

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**THERMOELECTRIC PROPERTIES INVESTIGATION OF COPPER
BASED CHALCOGENIDE AND COBALT BASED SKUTTERUDITE
STRUCTURES**



M.Sc. THESIS

TUĞBA TEMEL

Department of Nano Science and Nano Engineering

Nano Science and Nano Engineering Programme

DECEMBER 2019

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YAPILARININ TERMOELEKTRİK ÖZELLİKLERİNİN İNCELENMESİ**

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ABBREVIATIONS

TE	: Thermoelectric
ZT	: Figure of Merit
DOS	: Density of States
PGEC	: Phonon Glass Electron Crystal
PLEC	: Phonon Liquid Electron Crystal
SPS	: Spark Plasma Sintering
PXRD	: Powder X-ray Diffraction
SEM	: Scanning Electron Microscope



SYMBOLS

S	: Seebeck coefficient
V	: Voltage
T, T_h, T_c	: Temperature component
Π	: Peltier coefficient
Q	: Rate of heating or cooling
I	: Current
q	: Amount of heat per unit volume
σ	: Electrical conductivity
K	: Thermal conductivity
K_e	: Electronic component of thermal conductivity
K_l	: Lattice component of thermal conductivity
R	: Resistance
P	: Power
Φ	: Efficiency
Γ	: Coefficient of performance
f	: Boltzmann distribution function
T	: Time
K	: Wave vector
τ	: Relaxation time
E	: Energy
R	: Scattering parameter
x	: Position of a charge carrier
E_F	: Fermi energy
h	: Planck constant
m^*	: Effective mass
M	: Mass
$g(E)$	: Density of states
E	: Magnitude of charge particle
I	: Current density
w	: Heat flux density

$f(E)$	: Fermi-Dirac distribution
ε	: Electric field
ρ	: Resistivity
ξ	: Reduced energy parameter
$F_n(\xi)$	: Fermi-Dirac integrals
η	: Reduced Fermi energy
n	: Carrier concentration
μ	: Mobility of charge carrier
C_V	: Specific heat
l	: Mean free path
L	: Lorenz number
n_l	: Number of phonon modes
w_D	: Debye frequency
X	: Electronegativity
$f(D)$	: Debye integral
d	: Density
α	: Thermal diffusivity

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THERMOELECTRIC PROPERTIES INVESTIGATION OF COPPER BASED CHALCOGENIDE AND COBALT BASED SKUTTERUDITE STRUCTURES

SUMMARY

The need for clean and reliable energy sources is increasing day by day. To date the majority of the energy used is supplied by fossil fuels and the majority of this energy is lost as waste heat. Thermoelectric (TE) materials allow the conversion of waste heat directly into electrical energy or the use of electricity for cooling or heating purposes. TE generators or coolers have advantage of being compact, light weight, generally inexpensive, quiet operation, can operate in any season day/night without loss of efficiency. These advantages make TE materials among the most important alternatives considering the search for safe and sustainable energy resources for the future. TE materials are used in space studies (radioisotope thermoelectric generator-RTGs), automotive industry, nuclear batteries, temperature sensors, solar panels, coolers, wearable flexible devices using human body heat and much more.

A TE module is formed by electrically in series and thermally in parallel connection of an equal number of p and n type semiconductor materials. The efficiency of these materials is determined by the dimensionless ZT parameter called figure of merit. The modules that used today are generally bismuth telluride based and ZT parameter is about 1. In order to gain more space in our daily lives, for example, for generate energy from the exhaust gases of vehicles, the efficiency of a TE generator should be around 10% and the ZT value should be around 1.25, for power generation the efficiency should be 20% and the ZT value should be about 1.5. Although the ZT value of 2.8 has been reached in recent studies, but questions such as the temperature ranges where the material gives high efficiency is it applicable, is it non-toxic, abundant and cheap and is it possible for large scale production restrict the industrial use of these materials.

The ZT parameter is expressed as $ZT = (S^2\sigma / K).T$ where S; Seebeck coefficient, σ ; electrical conductivity, K; thermal conductivity and T; temperature. So it is clearly seen that a good thermoelectric material should have a high Seebeck coefficient and low electrical resistance and low thermal conductivity. However in an atomic scale balance these transport parameter create a dilemma. For instance, increase in electrical conductivity lead to decreasing in Seebeck coefficient. Therefore, it is not easy simultaneously to balance the Seebeck coefficient and electrical conductivity. And also thermal conductivity consist of electronic thermal conductivity and lattice thermal conductivity. The relation between electronic thermal conductivity and electrical conductivity (Wiedemann-Franz law) lead to restriction in lowering electronic thermal conductivity. Therefore, lattice thermal conductivity has critical role to obtain low thermal conductivity. Until this here it is understood that there are two ways to enhance the thermoelectric efficiency. These are increase in thermo power that expressed as $S^2\sigma$ and decrease in lattice thermal conductivity. Some approximations have been asserted to enhance the thermoelectric efficiency. Some of

these approximations are nanostructuring, phonon glass electron crystal (PGEC) and phonon liquid electron crystal (PLEC).

In briefly, use nano structure result in enhancement in thermo power via quantum confinement effect and low lattice thermal conductivity via more phonon scattering. PGEC property is that materials such as skutterudite structure (CoSb_3) conduct heat like in glass and conduct current similar to electron crystal PLEC material is such as copper chalcogenide (Cu_2Se) that conduct heat like in liquid and current similar to electron crystal.

The scope of this thesis includes these approaches. In this context, the thermoelectric properties of three different groups were investigated.

In group A, samples of different powder sizes of C- CoSb_3 , F- CoSb_3 and (C- CoSb_3) $1-x$ (F- Cu_2Se) $xx = 0.02, 0.05$ and 0.10 were synthesized by melting and annealing method. These samples were densified with applied heat treatment following cold press. Although the doped samples in this group had a higher ZT value than the C- CoSb_3 sample, they were lower than the F- CoSb_3 sample. Although the doped samples in this group had a higher ZT value than the C- CoSb_3 sample, they were lower than the F- CoSb_3 sample. In other words, one of the results can be drawn for this group that the particle size of the sample affects the TE properties under applied conditions.

In the B group, C- Cu_2Se and F- Cu_2Se and (C- Cu_2Se) $1-x$ (F- CoSb_3) $xx = 0.02, 0.05$ and 0.10 samples were synthesized by melting and annealing method. These samples were densified with applied heat treatment following cold press. In group B, ZT value of Cu_2Se 2% CoSb_3 sample was found to be 0.9 at 675 K. This value was higher than C- Cu_2Se and F- Cu_2Se values and resulted in an increase of ZT value by approximately 80%.

In the C group, the TE properties of the structures formed by the addition of nanomaterials with different crystal structure but having the same conductivity properties as the main structure were examined. In this group, nano Cu_2Se , nano $\text{Cu}_{1.8}\text{Se}$, nano Cu_2Se 2% and 5% FeCoSb doped materials were investigated. The maximum ZT value was obtained 2.1 that is recorded one of the highest value for $\text{Cu}_{1.8}\text{Se}$ sample. Although the ZT value of doped samples is better than the Cu_2Se sample that found in the literature, they are lower than nano Cu_2Se and nano $\text{Cu}_{1.8}\text{Se}$ synthesized in this group.

BAKIR TABANLI KALKOJENİT VE KOBALT TABANLI SKUTTERUDİTE YAPILARININ TERMoeLEKTRİK ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Sanayileşmenin ve artan nüfus yoğunluğunun getirdiği sorunlardan biri de temiz enerji kaynaklarına olan ihtiyaç olup, her geçen gün önemi artmaktadır. Bugün hala kullanılan enerjinin büyük çoğunluğu fosil yakıtlardan karşılanmakta ve bu enerjinin çoğunluğu da atık ısı olarak kaybolmaktadır. Termoelektrik (TE) malzemeler atık ısının doğrudan elektrik enerjisine dönüşümünü veya elektriğin soğutma ya da ısıtma amaçlı kullanılmasına olanak sağlar. Bir TE jeneratörünün veya TE soğutucunun atık ısıyı kullanmaları, sessiz çalışmaları, tek bir parça halinde üretilebilmeleri, fiziksel şartlara bağlı olmayışı (mevsime, rüzgâra veya alınan güneş miktarına) gibi unsurlar ciddi avantaj olarak karşımıza çıkmaktadır. Bu unsurlar geleceğe yönelik güvenilir ve sürdürülebilir enerji kaynakları arayışları dikkate alındığında TE malzemeleri en önemli alternatifler arasına sokmaktadır. TE malzemeler uzay çalışmalarında, (radioisotope thermoelectric genarator-RTGs), otomotiv sektöründe, nükleer bataryalarda, sıcaklık sensörlerinde, güneş panellerinde, soğutucularda, insanın vücut ısını kullanarak giyilebilir esnek cihazlarda ve daha pek çok alanda kullanılmaktadır.

Bir TE modül eşit sayıda p ve n tipi yarıiletken malzemenin elektriksel olarak seri termal olarak paralel bağlanmasıyla oluşur. Bu malzemelerin verimliliği figure of merit olarak adlandırılan boyutsuz ZT parametresi ile belirlenir. Bugün kullanılan modüllerin çoğu bizmut tellür tabanlı olup ZT parametreleri yaklaşık 1 değerindedir. Günlük hayatımızda daha çok yer edinmesi için mesela araçların egzoz gazlarından enerji üretmek için bir TE jeneratörün verimliliği yaklaşık %10 olup ZT değerinin 1.25 civarında olması, güç üretimi için ise verimliliği %20 olup ZT değerinin yaklaşık 1,5 olması gerekmektedir. Son çalışmalarda ZT değerinin 2,8 e ulaşılmasına rağmen, malzemenin yüksek verimlilik verdiği sıcaklık aralıklarının uygulanabilir olması, toksik olmayışı, bol ve ucuz olması, üretim metotlarının kolay uygulanabilir olması bu malzemelerin endüstriyel anlamda kullanılmasını kısıtlayan ölçütlerdir.

ZT parametresi, S; Seebeck katsayısı, σ ; elektriksel iletkenlik, K; termal iletkenlik ve T; sıcaklığa bağlı olup $ZT=(S^2\sigma/K).T$ şeklinde ifade edilir. O halde iyi bir termoelektrik malzemenin yüksek Seebeck katsayısına ve düşük elektriksel dirence ve düşük termal iletkenliğe sahip olması gerektiğini görürüz. Yalnız atomik mertebede bu parametrelerin birbirine bağlı olması TE verimliliğin artırılmasında ikilem oluşturmaktadır. Bunlara kısaca değinirsek, ilki, yarıiletken malzemenin elektriksel iletkenliğini arttırmanın yollarından biri taşıyıcı yük yoğunluğunu (n) arttırmaktır. Bu aynı zamanda elektriksel termal iletkenliğini de arttırmış olup, aşağıdaki formüllerden de anlaşıldığı üzere Seebeck değerini düşürmektedir, kısacası, Seebeck değeri ile elektriksel iletkenlik ters etkiye sahiptir diyebiliriz. Bu formüller sırasıyla malzemenin Seebeck katsayısının bağlı olduğu parametreleri, elektriksel iletkenliği ve Wiedemann-Franz kuralı olarak bilinen, bir iletkenin elektriksel termal iletkenliği ile

elektriksel iletkenliği arasında ki ilişkinin bir sabit olduğunu $L = 2.45 \times 10^{-8} W.\Omega.K^{-2}$ (Lorenz Sayısı) gösteren yasadır.

$$S = \pm \frac{8\pi^2 k^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}, \sigma = ne\mu, L = \frac{K_e}{\sigma T}$$

Dolayısıyla TE malzemenin verimliliğini arttırmak için geriye kalan diğer yol malzemenin elektriksel transport özelliklerini düşürmeden termal iletkenlik değerini düşürmektir. Termal iletkenlik elektronlardan gelen katkı (K_e) ve fononlardan (K_l ; örgü titreşimlerinden) gelen katkı olmak üzere iki bileşenin toplamıdır ($K = K_e + K_l$). Elektronik katkının optimizasyonu yukarıda verildiği gibi sınırlıdır. O halde geriye kalan malzemenin fononlardan gelen termal iletkenlik değerini düşürmektir. Gazların kinetik teorisinden bildiğimiz gibi örgü titreşimlerinden gelen termal iletkenlik matematiksel olarak $K_l = \frac{1}{3} C_V V l_{ph}$ denkleminde eşit olup malzemenin ısı kapasitesine (C_V), ses hızına (V) ve fononların aldığı ortalama serbest yola (l_{ph}) bağlıdır. Toparlarsak düşük termal iletkenlik fononların aldığı ortalama serbest yolun ve ısı kapasitesinin düşürülmesi ile elde edilir.

İyi bir termoelektrik verimlilik için öne sürülen yaklaşımlar malzemenin güç faktörü olarak adlandırılan $S^2 \sigma$ parametresini arttırmayı ve örgü titreşimlerden gelen termal iletkenlik değerini düşürmeyi kapsamaktadır. Bu doğrultuda malzemelerin kristal yapısı ve özellikleri optimizasyon için büyük önem taşır. Öne sürülen yaklaşımlar bu tezde de çalışılan yaklaşımlar olup ilki nano yapı (nanostucturing) diğer ikisi de malzeme özelliğine dayanan PLEC (phonon liquid electron crystal) ve PGEC (phonon glass electron crystal) yaklaşımlarıdır. Bu yaklaşımları kısaca inceleyelim.

İlk yaklaşım nano yapıları kapsamaktadır. Boyut olarak malzemenin nano yapılardan oluşması ya da malzemede nano yapıyı ara yüzler oluşturmak (nano malzeme ile katkılanarak), malzemenin hem elektriksel özelliklerinde hem de fononlardan gelen termal iletkenlik değerlerinde değişime yol açar. Malzemede nano yapıya gidildikçe malzemenin taşıyıcı parçacıklarının Fermi seviyesi civarında durum yoğununda (DOS; density of state) artışa sebep olmaktadır. Diğer bir ifadeyle malzemenin boyutu taşıyıcı parçacıkların de Broglie dalga boyuyla kıyaslanabilecek durumda olması, taşıyıcı parçacıkların hareketinde bir kısıtlanmaya yol açarak sonsuz potansiyel kuyusundaymiş gibi davranmalarına neden olur. Bu etki Kuantum tuzaklanma (Quantum Confinement) etkisi olarak bilinir ve TE malzemenin termo güç; σS^2 parametresinin artmasını sağlar. Bir diğer etki, nano malzemede fononların ortalama serbest yolu taşıyıcı parçacıkların ortalama serbest yolundan daha uzundur. Buda ara yüzlerde fonon saçılmalarının taşıyıcı parçacıkların saçılmasından daha baskın olduğunu, böylece fononların hem tane sınırlarından hem de oluşturulan ara yüzlerden saçılarak, elektriksel özelliklerin de korunarak termal iletkenliğin düşürülmesinde kilit rol oynadığı görülmüştür.

Bu “nano yapı” yaklaşımından sonra malzeme doğasına yönelik olan, PGEC yaklaşımı TE malzeme araştırmalarına yeni bir bakış açısı kazandırmıştır. Bu yapıya sahip malzemelerin termal iletkenlikleri camı malzemeler kadar düşük (phonon-glass), elektriksel iletkenlikleri ise tek kristal yapı malzemeler (electron crystal) kadar yüksek olmasıdır. PGEC özelliğine sahip malzemeler açık kristal (open framework) yapısına sahip olup içine atomların katılana bileceği boşlukların bulunmasıdır. Bu doldurulan boşlukların hepsi birer Einstein osilatörü gibi davranarak fonon saçılmalarını artırır (rattling effect). Dolayısıyla daha düşük bir termal iletkenlik elde edilir. PGEC özelliği taşıyan malzeme gruplarına skutterudite ve klatrat yapıları örnek verilebilir. Bu tezde çalıştığımız malzeme gruplarından biri de kobalt tabanlı

skutterudite yapılarıdır. $\square Co_4Sb_{12}$ hacim merkezli kübik kristal yapısına sahip olup, $\square$ yapıda bulunan boşlukları temsil etmektedir. Doldurulmamış hali p tipi bir yarıiletken iken boşlukların doldurulmasıyla hem p tipi hem de n tipi yarıiletkenler elde edilebilir. Ayrıca boşlukların birden fazla element ile doldurulması yani farklı frekanslarda fonon titreşim modlarının olması termal iletkenliğin düşürülmesinde daha etkili olduğu görülmüştür.

