Co}_{2.55}\text{Sb}_{12}$ mainly due to its lowest lattice thermal conductivity among all the Ca-Ce double filled skutterudites.

In recent years, comparable ZT were also reported in In based n-type double filling skutterudites, such as $\text{In}_x\text{Sn}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05, 0.1$ and 0.2), where their reported high Seebeck coefficient makes them good candidates for thermoelectric applications [75].

The high ZT values were also found in In-Yb n-type double filled skutterudites $\text{In}_{0.1}\text{Yb}_y\text{Co}_4\text{Sb}_{12}$ ($y=0.05, 0.10$, and 0.20) by Peng *et al.* [76]. In-Yb double filling was noted to reduce the lattice thermal conductivity while increasing the power factor, and Peng *et al.* reported a ZT value of 0.97 at 750K in $\text{In}_{0.1}\text{Yb}_{0.1}\text{Co}_4\text{Sb}_{12}$.

As shown in the literature, most of works focus on the study of the advantages of double filling as compared with single filling. The comparisons between each double filled skutterudite system are very limited also due to the difference in the sample compositions, synthesis methods and the temperature range of characterizations in each work. In the present work, Fe-doped Ca-La and Sr-La p-type double filled skutterudite systems are synthesized under similar experimental procedures and characterized in the same temperature range from 5K up to 800K. The compositions are properly controlled to be comparable. The advantages of Ca-La and Sr-La double filling, as compared with their parent single filling, are shown. Furthermore, the effects of different charge valence, atomic mass and radii of Ca and Sr in the two systems are studied to give a deeper understanding of double filling effects on thermoelectric properties of skutterudites.

Chapter 3 Experimental Procedures

3.1 Synthesis of Skutterudites

Polycrystalline samples of La, Ca, Sr single filled and Ca-La, Sr-La double filled skutterudites were prepared from elemental constituents of Ca granules (99%, Sigma-Aldrich), La powder (99.9%, Sigma-Aldrich), Sr distilled dendritic pieces (99.9%, Sigma-Aldrich), Fe powder (99.99%, American Elements), Co powder (99.995%, American Elements) and Sb powder (99.99%, American Elements). A thin layer of carbon was deposited on the inside of a round-bottomed quartz tube by the pyrolysis of acetone. Stoichiometric amounts of the metal elements were sealed in the quartz tube under vacuum at a pressure of 8×10^{-4} mbar. The quartz tube was heated to 630°C at 2°C/min and held for 1 hour. Then it was heated to 1000°C at 1°C/min and left for about 48 hours. It is important to slowly heat the tube because of the highly exothermic reaction between the rare-earth elements and Sb. The quartz tube was removed at 1000°C and water quenched. The same tube was then placed in a furnace and annealed at 650°C for 10 days.

For the measurements of thermal conductivity, electrical resistivity and Seebeck coefficient, the obtained ingots were crushed into powders and hot-pressed into high-density pellets under 50MPa at 600°C for 2 hours.

3.2 Characterizations

3.2.1 X-ray Diffraction, Surface and Compositional Analysis

X-ray diffraction (XRD) was employed for structural characterization using Shimadzu 6000 diffractometer with Cu K α radiation in a 2θ range (10° - 120°) with a 0.02° step and a counting time 4.43s/step.

The Rietveld refinement was done based on the XRD data and the skutterudite compositions determined from ICP-OES by using the TOPAS 3 software.

The microstructure of the fracture surfaces of the samples were examined using a scanning electron microscope (SEM) (JOEL JSM-6360).

The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Scientific Theta Probe spectrometer with a monochromatic Al anode X-ray source. Samples were cleaned by argon-ion sputtering to remove surface contaminants (mainly C and O). Because the samples are electrically conducting, charge neutralization was not required during the measurements and charge correction was not applied in the data analysis.

The chemical compositions of skutterudites were analyzed by inductively coupled plasma–optical emission spectroscopy (ICP-OES) (Varian Vista – MPX CCD Simultaneous ICP-OES).

3.2.2 High Temperature Electrical Resistivity and Seebeck Coefficient Measurement

ZEM-3 (ULVAC-RIKO) was used for high temperature electrical resistivity and Seebeck coefficient measurement. The rod-shaped specimen was sandwiched between two electrodes mounted on the upper and lower blocks, as shown in Figure 3-1.

Figure 3-1 Electrical resistivity and Seebeck coefficient measurement by ZEM-3.

The lower block has a heater and creates a temperature gradient in the specimen. Two pairs of thermocouples measure temperatures $T1$ and $T2$, and electric potential difference dV between them. The Seebeck coefficient S is calculated by the formula $S=dV/(T2-T1)$ against mean sample temperature. On the other hand, electrical resistivity is measured with four probe method. Using the electrodes, small electric current I runs through the specimen, and the thermocouple wires measure the

voltage difference dE created by the current in the specimen. The electrical resistivity ρ or electrical conductivity σ is calculated by the formula $1/\rho=\sigma=I/dE$. Electrical resistivity and Seebeck coefficient can be measured in the temperature range from room temperature to 800°C under Helium atmosphere.

3.2.3 High Temperature Thermal Conductivity

Measurement

High temperature thermal conductivity was measured by Laser Flash Method. Thermal conductivity can be calculated using the following function:

$$\kappa=a\times\rho\times C_p, \quad \text{Equation 3-1}$$

where κ is the thermal conductivity, a is the thermal diffusivity, ρ is the density and C_p is the specific heat capacity of the sample.

Thermal diffusivity a can be measured directly by using NETZSCH LFA 427. The front face of a cylindrically shaped sample is heated by an unfocused laser pulse. On the back face of the sample, the temperature increase is measured as a function of time. The mathematical analysis of this temperature/time function allows the determination of the thermal diffusivity a . For adiabatic conditions, a is determined by

$$a=0.1388\times l^2/t_{0.5}, \quad \text{Equation 3-2}$$

where l is the thickness of the sample, $t_{0.5}$, the half rise time, is the time for the back face temperature to reach 50% of its maximum value. The through-plane measurement is depicted in Figure 3-2.

Figure 3-2 Thermal diffusivity measurement by LFA 427.

Specific heat C_p can be measured with the Laser Flash Method by comparing the temperature rise of the sample to the temperature rise of a reference sample SRM 1461 of known specific heat tested under the same conditions. This temperature (voltage) rise is recorded during thermal diffusivity measurement. The specific heat of a material is defined as the amount of energy required to raise a unit mass of material by one unit of temperature at constant pressure by

$$C_p = Q / (m \times \Delta T), \quad \text{Equation 3-3}$$

where Q =energy, m =mass, ΔT =change in temperature. Assuming that the laser pulse energy and its coupling to the sample do not change between the test sample and the reference sample, we can obtain

$$Q = (m C_p \Delta T)_{\text{ref}} = (m C_p \Delta T)_{\text{sample}}, \quad \text{Equation 3-4}$$

$$(C_p)_{\text{sample}} = (m C_p \Delta T)_{\text{ref}} / (m \Delta T)_{\text{sample}} \text{ or } (C_p)_{\text{sample}} = (m C_p \Delta V)_{\text{ref}} / (m \Delta V)_{\text{sample}}, \text{Equation 3-5}$$

The reference sample SRM 1461 is measured at each temperature of interest to calibrate the change in output voltage of the IR detector (ΔV) resulting from the absorbed laser energy. The measured ΔV is proportional to the temperature rise

(ΔT). This calibration gives the absorbed energy in terms of the mass, specific heat and ΔV of the reference sample SRM 1461. The specific heat of the test sample can be calculated by the absorbed energy divided by the product of the mass and ΔV of the test sample as $(C_p)_{\text{sample}} = (mC_p\Delta T)_{\text{ref}} / (m\Delta T)_{\text{sample}}$ or $(C_p)_{\text{sample}} = (mC_p\Delta V)_{\text{ref}} / (m\Delta V)_{\text{sample}}$ (Equation 3-5). Coating the sample with a thin layer of graphite can eliminate the difference of the absorptive efficiency of the front surface of the test sample and reference sample to the laser pulse and the radiative efficiency of the back surface to the IR detector.

The density can be calculated using

$$\rho = m / (\pi r^2 l), \quad \text{Equation 3-6}$$

where r is the radius of the sample, m is the mass, l is the thickness.

The thermal conductivity of the sample can then be calculated using Equation 3-1 after the measurement of thermal diffusivity, specific heat and density as described above.

The thermal conductivity κ is related to the transfer of heat through a material, either by the electrons or by quantized vibrations of the lattice known as phonons. Hence, the total thermal conductivity, $\kappa = \kappa_e + \kappa_L$, where κ_e is the electronic thermal conductivity and κ_L is the lattice thermal conductivity. The electronic thermal conductivity κ_e is determined by the Wiedmann-Franz law $\kappa_e = L_0 T \sigma$, where L_0 is the Lorenz number, σ is the electrical conductivity, T is the temperature. The lattice thermal conductivity κ_L is calculated by subtracting the electronic thermal conductivity from the thermal conductivity.

3.2.4 Low Temperature Measurements

The low temperature electrical resistivity, Seebeck coefficient and thermal conductivity were measured with a Quantum Design Physical Property Measurement System (PPMS, Quantum Design). The Seebeck coefficient and thermal conductivity measurement was carried out simultaneously in the TTO mode (Thermal Transport mode). The electrical resistivity measurement was done by a 4-wire approach in the DC-R mode (DC Resistivity mode). The temperature range investigated is from 5K to 300K.

Chapter 4 Electrical Properties of Single and Double Filled Skutterudites

4.1 Electrical Properties of La, Ca and Sr Single Filled Skutterudites

A summary of room temperature electrical properties of La, Ca and Sr single filled skutterudites is given in Table 4-1. We tried to fix Fe/Co ratio to be 1.6/2.4 and then change the filling fraction of filler atoms. However, it was found that this ratio increased with the increase of the filling fraction, especially in Ca single filled skutterudites. Similar trend was also observed by Meisner *et al.* [32] and Uher [12] since the excess electrons introduced by filler atoms need to be neutralized by the substitution of Fe for Co in order to keep the structure stable. We also synthesized unfilled samples $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ under the same experimental procedures as the single filled samples and list the room temperature electrical properties in Table 4-1 for comparison. These two unfilled samples have similar thermoelectric properties as the reported unfilled samples with the same compositions [77]. The lattice parameter increased with the increase of La, Ca and Sr filling fraction in each group and all the single filled samples have higher lattice parameters than unfilled samples since filling in filler atoms can expand the lattice. On the other hand, the hole concentration decreased with the increase of filling fraction. This is related to the extra electrons introduced into the lattice by filling.

Every La^{3+} gives three electrons while every Ca^{2+} or Sr^{2+} gives two electrons. These electrons can compensate the holes produced by Fe substitution for Co. It is known that every Fe doping creates one hole. Therefore, the small deviation of Fe doping content in the samples is believed not to affect the hole concentration and electrical properties as much as the filling fraction variation of filler atoms. On the other hand, the similar mass and ionic radius of Fe and Co are reckoned to provide neglectable effects on thermal conductivity [32], which will be discussed in Chapter 5. Therefore, the discussion in this work mainly focuses on the effects of single and double filling. From Table 4-1, it is found that Seebeck coefficient and electrical resistivity usually increase with the increase of filling fraction in each group. The detailed discussion will be given in the following sections.