Son olarak PLEC yaklaşımını incelersek bu malzemelerin elektriksel iletkenlikleri elektron kristali gibi yüksek olup, termal iletkenlikleri sıvılar kadar düşük olan $A_{2-x}B$ chalcogen (A; Cu, Ag, Au ve B;Te, S,Se) gruplarıdır. Bu bileşiklerde B atomları kristalde sabit iken A atomları sıkı olmayan bağ yapıları nedeniyle B atomları etrafında serbestçe dolaşabilme özelliğine sahiptirler bu da titreşim modlarının azalmasına elektriksel özelliklerin artmasına neden olur. Süper iyonik iletkenler olarak bilinen bu yapılar hem kristal özelliklerinden hem de düşük termal iletkenliklerinden kaynaklı sıvı benzeri kristal (liquid like crystal) olarak adlandırılır. Cu_2Se bileşiği PLEC davranışı sergileyen TE malzemelerden biridir. Düşük sıcaklık fazı ve yüksek sıcaklık fazı olarak 400K de faz değişimi görülür. Düşük sıcaklık fazı birçok kristal formda bulunabilir iken yüksek sıcaklık fazı yüzey merkezli kübik yapıda olup süper iyonik haldedir. Cu_2Se p-tipi yarı iletken olup sadece TE sistemlerde değil güneş hücrelerinde, opto elektronikte, gaz sensörlerinde ve foto termal terapiler gibi birçok mühendislik alanlarında kullanılmaktadır. Dolayısıyla bileşiğin verimliliğinin artması hem tek başına hem de hibrit birçok sistemlerde kullanılmasını sağlar.

Bu tezin kapsamı bu yaklaşımları içermektedir. Bu bağlamda üç farklı grubun Termoelektrik özellikleri incelenmiştir.

A grubunda farklı toz boyutlarında olan C- $CoSb_3$, F- $CoSb_3$, $(C-CoSb_3)_{1-x}(F-Cu_2Se)_x$ $x=0.02, 0.05$ ve 0.10 numuneleri eritme ve tavlama yöntemi ile sentezlenmiş olup toz haline getirildikten sonra yoğunlaştırması soğuk pres ve ısıtma işlemi ile sağlanmıştır. Bu grupta her ne kadar katkılı numuneler C- $CoSb_3$ örneğinden daha yüksek ZT değerine sahip olsa da, bu grup içinde sentezlenen F- $CoSb_3$ numunesinden daha düşüktür. Bir diğer deyişle, bu grup için çıkarılacak sonuçlardan biri numunenin partikül boyutu uygulanan deney koşullarında TE verimlilik açısından önem taşımaktadır.

B grubunda C- Cu_2Se ve F- Cu_2Se ile $(C-Cu_2Se)_{1-x}(F-CoSb_3)_x$ örnekleri tekrar eritme ve tavlama methodu ile sentezlenmiş olup toz haline getirilmesi sonrasında soğuk presi takiben ısıtma işlemi uygulanarak yoğunlaştırılmıştır. İkinci grupta Cu_2Se %2 nano $CoSb_3$ katkılı örneğin ZT değeri 675 K de 0.9 olarak bulunmuştur. Bu değer C- Cu_2Se ve F- Cu_2Se değerlerinden daha yüksek olup yaklaşık %80 oranında ZT değerinde artma ile sonuçlanmıştır.

C grubunda ise nano malzemelerin içerisine farklı kristal yapıda ama esas yapı ile aynı iletkenlik özelliklerine sahip nano malzemelerin katkılanmasıyla oluşan yapıların TE özelliklerinin incelenmesidir. Bu grupta nano Cu_2Se , nano $Cu_{1.8}Se$, nano Cu_2Se %2 ve %5 oranında $FeCoSb$ katkılı malzemelerin TE özellikleri incelenmiştir Bu grupta sentezlenen nano $Cu_{1.8}Se$ ZT değeri 900 K de 2,1 olarak elde edilmiş olup en yüksek değerlerden biridir. Katkılı halleri ise literatürde yer alan bulk Cu_2Se formlarından daha iyi olmasına rağmen bu grup içinde sentezlenen nano Cu_2Se ve nano $Cu_{1.8}Se$ den daha düşüktür.



1. INTRODUCTION TO THERMOELECTRICITY

Today, energy consumption is the main problem in our world and increases day by day. An idea of using waste energy that is fundamentally heat emits from the industrial process, home heating or automotive exhaust offer a good solution for the alternative energy source. Thermoelectric (TE) materials can generate electric energy from waste heat and it can be used for heating /cooling by applying electrical energy to it. Thus, thermoelectricity is considered to have the potential to be reliable, sustainable, and cost-effective and silence energy resources. It has been used in many applications such as space exploration, medical applications environmental concerns or heat engine system[1–5].

A typical thermoelectric module consists of p-type and n-type semiconductor material that is electrically series and thermally parallel. The efficiency of these materials is characterized by the dimensionless figure of merit (ZT) value that is dependent on electrical (σ) and thermal conductivity (K) and Seebeck coefficient (S). For good thermoelectric material, it should exhibit low thermal conductivity, high Seebeck coefficient and high electrical conductivity. In the atomic scale, these transport parameters depend on each other so it is difficult simultaneously balance them. Therefore, the efficiency of the TE material is lower than other renewable energy resources [4-7]. Bismuth telluride is generally commercially available owing to work at a low-temperature scale (<400) that possesses ZT around 1 and efficiency is about 5% to 7% for most applications. To gain a place in our life, ZT should be higher than 2 to convert waste heat and higher than 3 for comparable refrigeration system [5–8].

Last two decades with the development of nanoscience, semiconductor industry and comprehensive study on structures paved the way for new approximations to optimize transport parameters and so enhance the ZT parameter. The Phonon-Glass-Electron-Crystal (PGEC) concept, phonon-phonon interaction and anharmonicity, complex bulk nanocomposite structures, effective mass and band engineering, the Phonon-Liquid-Electron-Crystal (PLEC) concept have been implemented to improve the efficiency. In this thesis PGEC, PLEC and nanostructure approximations were

investigated. Briefly, the properties of PGEC materials successfully applied on clathrate and skutterudite cage-like or open-frame structures is conduct electric current similar to electron crystal and conduct heat similar to in glass. The PLEC concept is an extension of PGEC approximation which expressed for firstly copper selenide superionic structure. The PLEC materials properties are again conducted electric current like electron crystal and have low thermal conductivity as much as liquids, so inherently have low thermal conductivity. Bulk nanostructure or filling bulk materials with nano inclusions lead to low thermal conductivity and improvement in power factor ($S^2\sigma$) [8–11].

A common purpose of researchers find non-toxic, earth-abundant, applicable and high efficiency of thermoelectric material and in this perspective, several materials have been researched. For low temperatures material (below 450 K) generally bismuth-based chalcogenide and silicon recently are studied. At medium temperature (450K-850K) lead of chalcogenide, copper and tin-based selenide, skutterudites, clathrates and half hausler alloys, for high temperature (>850 K) silicon-germanium alloys, zintl and oxide compound has been studied. The divided material according to the temperature range, is not effectual for all situation, however, provide a simple comprehension [1]. Figure 1.1 shows the most studied TE classes [12]. TE materials have been synthesized via various methods such as solid state reaction, solvothermal, high pressure high temperature synthesis, mechanical alloying, melt quenched, nano crystal synthesis and for consolidation of powder into pellets spark plasma sintering (SPS), self-propagating high-temperature synthesis (SHS) technique, hot and cold-pressed technique [13-17].

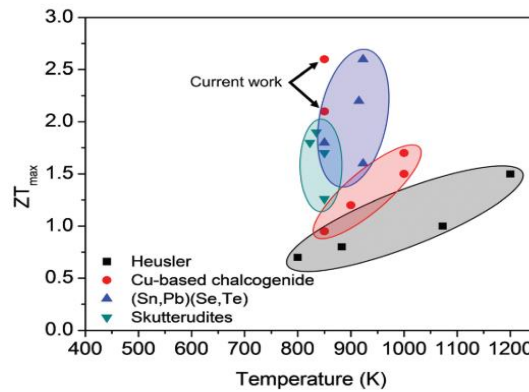


Figure 1. 1 : Study on the TE material classes [12].

Skutterudite and copper based chalcogenide are most appealing TE materials. In the recent study, it is achieved that ZT value is 1.7 and 2.6 for skutterudite ($\text{Co}_4\text{Sb}_{12}$) and copper selenide (Cu_2Se) structures respectively with substituting the materials [8]. In thesis, TE properties of these two materials will be investigated with different percentage of nano structures.





2. THERMOELECTRIC PHENOMENA

2.1. Thermoelectric Effects

A working principle of thermoelectric devices bases on three fundamental effects. The physical statement of these effects back to the 1800s, however, using in material and understand comprehensive nature's started at 1950s. This chapter gives brief information about these effects and how it can be used in the thermoelectric device.

2.1.1. Seebeck effect

The first principle of thermoelectricity was discovered by German physicist T. J. Seebeck, in 1821. He showed that temperature gradient at a junction between two different conductors creates a voltage difference. This phenomenon is called the Seebeck effect.

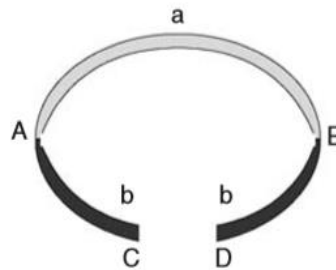


Figure 2. 1 : Seebeck effect on an open circuit.

Creation of voltage schematically illustrated in Figure 2.1 on an open circuit. Two dissimilar conductors (a and b) are connected thermally in parallel and electrically in series . When two junctions A and B have different temperature for example, T_1 , T_2 and $T_1 > T_2$, a voltage will be produced accross C and D. This situation mathematically is described as;

$$S = -\frac{\Delta V}{\Delta T} \quad (2.1)$$

Here S Seebeck coefficient or thermopower, V voltage and ΔT ($T_1 - T_2$) temperature difference. Seebeck coefficient can be either positive or negative depends on the

material type. For n-type material, the electrons diffuse from the hot side to cold side (clockwise direction) that it takes negative value, for p-type material holes diffuse from hot side to cold side that lead to positive value of Seebeck coefficient. The SI unit of Seebeck coefficient is V/K [15]–[18].

2.1.2. Peltier effect

The second principle of thermoelectricity, was discovered by Jean Peltier, in 1834. He showed a reversible relation of the Seebeck effect. In other words, when current passes through two different conductor materials, heat is either generated or absorbed at the junction. A direction of the current play an important role for which a junction is heated or cooled. The ratio between the rate of heating or cooling (Q) and current (I) gives the Peltier coefficient (Π). The SI unit of Peltier coefficient is V or W/A.

$$\Pi = \frac{Q}{I} \quad (2.2)$$

A comprehensive relationship of the thermoelectric effects between the Seebeck and Peltier effects was discovered in 1854 by a Mathematical physicist William Thomson (known as Lord Kelvin). He applied thermodynamic principles on thermoelectric effects to obtain connection between effects. The first Kelvin relation given as;

$$\Pi = S \cdot T \quad (2.3)$$

It is clearly seen from equation 2.3 that thermoelectric cooling (Π) and thermoelectric power generation (S) dependent of each other. Also Thomson's works concludes the third law of thermoelectricity known as Thomson Effects [15]–[18].

2.1.3. Thomson effect

The last and third principle of thermoelectricity relates to uniform conductor which has temperature gradient. When a current passes through the material, heat is either evolved or absorbed. This effect is called Thomson effect and defined as;

$$q = \pi \cdot I \cdot \Delta T \quad (2.4)$$

Here amount of heat per unit volume is q , ΔT is temperature gradient and τ is Thomson coefficient. The SI unit of Thomson coefficient is V/K [15], [16].

In Figure 2.2 shows that two types of Thomson effects. Positive Thomson effect occurs when hot side is at high potential and cold side at low potential. Typical materials that exhibit such as copper, zinc, tin and silver, when current is passed from hot side to cold side heat is evolved and when current flows from cold side to hot side, heat is absorbed. On the other hand metal such as iron, cobalt, bismuth and nickel have an opposite relation that hot side is at low potential and cold side is at high potential. When current flows from cold side to hot side, heat is evolved and the current flows from hot side to cold side, heat is absorbed. This is called negative Thomson Effect [19].

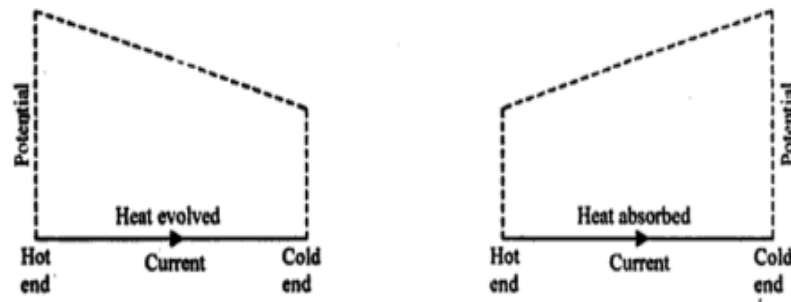


Figure 2. 2 : Positive and negative Thomson effect[19].

The first Kelvin relation gives relation between Seebeck and Peltier effects, while the second Kelvin relation gives a link between Seebeck and Thomson coefficients that is given in equation (2.5) [17].

$$\frac{dS}{dT} = \frac{\tau}{T} \quad (2.5)$$

2.2.Thermoelectric Figure of Merit

The discovery of the thermoelectrical effects given a new search area to science. In 1909 Edmund Altenkirch, found that efficiency of thermo electrical devices related to large Seebeck coefficient, low electrical resistivity and low thermal conductivity [1].

The mathematical expression of these requirements was formulated by Ioffe who introduced for the first time the dimensionless Figure of Merit.

$$ZT = \frac{\sigma S^2}{K} T \quad (2.6)$$

Here σ is the electrical conductivity and S is Seebeck coefficient and K is thermal conductivity. σS^2 is called as power factor. Thermal conductivity is the sum of a two components which are electronic thermal conductivity (K_e) and lattice thermal conductivity (K_l).

$$K = K_e + K_l \quad (2.7)$$

If we compare the metals and semiconductors, metals have a high electrical conductivity. However, the electrical conductivity relates to the carrier concentration and any increasing in the carrier concentration result in a low Seebeck coefficient and a high electronic thermal conductivity. On the other hand, semiconductors have low carrier concentration, high Seebeck coefficient and low thermal conductivity than metals. Owing to these properties, semiconductors are the most researched materials for thermoelectrics. Figure 2.3 shows dependence of transport parameter depends on charge carrier concentration [15], [16].

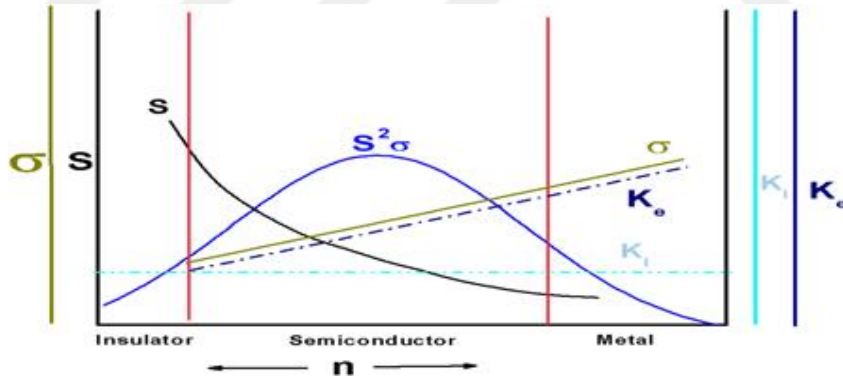


Figure 2. 3 : Dependence of electrical conductivity, Seebeck coefficient, and thermal conductivity on concentration of carriers [8].

2.3. Thermoelectric Device and Efficiency

Thermoelectric devices that consist of several TE module can be used either for power generation or for purposes of heating/cooling. A TE module consists of pairs n-type and p-type semiconducting legs as shown in Figure 2.4. Single couple (just one n and p legs) is connected electrically in series and thermally in parallel with other couples [4], [5].

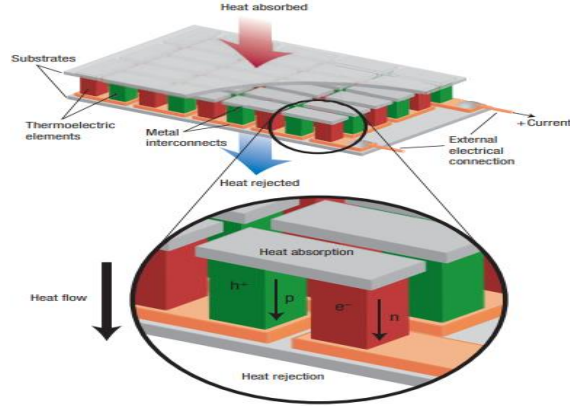


Figure 2. 4 : A typical TE module consist of equal number of p and n type thermo elements that are connected with electrical conductor generally copper [3].

TE materials are used in space exploration (radioisotope thermoelectric generator-RTGs), automotive industry, nuclear batteries, heat sensor, solar cells, cooling systems, wearable flexible devices and many other areas. In order to gain more space in our daily lives, for example, for generate energy from the exhaust gases of vehicles, the efficiency of a TE generator should be around 10% and the ZT value should be around 1.25, for power generation the efficiency should be 20% and the ZT value should be about 1.5. Of course, to reach these values, the material used in the temperature range in which high efficiency is applicable, non-toxic, abundant and cheap are among the desired properties [4], [23-24].

As shown in Figure 2.5 the power generation device works based on the Seebeck effect. If a temperature gradient occurs across the couple, the power is generated. The thermo couple is connected with an electrical load resistance R_L and so the current is equal to;[4]

$$I = \frac{S_{pn}(T_H - T_C)}{R_p + R_n + R_L} \quad (2.8)$$

Here S_{pn} is Seebeck coefficient and equal to $(S_p - S_n)$, T_H hot side temperature and T_C cold side temperature, R_p and R_n are the electrical resistance of the p-n legs. The power is given by;[15]–[18], [22]

$$P = I^2 \cdot R_L \quad (2.9)$$

The total rate of hate given as;

$$q = (K_p + K_n)(T_H - T_C) + S_{pn} \cdot I \cdot T_H \quad (2.10)$$

Where K_p, K_n are thermal conductance for legs that occurs along the heat source and sink. The maximum power is obtained when the load resistance is equal to the generator resistance. The maximum efficiency of thermo electric power generation is determined as ratio of generated power delivered to the load resistance to heat. Ioffe showed that the highest efficiency is that is given by;

$$\Phi = \frac{P}{q} = \frac{(T_H - T_C)}{(T_H)} \frac{(1 + ZT)^{1/2}}{\frac{T_H}{T_C} + (1 + ZT)^{1/2}} \quad (2.11)$$

where T is average temperature equal to $(T_H + T_C)/2$. It is seen if $(1 + ZT)^{1/2}$ is very large, the efficiency approaches Carnot cycle value, $\frac{(T_H - T_C)}{(T_H)}$ [15]–[17], [22].

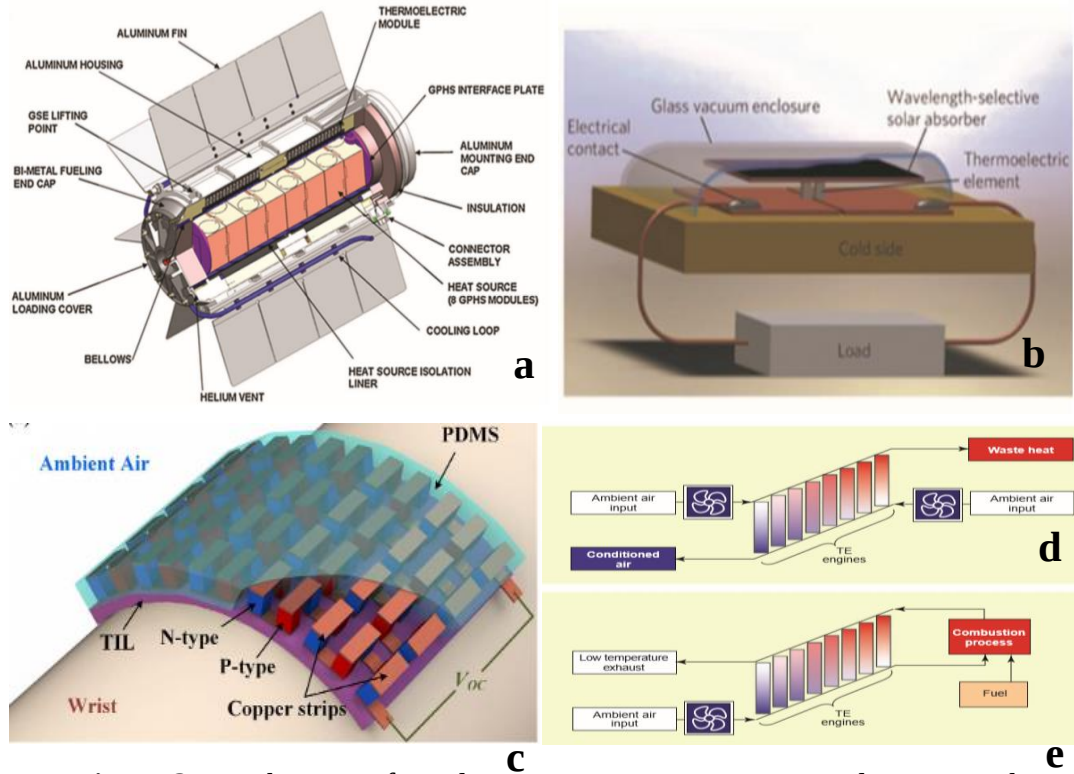


Figure 2. 5 : The uses of TE devices in some area; space exploration as the Rtegs(a), solar generators (b), flexible and wearable generators which using body heat (c), heating/cooling (d) and power generation for gas turbine [4], [20], [21].

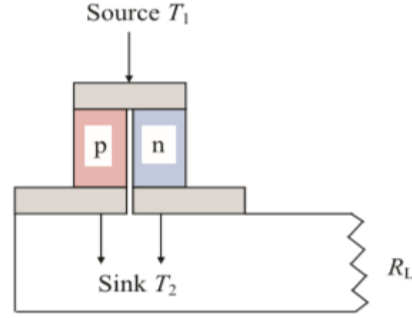


Figure 2. 6: Thermo couple for power generation mode connected a resistive load [22].

Refrigeration mode of thermoelectrics work based on Peltier effect. If we assume that a current (I) flows the direction as given in Figure 2.6 the bottom is cooled at temperature T_C and the lower is heated at temperature T_H . Then the maximum coefficient of performance (COP) is given as; [15], [17], [22]

$$COP = \Gamma = \frac{T_C[(1 + ZT)^{1/2} - T_H/T_C]}{(T_H - T_C) \cdot [(1 + ZT)^{1/2} + 1]} \quad (2.12)$$

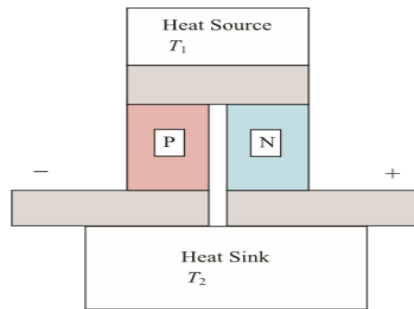


Figure 2. 7 : Refrigeration mode of thermo couple[22].

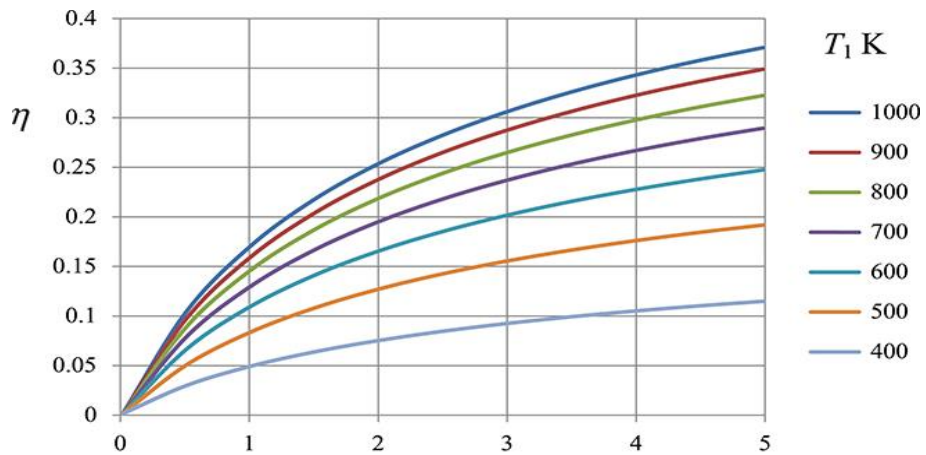


Figure 2. 8 : Plot of efficiency against for thermoelectric generation. The heat sink temperature, is set at 300 K [22].

In Figure 2.7. The maximum efficiency is plotted according to the ZT for The maximum efficiency change with ZT for a heat sink temperature at 300 K. It is clearly seen that when the efficiency is 5%,The ZT value equal to 1 at temperature differences 100 K [22].



3. TRANSPORT THEORY in SOLIDS

Prior to the focus to the relation of transport parameters and effectiveness on thermoelectricity; it should be better to revise the transport theory of conductivity for a better understanding.

3.1.Transport Equation

The flux of carrier particles in solids consist of two steps with opposite effects. First, the driving force of external field and the second dissipative effect of the scattering of the carrier particles with electron, phonon and defects. The relation between two steps is defined by the Boltzmann transport equation. The distribution function f gives probability of finding carrier particles at position r , with momentum P and at time t and the Boltzmann equation given as;

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{k} \frac{\partial f}{\partial k} + \dot{r} \frac{\partial f}{\partial r} = \left(\frac{df}{dt}\right)_{collision} \quad (3.1)$$

For solution of this equation use the relaxation time approximation (RTA).Relaxation time is defined as the passed time of success scattering between electron and electron, phonon or impurity. The relaxation time is dependent of an energy. Relaxation time can be expressed as $\tau_0 E^r$. Here; τ_0 is a constant that is independent from energy, however it can be dependent temperature or effective mass. r is scattering parameter that takes value according to scattering type. There are three main scattering mechanism;[23], [24][25] [18].

$r = -1/2$ for acoustic-phonon scattering

$r = 3/2$ for ionized-impurity scattering

$r = 1/2$ for polar optical phonon scattering [18].

$$\left(\frac{df}{dt}\right)_{collision} = -\frac{f-f_0}{\tau} \quad (3.2)$$

Here the distribution function, f it will relax towards its equilibrium state f_0 .Solution for this equation involve assumption that a conductor is isotropic and flows are in the

direction of the x axis. In order to get $f - f_0$ in terms of the electric field and the temperature gradient [15], [17], [18], [26].

$$\frac{f(E) - f_0(E)}{\tau} = v \cdot \frac{df_0(E)}{dE} \left[\frac{dE_F}{dx} + \frac{(E - E_F)}{T} \frac{dT}{dx} \right] \quad (3.3)$$

This equation can be applied both for holes and electrons. V is the velocity of charge carrier particle and $f(E)$ Fermi distribution function that has the equilibrium state $f_0(E)$. In order to get electrical conductivity and the Seebeck coefficient, we use the parabolic band model. It means the energy of solids, change with square of wave vector, k^2 . Thus, energy is given as; [15], [17], [18], [26].

$$E = \frac{\hbar^2 k^2}{2m^*} \quad (3.4)$$

Here $\hbar$ is Plank constant, the interaction between the carrier particles and crystal lattice give in result with effective mass (m^*). In this frame, write number of electron allowed per unit volume within energy interval from E to $E+dE$. In other words, Density of states (DOS) near the maxima of valance band or minima of conduction band given as;

$$g(E)dE = \frac{4\pi(2m^*)^{3/2}E^{1/2}dE}{\hbar^3} \quad (3.5)$$

For determine the transport parameter we should use the equation (3.3). The current density and heat flux density are given in (3.6) and (3.7). Here e is magnitude of charge carrier. The positive sign for hole carriers and negative sign for electrons in current density formula.

$$i = \pm \int_0^\infty e \cdot v \cdot f(E) \cdot g(E) \cdot dE \quad (3.6)$$

$$w = \int_0^\infty v(E - E_F) \cdot f(E) \cdot g(E) \cdot dE \quad (3.7)$$

$(E - E_F)$ is the energy transported by each carrier. If assumed no flow of any charge or heat in other words $i = w = 0$, it can be replaced f by $f - f_0$ and the drift velocity of charge carrier it can be ignorable compare to the thermal velocity of charge carrier.

Thus, it can rewrite the v as the $\frac{2E}{m^*}$. If rearranged the Equations (3.6) and (3.7); [15], [17], [18], [26].

$$i = \pm \frac{2e}{3m^*} \int_0^\infty g(E) \tau E \frac{df_0(E)}{dE} \left\{ \frac{dE_F}{dx} + \frac{(E - E_F)}{T} \frac{dT}{dx} \right\} dE \quad (3.8)$$

$$w = \mp \frac{E_F}{e} i + \frac{2e}{3m^*} \int_0^\infty g(E) \tau E^2 \frac{df_0(E)}{dE} \left\{ \frac{dE_F}{dx} + \frac{(E - E_F)}{T} \frac{dT}{dx} \right\} dE \quad (3.9)$$

3.2. The Electrical Conductivity and Seebeck Coefficient

In order to find the electrical conductivity, boundary conditions are used. Hence, the electrical conductivity given as the ratio of i over the electric field when the change in the temperature according to the direction is equal to zero. Then electric field expressed as; [15], [17], [18], [26]

$$\varepsilon_x = \pm \frac{\frac{dE_F}{dx}}{e} \quad (3.10)$$

So that;

$$\sigma = \frac{i}{\varepsilon} = \frac{1}{\rho} = - \frac{2e^2}{3m^*} \int_0^\infty g(E) \tau \frac{df_0(E)}{dE} dE \quad (3.11)$$

The condition for the Seebeck coefficient is the electric current is zero. The Seebeck coefficient is equal to ratio of electric field to temperature gradient.

$$S = \frac{\varepsilon_x}{\frac{dT}{dx}} = \pm \frac{\frac{dE_F}{dx}}{e \cdot \frac{dT}{dx}} \quad (3.12)$$

$$S = \pm \frac{1}{eT} \left\{ E_F - \int_0^\infty g(E) \tau E^2 \frac{df_0(E)}{dE} dE / \int_0^\infty g(E) \tau E \frac{df_0(E)}{dE} dE \right\} \quad (3.13)$$

Transport parameter consist of same integral forms. For simplification this equation defined this integral as;

$$K_s = -\frac{2T}{3m^*} \int_0^\infty g(E) \tau E^{s+1} \frac{df_0(E)}{dE} dE \quad (3.14)$$

It can be rearranged this integrals with using the relaxation time and density of states expressions. Thus;

$$K_s = \frac{8\pi}{3} \left(\frac{2}{h^2}\right)^{3/2} (m^*)^{1/2} T \tau_0 \left(s + r + \frac{3}{2}\right) (kT)^{s+r+3/2} F_{s+r+1/2} \quad (3.15)$$

Where

$$F_n(\xi) = \int_0^\infty \xi^n f_0(\xi) d\xi \quad (3.16)$$

This equation change with the ξ parameter that is reduced energy equal to E/kT . $F_n(\xi)$ the function is known as Fermi-Dirac integrals. Also used the symbol η to show the reduced Fermi energy, E_F/kT . In term of K_s definetation the transport parameters are expressed as;

$$\sigma = \frac{e^2}{T} K_1 \quad (3.17)$$

$$S = \pm \frac{1}{eT} \left(E_F - \frac{K_1}{K_0}\right) \quad (3.18)$$

In order to determine the transport parameter from equation (3.17) and (3.18), numerical method is used. However, when the Fermi energy less or higher than 0 that is depending on material, it gives the enable use some approximation to Fermi-Dirac distribution. Next step this approximations will be used to determine the transport parameter [15], [17], [18], [26].