Table 4-1 Actual composition determined from ICP-OES quantification, lattice parameter a , hole concentration n , Seebeck coefficient S , electrical resistivity ρ , power factor PF at room temperature in La, Ca and Sr single filled skutterudites. ($\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are the nominal compositions.)

<i>Actual Composition</i>	<i>a ($\text{\AA}$)</i>	<i>n (10^{19}cm^{-3})</i>	<i>S ($\mu\text{V/K}$)</i>	<i>ρ ($\text{m}\Omega.\text{cm}$)</i>	<i>PF ($\text{mW}/(\text{m.K}^2)$)</i>
$\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$	9.0715	1.77	88.7	0.99	0.79
$\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$	9.0741	1.44	97.8	1.10	0.87
$\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$	9.0864	0.91	112.0	2.86	0.44
$\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$	9.0716	2.83	59.7	0.98	0.36
$\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$	9.0826	2.61	85.3	0.93	0.78
$\text{Ca}_{0.67}\text{Fe}_{1.63}\text{Co}_{2.37}\text{Sb}_{11.36}$	9.0987	1.23	119.0	2.02	0.71
$\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$	9.0825	5.62	79.4	0.91	0.69
$\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$	9.0887	2.38	85.5	0.90	0.82
$\text{Sr}_{0.42}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.60}$	9.0917	1.92	83.5	1.01	0.69
$\text{FeCo}_3\text{Sb}_{12}$	9.0358	9.89	42.4	0.99	0.18
$\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$	9.0600	14.64	64.9	0.90	0.47

4.1.1 X-ray Diffraction Patterns and Rietveld Refinements

Figure 4-1 shows the X-ray diffraction (XRD) results of La, Ca and Sr single filled skutterudites. Skutterudite phase is the major phase in all the samples. Less than 5wt% of Sb was detected in most of samples except $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$. It has been reported that this amount of impurities do not have a significant effect on the thermoelectric properties [63, 64, 71]. For $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$, some $\text{Fe}_{1-x}\text{Co}_x\text{Sb}_2$ was also detected. We used diluted aqua regia to wash this sample. After acid wash, $\text{Fe}_{1-x}\text{Co}_x\text{Sb}_2$ was removed completely and the Sb amount was reduced to less than 5wt%. The X-ray diffraction patterns of $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ before and after acid wash are shown in Figure 4-1 (d) for comparison.

(b)

(c)

(d)

Figure 4-1 X-ray diffraction patterns of (a) La, (b) Ca, and (c) Sr single filled skutterudites.
(d) X-ray diffraction patterns of $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ before and after acid wash.

(a)

Figure 4-2 X-ray diffraction pattern and Rietveld refinement of (a) $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$ (b) $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ and (c) $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$. Inset: the fitting results at the high 2θ angle range from 86° to 98° . The blue lines are the experimental results. The red lines are the calculated results. The bottom curves are their difference.

The Rietveld refinement method was used to study the skutterudite lattice structure. In refinement process, occupancy factors of La, Ca, Sr, Fe, Co and Sb were fixed according to ICP-OES quantification. The lattice parameter, thermal parameter (B) and coordinates of Sb atom were refined. The X-ray diffraction patterns and Rietveld refinements of $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$, $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$, and $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$ are exemplified in Figure 4-2. The insets show that there is no broadening or shift of the Bragg peaks at the high 2θ angle range from 86° to 98° , which reveals that the skutterudite phases were

well crystallized and homogeneous. The data collection conditions and refinement results are listed in Table 4-2, Table 4-3 and Table 4-4, respectively. The thermal parameters (B) of La, Ca and Sr are much larger than Fe, Co and Sb, revealing their rattling motion in the over-sized cage. The B value of La is comparable to the reported value in $\text{La}_y\text{Co}_{3.5}\text{Fe}_{0.5}\text{Sb}_{12}$ [78]. Also, the results show that Ca and La have similar B values due to the similar ionic radius of Ca^{2+} (1.34Å) and La^{3+} (1.36Å). The B value of Sr is less than those of La and Ca due to the smaller amplitude of Sr in the void, since the radius of Sr^{2+} (1.44Å) is larger than those of Ca^{2+} and La^{3+} [79, 80]. This phenomenon of rattling will be discussed further in Chapter 5.

Table 4-2 Rietveld refinement condition and results of $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$

X-ray radiation	Cu K_α
Monochromator	Graphite
Temperature	Room temperature
2θ range (deg)	10.000-120.000
Step width (deg)	0.02
Counting time (s/step)	4.43
Structure type	$Im\bar{3}$
Lattice parameter (Å)	9.07405(93)
R_{wp}	0.1134
R_p	0.0858
R_{Bragg}	0.02421
GOF	1.55

Atom	Position	Occu.	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
La	2a	0.28	0	0	0	3.03(30)
Fe/Co	8c	0.385/0.615	0.25	0.25	0.25	0.93(13)
Sb	24g	0.976	0	0.33582(10)	0.15901(11)	0.93(12)

Table 4-3 Rietveld refinement condition and results of $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$

X-ray radiation	Cu K_{α}
Monochromator	Graphite
Temperature	Room temperature
2θ range (deg)	10.000-110.000
Step width (deg)	0.02
Counting time (s/step)	4.43
Structure type	$Im\bar{3}$
Lattice parameter (Å)	9.08259(92)
R_{wp}	0.1222
R_p	0.0931
R_{Bragg}	0.04574
GOF	1.92

Atom	Position	Occu.	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Ca	2a	0.35	0	0	0	2.75(78)
Fe/Co	8c	0.37/0.63	0.25	0.25	0.25	1.23(20)
Sb	24g	0.9617	0.15923(11)	0.33574(11)	0	0.93(20)

Table 4-4 Rietveld refinement condition and results of $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$

X-ray radiation		Cu K_{α}				
Monochromator		Graphite				
Temperature		Room temperature				
2θ range (deg)		10.000-120.000				
Step width (deg)		0.02				
Counting time (s/step)		4.43				
Structure type		$Im\bar{3}$				
Lattice parameter ($\text{\AA}$)		9.08873(91)				
R_{wp}		0.1107				
R_p		0.0857				
R_{Bragg}		0.01819				
GOF		1.70				

Atom	Position	Occu.	x	y	z	B
Sr	2a	0.36	0	0	0	1.99(31)
Fe/Co	8c	0.38/0.62	0.25	0.25	0.25	0.342(77)
Sb	24g	1.005	0	0.15900(11)	0.33614(10)	0.644(52)

4.1.2 Seebeck Coefficient

The temperature dependence of Seebeck coefficient in La, Ca and Sr single filled skutterudites as well as unfilled ternary skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ is shown in Figure 4-3. All of the samples show positive Seebeck coefficients, S , indicating that they are p -type thermoelectric materials. The Seebeck coefficient of unfilled ternary skutterudites increased with the increase of temperature. It can be seen that no maximal value is observed. As a result, as mentioned in Section 2.2.1, it is reckoned to have single carrier (hole) conduction at the temperature range investigated. On the other hand, a maximal Seebeck coefficient is observed in high filling fraction samples at the temperature range of 675-790K. The reduction in Seebeck coefficient at higher temperature is related to the activation of minority carriers since both electron and hole conduction appear at high temperatures [81], which is described as a two-carrier system in Section 2.2.1. The Mott relation

($S = \frac{S_n \sigma_n + S_p \sigma_p}{\sigma_n + \sigma_p}$ (Equation 2-5)) can be used to describe this phenomenon, where

above certain temperature (675-790K in the case of our single filled samples), a lot of the minority carriers (electrons) are thermally excited. As a result, the Seebeck coefficient is reduced due to the opposite sign of electron Seebeck coefficient (S_n) and hole Seebeck coefficient (S_p). As compared to unfilled $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$, the single filled skutterudites with similar Fe content have lower

hole concentrations. As a result, according to $S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$ (Equation 2-6),

they possess higher Seebeck coefficients. It is noted that $\text{Ca}_{0.67}\text{Fe}_{1.63}\text{Co}_{2.37}\text{Sb}_{11.36}$

has the highest Seebeck coefficient among all of La, Ca and Sr single filled samples due to its relatively high filling fraction and low hole concentration.

(a)

(b)

(c)

Figure 4-3 Temperature dependence of Seebeck coefficient in (a) La, (b) Ca and (c) Sr single filled skutterudites. Unfilled ternary skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are included for comparison.

4.1.3 Electrical Resistivity

The temperature dependence of electrical resistivity in La, Ca and Sr single filled skutterudites, as well as unfilled ternary skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$, is shown in Figure 4-4. For samples with similar Fe content in each group, the electrical resistivity increases with the increase of filling fraction due to the decrease in hole concentration. There is a crossover at 250K-300K for the electrical resistivity of $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ and $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$. From Hall Effect measurement, $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ is noted to have lower hole concentration than $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$. Therefore, according to Equation 2-7

($1/\rho = \sigma = ne\mu$), the carrier mobility of $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ should be higher than $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ when the temperature is above 300K, hence resulted in the phenomenon. Except $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$ and $\text{Ca}_{0.67}\text{Fe}_{1.63}\text{Co}_{2.37}\text{Sb}_{11.36}$, the electrical resistivities of most of samples increase with the increase of temperature in the whole temperature range investigated. This is a consequence of the enhancement in the scattering effect of the charge carriers on the crystal lattice. On the other hand, for $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$ and $\text{Ca}_{0.67}\text{Fe}_{1.63}\text{Co}_{2.37}\text{Sb}_{11.36}$, the electrical resistivities reach a maximum at about 700K and then decrease slightly with the increase of temperature. It is noted that this is also the same temperature for the maximum Seebeck coefficient. This could be attributed to the two-carrier conduction mechanism, which arises from the relatively higher La and Ca filling fraction. Similar behavior has also been observed in a Ba filled p-type skutterudite [49] and a Ca filled n-type skutterudite [44]. At the same time, because of their low hole concentrations, their electrical resistivities are much higher than the other samples. It is noted that the electrical resistivity of $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$ is almost three times higher than the other two La single filled samples. Such high electrical resistivity should be not only due to its low hole concentration (n), but also due to the reduced hole mobility (μ), which is ascribed to its high filling fraction [82].

(a)

(b)

(c)

Figure 4-4 Temperature dependence of electrical resistivity in (a) La, (b) Ca and (c) Sr single filled skutterudites. Unfilled ternary skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are included for comparison.

4.1.4 Power Factor

A plot of the power factor (PF) of La, Ca and Sr single filled skutterudites along with the unfilled ternary skutterudites is shown in Figure 4-5. It is found that La, Ca and Sr single filling can improve the power factor effectively. Moreover, the largest improvement in these three groups happens at the medium filling fraction. It is due to the trend that both of Seebeck coefficient and electrical resistivity usually increase with the increase of filling fraction. The improvement decreases with the increase of temperature, which follows the same trend as the temperature

dependence of Seebeck coefficient. In general, La, Ca and Sr filled skutterudites show improved power factor when the filling fraction is controlled properly.