3.2.1. Degenerate and non-degenerate conductors

If stared with non-degenerate conductors. If $\frac{\xi}{kT} \ll 0$, that is the Fermi level lies within the forbidden gap, in other words, semiconductor does not include too many impurities. In semiconductor Fermi level can be changed with changing carrier concentration. Then Fermi-Dirac integrals; [15], [17], [18], [26]

$$F_n(\eta) = \exp(\eta) \int_0^\infty \xi^n \exp(-\xi) d\xi = \exp(\eta) \Gamma(n+1) \quad (3.19)$$

And the transport integrals with new condition;

$$K_s = \frac{8\pi}{3} \left(\frac{2}{h^2}\right)^{\frac{3}{2}} (m^*)^{\frac{1}{2}} T \tau_0 \Gamma(s+r+\frac{5}{2}) (kT)^{s+r+\frac{3}{2}} \exp(\eta) \quad (3.20)$$

Then electrical conductivity;

$$\sigma = \frac{8\pi}{3} \left(\frac{2}{h^2}\right)^{\frac{3}{2}} e^2 (m^*)^{\frac{1}{2}} \tau_0 (kT)^{r+\frac{3}{2}} \Gamma(r+\frac{5}{2}) \exp(\eta) \quad (3.21)$$

It is suitable way to define the electrical conductivity as;

$$\sigma = ne\mu \quad (3.22)$$

Here n is carrier concentration, e is the electron charge and μ is the mobility that is defined mean drift speed of the charge carriers in an electric field. The concentration of a charge carrier given as;

$$n = \int_0^\infty f(E)g(E)dE = 2 (2\pi m^* kT/h^2)^{3/2} \exp(\eta) \quad (3.23)$$

And from two previous equation it can conclude with the expression of the mobility;

$$\mu = \frac{4}{3\pi^{1/2}} \Gamma\left(r+\frac{5}{2}\right) e \tau_0 (kT)^r / m^* \quad (3.24)$$

It is understood from the equation (3.24) that mobility does not direct the Fermi energy. It is depend on τ_0 and scattering parameter. It is expressed before that τ_0 may be depends on carrier concentration.

The other conclusion comes from equation (3.23). $(2\pi m^* kT/h^2)^{\frac{3}{2}}$ quantity involve m^* and it is expected that this quantity has different value for different semiconductors. This quantity is known as effective density of states.

Now turned the Seebeck coefficient for the non-degenerate semiconductor is related to the reduced Fermi energy and scattering parameter.

$$S = \pm \frac{k}{e} \left[\eta - \left(r + \frac{5}{2} \right) \right] \quad (3.25)$$

The condition for degenerate conductor is $\xi/kT \gg 0$. The Fermi level energy for electrons well above the conduction band edge and for holes well below the valance band edge. If expressed in other words, the conductor has too many impurities and exhibits metallic behaviour. Under this situation, the Fermi-Dirac integrals expressed as converging series. Same manner is applied as in non-degenerate conductor and the expression of electrical conductivity and Seebeck coefficient are given as ;[15], [17], [18], [22], [26], [27]

$$\sigma = \frac{8\pi}{3} \left(\frac{2}{h^2} \right)^{\frac{3}{2}} e^2 (m^*)^{\frac{1}{2}} \tau_0 \xi^{r+3/2} \quad (3.26)$$

$$S = \pm \frac{\pi^2 k}{3 e} \frac{\left(r + \frac{3}{2} \right)}{\eta} \quad (3.27)$$

In order to seen the relation easily, assumed no any scattering process and if continued with non-degenerate conductors the Seebeck coefficient is found as;

$$S = \pm \frac{8\pi^2 k^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (3.28)$$

- Mobility is inversely proportional to effective mass, from equation 3.24.
- Electrical conductivity is direct proportional to the carrier concentration and mobility, from equation 3.22.
- Carrier concentration is to proportional effective mass from equation 3.23.
- Seebeck coefficient is directly proportional to the effective mass and inversely proportional to charge carrier concentration, from equation 3.28.

3.3. Thermal Conductivity

Heat energy can be conducted in solids with electrical charge carriers (electron and hole), phonons, electromagnetic waves or other excitation. In metal charge carriers conduct the heat energy whereas in insulator lattice waves (phonons) predominant except diamond. Just electrical and lattice component of thermal conductivity are

focused. Thermal conductivity defined flow of heat down a road with temperature gradient that is expression as;[28-29]

$$K = -\frac{\vec{Q}}{\vec{\nabla}T} \quad (3.29)$$

Here Q is heat flux vector and T absolute temperature. From the Kinetic Theory thermal conductivity is given as;

$$K = \frac{1}{3} C_v V l \quad (3.30)$$

Here C the heat capacity per unit volume, V is the sound velocity and l is the mean free path of the particles.

3.3.1. Electronic thermal conductivity

The electronic component of the thermal conductivity comes from charge carrier particles (electrons or holes). In order to understand Wiedmann Franz Law and state the Lorenz Number, it will begin with metals.

From kinetic theory of gases the heat capacity is found that $C_v = \frac{3}{2}nk$, here n is carrier concentration and k is defined as before Boltzmann constant. If substituted this quantity in equation (3.29), it is found that;

$$K_e = 1/2 n V^2 k \tau \quad (3.31)$$

The thermal electrical conductivity depends on velocity of charge carrier, carrier concentration and mean free time ($l = v \cdot \tau$).

The Wiedmann Franz Law specify that the ratio of electrical thermal conductivity to electrical conductivity is proportional to the temperature with a constant number that is known as Lorenz Number. In order to get this number it is used the definition of electrical conductivity and energy that is found from kinetic theory.

$$\sigma = \frac{ne^2\tau}{m} \quad (3.32)$$

$$E = \frac{\pi^2}{3} \cdot kT \quad (3.33)$$

$$L = \frac{K_e}{\sigma T} = \frac{3}{2} \left(\frac{k}{e} \right)^2 = 2.45 \times 10^{-8} W. \Omega. K^{-2} \quad (3.34)$$

This conclusion is important for metals. It is clearly understood that the ratio does not depend on carrier concentration, scattering parameter, mobility or mass [28-29].

In order to grasp physical background of Wiedmann Franz-Lorenz Number, Kinetic Theory and metallic behaviour were used. Indeed, calculations of these parameter based on perturbation theory and Boltzmann transport equation. Boundary condition for electronic thermal conductivity is equal to the ratio of w which is given in equation (3.9) to $\frac{dT}{dx}$ when the electric current is zero. Thus electrical thermal conductivity is:

$$\lambda_e = \frac{2}{3m^*T} \left[\frac{\left[\int_0^\infty g(E) \tau E^2 \frac{df_0(E)}{dE} dE \right]^2}{\int_0^\infty g(E) \tau E \frac{df_0(E)}{dE} dE} - \int_0^\infty g(E) \tau E^3 \frac{df_0(E)}{dE} dE \right] \quad (3.35)$$

The electrical thermal conductivity is given as in terms of Fermi-Dirac integrals like:

$$\lambda_e = \frac{1}{T^2} \left(K_2 - \frac{K_1^2}{K_0} \right) \quad (3.36)$$

Here K_2, K_1, K_0 Fermi-Dirac integrals.

It is conventional method for define electronical thermal conductivity in terms of the Lorenz Number. For non-degenerate conductor the Lorenz number is described as;

$$L = \left(\frac{k}{e} \right)^2 \left(r + \frac{5}{2} \right) \quad (3.37)$$

It is found that the Lorenz Number does not depend on Fermi energy, however depend on scattering parameter.

For degenerate conductors the Lorenz Number is given in Equation (3.38). It is found that this quantity is same for all metals at low temperature. It is fully agree with Wiedmann Franz law. Other fundamental conclusions this quantity does not depend on scattering parameter [17], [18], [22], [26].

$$L = \frac{\pi^2}{3} \left(\frac{k}{e} \right)^2 \quad (3.38)$$

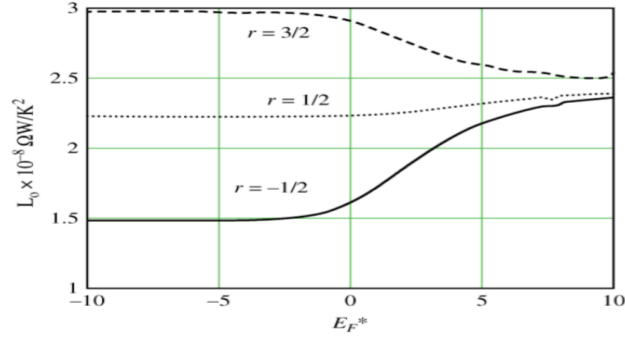


Figure 3.1: The reduced Fermi energy according to the Lorenz number [18].

In figure (3.1) shows the Lorenz Number is plotted according to the reduced Fermi energy for three main scattering mechanism. It is clearly seen from graph; for metals at high of Fermi energy the Lorenz Number equal to $2.45 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$. For reduced Fermi energies below to zero and $r = -1/2$, in other saying for semiconductor, Lorenz Number decrease to $1.5 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ that is lowest value that come from acoustic-phonon scattering [18].

3.3.2. Lattice thermal conductivity

In this part heat conduction with lattice vibration will be investigate. The quanta of a lattice vibration is known as a phonon. If we draw an analogy between the Kinetic Theory of Gases and the lattice thermal conductivity that is expressed as;

$$K_{ph} = \frac{1}{3} C_V V l_{ph} \quad (3.39)$$

Here C_V specific heat of solid per unit volume, V speed of a sound and l_{ph} the mean free path of phonons. In order to understand lattice thermal conductivity, we should examine specific heat of solids [15], [17], [18], [22], [26].

The atom in crystal is bonded with its neighbours. This result in that if any displacement occurs in one atom that is cause to be seen other atoms. Owing to that and nature of the crystals the atoms in vibration mode can be represented by a waves. An increasing in a temperature of crystal result in increasing amplitude of vibration wave. This result was used by Debye who explain the specific heat of solids. Also Debye identified the crystal as an elastic continuum. It is expected if the crystal is

continuum, the vibrational mode should be infinitive. However, a lower limit to the wavelength is fixed by discrete nature of atoms. He prove that only certain modes of vibration occurs as boundary conditions are applied. The total number of vibrational modes equal to $3N$, here N is the number of atoms [15], [17], [18], [22], [26].

The dispersion curve that is plotted the lattice vibration frequency based on the wave vector (k) as shown in Figure (3.2). The dispersion curve of 3-d lattice has three acoustic branch (two transverse and one longitudinal mode) and $(3N-3)$ optical branch.

In Debye Theory the number of modes per unit volume that have frequencies between w and $w+dw$ is given as;

$$n_l == \frac{2\pi w^3 dw}{V^3} \quad (3.40)$$

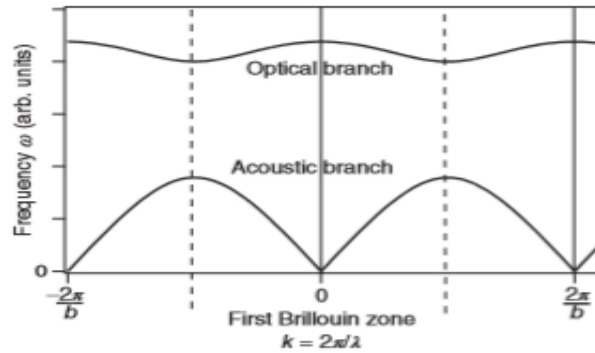


Figure 3.2: The dispersion curve at first Brillouin zone for diatomic structure[30].

After integrated this equation it is found the total number of modes and it should be equal to $3N$. Here w_D is the upper limit of frequency.

$$\frac{4\pi w_D^3}{V^3} = 3N \quad (3.41)$$

Phonons are Bose particle thus they obeys Bose-Einstein statistics. Owing to that Debye used the quantum theory in order to identified energy in mode of frequency. Specific heat is the differentiating of the internal energy according to the temperature. Then specific heat is given as;

$$C_v = 9Nk \left(\frac{T}{\theta_D} \right)^3 f_D \left(\frac{\theta_D}{T} \right) \quad (3.42)$$

Here θ_D is the Debye temperature and f_D Debye Function defined as;

$$\theta_D = \frac{hw_D}{k} \quad (3.43)$$

$$f_D \left(\frac{\theta_D}{T} \right) = \int_0^{\theta_D} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \quad (3.44)$$

Debye Theory consistent with experimental result. Thus, this elementary model is used today. However, one of Debye's assumption that the crystal is a continuum and result with the lattice thermal conductivity is infinite. But it is known from experimental result the thermal conductivity of solid should be finite. In order to solve this problem, anharmonicity should be considered [17], [29][28].

Pierls who firstly showed that the phonons interact with others in two ways with absence of impurity shown as in Figure (3.3). In normal process also is called N-scattering, the momentum of phonon is conserved. In Umklapp also is known U-scattering, momentum is not conserved. The thermal conductivity occurs with U-process [28][17].

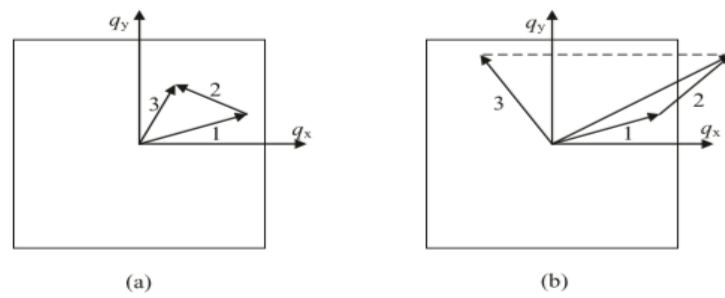


Figure 3.3 : Phonon interactions with others. (a) N-scattering (b) U-scattering [22].

It is clearly seen in Figure (3.3). k is used for wave vector of phonons. The interaction between two phonons produced a third phonon. In N-scattering third phonon is occurred with simple vector additions, in U-scattering, the reciprocal lattice vector produce third phonon in the first Brillouin zone [28][29].

$$k_1 + k_2 = k_3 \text{ (N-scattering mechanism)} \quad (3.45)$$

$$k_1 + k_2 = k_3 + G \text{ (U-scattering mechanism)} \quad (3.46)$$

3.4.Ways for Optimization

It is understood until this section that the optimization strategies base on reducing the lattice thermal conductivity without drastically lowering in power factor and improvement in electrical properties. In this perspective some novel strategies were presented.

3.4.1. Nano structure

In 1990, Hicks and Dresselhaus showed that thermoelectric performance of material can be increased by using a low-dimensional system such as nanowire, nanotubes, quantum wells or quantum dots. There are two main strategies affect the TE properties of the material in nanostructuring.

- 1.Enhancement of power factor via quantum confinement effect; if size of the material is comparable to the de Broglie wave length of the charge carriers in certain direction, the motion of charge carriers are limited. In other words, the charge carriers are placed in infinitely potential well and therefore lead to drastically change in DOS near the Fermi level that is known as quantum confinement effect. In this way, the thermo power of material is improved.

2. Reducing the thermal conductivity; in a low dimensional system the mean free path of phonons is longer than the charge carriers. Thus, phonon scattering become significant at the boundaries and that is result in low lattice thermal conductivity without changing in electronical conduction and carrier mobility [32–37].

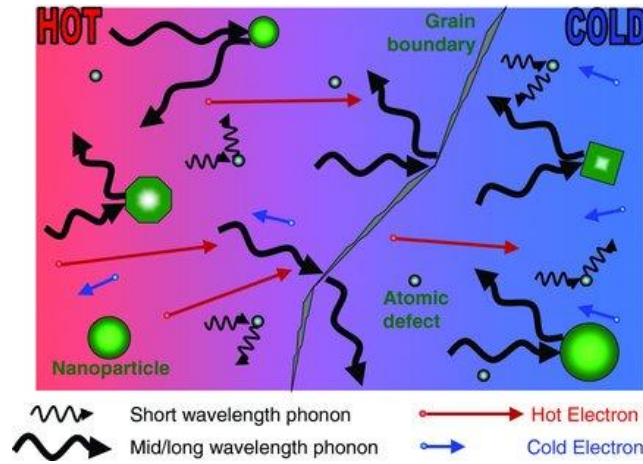


Figure 3.4 : The phonon scattering mechanism and transport of hot and cold electrons through thermoelectric material[35].

3.4.2. Phonon glass electron crystal and complex structure

Phonon-glass electron crystal (PGEC) approximations was proposed by Slack. The properties of PGEC materials, such as skutterudites and clathrates conduct electric current similar to a crystal and conduct heat like in glass. These materials have complex crystal structures that can be associated with large unit cell and voids, so alloying with isoelectronic elements result in disordered structure. The voids can be filled with heavy atoms and these atoms acting as rattlers. Therefore, low thermal conductivity is obtained with the increasing in scattering of phonons, in other words, reduction in mean free path of phonons [8],[37].