(a)

(b)

Figure 4-5 Temperature dependence of power factor in (a) La, (b) Ca and (c) Sr single filled skutterudites. Unfilled ternary skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are included for comparison.

4.1.5 Comparison of La, Ca and Sr Single Filling

In general, the single fillings of La, Ca and Sr increase Seebeck coefficient and electrical resistivity due to the decrease of hole concentration. Since power factor is proportional to the square of Seebeck coefficient and inversely proportional to electrical resistivity, Seebeck coefficient is a more dominating factor in the final power factor. As a result, the single fillings of La, Ca and Sr showed overall improvement in power factor as compared to unfilled skutterudites. However, at high temperatures, the single filled skutterudites favor the two-carrier conduction, which compromises Seebeck coefficient. As a result, the enhancement of power factor at high temperatures is limited. Moreover, it is noted that when the filling

fraction is higher than a certain value, the electrical resistivity is largely increased, which results in poor power factor.

The room temperature electrical properties of La, Ca and Sr single filled skutterudites with the filling fraction about 0.35 are listed in Table 4-5. It can be seen that $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ and $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$ have similar hole concentration, room temperature Seebeck coefficient, electrical resistivity and power factor. Sr filling expands the lattice parameter more than Ca and La filling due to its larger ion radius. $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$ has the highest room temperature Seebeck coefficient and electrical resistivity due to its lowest hole concentration.

Table 4-5 Actual composition determined from ICP-OES quantification, filler ion radius R , lattice parameter a , hole concentration n , Seebeck coefficient S , electrical resistivity ρ , power factor PF at room temperature in Ca, La and Sr single filled skutterudites when the filling fraction is about 0.35.

<i>Actual Composition</i>	R (Å)	a (Å)	n (10^{19} cm^{-3})	S ($\mu\text{V/K}$)	ρ ($\text{m}\Omega\cdot\text{cm}$)	PF ($\text{mW}/(\text{m}\cdot\text{K}^2)$)
$\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$	1.36	9.0864	0.91	112.0	2.86	0.44
$\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$	1.34	9.0826	2.61	85.3	0.93	0.78
$\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$	1.44	9.0887	2.38	85.5	0.90	0.82

The temperature dependence of Seebeck coefficient and electrical resistivity in these La, Ca and Sr single filled skutterudites with the filling fraction about 0.35 is shown in Figure 4-6 and Figure 4-7, respectively. $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ and $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$ have the Seebeck coefficient and electrical resistivity comparable in the whole temperature range investigated. According to Equation

2-6 ($S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T (\frac{\pi}{3n})^{2/3}$) and Equation 2-7 ($1/\rho = \sigma = ne\mu$), as they possess similar hole concentration, similar electrical properties are expected. $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$, on the other hand, has the highest Seebeck coefficient and electrical resistivity among these three samples due to its lowest hole concentration.

Figure 4-6 Temperature dependence of Seebeck coefficient in La, Ca and Sr single filled skutterudites when the filling fraction is about 0.35.

Figure 4-7 Temperature dependence of electrical resistivity in La, Ca and Sr single filled skutterudites when the filling fraction is about 0.35.

The temperature dependence of power factor in these La, Ca and Sr single filled skutterudites with the filling fraction about 0.35 is shown in Figure 4-8. Due to the comparable Seebeck coefficient and electrical resistivity in Ca and Sr single filled skutterudites, they have the similar power factor. Although $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$ has the highest Seebeck coefficient, its power factor is much lower than both Ca and Sr single filled skutterudites above room temperature due to its nearly three times higher electrical resistivity compared to the other two. It can be noted is that a lower La filling fraction (0.28) would induce comparable improvement of power factor in Figure 4-5 (a) as Ca and Sr single filling as shown in Figure 4-8.

Figure 4-8 Temperature dependence of power factor in La, Ca and Sr single filled skutterudites when the filling fraction is about 0.35.

From the above discussion, it is noted that the electrical properties of single filled skutterudites are mainly determined by the charge valences of filler atoms. Ca and Sr, which come from the same elemental group and thus possess the same charge valence (+2), have similar effects on electrical properties of skutterudites. On the other hand, La, which has higher charge valence (+3), can induce higher Seebeck coefficient and electrical resistivity as compared to Ca and Sr.

4.2 Electrical Properties of Ca-La and Sr-La Double Filled Skutterudites

The room temperature electrical properties are summarized in Table 4-6. The lattice parameters of the samples were determined using Rietveld refinement. The lattice parameters of Ca single, La single and Ca-La double filled skutterudites are found to vary only slightly from 9.0715 to 9.0778 Å, and the small variation is attributed to the similar ionic radii of Ca^{2+} (1.34 Å) and La^{3+} (1.36 Å). As a result, it is reckoned that variation of their compositions does not result in too much distortion to the crystal structure. In contrast, Sr-La double filling expands the lattice parameter as compared to the La single filled skutterudite. It is due to the larger radius of Sr^{2+} ion (1.44 Å). The detailed discussion of electrical properties of Ca-La and Sr-La double filled skutterudites will be presented in the following sections.

Table 4-6 Actual composition determined from ICP-OES quantification, lattice parameter a , hole concentration n , Seebeck coefficient S , electrical resistivity ρ , power factor PF at room temperature in Ca-La and Sr-La double filled skutterudites as well as La, Ca and Sr single filled skutterudites.

<i>Actual Composition</i>	a (Å)	n (10^{19}cm^{-3})	S ($\mu\text{V/K}$)	ρ ($\text{m}\Omega.\text{cm}$)	PF ($\text{mW}/(\text{m.K}^2)$)
$\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$	9.0755	2.27	80.0	1.00	0.64
$\text{Ca}_{0.17}\text{La}_{0.11}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.91}$	9.0778	1.61	84.0	1.25	0.56
$\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$	9.0738	1.74	90.0	1.14	0.71
$\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$	9.0824	2.97	84.1	1.02	0.69
$\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$	9.0855	4.87	78.0	0.97	0.63
$\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$	9.0715	1.77	88.7	0.99	0.79
$\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$	9.0716	2.83	59.7	0.98	0.36
$\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$	9.0825	5.62	79.4	0.91	0.69

4.2.1 X-ray Diffraction Patterns, Rietveld Refinements and X-ray Photoelectron Spectroscopy Study

The compositions of the samples were denoted according to the chemical analysis results obtained from ICP-OES. The total filling fraction in the Ca-La double filled skutterudites is between 0.23 and 0.28, while the total filling fraction in the Sr-La double filled skutterudites is 0.20. Ca, Sr and La single filled skutterudites with similar filling fraction are also chosen for comparison with the double filled samples.

(a)

(b)

Figure 4-9 X-ray diffraction patterns of (a) Ca-La and (b) Sr-La double filled skutterudites.

(a)

Figure 4-10 X-ray diffraction pattern and Rietveld refinement of (a) $\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$ and (b) $\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$. Inset: the fitting results at the high 2θ angle range from 86° to 98° . The blue lines are the experimental results. The red lines are the calculated results. The bottom curves are their difference.

The X-ray diffraction patterns of Ca-La and Sr-La double filled skutterudites are shown in Figure 4-9. It can be seen that less than 4wt% of Sb determined by Rietveld refinement from XRD data was detected in all the samples. Only less than 3wt% $\text{Fe}_{1-x}\text{Co}_x\text{Sb}_2$ was detected in $\text{Ca}_{0.17}\text{La}_{0.11}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.91}$, and this is reckoned not to affect the properties significantly [64]. The XRD pattern and Rietveld refinement of $\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$ and $\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$ are exemplified in Figure 4-10. The inset of Figure 4-10 shows that there is no broadening or shift in the diffraction peaks at high 2θ angle ranging from 86° to 98° . This indicates that the samples contained a single skutterudite phase which was well crystallized and homogeneous, rather than multiple skutterudite phases of different lattice parameters [83, 84]. Rietveld refinement condition and results of $\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$ and $\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$ are also listed in Table 4-7 and Table 4-8, respectively. The occupancies of Ca, Sr, La, Fe, Co and Sb are fixed according to the ICP-OES

results. Sb position has been refined and is noted to be comparable to Ca and La single filled skutterudites. The thermal parameters (B) of Ca and La in Ca-La double filled samples were refined simultaneously and fixed to be the same value. This is expected as the radii of Ca^{2+} (1.34Å) and La^{3+} (1.36Å) are comparable and thus their rattling amplitudes will be similar. The thermal parameters (B) of Ca and La (6.09) are much higher than those of Fe/Co (0.873) and Sb (0.994), which will facilitate the rattling effect of Ca and La in the lattice. Similarly, the thermal parameters (B) of Sr and La in Sr-La double filled samples are higher than the other elements.

Table 4-7 Rietveld refinement condition and results of $\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$.

X-ray radiation		Cu K_{α}				
Monochromator		Graphite				
Temperature		Room temperature				
2θ range (deg)		10.000-140.000				
Step width (deg)		0.02				
Counting time (s/step)		4.43				
Structure type		$Im\bar{3}$				
Lattice parameter (Å)		9.07555(27)				
R_{wp}		0.1026				
R_p		0.0722				
R_{Bragg}		0.02096				
GOF		2.50				

Atom	Position	Occu.	x	y	z	B
Ca	2a	0.12	0	0	0	6.09(61)
La	2a	0.11	0	0	0	6.09(61)
Fe/Co	8c	0.3275/0.6725	0.25	0.25	0.25	0.873(39)
Sb	24g	0.9742	0.158532(78)	0.335236(77)	0	0.994(23)

Table 4-8 Rietveld refinement condition and results of $\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$.

X-ray radiation	Cu K_{α}
Monochromator	Graphite
Temperature	Room temperature
2θ range (deg)	10.000-120.000
Step width (deg)	0.02
Counting time (s/step)	4.43
Structure type	$Im\bar{3}$
Lattice parameter ($\text{\AA}$)	9.0855(13)
R_{wp}	0.1450
R_p	0.1053
R_{Bragg}	0.04401
GOF	4.31

Atom	Position	Occu.	x	y	z	B
Sr	2a	0.16	0	0	0	1.00(59)
La	2a	0.04	0	0	0	1.00(59)
Fe/Co	8c	0.36/0.64	0.25	0.25	0.25	0.69(23)
Sb	24g	1	0	0.15882(13)	0.33556(12)	0.71(21)

Due to the possible existence of multi-valence of Co and Fe in double filled skutterudites, X-ray photoelectron spectroscopy (XPS) study was applied to examine the valence states of Co and Fe. The Co and Fe 2p XPS spectra of $\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$ and $\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$ are exemplified in Figure 4-11 and Figure 4-12, respectively. The Co 2p_{3/2} binding energies of 778.1eV for both two samples are exactly same to that in CoSb₃ [85]. It means that

the Co valence state in our double filled samples is +3, the same as that in CoSb_3 . Also, it is found that the Fe $2p_{3/2}$ binding energies of 706.8eV for $\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$ and 706.7eV for $\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$ are comparable to those in $\text{LaFe}_4\text{Sb}_{12}$ (706.7eV) and $\text{CeFe}_4\text{Sb}_{12}$ (706.8eV) [85]. Thus, it is confirmed that the valence state of Fe in our double filled samples is +2, the same as that in the single filled samples. In other words, the double filling does not change the valence states of Fe and Co in skutterudites.

Figure 4-11 High-resolution Co 2p XPS spectra of (a) $\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$ and (b) $\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$.

Figure 4-12 High-resolution Fe 2p XPS spectra of (a) $\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$ and (b) $\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$.

4.2.2 Seebeck Coefficient

(a)

(b)

Figure 4-13 Temperature dependence of Seebeck coefficient in the (a) Ca-La and (b) Sr-La double filled skutterudites as well as Ca, Sr and La single filled skutterudites.

The temperature dependence of the Seebeck coefficient of all the samples is shown in Figure 4-13. All the samples show positive Seebeck coefficients (S), indicating that they are p -type thermoelectric materials. In general, the Seebeck coefficient is observed to increase with the increase of temperature and reaches a maximum at around 730K to 780K. With further increase in temperature, the Seebeck coefficient decreases. The reduction in Seebeck coefficient at higher temperature, as discussed earlier, is related to the activation of minority carriers since both electron and hole conduction appear at high temperature [81]. The Seebeck coefficient of the Ca-La double filled samples is noted to be higher than the Ca single filled sample. This is due to the hole carrier concentration difference caused by the difference in the charge valence of Ca and La ions in the lattice. In

general, the Seebeck coefficient increases as charge carrier concentration decreases. La^{3+} filling provides 3 electrons to the lattice and will compensate more holes than Ca^{2+} filling, which gives 2 electrons. As a result, the Ca single filled sample have the highest hole concentration, as shown in Table 4-6. All the Ca-La double filled samples have hole carrier concentrations lower than the Ca single filled sample. This attributes to the higher Seebeck coefficient of the Ca-La double filled samples than that of the Ca single filled sample. The La single filled skutterudite sample does not show the lowest hole concentration because its La filling fraction is lower than the total Ca-La filling fraction of double filled samples. Hence, the Seebeck coefficient of the La single filled sample is similar to that of the Ca-La double filled samples due to their comparable hole concentration. On the other hand, the La single filled sample has higher Seebeck coefficient than both of the Sr-La double filled samples and the Sr single filled sample above room temperature due to its lower hole concentration. $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$ possesses higher Seebeck coefficient than the Sr single filled sample in the whole temperature range investigated. This is mainly due to the lower hole concentration of $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$. The other Sr-La double filled skutterudite $\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$ also has the hole concentration comparable to the Sr single filled sample. Thus their Seebeck coefficient is similar in the whole temperature range investigated. For the double filed skutterudites $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$ and $\text{Sr}_{0.16}\text{La}_{0.04}\text{Fe}_{1.44}\text{Co}_{2.56}\text{Sb}_{11.27}$, the Seebeck coefficient decreases with the increase of the ratio of Sr/La due to the increase of hole concentration.

4.2.3 Electrical Resistivity

Figure 4-14 shows the temperature dependence of the electrical resistivity of the samples. The electrical resistivity (ρ) of all the samples is observed to increase with the increase of temperature for the temperature range investigated. This is a consequence of the enhancement in the scattering effect of the charge carriers on the crystal lattice as the temperature increases. The Ca single filled sample has lower electrical resistivity than all the Ca-La double filled samples at low temperature, which is consistent with its higher hole concentration. But its electrical resistivity increases very fast with the increase of temperature. This should be attributed to its temperature dependence of hole mobility according to Equation 2-7 ($1/\rho = \sigma = ne\mu$). The electrical resistivity of Ca-La double filled skutterudites was also observed to have similar trend in the temperature range investigated. At the same temperature, the electrical resistivity increases with the decrease of hole concentration. As a result, $\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$ exhibited the lowest electrical resistivity among all the Ca-La double filled samples, while $\text{Ca}_{0.17}\text{La}_{0.11}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.91}$ has the highest electrical resistivity. On the other hand, the Sr single filled sample has lower electrical resistivity than both of the Sr-La double filled samples due to its higher hole concentration. Filling in La with higher charge valence (+3) is noted to decrease the hole concentration, hence increase the electrical resistivity.

(a)

(b)

Figure 4-14 Temperature dependence of electrical resistivity in the (a) Ca-La and (b) Sr-La double filled skutterudites as well as Ca, Sr and La single filled skutterudites.

4.2.4 Power Factor

The temperature dependence of power factor of the samples is shown in Figure 4-15. All the Ca-La double filled skutterudites have power factor much higher than Ca single filled skutterudite. It is because they have much higher Seebeck coefficient than Ca single filled sample in the temperature range investigated. But at the high temperature range they cannot surpass the power factor of La single filled skutterudite. It is ascribed to the low electrical resistivity of the La single filled sample at the high temperature range. For the Sr-La double filled samples, although their power factors do not surpass the power factor of the Sr or La single filled samples at high temperature, it is essential to noted that they are not compromised significantly. The overall effect on thermoelectric property will be discussed in Chapter 6.

(a)

(b)

Figure 4-15 Temperature dependence of power factor in the (a) Ca-La and (b) Sr-La double filled skutterudites as well as Ca, Sr and La single filled skutterudites.

4.2.5 Ca-La and Sr-La Comparison

In general, the filling fraction and the charge valence of filler atoms have determining effects on Seebeck coefficient, hence the power factor of the system. On the other hand, maintaining a low electrical resistivity is also essential. It is noted, in the present work, that double filling does not really facilitate superior final electrical properties compared to the single filled ones. However, it does not compromise much on the properties either.

A summary of the room temperature electronic properties of Ca-La and Sr-La double filled skutterudites with the similar filling fractions is listed in Table 4-9. The Sr-La double filled skutterudite has larger lattice parameter than the Ca-La double filled skutterudite since the radius of Sr^{2+} (1.44Å) is larger than La^{3+}

(1.34Å). They have comparable room temperature Seebeck coefficient, electrical resistivity and power factor.

Table 4-9 Actual composition determined from ICP-OES quantification, lattice parameter a , hole concentration n , Seebeck coefficient S , electrical resistivity ρ , power factor PF at room temperature in Ca-La and Sr-La double filled skutterudites.

<i>Actual Composition</i>	<i>a (Å)</i>	<i>n (10^{19}cm^{-3})</i>	<i>S ($\mu\text{V/K}$)</i>	<i>ρ ($\text{m}\Omega.\text{cm}$)</i>	<i>PF ($\text{mW}/(\text{m}.\text{K}^2)$)</i>
$\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$	9.0738	1.74	90.0	1.14	0.71
$\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$	9.0824	2.97	84.0	1.02	0.69

The temperature dependence of Seebeck coefficient in the Ca-La and Sr-La double filled skutterudites is shown in Figure 4-16. Both of them have almost the same and linear Seebeck coefficient as a function of temperature at the temperature range from 5K to 300K. Above 300K, the slope of Seebeck coefficient vs. temperature is greatly reduced and above 650K the slope is almost independent of temperature. This reduced slope results from the two-carrier conduction mechanism at high temperatures due to intrinsic semiconducting behavior. $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$ has the slightly lower Seebeck coefficient than $\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$ above 300K due to the higher hole concentration of the former.

Figure 4-16 Temperature dependence of Seebeck coefficient in the Ca-La and Sr-La double filled skutterudites.

Figure 4-17 Temperature dependence of electrical resistivity in the Ca-La and Sr-La double filled skutterudites.

The temperature dependence of electrical resistivity in the Ca-La and Sr-La double filled skutterudites is given in Figure 4-17. Both of them increase with the increase of temperature. $\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$ has a slight higher value than $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$ due to their difference in hole concentration.

The higher Seebeck coefficient and electrical resistivity in $\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$ makes its power factor comparable to $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$, shown in Figure 4-18. We can estimate that all the electronic properties of the Ca-La and Sr-La should be the same if they have the same filling fractions. In other words, Ca and Sr filling have the similar effect on the electronic properties in the double filled skutterudites due to the same charge valence (+2) in both of their ions. In conclusion, the charge valences of filler atoms have a determining effect on the electrical properties of double filled skutterudites with similar compositions, as that of the single filled skutterudites.

Figure 4-18 Temperature dependence of power factor in the Ca-La and Sr-La double filled skutterudites.

Chapter 5 Thermal Properties of Single and Double Filled Skutterudites

5.1 Thermal Properties of La, Ca and Sr Single Filled Skutterudites

5.1.1 La Single Filled Skutterudites

The temperature dependence of total thermal conductivity in La single filled skutterudites in the temperature range from 5K to 730K is shown in Figure 5-1. The total thermal conductivity of $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ is plotted for comparison. There is a peak at around 28-40K for $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$, $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$ and $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$. This peak corresponds to the behaviour of a dielectric crystal [86]. The peak intensity indicates the disorder in the sample as discussed in Section 2.2.3 and can be suppressed as the defects (disorder) increase because at such low temperatures the thermal conductivity is determined by phonon scattering against defects, which limits the mean free path of phonons [87]. The filler atom La can be viewed as defect in the lattice. Therefore the peak intensity reduces quickly when the La filling fraction increases from 0 to 38%. No peak at such low temperature is observed in $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$, which was also reported in Ce [88] and Ba [89] p-type skutterudites as well as Ca [61] and Ba [90] single filling for n-type skutterudites, as the characteristic of substantially filled skutterudites.

When the La filling fraction increases, the total thermal conductivity of La single filled skutterudites decreases in the whole temperature range investigated. As compared to unfilled $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$, La filling can effectively reduce the total thermal conductivity. The value at 730K is lowered by 17%, 35% and 64% for $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$, $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$ and $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$, respectively.