3.4.3. Phonon liquid electron crystal

The thermal conductivity of solid is limited to the thermal conductivity of glass, but structurally glass and liquid have short range order, just glass does not have capacity to flow. The idea of Phonon liquid electron crystal (PLEC) proposed first time for copper based super ionic chalcogenide structures that have heat capacity lower than glass limit. The random diffusion of energy located at fixed atomic positions with sequentially atomic jumps from one equilibrium position to another lead to the thermal transport in disordered systems. Local atomic jumps and rearrangement of liquid, result in eliminating some transverse waves that suppress propagation of heat by phonons and so leading substantial reduction in specific heat (C_v). While for solid, specific heat is equal to $3Nk_B$ at high temperature (Dulong-Petit Law), where N number of particles and k_B Boltzmann constant, C_v reduce to $2 Nk_B$ - $2.5 Nk_B$ for liquid. While the frequency is below the cut-off frequency, the transverse phonons are muted and vanish, resulting in C_v between that of a liquid and a solid as show in Figure

3.5. Moreover, copper atoms can move freely in sub lattice of these structure (liquid-like) and thus lead to more scattering of longitudinal phonons. Such liquid like behaviour result in shorten mean free path of phonons so decreasing in lattice thermal conductivity. In substance, the PLEC materials conduct electric current like electron crystals and conduct heat like liquids [41–45].

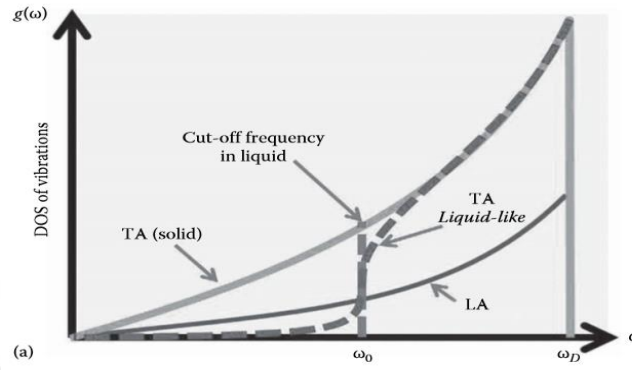


Figure 3. 5 : Phonon density of states for liquid-like behaviour structures [39].

3.4.4. Phonon-phonon interaction and anharmonicity

Consider in three dimension array of atoms linked with spring as shown in Figure 3.6. If an atom pulled from its equilibrium position during passage of phonons, the force that the atom is exposed to is proportional to its displacement. The proportional value for harmonicity does not change and that is called spring constant. For anharmonicity when two phonon run into each other, the spring constant change with atomic displacement. Anharmonicity is considered consequence of enhancement of phonon-phonon scattering that lead to reducing lattice thermal conductivity and without any disrupting in electrical properties. Grüneisen γ parameter is used to measure anharmonic nature of bonds as given in equation 3.45. Here β is the volume thermal expansion coefficient, B is the isothermal bulk modulus, C_v the isochoric specific heat per mole, and V_m is the molar volume. The rock salt structures that have PbTe or I-V-VI₂ group semiconductors structures, where the group V element can be P, As, Bi or Sb, the group VI element Te, Se or S and the group I element Au, Ag or Cu, have high Grüneisen parameter [41], [46–48].

$$\gamma = \frac{3\beta B V_m}{C_v} \quad (3.47)$$

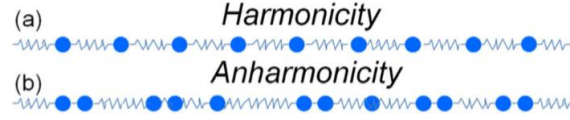


Figure 3. 6 : Atomic displacement and anharmonicity [43].

3.4.5. Effective mass and band convergence

In previous chapter some difficulties was mentioned for optimize transport parameters. These are that;

- Band effective mass of charge carriers (m_{band}^*) is inversely proportional to carrier mobility (μ).
- Seebeck coefficient (S) directly proportional to density of states effective mass (m_{DOS}^*).

The relation between m_{DOS}^* and m_{band}^* given as $m_{DOS}^* = N_v^{2/3} m_{band}^*$ here N_v represent the valley degeneracy. When the relationship between m_{DOS}^* and m_{band}^* is examined according to the given above, large density of state effective mass result in increasing in power factor, however, large band effective mass of charge carriers lead to lower electrical conductivity. Therefore, low band effective mass is required for thermoelectric materials. The maximum ZT depends on atomic and electronic structure and its quality factor B defined as;

$$B = \frac{2k_B^2 \hbar}{3\pi} \cdot \frac{N_v C_l}{m_b^* \equiv^2 K_l} T \quad (3.48)$$

Here, k_B is Boltzman constant, $\hbar$ Planck constant, K_l lattice thermal conductivity, C_l longitudinal elastic moduli and $\equiv$ is deformation potential coefficient which arises from weak scattering of charge carriers. It is clearly seen from equation 3.46 for high ZT the small band effective mass, low deformation potential coefficient, low lattice thermal conductivity and high degeneracy is required. Complex or multiband structures show high degeneracy and it can be obtain with higher doping concentration. Lead chalcogenide and their alloys exhibit multi band systems, comprise two valance band, convergence or overlapping these band lead to increasing in valley degeneracy [8], [45]–[47].

3.5. State of Art Thermoelectric Materials

In this section, not all TE classes, the most studied thermoelectric material classes will be discussed. Brief information such as crystal structure, chemical composition or TE value will be given for chalcogenide, clathrate and half hausler structures. The skutterudite and copper based selenide structures within the context of this thesis will be examined in detail.

3.5.1. Chalcogenide structure

In order to simple comprehension, the chalcogenide structures will be examined in three subtitle. One of chalcogenide class that is copper based structure will be given in detail at another title. All chalcogenide groups have narrow band gaps. Firstly, binary chalcogenide include of bismuth telluride, antimony telluride and bismuth selenide structures. Bi_2Te_3 that firstly studied by Goldsmid in 1954 is the most used materials until this day in TE applications due to have high efficiency at room temperature. Bi_2Te_3 that has layered structure as shown in Figure 3.7-a, exhibits strong ionic covalent bonding between T2 and Bi atoms, however, bonding between the neighbouring Te1 layers is weak van der waals bond. Bi_2Te_3 and its alloys such as $Bi_{2-x}Sb_xTe_3$ and $Bi_2Te_{3-x}Se_x$ show p and n type semiconductor behaviour sequentially with ZT around 1. The highest ZT=1.9 at 323 K was obtained for $Bi_{0.5}Sb_{1.5}Te_3$ with dense dislocation arrays formed at grain boundaries [51-52].

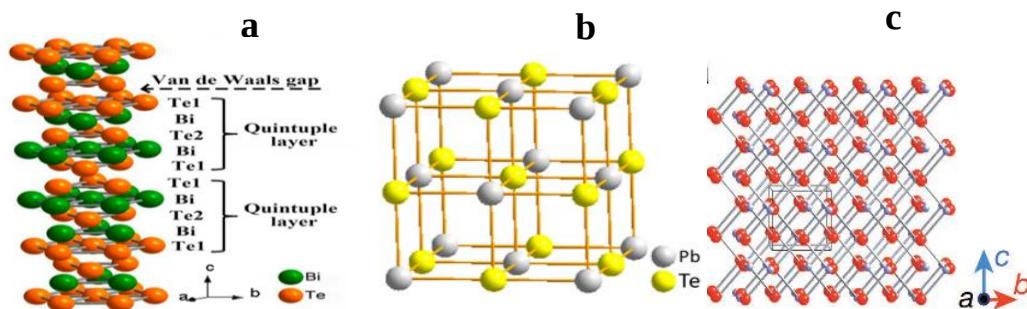


Figure 3. 7: Bismuth based, lead based and tin based TE chalcogenide structure respectively [48],[50],[51].

Second group that consist of lead chalcogenide materials generally effective at medium temperature (450K-900K) have PbA structure, in here A represent Te, Se or S atoms. It is mentioned before for good thermoelectrical properties narrow band gap is required and for PbTe, PbSe and PbS are 0.29 eV, 0.27 eV, 0.37 eV respectively. PbTe structure have two valance band and it is enable to studying band convergence approximations in order to optimize. The crystal structure of PbTe as shown in Figure

3.7-b is NaCl crystal structure with space group $Fm\bar{3}m$. The unit cell is face centered cubic structure and exhibits high symmetry. It is classified polar semiconductors due to chemical bonding which is mix of covalent and ionic bond. It is used for generally NASA space mission as RTEGs since 1950. It found $ZT=2.5$ for PbTe-SrTe compound at 923K [50], [52], [53].

Last and third group is lead free tin based chalcogenide structures such as *SnSe*, *SnTe* and *SnS* which effective at medium temperature. A study that conducted by Zhao et al. in 2014, surprisingly found $ZT=2.6$ at 923 K for *SnSe* structure. The two dimensional layered structure of *SnSe* as shown in Figure 3.7-c, possesses intrinsically low thermal conductivity due to have distorted rock salt structure, high anisotropy and high anharmonicity (high Grüneisen parameter). The bonding between Sn-Se is covalent bonding around b-c plane and weak Van der Waals bond along a-axis. There is advantage sides of these group such as more environmentally and available according to the lead based chalcogenide. *SnSe* is p type semiconductor and n type material with nearly same ZT value is required in order to balance with p-type *SnSe* in TE applications. This n-type material that found add of bromine to *SnSe* have high TE properties with $ZT=2.8$ at 773 K [51], [54], [55].

3.5.2. Half Heusler structure

Half Heusler (HH) compounds are defined as with the composition of XYZ which X and Y are transitional metal and Z is main group element. Generally the most studied half-heusler compound are XCoSb and XNiSn, in here X being Ti, Zr and Hf. HH compounds are classified intermetallic compounds. Due to their complex crystal structure, narrow band gap, high electrical conductivity, inexpensive and non-toxic element and powerful physical properties make them a candidate for TE material classes. The crystal structure of this compound that is shown in Figure 3.8-a is Zintl compound and have covalent bond diamond like substructures with space group $F\bar{4}3m$. Besides good properties, it exhibits high thermal conductivity that is drawback and so many studies have been conducted to reduce thermal conductivity such as enhancement the scattering at grain boundary. In literature $ZT=1.5$ at 700 K for Sb-doped HfZrNiSn is recorded [59-60].

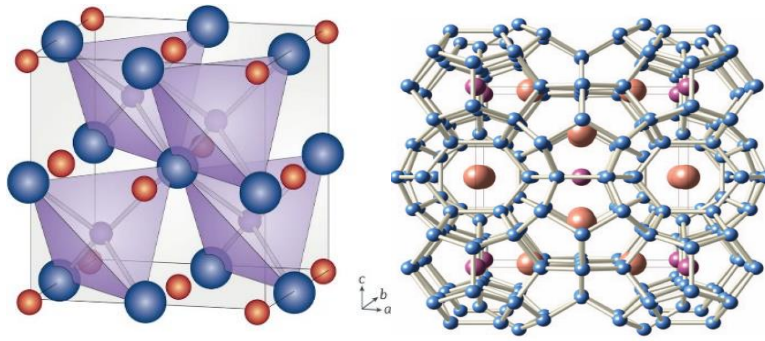


Figure 3. 8 : (a) HH XYZ structure; X atoms are in red, y atoms purple and z atoms blue (b) Type-I clathrate framework atoms are in blue and guest atoms are orange and purple [60-61].

3.5.3. Clathrate structure

Intermetallic clathrate structures exhibit very low PGEC materials properties. Its open framework structures enable to host guest atoms. The guest atom that we mentioned before have rattle effect and so decrease in lattice thermal conductivity. Even though there are several of clathrates classes, The Type I will be examined. The chemical form is $A_2B_6C_{46}$ that is shown in Figure 3.8-b, in here A and B are guest atoms and C is tetrahedrally bonded framework atom generally Al, Si, Ga, Ge and Sn. In literature $ZT=1.41$ at 700 K for ZnInSb compound is recorded [8], [58].

3.5.4. Skutterudite structure

One of novel thermoelectric material classes is skutterudite structure. The name of Skutterudite structure comes from a town in Norway called as Skutterud where the crystalline structure of $CoAs_3$ was firstly discovered. The general formula of the skutterudite structure is AX_3 here A is transition metal (Co group (Rh, Ir)) and X (P, As or Sb) is a pnictogen atoms. The unit cell is body centered cubic structure consist of 32 atoms with space group $Im\bar{3}$. The unit cell has eight cubes of transition material (1/4, 1/4, 1/4) that is seen in Figure 3.9. Six of this cubes filled with rectangle pnictogens and the remain of two cubes have large void that can be filled by guest atoms surrounded by 12 X atoms. Unfilled skutterudite structure exhibit diamagnetic p type semiconductor behaviour. If the bonding properties is examined, because the distance of metal atoms is too large there is no important bonding between metal atoms. The pnictogen rings are bonded with Sigma bonds [37],[62–64].

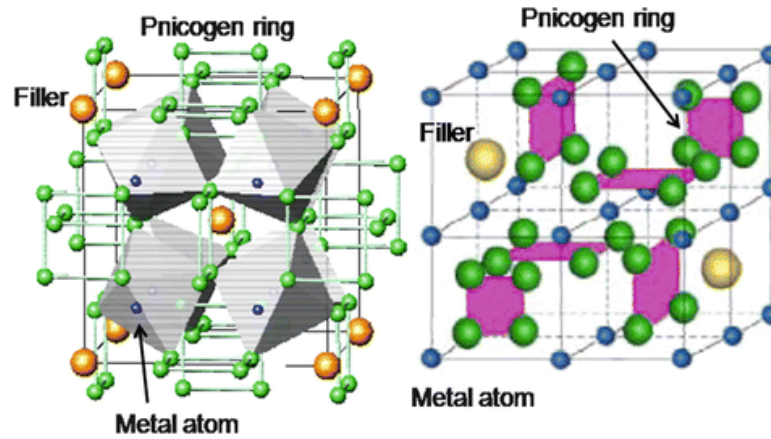


Figure 3.9 : Crystal structure of a filled skutterudite viewed from different perspectives [61].

Owing to their high mobility, high electrical conductivity the most studied structure is CoSb_3 compound in order to power generation at intermediate temperature. Generally unfilled CoSb_3 show p type semiconductor behaviour with 0.5 eV. Therefore the conducting behaviour varies with filler atom, synthesis and densification methods, it can be change to n type conductivity. Sometimes it can show both two conducting behaviours that changing with temperature. However a major drawback of this unfilled structure show high thermal conductivity around 8.9 W/mK at 300K. In literature the highest ZT value for unfilled structure that conducted by Toprak et al. is 0.17 at 611 K with average particle size 220 nm. Filled the voids and doped Cobalt or Antimony sides are effective way to diminish the thermal conductivity[37], [60], [62].

The general formula of filled skutterudite is AM_4X_{12} , here A shows the void which can be filled with rare-earth, alkali-metal to alkaline-earth elements. The filler atoms have rattle effects and interact with the phonon modes. Thus lead to decreasing in thermal conductivity. Partly filled skutterudites does not have charge-deficient atoms in the structure. In other words the filler atoms donates valance electrons to the valance band of structure and so lead n-type conductivity. The physical and chemical properties of filling atoms such as ionic radius, valance states and electronegativity as well play critical role to TE properties of structure. If the fillers have smaller ionic radius than the void=1, 9Å, it can be easily escape from voids. If have bigger radius, it is difficult obtain thermodynamically stable phase because of the lattice expansion. The study that is conducted by Chen showed range of $r_{\text{ion}}/r_{\text{cage}}$ various between 0.6 and 0.9. Filling fraction rate that depends on this range and ion valance (n) is expressed as in equation 3.49.

$$\gamma_{\max} = r_{\text{ion}}/r_{\text{cage}} - 0.86n - 0.24 \quad (3.49)$$

Another study is conducted by Shi et al. found that the difference of electronegativity between fillers and antimony atoms have role for filling fraction limit and also thermodynamic stability. The simple rule is given as $X_A - X_{\text{Sb}} > 0.8$ in here X_A and X_{Sb} the electronegativity of fillers and antimony atom respectivel [66–70].

In literature, many work have been presented that with fillers atoms such as Ba, Yb, In, Eu and Tl as well for partly filled skutterudite structures. Some filler atoms do not effect only thermal conductivity, but also improve the electronic properties. Na as a filler atoms, drive in extra electronic states close to conduction band and lead to increasing in electron mobility. Therefore, $ZT=1.25$ was achieved at 850 K for $\text{Na}_{0.48}\text{Co}_4\text{Sb}_{12}$ compounds. In literature, the highest $ZT=1.5$ was obtained at 725 K for $\text{InCo}_4\text{Sb}_{12}$ compounds with excess of antimony.[68], [71-72]

Recent year double-filled or multifilled approach has been more studied to great impact on lattice thermal conductivity. It is known that weakly bounded fillers atoms interact with the normal phonon mode of structure (Einstein oscillator).In detail, each filler ions have specific frequency and it can be seen phonon resonance scattering mechanism. Normal phonon mode frequencies of structure close to the local resonant frequency. Interaction between these modes, result in low lattice thermal conductivity and it can be attributed difference local resonant frequency if there is more than one filler. Again filling the voids structure with one or more than one atoms lead to n type conductivity. There are many studies available in literature. A study conducted by Shi et al found $ZT= 1.36$ at 800 K for $\text{Ba}_x\text{Yb}_y \text{Co}_4\text{Sb}_{12}$. Another study is conducted by Yang et al. studied on $\text{Ba}_x \text{R}_y \text{Co}_4\text{Sb}_{12}$ in here $\text{R} = \text{La}, \text{Ce}, \text{and Sr}$ and found (Ba, La) or (Ba, Ce) combination is more effective according to the single filler There is no restriction on filler atoms and many studied showed that multi filling system enhance the thermoelectric properties of this structures. CoSb_3 with multiple co-fillers Ba, La, and Yb thermoelectric figure of merit $ZT = 1, 7$ at 850 K. There is another study that conducted by Rogl et al. work on $(\text{R}\text{BaYb}) \text{Co}_4\text{Sb}_{12.3}$ compound R being Sr, La, DD, MM, SrMm, and SrDD. The highest $ZT=1.9$ at 835 K was achieved after severe plastic deformation [73–78].

Until here, the filled skutterudites were investigated. It was mentioned that filling void always lead n type conductivity. It is required find p type material with nearly same

ZT at same working temperature. P-type materials are obtained with substitute of different chemicals to cobalt side, antimony side or both side of structure. These chemicals are electron deficient elements in order to balance charge. The Co side is doped generally with Fe or Ni and Sb side is doped with such as Te, Se, and Sn etc. Substitution atoms in structure enhance the point defect scattering and so lead lower lattice thermal conductivity. In order to get high efficiency materials both strategy are used on the same materials. Mallik et al. substituted Co side with Fe and Sb side with Te which result in $ZT = 1, 3$ at 820 K with after severe plastic deformation via high pressure torsion for $\text{Fe}_{0.2}\text{Co}_{3.8}\text{Sb}_{11.5}\text{Te}_{0.5}$ skutterudites. Another study which is conducted by Rogl et al. achieved $ZT=1.45$ at 850 K with substituting and filling for p type $\text{DD}_{0.7}\text{Fe}_{2.7}\text{Co}_{1.3}\text{Sb}_{11.8}\text{Sn}_{0.2}$ skutterudite [66], [78-79].

Another effective way to use nano inclusions in the matrix enhance the phonon scattering at grain boundaries with rattlers effects. Such as, using multilayer graphene (even at micron size) show $ZT = 1, 5$ was found for n-type $\text{Yb}_{0.72}\text{Co}_4\text{Sb}_{12}$, while $ZT=1.06$ was found for p-type $\text{Ce}_{0.56}\text{Fe}_3\text{CoSb}_{12}$ [78].

Table (3.1) show some high ZT value for skutterudite structure. It is understood from the table that substitute/filled or multi filled the structure exhibit great improvement thanks to the rattlers with lowering the thermal conductivity. The transport parameter value also depend on experimental methods and densification the material play important role to lowering the resistivity and thermal conductivity. Therefore several methods have been attempted to find applicable method and conditions.

3.5.5. Copper based chalcogenide structure

Super ionic conductors are a class solids that exhibit remarkable high ionic conductivity similar to liquids or molten salts. One of important properties of super ionic conductors undergo order- disorder phase transition. It is used for such as batteries, photovoltaic systems, super capacitors, thermoelectric applications, electrolyzes etc [79].

Copper based chalcogenide Cu_{2-x}A A= S, Se, Te have great potential therefore their thermoelectric performance and interesting physical properties that is not fully understood yet [39].

Table 3. 1: Some ZT and thermal conductivity values observed in the literature.

Compound	ZT	T(K)	K(W/mK)	Methods
DD _{0.7} Fe _{2.7} Co _{1.3} Sb _{11.8} Sn _{0.2}	1.3	780	1.9	MQA+HP+HPT
Sr _{0.09} Ba _{0.11} Yb _{0.05} Co ₄ Sb ₁₂	1.9	835	1.6	MG+HP+HPT
Ba _{0.08} La _{0.05} Yb _{0.04} Co ₄ Sb ₁₂	1.7	850	2.7	IM+HTA+SPS
Fe _{0.2} Co _{3.8} Sb _{11.5} Te _{0.5}	1.3	820	2.8	MQG+HP+HPT
InCo ₄ Sb ₁₂	1.5	725	1.3	IM+SPS

MQA: melting, quenching, annealing; HP: hot press; HPT: high-pressure torsion; MG: melting, grinding; IM: injection melting; HTA: high temperature annealing; SPS: spark plasma sintering; k: thermal conductivity; T: temperature [69], [70], [73], [76], [77].

Although the simple chemical formula of copper selenide structure has complex atomic unit cell. Cu₂Se has two phase dependent of temperature that α and β phase at low and high temperature respectively. α phase is stable around at 400K and many studies have been presented to understanding of crystal structure. The conclusion result in both theoretical and experimental studies showed that low symmetry of α - Cu₂Se phase has multiform structure, in other words, it can be either monoclinic or trigonal or orthorhombic. High symmetry of β phase has cubic anti-fluorite structure with space group Fm3m. The Se ions crystallize as face centered cubic structure while the cations namely super ionic Cu atoms are kinetically disordered exact atomic position. In 2015, the study conducted by Lu et al. showed that the layered structure of both phase of copper selenide that is shown in Figure 3.10. Low temperature- α phase that is shown in Figure 3.10-b has no copper layers between the selenium layers obviously seen Se-Se bonds. High temperature- β phase given as Figure 3.10-a has two copper layers between the selenium layers In figure, while coppers ions are illustrated in blue, selenium ions are in red. Ordering of copper ions with considering energy situation result in multiform structure [11], [42], [81–83].

It is mentioned previous section, for reminder briefly, the origin of good TE properties of copper selenide come from low thermal conductivity. The PLEC approximation was proposed for clarify this structure behaviour. β phase is known super ionic conductor because high mobility of Cu ions. The fast of copper ions diffusivity result in the decreasing in thermal conductivity and increasing in power factor. Copper selenide normally is zero band gap materials (1.23 eV) and p type conductivity increases with Cu deficiency [11], [82].

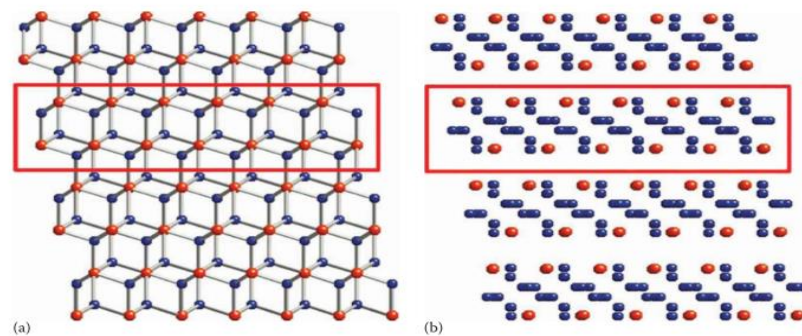


Figure 3. 10 : Layered structure of Cu_2Se with high temperature β phase (a) and low temperature α phase (b)[39].

Some ZT values for bulk copper selenide structure is given in Table 3.2. The synthesising method effect the crystal structure, morphology and so thermoelectric properties. However, besides good thermoelectric properties, Cu migration under high current and the time consuming process steps major drawbacks for copper based structures.

Table 3. 2: The ZT and thermal conductivity values measured for Cu_2Se prepared via different technique.

Compound	ZT	T(K)	K(W/mK)	Method
Cu_2Se	1.5	1000	$\approx 0,7$	Melting+Annealing+SPS
	1.6	700	≈ 0.6	HEBM+ HP
	1.19	723	≈ 0.82	HPHT+ Annealing
	1.2	823	≈ 0.8	SSR + CP

SPS; Spark plasma sintering, HEBM; High energy ball mill, HP; Hot press, HPHT; High pressure high torsion, SSR; solid state reaction, CP; cold press K; total thermal conductivity, T; Temperature, ZT; Figure of merit [11], [83]–[85].

In Table 3.2 some compaction method are presented that SPS, HP and CP. Using high current in SPS, graphite paper in HP and lower material density according to the other system in CP and high cost of SPS and HP systems negative sides of fabrication. new methods have being implemented in order to find optimum conditions such as easy fabricating, no time consuming, cheaper methods etc. Another synthesising methods are using chemical routes such as solvothermal, microwave assisted thermolysis method etc. In 2016 Tafti et al, showed for nano copper selenide that the particle size

vary between 200 nm to 50 nm synthesised with microwave assisted thermolysis method and compacted with SPS achieved $ZT=2$ and total thermal conductivity with 0.38 at 900K [15], [86-87].

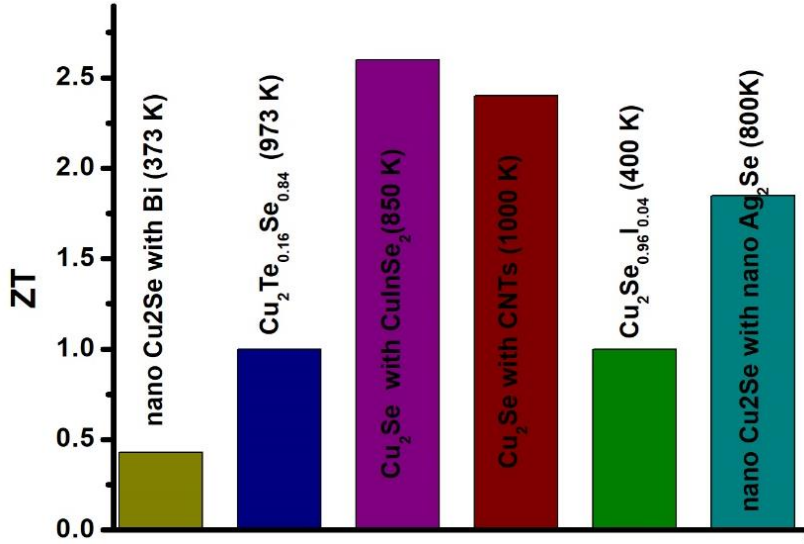


Figure 3. 11: Some ZT values measured for Cu₂Se in the literature. [12], [82], [88–91].

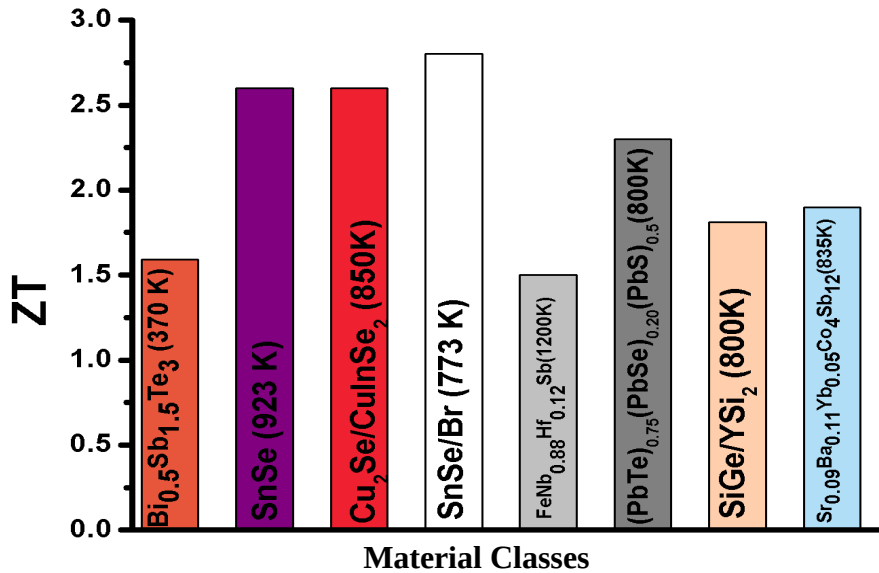


Figure 3. 12: Some ZT values according to the material classes [12], [54], [58], [76], [92–95].

There have been great effort in order to improve thermoelectric properties of copper selenide at medium temperature. The Cu migration have a positive effect to reduce in thermal conductivity, however, its leads to low carrier mobility and so lowering in thermal conductivity. Again Cu migration result in impairment in chemical stability.

Doping cations or nano structure can be assist to these problems. Many works have been presented such as substitute copper or selenide or both side with Bi, Te, I, CuISe, carbon nano tubes, nano Ag_2Se . These works are presented in Figure 3.11. [12], [85], [86]. Some ZT value in literature according to the classes are given in Figure 3.12.





4. EXPERIMENTAL METHODS

The experimental steps of this thesis include the synthesis samples and their structural and TE characterization. The flow chart of the conducted experiments is given in Figure 4.1.

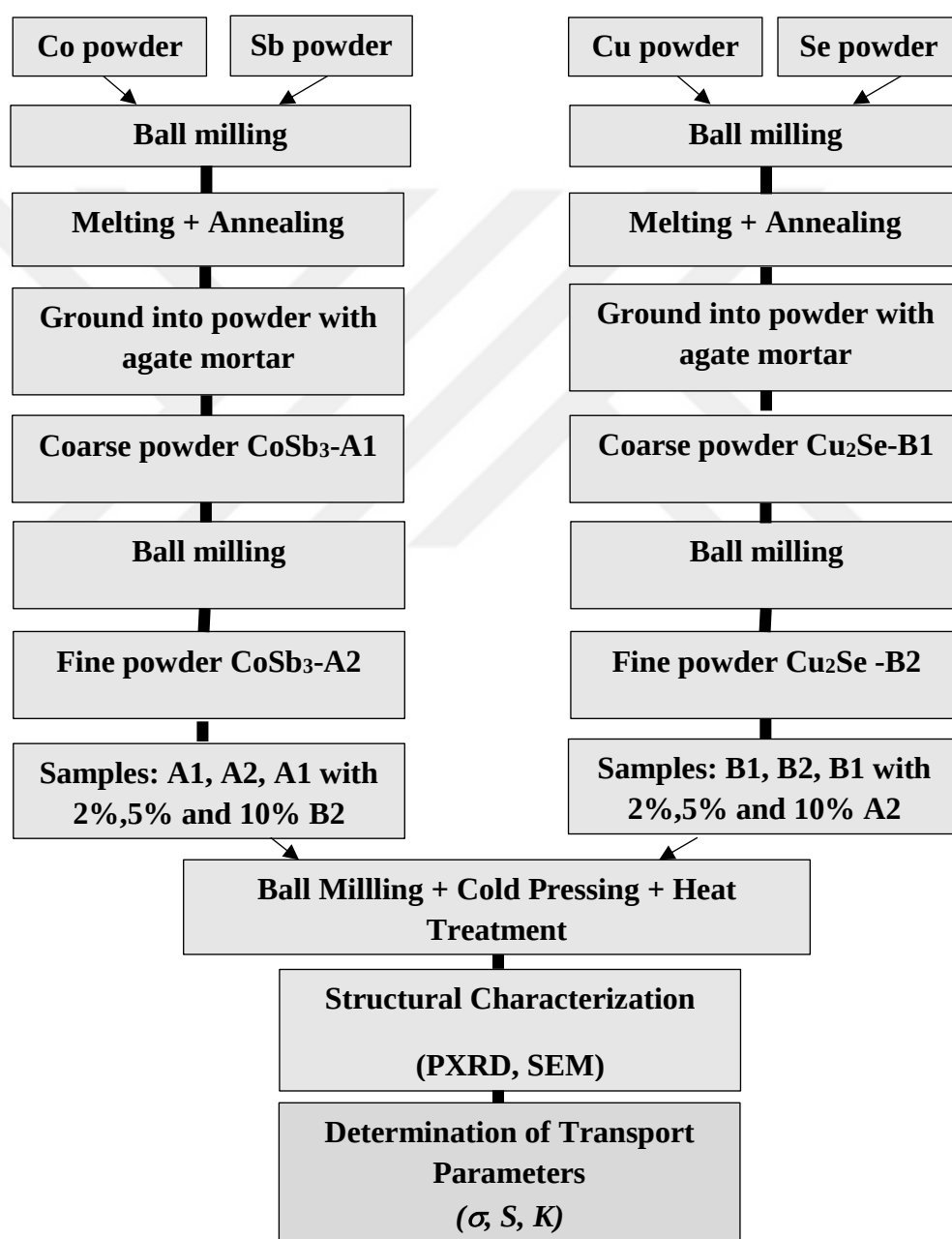


Figure 4. 1 : The flow chart of experimental steps.