Figure 5-1 Temperature dependence of total thermal conductivity in La single filled skutterudites as well as unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

Figure 5-2 Temperature dependence of lattice and electronic thermal conductivity in La single filled skutterudites as well as unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

The temperature dependence of lattice thermal conductivity (κ_L) in La single filled skutterudites is calculated by subtracting the electronic thermal conductivity (κ_E) from the total thermal conductivity (κ_T), as shown in Figure 5-2. The electronic thermal conductivity, also shown in Figure 5-2, can be estimated from the Wiedemann-Franz law ($\kappa_E = L_0 T / \rho$, where κ_E is the electronic thermal conductivity, L_0 is the Lorenz number $2 \times 10^{-8} \text{ V}^2/\text{K}^2$, T is the temperature and ρ is the electrical resistivity). It can be seen that κ_E increases with the increase of temperature, hence has an important role at high temperature range. At a certain temperature, κ_E increases when the electrical resistivity is decreased. Due to its high electrical resistivity among the La single filled skutterudites, $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$ shows the lowest electronic thermal conductivity, only

about half of that of the other two samples. $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$ and $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$ have similar electronic thermal conductivity since they have comparable electrical resistivity (as shown in Figure 4-4 (a)) in the whole temperature range investigated. The lattice thermal conductivity decreases with the increase of La filling fraction. This reduction in lattice thermal conductivity is attributed to the increase in the number of “rattlers” with the increase in filler atom amount, and it is the most obvious at temperatures below 300K. Yang *et al.* [51] and Puyet *et al.* [61] have used the Debye model to fit their experimental results, proven that increasing the rattler atom filling fraction could enhance phonon resonance scattering. The room temperature lattice thermal conductivity is 80%, 77% and 88% of the total thermal conductivity in $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$, $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$ and $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$, respectively. At about 730K, the value is reduced to 58%, 51% and 72% in these samples, respectively. As a result, at below room temperature, the lattice thermal conductivity plays an important part in the total thermal conductivity. When the temperature increases, it decreases due to the phonon-phonon Umklapp scattering [24]. Meanwhile, the electronic thermal conductivity increases with the increase of temperature and becomes comparable to lattice thermal conductivity at 730K, such as in $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$ and $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$. Nevertheless, as compared to the unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$, the electronic thermal conductivity of $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$ and $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$ system is only reduced slightly. The reduction of their total thermal conductivity mainly comes from the reduction of their lattice thermal conductivity due to La rattling effect. The value of their

lattice thermal conductivity is reduced by 7% and 36% at 730K, respectively. However, it is noted that for $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$, both the lattice thermal conductivity (32% reduction) and electronic thermal conductivity (71% reduction) have reduced significantly as it has the largest amount of filler atom (La), which gives its lowest total thermal conductivity among all the samples.

5.1.2 Ca Single Filled Skutterudites

The temperature dependence of total thermal conductivity in Ca single filled skutterudites in the temperature range from 5K to 730K is shown in Figure 5-3. The results of the unfilled skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are also included for comparison. A peak at low temperature is noted in all the unfilled and Ca single filled skutterudites, similar to that observed in the La single filled skutterudites. The peak is much lower in the case of $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ and $\text{Ca}_{0.67}\text{Fe}_{1.63}\text{Co}_{2.37}\text{Sb}_{11.36}$ as compared to $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$, as the total thermal conductivity decreases a lot when the Ca filling fraction increases from 0.25 to 0.67. With similar Fe content, $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ and $\text{Ca}_{0.67}\text{Fe}_{1.63}\text{Co}_{2.37}\text{Sb}_{11.36}$ have lower thermal conductivity than $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ while $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ has lower thermal conductivity than $\text{FeCo}_3\text{Sb}_{12}$, since Ca filling can reduce the total thermal conductivity as La filling. However, due to the low filling fraction of 0.25, $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ has limited reduction of lattice thermal conductivity. Thus, above 150K, its lattice thermal conductivity is still higher than $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ sample, which has higher Fe content. The reduction in thermal conductivity was also reported by Puyet *et al.* [44] on Ca single filled n-type skutterudites such as

$\text{Ca}_{0.05}\text{Co}_4\text{Sb}_{12.43}$, $\text{Ca}_{0.08}\text{Co}_4\text{Sb}_{12.45}$ and $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$, when compared to the unfilled CoSb_3 skutterudite. The total thermal conductivity of $3.5\text{W}/(\text{m}\cdot\text{K})$ at 730K in $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$ is comparable to that in our $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ sample with similar Ca filling fraction. Nevertheless, it is still much higher than the other two filled samples $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ ($2.7\text{W}/(\text{m}\cdot\text{K})$) and $\text{Ca}_{0.67}\text{Fe}_{1.63}\text{Co}_{2.37}\text{Sb}_{11.36}$ ($1.6\text{W}/(\text{m}\cdot\text{K})$) due to their higher Ca filling fraction. In the next section, the lattice thermal conductivity is separately looked at from the total thermal conductivity to gain more insight on the Ca single filling effect on thermal conductivity.

Figure 5-3 Temperature dependence of total thermal conductivity in Ca single filled skutterudites as well as unfilled skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

Figure 5-4 Temperature dependence of lattice and electronic thermal conductivity in Ca single filled skutterudites as well as the unfilled skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

The electronic thermal conductivity of the Ca single filled skutterudites is calculated by using the Wiedemann-Franz law. The lattice thermal conductivity is obtained by subtracting the electronic thermal conductivity from the total thermal conductivity. Both results are shown in Figure 5-4. The data of the unfilled skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are also plotted. The electrical resistivities of $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$, $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$, and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are comparable (as shown in Figure 4-4 (b)), hence they have similar electronic thermal conductivity. $\text{Ca}_{0.67}\text{Fe}_{1.63}\text{Co}_{2.37}\text{Sb}_{11.36}$, on the other hand, has electronic thermal conductivity nearly 50% lower than other samples, since its electrical resistivity is about twice higher than that of the other samples. When having similar Fe content, $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ is noted to have lower lattice thermal conductivity than that of $\text{FeCo}_3\text{Sb}_{12}$ (7% reduction at 730K) while

$\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ and $\text{Ca}_{0.67}\text{Fe}_{1.63}\text{Co}_{2.37}\text{Sb}_{11.36}$ are noted to have lower lattice thermal conductivity than that of $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ (about 18% and 39% reduction respectively at 730K). This shows that Ca behaves as a good “rattler” to scatter the phonons. As Ca filling fraction increases from 0.25 to 0.67, the lattice thermal conductivity decreases due to the increase of the amount of phonon scattering oscillators. The maximal Ca filling fraction was reported to be 0.20 in skutterudites without Fe doping [45, 62]. However, in the present work, due to the Fe doping, our Ca filling fraction can reach up to 0.67. This triple amount of Ca filling is mainly responsible for the 37% and 39% reduction in lattice thermal conductivity at 300K and 730K respectively as compared to $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

5.1.3 Sr Single Filled Skutterudites

The temperature dependence of total thermal conductivity in Sr single filled skutterudites and unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ is shown in Figure 5-5. The peak value at about 40K is strongly reduced as the Sr filling fraction increases. All the Sr single filled skutterudites have lower total thermal conductivity than unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. The total thermal conductivity reduction induced at 730K is about 19%, 30% and 40% in $\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$, $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$ and $\text{Sr}_{0.42}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.60}$ samples, respectively. The reduction of total thermal conductivity due to Sr filling was also observed by Zhao *et al.* [62] in n-type skutterudites $\text{Sr}_y\text{Co}_4\text{Sb}_{12}$ ($y=0.12, 0.17, 0.22, 0.28$ and 0.40) without Fe doping. As compared to $\text{Sr}_{0.22}\text{Co}_4\text{Sb}_{12}$ and $\text{Sr}_{0.40}\text{Co}_4\text{Sb}_{12}$ with similar Sr filling fractions, which have thermal conductivity $> 5\text{W}/(\text{m.K})$ at room temperature,

the present samples $\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$ and $\text{Sr}_{0.42}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.60}$ have much lower total thermal conductivity of 2.9 and 2.1 W/(m.K) at room temperature. In order to further understand the mechanism, the total thermal conductivity needs to be separated into the lattice and electronic thermal conductivity.

Figure 5-5 Temperature dependence of total thermal conductivity in Sr single filled skutterudites as well as unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

Figure 5-6 Temperature dependence of lattice and electronic thermal conductivity in Sr single filled skutterudites as well as unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

Using the computation relationships described earlier, Figure 5-6 shows the temperature dependence of lattice and electronic thermal conductivity in Sr single filled skutterudites. The results of unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are also plotted. The electronic thermal conductivity of $\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$ and $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$ is comparable to $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ due to their similar electrical resistivity. $\text{Sr}_{0.42}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.60}$ has the lowest electronic thermal conductivity since it has the highest electrical resistivity (as shown in Figure 4-4 (c)). Determined by subtracting the electronic thermal conductivity from the total thermal conductivity, it is noted that the lattice thermal conductivity decreases with increase of Sr filling fraction in the whole temperature range investigated. This is attributed to the increase of the amount of oscillators (Sr) for the resonant phonon scattering. The same trend was also observed in n-type Sr single filled skutterudites

$\text{Sr}_y\text{Co}_4\text{Sb}_{12}$ ($y=0.12, 0.17, 0.22, 0.28$ and 0.40) reported [62]. All our Sr single filled skutterudites were also noted to have much lower lattice thermal conductivity than the unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ due to the resonant phonon scattering arising from Sr rattling in the oversized lattice voids. The reduction of thermal conductivity at 730K is measured to be 25%, 39% and 45% for $\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$, $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$ and $\text{Sr}_{0.42}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.60}$ samples, respectively. These values are higher than that of the total thermal conductivity reduction, which means that the main reduction in the total thermal conductivity comes from the reduction in lattice thermal conductivity.

Figure 5-7 The comparison of the lattice thermal conductivity between our p-type Fe doping samples $\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$, $\text{Sr}_{0.42}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.60}$ and n-type $\text{Sr}_{0.22}\text{Co}_4\text{Sb}_{12}$, $\text{Sr}_{0.40}\text{Co}_4\text{Sb}_{12}$ [62].

Figure 5-7 compares the lattice thermal conductivity of our p-type Fe doped samples $\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$ and $\text{Sr}_{0.42}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.60}$ with n-type samples $\text{Sr}_{0.22}\text{Co}_4\text{Sb}_{12}$ and $\text{Sr}_{0.40}\text{Co}_4\text{Sb}_{12}$ in the literature [62]. It is noted that the lattice

thermal conductivity of n-type samples is more temperature dependent than the p-type samples. At room temperature, the values in the n-type samples are about twice as high as our p-type samples with similar Sr filling fraction. However, as the temperature increases, the difference decreases. At 730K, the value in $\text{Sr}_{0.22}\text{Co}_4\text{Sb}_{12}$ is close to $\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$, while at about 630K, the lattice thermal conductivity curve of $\text{Sr}_{0.40}\text{Co}_4\text{Sb}_{12}$ intercepts that of $\text{Sr}_{0.42}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.60}$. The variation of lattice thermal conductivity reduction in our p-type samples at room temperature as compared to the n-type samples with similar Sr filling fraction should be ascribed to the extra phonon scattering due to Fe doping. This Fe-doping effect on the room temperature lattice thermal conductivity has been reported by Morelli *et al.* [45] in Ce single filled skutterudites and by Katsuyama *et al.* [77] in $\text{Co}_{1-x}\text{Fe}_x\text{Sb}_3$. Yang *et al.* applied the Debye model to fit the lattice thermal conductivity in $\text{Co}_{1-x}\text{Fe}_x\text{Sb}_3$ and concluded that the reduction of lattice thermal conductivity is due to the lattice defects which are created by Fe doping [91].

5.1.4 Comparison of La, Ca and Sr Single Filling

In general, a peak at low temperatures can be observed in the temperature dependence of lattice thermal conductivity in all the single filled samples, which corresponds to the behaviour of a dielectric crystal. Above room temperature, the lattice thermal conductivity decreases with the increase of temperature, which is due to the phonon-phonon Umklapp scattering. As the filling fraction increases, the lattice thermal conductivity is reduced, which is ascribed to the increase of the “rattler” amount. The electronic thermal conductivity increases with the increase of

temperature and is much lower than the lattice thermal conductivity at low temperatures. Hence, the reduction of the lattice thermal conductivity due to La, Ca and Sr single filling leads to the reduction of the total thermal conductivity, especially at low temperatures.