There group samples were investigated according to the TE properties. The flow chart shows experimental steps of Group A and Group B. Group C samples were obtained from another research group for a comparison set for the TE properties. Details of the powder preparation (nano $\text{Fe}_{3.25}\text{Co}_{0.75}\text{Sb}_{12}$ and nano Cu_{2-x}Se) were mentioned in references [86][95]. Powder samples of Group C were densified by this group with the following conditions; 450 °C for 15 minutes under 50 MPa pressure with SPS system.

Group	Sample Code	Samples
G R O U P A	C- CoSb_3	Coarse Powder CoSb_3
	F- CoSb_3	Fine Powder CoSb_3
	CoSb_3 2% Cu_2Se	Coarse Powder CoSb_3 with 2% fine Powder Cu_2Se
	CoSb_3 5% Cu_2Se	Coarse Powder CoSb_3 with 5% fine Powder Cu_2Se
	CoSb_3 10% Cu_2Se	Coarse Powder CoSb_3 with 10% fine Powder Cu_2Se
G R O U P B	C- Cu_2Se	Coarse Powder Cu_2Se
	F- Cu_2Se	Fine Powder Cu_2Se
	Cu_2Se2% CoSb_3	Coarse Powder Cu_2Se with 2% Fine Powder CoSb_3
	Cu_2Se5% CoSb_3	Coarse Powder Cu_2Se with 2% Fine Powder CoSb_3
	Cu_2Se10% CoSb_3	Coarse Powder Cu_2Se with 2% Fine Powder CoSb_3
G R O U P C	nano $\text{Cu}_{1.8}\text{Se}$	nano $\text{Cu}_{1.8}\text{Se}$
	nano Cu_2Se	nano Cu_2Se
	nano Cu_2Se 2% FeCoSb	nano Cu_2Se with 2% nano FeCoSb
	nano Cu_2Se 5% FeCoSb	nano Cu_2Se with 5% nano FeCoSb

Figure 4. 2 : The examined samples as per group.

4.1. Samples Synthesis

4.1.1. Synthesis micron coarse Cu_2Se and CoSb_3

The powder form of Co, Sb, Cu and Se (99.99% purity-Sigma Aldrich) were mixed according to their stoichiometric ratio to get CoSb_3 and Cu_2Se . All steps carried out in the glove box which is filled with inert gases and oxygen level around 0.1 ppm given as Figure 4.3-(a). To get homogeneous composition, the ball mill was used at 200 rpm, one hour and ball to powder ratio was 5 as shown in Figure 4.3-(b). The ball mill jars were sealed and opened at glove box for avoiding any contamination during synthesising of samples.

The prepared samples were placed in a quartz tube and sealed under vacuum remains at least twenty minutes at 10^{-2} Torr to remove oxygen and avoid any oxidation during the sealing step. Figure 4.3-(c) represent the sealing mechanism. Propane and oxygen gases were used for sealing the quartz tubes. Then the sealed samples were loaded a box furnace which is shown in Figure 4.3 (d). The furnace was heated slowly up to 1100°C ($1^\circ\text{C}/\text{minute}$), held at 1100°C at 10 hours, cooled down at 800°C ($4^\circ\text{C}/\text{minute}$) held at 800°C 144 hours. Then the furnace was naturally cooled down at room temperature. The as-prepared powders were ground into fine powder using an agate mortar.

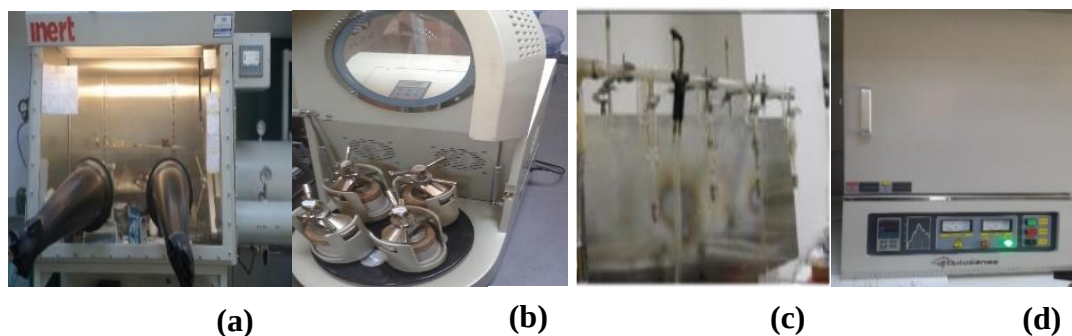


Figure 4. 3 : (a)-glove box, (b)-ball mill machine, (c)-sealing system, (d)-box furnace.

4.1.2. Synthesis of sub micron Cu_2Se and CoSb_3 with ball milling

The fine powder samples were prepared from coarse powder CoSb_3 and Cu_2Se compound. For reducing the dimension planetary ball mill was used at 400 rpm and 2 hours and ball powder ratio was 5. To avoid any contamination all steps were carried out in the glove box.

The substituting step was conducted according to the percentage ratio of group A and group B samples obtained. This step was carried out in the glove box. After substituting to get homogenous composition ball mill was used at 200 rpm 1 hour.

4.2. Samples Compaction

Group A and Group B all powder samples were pressed at 350 MPa in a rigid cylindrical container which radius is 12.7 mm and 2mm thickness, by using hydraulic press given as Figure 4.4-(a). After cold pressing, heat treatment was conducted at inert gases medium (Ar) by using a tube furnace given in Figure 4.4-(b). The samples were heated up to 600°C within 2 hours. Then furnace naturally cooled down to room temperature.

Group A and Group B samples were cut into disc and rectangular bar shapes with cutting machine for high temperature transport measurements. Archimedes law was used to determine the density.

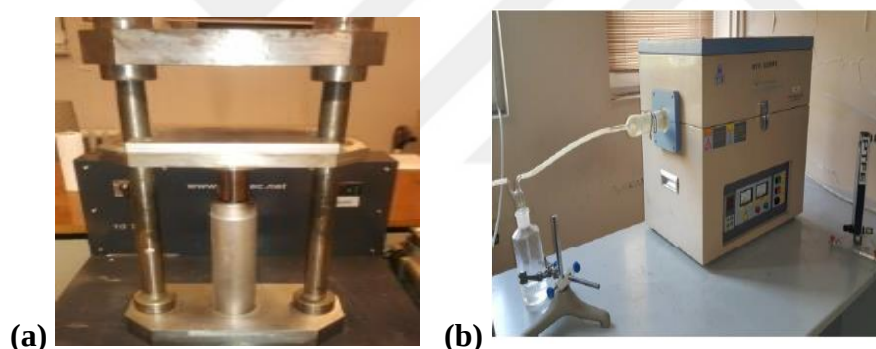


Figure 4. 4 : Hydraulic press-(a), (b)-tube furnace.

4.3. Characterization Methods

4.3.1. Structural and morphological analysis

The particle size of powder chemicals was measured in Malvern Mastersizer Laser particle size analyser Figure 4.5-(a). The particle size of fine powder samples was determined by Nano Flex particle size analyser given in Figure 4.5-(b).



Figure 4. 5 : (a) and (b) particle size analysers.

Phase analysis of the samples were characterised by using X-ray Diffractometer as shown in Figure 4.6 with $\text{CuK}\alpha$ ($\lambda = 0,154 \text{ nm}$) radiation in the 2θ range of 20° - 60° steps at rate of 2° .



Figure 4. 6 : X-Ray diffraction system.

To realize microstructural characterization of samples Scanning Electron Microscope (SEM) was used as shown in Figure 4.7. The microstructural properties of all samples were determined from the fractured surface.



Figure 4. 7 : Scanning electron microscope (SEM).

4.3.2. Determination of Transport Parameter

Four probe method is used to determine the resistivity of the samples. In other words, current is applied ends of the sample to determine the voltage drop between the same wires of thermocouple. The sample placed within the copper blocks that is a bar shaped with 2-3 mm width and 10-12 mm height [16], [22], [96].

$$\sigma = \frac{1}{\rho} = \frac{l}{R \cdot A} \quad (4.1)$$

The electrical conductivity is inversely proportional to resistivity of material that is given in equation (4.1) here σ electrical conductivity, ρ resistivity, l the space between the thermocouple, R resistance and A area of sample.

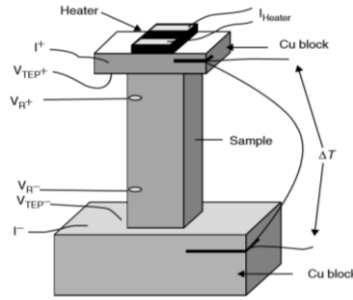


Figure 4. 8 : Experimental setup for Seebeck and resistivity measurement [16].

4.3.2.2. Seebeck coefficient

A sample is set in a vertical position between the upper and lower copper blocks in the heating furnace. While the sample is heated at a specified temperature, the temperature gradient occurs, owing to heater at lower block. Seebeck coefficient is measured by measuring the upper and lower temperatures T_1 and T_2 with the thermocouples pressed against the side of the sample in order to generate electromotive force. An experimental setup can be established same device which is shown in Figure 4.8 [16], [22], [96]. In laboratory the Seebeck coefficient and resistivity measured with same device Ulvac ZEM-3 that were given in Figure 4.9.



Figure 4. 9 : Measurement of resistivity and Seebeck coefficient.

4.3.2.3. Thermal conductivity

Laser flash thermal diffusivity (LFTD) method is used for measured thermal properties of samples. The LFTD method measure both thermal diffusivity and specific heat of sample. For suitable measurement sample should be disc shaped with around 6.5 mm radius and 1 to 2 mm thickness. The working principle is that one side of sample is exposed with short laser pulse and the temperature rise of the opposite side of the sample is recorded by detector. Then thermal conductivity is calculated from $K = \rho \cdot a \cdot C_v$. Here a thermal diffusivity, K thermal conductivity, ρ density of samples and C_v specific heat of sample. The thermal diffusivity and specific heat of samples were measurement via Linsesis LFA device that were given in Figure 4.10. Sample surfaces are coated with graphite to make them highly absorptive and emissive [16], [22], [96].



Figure 4. 10 : Equipment used for thermal diffusivity and specific heat determination.



5. RESULT AND DISCUSSION

The mean particle size of starting chemicals Co, Sb, Cu and Se were measured at 142 μm , 62,6 μm , 192 μm and 106 μm respectively. The mean particle size of the fine powder A2 and B2 were measured as 520 nm and 620 nm.

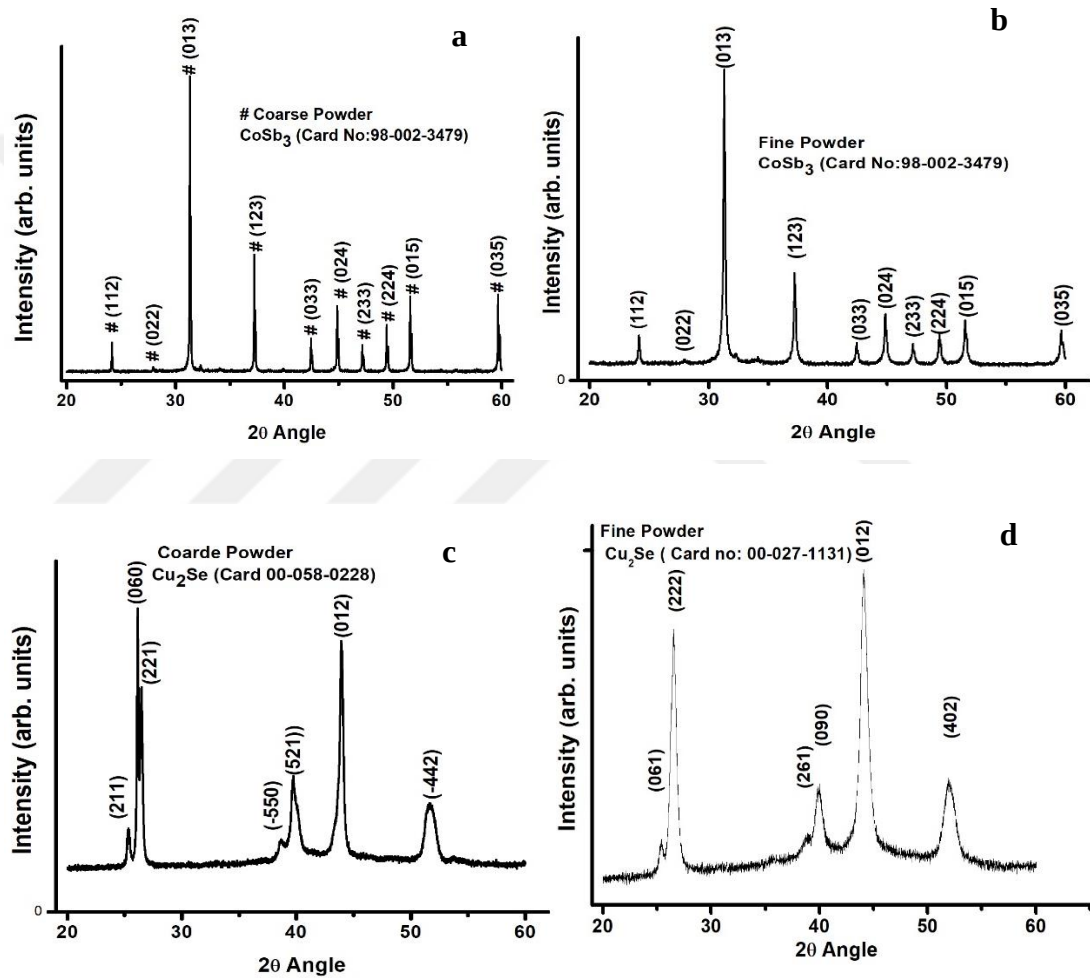


Figure 5. 1 : PXRD patterns of A1-(a), A2-(b), B1-(c) and B2-(d).

The PXRD diffraction patterns of the samples A1, A2, B1, B2 were given in Figure 5.1. The diffraction peaks of A1 and A2 are consistent for the characteristic positions of materials, showing cubic structure. The diffraction patterns of B1 and B2 samples exhibit the same diffraction peaks according to the pdf card, showing monoclinic structure.

5.1. Coarse Powder Cobalt Antimony with Fine Powder Cu₂Se (Group-A)

5.1.1. Structural analysis

The PXRD patterns of Group A samples were given in Figure 5.2. The patterns show identical diffraction peaks of skutterudite as well as secondary phase of CoSb₂. The Group A samples were formed from A1, A2 and A1 with 2%, 5% and 10% B2 powder samples. These powder samples were densified with the following parameters; one-hour ball milling, cold pressing and heat treatment. The CoSb₂ phase may have formed during these experimental steps.