Figure 5-8 Temperature dependence of total thermal conductivity in La, Ca and Sr single filled skutterudites when the filling fraction is about 0.35.

Figure 5-9 Temperature dependence of lattice thermal conductivity in La, Ca and Sr single filled skutterudites when the filling fraction is about 0.35.

The total and lattice thermal conductivities of the La, Ca and Sr single filled skutterudites with a common filling fraction of about 0.35 are compared in Figure 5-8 and Figure 5-9, respectively. It is generally accepted that for phonon transportation in filled skutterudites, there exists four kinds of phonon scattering effects. They are, namely, grain boundary scattering, point defect scattering, phonon-phonon Umklapp scattering and phonon resonance scattering [44, 52]. The grain sizes of these three samples are in the same range of 1-5 μm , as shown in Figure 5-10. It is reported that the lattice thermal conductivity of skutterudites was noted to be insensitive to the grain size in the range of 0.8-6.7 μm [92]. Also, the densities of these three samples are higher than 95%. Thus the grain boundary scattering in these three samples is comparable. In this section, we have selected samples of similar filling fractions, hence the phonon scattering effect due to the

resonant rattling of filler atom should be comparable. The phonon-phonon Umklapp scattering is determined by many factors such as the Debye temperature, the Grüneisen constant and the average number of atoms in the unit cell [93, 94], and it generally dominates at high temperatures. As a result, at low temperatures, it is noted that point defect scattering is the key effect to lattice thermal conductivity, which is reckoned to be responsible for the difference in the present three kinds of single filled skutterudites. Point defect scattering consists of two components [95], namely, mass fluctuation scattering and strain field scattering. The mass fluctuation in the single filled skutterudites comes from the mass difference between the filler atoms and the remaining voids. In this effect, the heavier filler atom makes stronger mass fluctuation scattering. As a result, the La single filled skutterudite $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$ is expected to show the strongest mass fluctuation scattering while the Ca single filled skutterudite $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ exhibits the weakest mass fluctuation scattering among these three samples. Since the lattice parameter difference between all of our single filled skutterudites and unfilled CoSb_3 or $\text{Fe}_{1-x}\text{Co}_x\text{Sb}_{12}$ is less than 1%. The strain field influence will be very small in comparison to the mass fluctuation and hence can be neglected [32]. It is noted that the Ca single filled sample $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ has the highest total and lattice thermal conductivities among these three samples at the whole temperature range investigated. The La single filled sample $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$ has the lowest total thermal conductivity at the whole temperature, however, its lattice thermal conductivity only shows the lowest values when the temperature is below 450K. These phenomena can be attributed to the mass fluctuation scattering

due to the mass difference of these filler atoms which is also more pronounced at higher filling fraction. Above 450K, the lattice thermal conductivity of $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$ is comparable to $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$.

(a)

(b)

(c)

Figure 5-10 SEM images of the fracture surfaces of (a) $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$, (b) $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$, (c) $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$.

5.2 Thermal Properties of Ca-La and Sr-La Double Filled Skutterudites

Section 5.1 has shown the promising thermal conductivity reduction by using La, Ca and Sr single filling for skutterudite. In this section, double filling, which means the filling in of two kinds of filler atoms, such as Ca-La and Sr-La, is applied in order to further reduce the thermal conductivity of skutterudite. It is expected that these dual filler atoms from different elemental groups possess different “rattling” frequencies in the lattice, and can thus result in the broadening of the resonant frequency range for phonon scattering. In order to give a reasonable comparison for the single and double filling effects on the thermal conductivity of skutterudite, similar total filling fraction in the double filled samples to that of the single filled samples is attempted.

5.2.1 Ca-La Double Filled Skutterudites

The temperature dependence of the total thermal conductivity (κ_T) for Ca-La double filled skutterudites is shown in Figure 5-11. The data for La and Ca single filled skutterudites with similar filling fraction are also plotted for comparison. It can be seen that all the Ca-La double filled samples exhibit much lower total thermal conductivity than the single filled skutterudites over the temperature range of 5 to 730K. The maximum reduction is found at about 40K, where a peak is observed in all the samples, which is the characteristic of a dielectric crystal. All the double filled samples showed similar thermal conductivities, which could be due to the similar fraction amount of total filling. The reduction of total thermal

conductivity in double filled samples at 730K is noted to be as high as 46% and 57%, as compared to the single filled $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$ and $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ samples, respectively. In order to have a clearer picture of the phonon scattering mechanism, the electronic thermal conductivity (κ_E) and lattice thermal conductivity (κ_L) of all the samples were separated before comparing among the samples.

Figure 5-11 Temperature dependence of total thermal conductivity in Ca-La double filled skutterudites as well as Ca and La single filled skutterudites.

Figure 5-12 Temperature dependence of electronic thermal conductivity in Ca-La double filled skutterudites as well as Ca and La single filled skutterudites.

Figure 5-13 Temperature dependence of lattice thermal conductivity in Ca-La double filled skutterudites as well as Ca and La single filled skutterudites.

As discussed earlier, the electronic thermal conductivity (κ_E) and lattice thermal conductivity (κ_L) can be calculated by Wiedmann-Franz law. They are shown in Figure 5-12 and Figure 5-13, respectively. For the lattice thermal conductivity, it is noted that all the double filled samples have lower lattice thermal conductivity than the single filled samples in the whole temperature range investigated. The lattice thermal conductivity of $\text{Ca}_{0.17}\text{La}_{0.11}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.91}$ is lower than $\text{Ca}_{0.12}\text{La}_{0.11}\text{Fe}_{1.31}\text{Co}_{2.69}\text{Sb}_{11.69}$ due to the higher Ca filling fraction in the former. Nevertheless, it is also noted to have a lower lattice thermal conductivity than $\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$ sample. This could be due to its having a ratio of Ca/La closer to 1:1, hence resulted in a more inordinate distribution of the two kinds of filler atoms. This superior effect induced by a more balancing ratio was also observed and reported in Ca-Ce double filled skutterudites [74]. Meanwhile, the higher Fe content in $\text{Ca}_{0.17}\text{La}_{0.11}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.91}$ also plays a role in the reduction of its lattice thermal conductivity. The room temperature lattice thermal conductivities of all our Ca-La double filled samples achieved on average of 50% reduction compared to that of the single filled samples. When the temperature is increased to 730K, the reduction of lattice thermal conductivity in double filled samples can be as much as 76% lower as compared to the Ca single filled sample and 63% lower as compared with the La single filled sample, even for similar filling fractions. The lowest κ_L value of 1.3 W/(m.K) at room temperature is found in sample $\text{Ca}_{0.17}\text{La}_{0.11}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.91}$. When compared to other reported n-type single filled skutterudites of similar filling fraction, such as $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$ (4.2 W/(m.K) at room temperature) [44] and $\text{La}_{0.23}\text{Co}_4\text{Sb}_{11.6}$ (2.5 W/(m.K) at room

temperature) [28], all the present Ca-La double filled skutterudites again exhibit much lower lattice thermal conductivities (1.3-1.6 W/(m.K) at room temperature). Moreover, their room temperature lattice thermal conductivities are also lower than other double filled skutterudites reported [70, 71] of similar total filling fraction such as Ce-La and Ba-Sr as shown in Figure 5-14. These experimental data have clearly shown that the reduction of κ_L in Ca-La double filled samples is larger than that of either RE-RE or AE-AE double filled skutterudites, where RE and AE stand for rare-earth and alkaline-earth elements, respectively. Yang *et al.* [70] have calculated the resonant frequencies of alkaline-earth filler atoms Sr and Ba (90cm^{-1} and 93cm^{-1} in [111] direction) using a lattice dynamical model based on density-functional calculations, and proposed that the resonant frequencies for filler atoms from the same elemental group should be comparable. As a result, it is deduced that Ca has the similar resonant frequency of about 90cm^{-1} as those of Sr and Ba. Yang *et al.*'s calculations also gave the La resonant frequency of about 70cm^{-1} , which is consistent with the calculation from Feldman *et al.* [96]. These two distinguish domains of the resonant frequencies are believed to scatter a broader spectrum of heat-carrying phonons, with frequencies close to these resonant frequencies [70]. As a result, the Ca-La double filling provides remarkable reduction in lattice thermal conductivity as compared to either their parent Ca and La single filling or the double filling from the same elemental group.

Figure 5-14 Room temperature lattice thermal conductivity as a function of the total filling fraction (x+y) for our Ca-La double filled samples, the reported Ce-La [71] and Ba-Sr [70] double filled samples.

5.2.2 Sr-La Double Filled Skutterudites

The temperature dependence of total thermal conductivity in Sr-La double filled skutterudites is shown in Figure 5-15. The results of Sr and La single filled samples with similar filling fraction are also shown for comparison. It can be seen that Sr-La double filling has also effectively reduced the total thermal conductivity at the whole temperature range investigated as compared with Sr or La single filling. The peak at low temperature, which is the characteristic of a dielectric crystal, can be observed in both La and Sr single filled samples, but is not found in Sr-La double filled samples. This is attributed to the remarkable reduction at the corresponding temperature where the dielectric maximum is diminished. Although the La percentage in total filling fraction is small (20% and 30%) in both of our double

filled samples, it is enough to give about 33% total thermal conductivity reduction at 730K from that of the Sr or La single filled sample.

Figure 5-15 Temperature dependence of total thermal conductivity in Sr-La double filled skutterudites as well as Sr and La single filled skutterudites.

The electronic thermal conductivity and lattice thermal conductivity are separately shown in Figure 5-16 and Figure 5-17, respectively. $\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$ has shown the highest electronic thermal conductivity in the whole temperature range investigated due to its lowest electrical resistivity among all the samples. The other samples have comparable electronic thermal conductivity since their electrical resistivities are similar. A peak at low temperature in the lattice thermal conductivity of Sr-La double filled samples can still be seen, despite the intensity is much lower than the Sr and La single filled samples.

Figure 5-16 Temperature dependence of electronic thermal conductivity in Sr-La double filled skutterudites as well as Sr and La single filled skutterudites.

Figure 5-17 Temperature dependence of lattice thermal conductivity in Sr-La double filled skutterudites as well as Sr and La single filled skutterudites.

The lattice thermal conductivity of our Sr-La double filled skutterudites can reach to about 0.5W/(m.K)) at 730K, which is 63% and 70% lower than the Sr single filled sample $\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$ and the La single filled sample $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$, respectively. As compared to the Ce-La double filled sample $\text{Ce}_{0.1}\text{La}_{0.1}\text{FeCo}_3\text{Sb}_{12}$ (about 1.0W/(m.K) at 730K) [71], the lattice thermal conductivity of our Sr-La samples is much lower. The reduction effect from Sr-La double filling is even stronger than the previous Ca-La double filled skutterudites. The room temperature lattice thermal conductivity in both of the present Sr-La double filled samples is about 1.2W/(m.K). This value is only about half of Ba-Sr double filled skutterudites $\text{Ba}_{0.15}\text{Sr}_{0.14}\text{Co}_4\text{Sb}_{12.03}$, $\text{Ba}_{0.17}\text{Sr}_{0.08}\text{Co}_4\text{Sb}_{12.07}$ and $\text{Ba}_{0.20}\text{Sr}_{0.17}\text{Co}_4\text{Sb}_{12.08}$ reported by Yang *et al.* [70]. These results confirm that the filler atoms from two different elemental groups, especially the pairing from rare-earth and alkaline-earth, can scatter a broader frequency range of phonons than those from the same elemental group, and facilitate property improvement.

5.2.3 Ca-La and Sr-La Comparison

In general, it is noted that Ca-La and Sr-La double fillings further reduce the lattice thermal conductivity as compared with their parent single fillings. When compared with other reported double fillings, such as Ce-La and Ba-Sr, whose dual filler atoms are from the same elemental group, Ca-La and Sr-La double fillings, whose dual filler atoms are from the different elemental groups, result in more effective phonon scattering. These results support the proposed mechanism that a broader frequency range of phonons can be scattered by choosing the dual filler

atoms from two different elemental groups than from the same elemental group for double filled skutterudites.

Figure 5-18 Temperature dependence of lattice thermal conductivity in $\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$ and $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$.

In this section, $\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$ and $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$ are chosen for comparison since they have the most similar compositions in our Ca-La and Sr-La double filled samples. Their lattice thermal conductivities are shown in Figure 5-18, and it can be seen that $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$ has much lower lattice thermal conductivity than $\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$ in the whole temperature range investigated. It hence can deduce that Sr-La double filling is more effective on phonon scattering than Ca-La double filling. From Yang's [70] finding that Ca, Sr and Ba exhibit similar resonant frequency about 90cm^{-1} , Ca-La and Sr-La double filling should have similar resonant frequency range for the

phonon scattering. The grain boundary scattering of these two samples is similar since their grain sizes are in the same range of 1-5 μm , as shown in Figure 5-19. Their differences hence mainly lie on the atomic mass and ionic radius of Ca and Sr. Sr atom (87.62g/mol) is almost twice as heavy as Ca atom (40.08g/mol). The ionic radius of Sr^{2+} (1.44 $\text{\AA}$) is larger than the ionic radius of Ca^{2+} (1.34 $\text{\AA}$). If Ca-La and Sr-La are randomly distributed in the samples, Sr-La filling will provide stronger point defect phonon scattering than Ca-La filling since Sr-La filling produces more mass fluctuation (mass difference between the filler atoms and the remaining voids) and strain field (the lattice parameter difference between filled and unfilled unit cells) in the lattice. It should be noted that the filling fraction of Sr (0.14) is lower than that of Ca (0.19). If the filling fraction of Sr is increased to 0.19, as the same value as that of Ca, the lattice thermal conductivity of the Sr-La double filled sample should be further reduced. As a result, the difference of the lattice thermal conductivities in these two samples will be even larger.

Figure 5-19 SEM images of the fracture surfaces of (a) $\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$ and (b) $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$.

Chapter 6 Dimensionless Figure of Merit

ZT in Single and Double Filled

Skutterudites

In Chapter 4 and 5, the electrical and thermal properties of the single and double filled skutterudites have been measured. In this chapter, we combine all these properties to get the dimensionless figure of merit ZT , which can be used to determine the performance of the single and double filled samples. The larger the ZT value, the higher TE efficiency a material has.

The dimensionless figure of merit ZT can be calculated by

$$ZT = \frac{S^2 T}{\rho \kappa_T} = \frac{PF \times T}{\kappa_T}, \quad \text{Equation 6-1}$$

where S is the Seebeck coefficient, T is the temperature, ρ is the electrical resistivity, κ_T is the total thermal conductivity, PF is the power factor. Hence ZT is proportional to power factor and inversely proportional to the total thermal conductivity.

6.1 *ZT* Values of Single Filled Skutterudites

6.1.1 La Single Filled Skutterudites

The temperature dependence of *ZT* in La single filled skutterudites is calculated and shown in Figure 6-1. Results of unfilled ternary skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are added for comparison. It can be seen that all the La single filled skutterudites have higher *ZT* values than unfilled ternary skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. Among them, $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$ has the highest *ZT* value at the whole temperature range investigated. It reaches the maximal value about 0.6 at 730K, which is almost 70% higher than that of $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. The improved *ZT* in the La single filled skutterudites is mainly attributed to the reduced thermal conductivity due to La filling, as shown in Section 5.1.1. Although $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$ has lower power factor than $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ due to its high electrical resistivity, as shown in Section 4.1, its largely reduced thermal conductivity has made its final *ZT* higher than $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. The other two samples $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$ and $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$ have even improved power factor as compared with $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. As a result, combining the lower thermal conductivity with higher power factor, both of them achieved higher *ZT* than $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

Figure 6-1 Temperature dependence of ZT in La single filled skutterudites. Unfilled ternary skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ is included for comparison.

Although our La single filled samples have improved ZT values as compared to the unfilled sample $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. The maximal ZT value of 0.6 at 730K in $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$ is still lower than the reported ZT value of 0.8 at 730K in $\text{LaFe}_3\text{CoSb}_{12}$ [33]. It is found that they have similar power factors at 730K. However, the thermal conductivity (1.6W/(m.K)) in $\text{LaFe}_3\text{CoSb}_{12}$ is lower than that (2.2 W/(m.K)) in our $\text{La}_{0.28}\text{Fe}_{1.54}\text{Co}_{2.46}\text{Sb}_{11.71}$ due to the higher La filling fraction of the former.

6.1.2 Ca Single Filled Skutterudites

The temperature dependence of ZT in Ca single filled skutterudites is shown in Figure 6-2. It can be seen that the ZT value increases as the Ca filling fraction increases from 0.25 to 0.67 in the temperature range investigated. It is noted that

the results follow similar trend as that observed in the thermal conductivity. $\text{Ca}_{0.67}\text{Fe}_{1.63}\text{Co}_{2.37}\text{Sb}_{11.36}$ is noted to have the highest ZT value among these Ca single filled samples. The maximal ZT value of 0.65 is achieved at 730K, which is 80% higher than that of unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ at the same temperature. Although its power factor is lower than that of $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ sample when the temperature is higher than 600K, as shown in Section 4.1.4, its superior thermal conductivity (only half of that of $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ at this temperature range) has resulted in the higher ZT value. On the other hand, $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ has higher ZT values than $\text{FeCo}_3\text{Sb}_{12}$ due to its higher power factor and lower thermal conductivity.

Figure 6-2 Temperature dependence of ZT in Ca single filled skutterudites. Unfilled ternary skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are included for comparison.

6.1.3 Sr Single Filled Skutterudites

The temperature dependence of ZT in Sr single filled skutterudites is shown in Figure 6-3. All the Sr single filled samples have shown higher ZT than unfilled sample $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$ and $\text{Sr}_{0.42}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.60}$ have comparable ZT in the whole temperature range investigated. Both of them can reach the maximal ZT value of 0.55 at 730K, which is 53% higher than that of $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ at the same temperature. $\text{Sr}_{0.25}\text{Fe}_{1.47}\text{Co}_{2.53}\text{Sb}_{11.94}$ has relatively lower ZT as compared with the other two Sr single filled samples mainly due to its high thermal conductivity as shown in Section 5.1.3.

Figure 6-3 Temperature dependence of ZT in Sr single filled skutterudites. Unfilled ternary skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ is included for comparison.

6.1.4 Comparison of La, Ca and Sr Single Filling

In general, it is noted that La, Ca and Sr single fillings improve ZT values as compared with the reported unfilled $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ sample with similar Fe content. It is found that the improvement is mainly due to the significant reduction of lattice thermal conductivity by La, Ca and Sr single fillings since the enhancement of power factor is limited at high temperatures, which is ascribed to the reduction of Seebeck coefficient at high temperature due to the two-carrier conductivity mechanism in the single filled skutterudites. This also indicates that single filling provides more benefits on thermal properties than on electrical properties for thermoelectric applications.

The temperature dependence of ZT in La, Ca and Sr single filled skutterudites with the filling fraction of about 0.35 are shown in Figure 6-4. $\text{Sr}_{0.36}\text{Fe}_{1.52}\text{Co}_{2.48}\text{Sb}_{12.06}$ has the highest ZT in the whole temperature range investigated. Though its power factor is comparable to that of $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$ as shown in Section 4.1.4, its lower thermal conductivity makes higher ZT than $\text{Ca}_{0.35}\text{Fe}_{1.48}\text{Co}_{2.52}\text{Sb}_{11.54}$. $\text{La}_{0.38}\text{Fe}_{1.58}\text{Co}_{2.42}\text{Sb}_{11.54}$ has the lowest ZT above 450K due to its poor electrical resistivity and thus power factor.

Figure 6-4 Temperature dependence of ZT in La, Ca and Sr single filled skutterudites when the filling fraction is about 0.35.

6.2 *ZT* Values of Ca-La and Sr-La Double Filled Skutterudites

6.2.1 Ca-La Double Filled Skutterudites

The temperature dependence of *ZT* in the Ca-La double filled skutterudites is shown in Figure 6-5. The Ca and La single filled skutterudites with similar filling fraction are added in for comparison. All the double filled skutterudites have similar improved *ZT* values as compared to the single filled ones. $\text{Ca}_{0.17}\text{La}_{0.11}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.91}$ has the highest *ZT* among all the samples. The highest *ZT* value of 0.65 can be reached at 730K in $\text{Ca}_{0.17}\text{La}_{0.11}\text{Fe}_{1.53}\text{Co}_{2.47}\text{Sb}_{11.91}$, which is 140% and 44% higher than those of the single filled $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$ and $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$ samples at the same temperature. $\text{La}_{0.22}\text{Fe}_{1.49}\text{Co}_{2.51}\text{Sb}_{11.92}$ possesses higher *ZT* than $\text{Ca}_{0.25}\text{Fe}_{1.26}\text{Co}_{2.74}\text{Sb}_{11.93}$, since the former not only has better power factor due to its much higher Seebeck coefficient, which is attributed to the higher charge valence of La (+3), but also shows the much lower thermal conductivity due to the heavier mass of La. The improved *ZT* in the Ca-La double filled samples benefits mainly from their largely reduced thermal conductivity as shown in Section 5.2.1. Meanwhile their power factors fall between the La and Ca single filled samples as shown in Section 4.2.4. So Ca-La double filling enhances *ZT* as compared with the Ca and La single filled samples since it can effectively reduce the thermal conductivity and does not compromise their power factor.

Figure 6-5 Temperature dependence of ZT in the Ca-La double filled skutterudites as well as Ca and La single filled skutterudites.

6.2.2 Sr-La Double Filled Skutterudites

The temperature dependence of ZT in the Sr-La double filled skutterudites is shown in Figure 6-6. The La and Sr single filled samples with similar filling fractions are added in for comparison. Both of the Sr-La double filled samples have higher ZT than the single filled samples. This is attributed to the low thermal conductivity induced by Sr-La double filling, as shown in Section 5.2.2. The maximal ZT value of 0.66 is obtained at 730K in $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$, which is about 47% higher than the Sr and La single filled samples.

Figure 6-6 Temperature dependence of ZT in the Sr-La double filled skutterudites as well as Sr and La single filled skutterudites.

6.2.3 Ca-La and Sr-La Comparison

In general, it is noted that Ca-La and Sr-La double filled skutterudites have higher ZT values than their parent single filled skutterudites. The ZT improvement is found to be mainly due to the effective reduction of lattice thermal conductivity by double filling as compared with single filling, since the power factors of the double filled samples do not surpass that of their parent single filled samples. The results reflect the even more significant influence from thermal properties than electrical properties by double filling.

The ZT of $\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$ and $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$ are compared in Figure 6-7. In the whole temperature range investigated, $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$ has higher ZT than $\text{Ca}_{0.19}\text{La}_{0.07}\text{Fe}_{1.39}\text{Co}_{2.61}\text{Sb}_{12.08}$.

Since their power factor is comparable as shown in Section 4.2.5, the lower lattice thermal conductivity of $\text{Sr}_{0.14}\text{La}_{0.06}\text{Fe}_{1.43}\text{Co}_{2.57}\text{Sb}_{11.31}$ makes its ZT higher.

Figure 6-7 Temperature dependence of ZT in the Ca-La and Sr-La double filled skutterudites.

Chapter 7 Conclusions and Future Work

7.1 Conclusions

The Skutterudite is reckoned to be one of the most promising thermoelectric (TE) materials for thermoelectric refrigeration and power generation applications at high temperature range. It contains elements with low electronegativity differences and high degree of covalent bonding, hence enabling high carrier mobilities and exhibiting good electron-crystal properties. In addition, there are two large voids in a unit cell, which allow the filling in of some filler atoms, such as rare-earth or alkaline-earth atoms. These filler atoms are weakly bonded with the matrix elements, and therefore could have a “rattling” motion in the oversized voids. This “rattling” is noted to be able to scatter the low frequency phonons, which in turn gives rise to good phonon-glass properties. The present work has concluded that the skutterudite can be made into a “phonon-glass electron-crystal” (PGEC), which could facilitate good TE applications.

In this thesis, we synthesized La, Ca and Sr single filled skutterudites and Ca-La, Sr-La double filled skutterudites. The single and double filling not only affect the electrical properties, but also the thermal properties. Our main purpose is to study the effects of single and double filling in the skutterudites and to give a more complete picture of the composition design for better TE performance.

For the La, Ca and Sr single filled skutterudites, the lattice parameter increased with the filling fraction of these filler atoms, which means that filling of the voids

can expand the lattice. The lattice parameters of the Sr single filled skutterudites are larger than the La and Ca single filled skutterudites with similar filling fraction. It is due to the larger radius of Sr^{2+} than La^{3+} and Ca^{2+} . The lattice parameters of the La single filled skutterudites are comparable to the Ca single filled skutterudites with similar filling fraction since the radii of La^{3+} and Ca^{2+} are similar. The effect of “rattling” of these filler atoms can be seen in their much higher thermal parameters than those of the matrix elements Fe, Co and Sb. If we assume that the sizes of voids in all the samples are the same, larger radius of the filler atom will have less vibration amplitude and thus smaller thermal parameter. As a result, the thermal parameter of Sr is smaller than La and Ca, while La and Ca have similar thermal parameters, which is consistent with the findings of the present work.

The La, Ca and Sr single filling has not only changed the lattice structure, but also varied the electrical properties. In all of our single filled samples, Fe doping contents are kept to about 1.5. This doping of Fe on the Co sites results in holes in the lattice since every Fe atom has one electron less than every Co atom. On the other hand, the La, Ca and Sr single filling introduce extra electrons into the lattice to neutralize the holes. As a result, the hole concentration decreases as the filling fraction increases. The electrical resistivity usually increases when the filling fraction increases, as it is inversely proportional to the hole concentration which gives a deteriorating effect to the power factor. The Seebeck coefficient, at the same time, also increases with the decrease of hole concentration as filling fraction increases. As compared to the unfilled skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$, the present La, Ca and Sr single filled samples generally show a higher Seebeck

coefficient since the filling reduces the hole concentration. Nevertheless, this also increases the electrical resistivity, which is undesirable. In our work, it is noted that when the hole concentrations of the filled samples were kept in the order of 10^{19} cm^{-3} , the increase in electrical resistivity can be minimized. As a result, the La, Ca and Sr single filling can result in an overall enhancement of the power factor as compared with the unfilled skutterudites $\text{FeCo}_3\text{Sb}_{12}$ and $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ due to the more significant improvement in Seebeck coefficient. For the similar filling fraction and Fe doping content, La single filled skutterudites are noted to have higher Seebeck coefficient and electrical resistivity than the Ca and Sr single filled skutterudites as every La filling provides 3 electrons while every Ca or Sr filling only provides 2 electrons to the lattice. It is also found that the Ca and Sr single filled skutterudites have comparable electrical properties if they have similar composition since they give the same electron amount to the lattice.

For the effect of double filling, the power factors of Ca-La double filled skutterudites are observed to be higher than the Ca single filled sample, but lower than the La single filled sample with similar filling fraction. This is mainly attributed to their intermediate Seebeck coefficient as compared with the two single filled samples. The power factors of Sr-La double filled skutterudites are quite comparable to the Sr and La single filled samples with similar filling fraction. Generally speaking, the double filled samples do not show more advantage than the single filled ones as the electrical properties are largely determined by hole concentration.

The superiority of the filling approach is expected to be seen in the thermal properties. La, Ca and Sr single filling's effective reduction of the thermal conductivity confirms the theory that the filler atoms can "rattle" in the oversized voids to scatter the phonons. The higher the filling fraction, the lower thermal conductivity the single filled skutterudites possess as there are more "rattlers" in the samples. A 38% of La single filling can result in 64% total thermal conductivity and 32% lattice thermal conductivity reduction. The Ca filling fraction can reach to 67%, and achieve a 52% total thermal conductivity reduction with 39% reduction in lattice thermal conductivity. For the Sr single filled samples, the maximum reduction of 40% for the total thermal conductivity and 45% lattice thermal conductivity are found when the Sr filling fraction is 42%. Among these three kinds of filler atoms, La makes the most effective reduction in the thermal conductivity and the reduction of thermal conductivity by Ca single filling is found to be the lowest. This effect of different atomic mass of the filler atoms was also verified in the present work. The filler atoms can be considered as point defects and distributed randomly in the samples, and there exists mass fluctuation between the filler atoms and the remaining unfilled voids, which induces point defect phonon scattering. It is noted that with heavier filler atom, better point defect phonon scattering can be achieved. Among the present fillers used, La is the heaviest while Ca is the lightest. As a result, the La single filled skutterudites that have the largest mass fluctuation thus give rise to the highest thermal conductivity reduction. On the other hand, Ca single filled samples have the smallest mass fluctuation and

hence the lowest thermal conductivity reduction. Sr has the intermediate atomic weight and thus provides intermediate thermal conductivity reduction.

We have also quantitatively shown that Ca-La and Sr-La double filling, when compared with the single filled skutterudites of similar filling fraction, possess much lower thermal conductivity. At 730K, the reduction of lattice thermal conductivity in our Ca-La double filled samples can reach up to 76% as compared with our Ca single filled sample, and 63% as compared with our La single filled sample. The lattice thermal conductivity of our Sr-La double filled skutterudites is 63% and 70% lower than the Sr and La single filled sample, respectively. The reduction mainly comes from the broadening of the resonant rattling frequency range by having two kinds of filler atoms from different elemental groups (alkaline-earth and rare-earth respectively). As a result, our Ca-La and Sr-La double filling are more effective on thermal conductivity reduction than the reported Ce-La and Ba-Sr double filling whose filler atoms are from the same elemental group. With similar composition, the Sr-La double filling is found to be better than the Ca-La double filling at reducing the lattice thermal conductivity. The heavier mass and larger size of Sr in Sr-La filled samples create more mass fluctuation and strain field difference in the lattice, hence produce stronger point defect phonon scattering than the Ca-La double filling.

By combining the electrical and thermal properties, the dimensionless figure of merit ZT values in our single and double filled skutterudites were calculated. The performance of a TE material is generally represented by the ZT values. The higher ZT value, the better TE performance the material has. The La, Ca and Sr single

filling can improve the ZT values up to around twice as high as that of the unfilled skutterudite $\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. It is mainly attributed to the dramatic reduction of the thermal conductivity due to the single filling. The Ca-La and Sr-La double filling can further enhance the ZT values due to further reduction in the thermal conductivity. The maximum ZT enhancement of our Ca-La samples can achieve 140% higher than that of the Ca single filled sample and 44% higher than the La single filled sample with the similar filling fraction at 730K. The ZT enhancement of our Sr-La samples can reach up to about 47% higher than the Sr and La single filled samples with the similar filling fraction at 730K.

7.2 Future Work

The filling approach has been proven to be a good method to reduce the thermal conductivity of skutterudites in our work. Significant reduction of the thermal conductivity has been shown by double filling using two kinds of filler atoms which come from the different elemental groups. Further work can be done to study the detailed phonon scattering effects (grain boundary scattering, point defect scattering, phonon-phonon Umklapp scattering, resonant scattering and electron-phonon scattering) on the lattice thermal conductivity. The Debye model, which has been successfully applied for the studying of lattice thermal conductivity in Fe-doped skutterudites $\text{Co}_{1-x}\text{Fe}_x\text{Sb}_3$ [91], Ni-doped skutterudites $\text{Co}_{1-x}\text{Ni}_x\text{Sb}_3$ [97] and n-type Ca single filled skutterudites $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ [61], can be employed to study the lattice thermal conductivity of double filled skutterudites, by considering the dual resonant scattering in the calculation.

In recent years, nanocomposites are found to be another effective approach to reduce the thermal conductivity by enhancing grain boundary scattering. Unfilled skutterudites as the matrix material and some kinds of oxide nanoparticles like nano- ZrO_2 and nano- TiO_2 as inclusions were reported [98, 99]. Nano-fullerene and nano- CoSb_3 was also found to be good inclusion to reduce the thermal conductivity of unfilled skutterudites [100, 101]. Most recently, single filled skutterudites $\text{Yb}_{0.15}\text{Co}_4\text{Sb}_{12}$ [102] and $\text{La}_{0.9}\text{CoFe}_3\text{Sb}_{12}$ [103] were chosen as the matrix materials with nano- CoSb_3 inclusions. The ZT values were improved due to the additional grain boundary scattering by nanoparticles while the power factors were not compromised. It is also noted that nanostructure can produce a positive effect on

Seebeck coefficient. As a result, adding nanoparticles in single and double filled skutterudites can be an effective way to further reduce the thermal conductivity and to optimize the power factor.

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