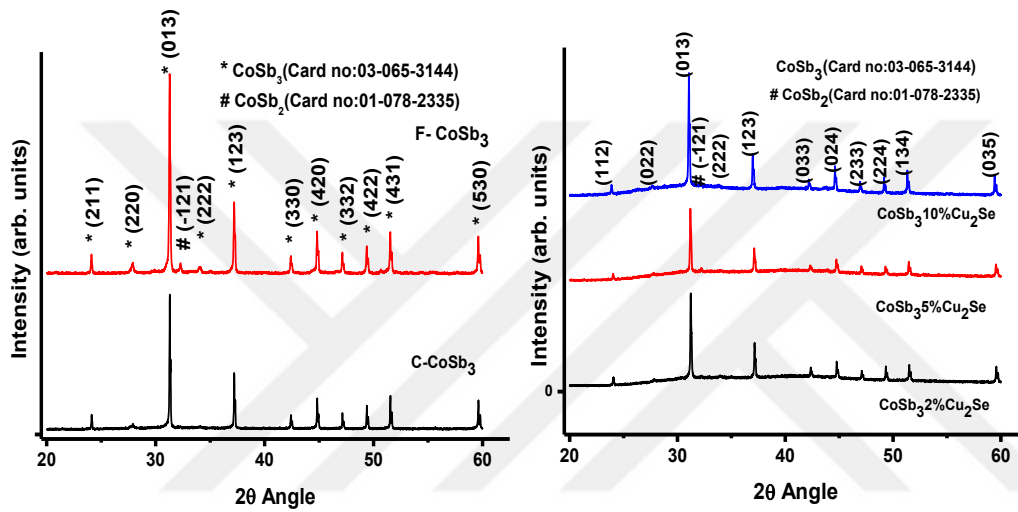
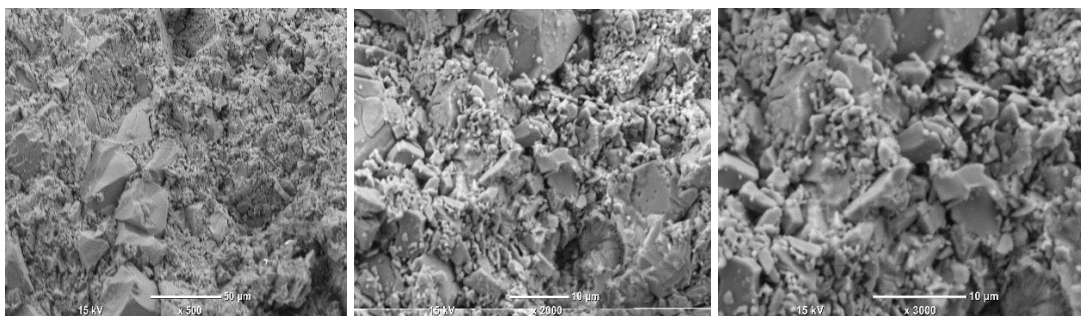
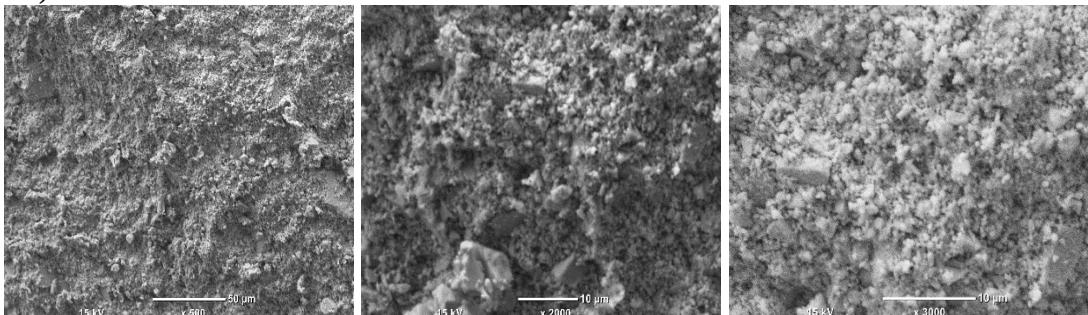


Figure 5. 2 : PXRD patterns of Group A samples.

Figure 5.3 shows the SEM images of group A samples at different magnifications.



a)



b)

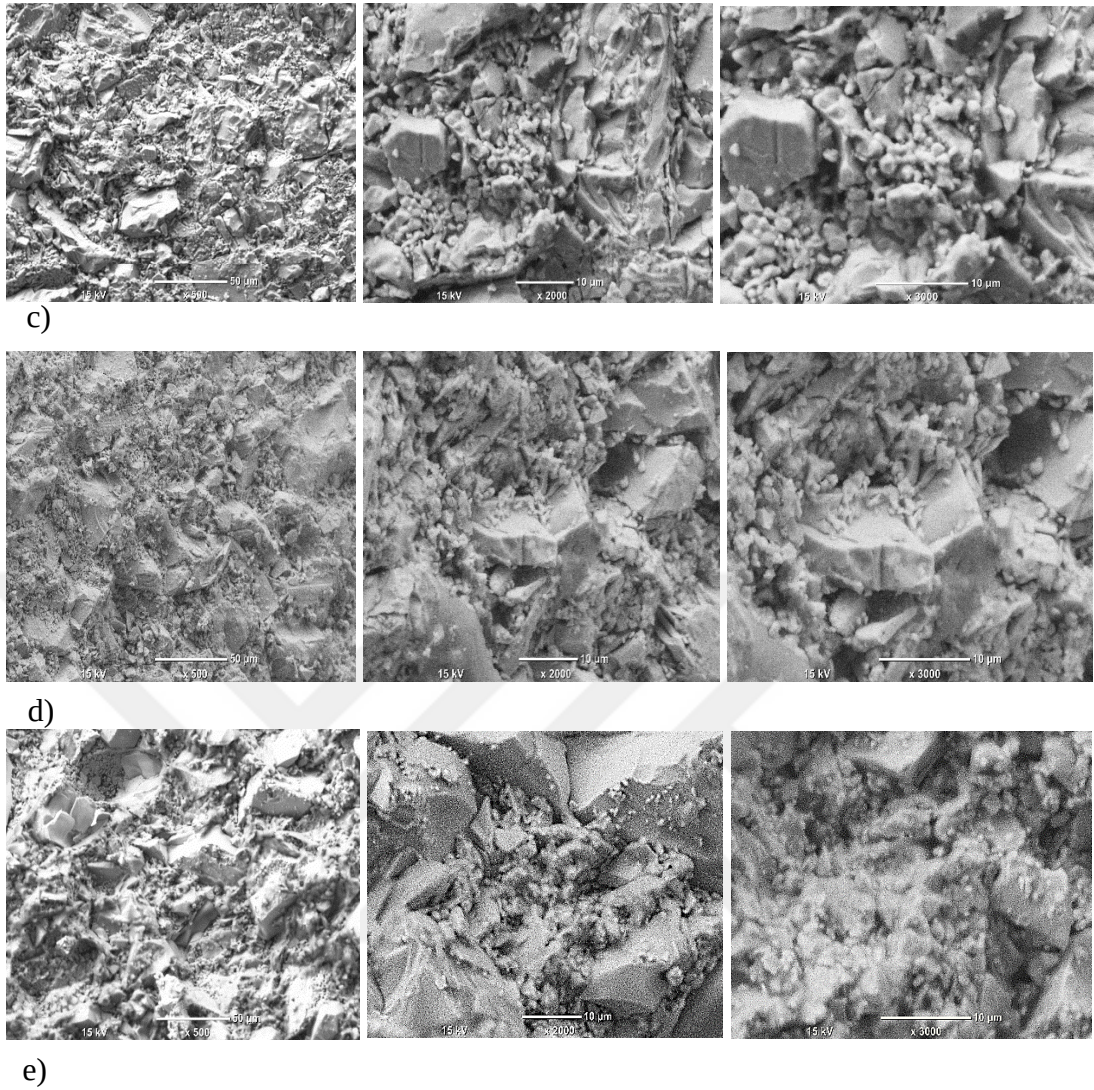


Figure 5. 3 : The SEM images of (a) C- CoSb_3 , (b) F- CoSb_3 , (c) CoSb_3 2% Cu_2Se , (d) CoSb_3 5% Cu_2Se , (e) CoSb_3 10% Cu_2Se , respectively.

When the SEM images of (b) F- CoSb_3 were examined, it was observed which composed of smaller particle compared to the (a) C- CoSb_3 . The SEM images of doped samples are given in Figure 5-(c), (d) and (e). It was observed that the addition of Cu_2Se led to the crystallization and as well the grain size grows compared to the C- CoSb_3 and F- CoSb_3 . It should be seen that fine particles are in existence among with coarse particles for doped samples.

5.1.2. Transport data

5.1.2.1. Electrical conductivity and Seebeck coefficient

Figure 5.4 shows the plot of electrical conductivity (a) and Seebeck coefficient (b) as a function of temperature. As seen in the electrical conductivity vs temperature graph,

Group A samples behave as semiconducting material, increase with increasing temperature. The highest electrical conductivity value in the group was observed for the CoSb₃10% Cu₂Se sample.

Figure 5.4-(b) shows the Seebeck coefficient of samples vs temperature. The positive sign of Seebeck coefficient shows dominance of holes in conductivity. C- CoSb₃ and F- CoSb₃ show p-type electrical conductivity. The conductivity type can be change with synthesising method, amount of Sb or point defects. It is seen from graph doped samples with Cu₂Se show n-type electrical conductivity up to 450 K for 5% and 10% doped samples and 475K for 2% sample. In other words, electrons are the dominance charge carriers up to these temperature. However beyond this temperature is seen the changing in conductivity transform to p-type. The group samples showed nearly same Seebeck coefficient with 100 μ V/K at 675 K.

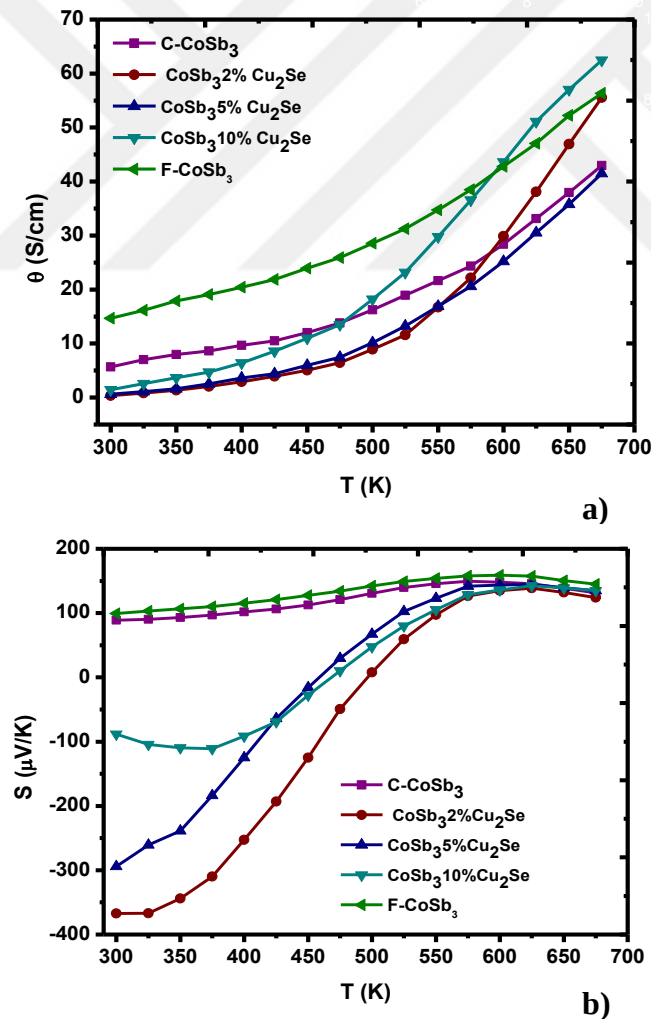


Figure 5. 4 : The electrical conductivity (a) and the Seebeck coefficient (b) of Group A samples.

5.1.2.2. Thermal conductivity

The thermal conductivity of group samples was given in Figure 5.5. When the thermal conductivity data was examined, the thermal conductivity value of all doped samples was found lower than the C- CoSb₃ sample but also higher than the F- CoSb₃ except CoSb₃5% Cu₂Se sample. The lowest thermal conductivity value in group was obtained for the CoSb₃5% Cu₂Se sample with 0.88 W/m-K at 675 K.

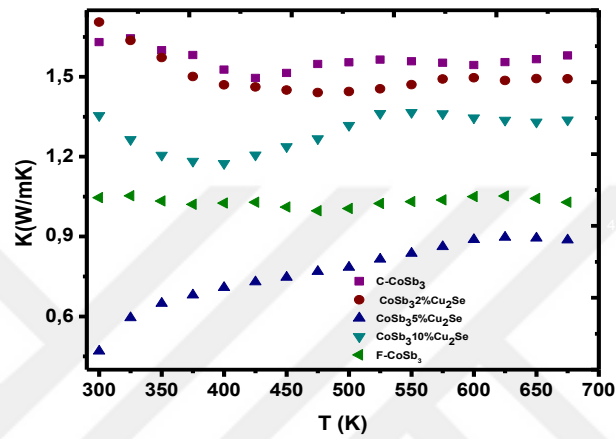


Figure 5. 5 : The total thermal conductivity of all Group A samples.

5.1.2.3. Power factor and ZT

The power factor (PF) and figure of merit (ZT) value of the group samples versus the temperature are given in Figure 5.6-(a) and (b), respectively.

The power factor was calculated with electrical conductivity combined with Seebeck coefficient, achieves 1.88 μ W/ (m-K²) at 675 K for F- CoSb₃. However, when all doped samples are examined, the PF value obtained is found to be lower than the F- CoSb₃ sample. The PF value of CoSb₃ 5% Cu₂Se sample was found equal to the C- CoSb₃ sample.

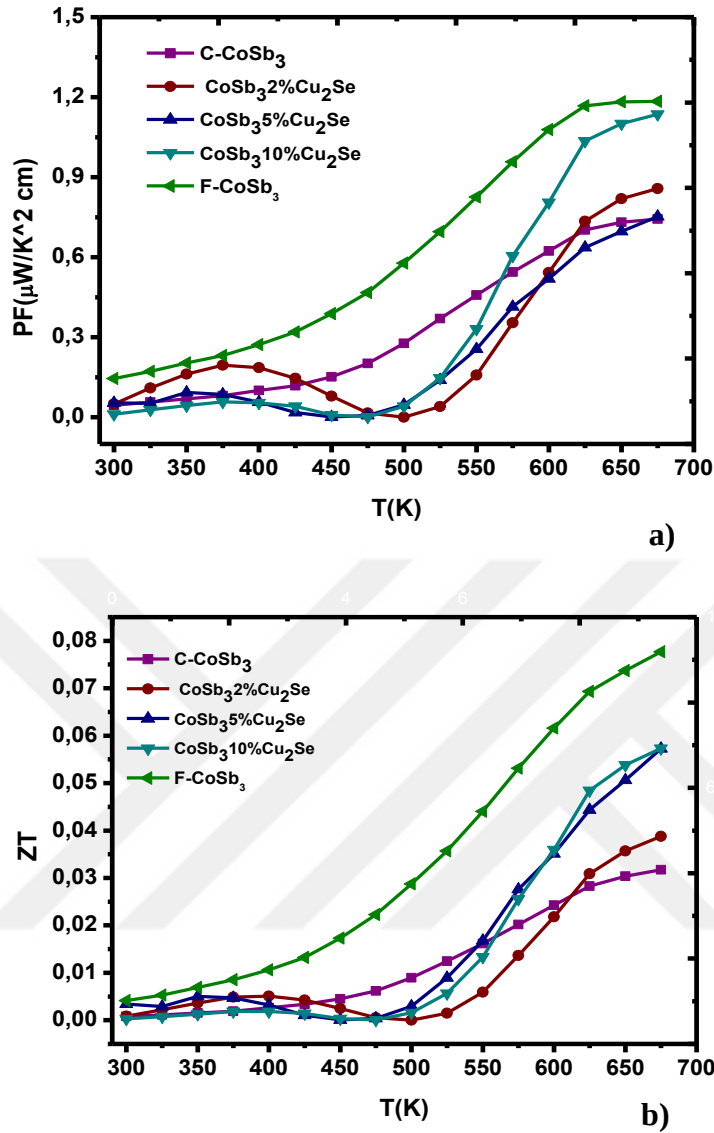


Figure 5. 6 : Power factor (a) and the ZT value (b) of group A samples.

When the ZT value of the samples was examined, all group A samples showed almost same ZT value at room temperature. While C-CoSb₃ and CoSb₃5% Cu₂Se samples showed the same PF value, thanks to the lower thermal conductivity of CoSb₃5% which was observed the higher ZT value with 0.065 at 675 K than C-CoS₃. This ZT value was the same for CoSb₃10% Cu₂Se sample. The ZT value of doped group samples was found higher than the C- CoSb₃ sample, however, lower than the F- CoSb₃ sample. The highest ZT value was observed for the C- CoSb₃ sample with 0.08 at 675 K.

5.2. Coarse Powder Copper Selenide with Fine Powder CoSb₃ (Group B)

5.2.1. Structural analysis

The PXRD patterns of Group B samples were given in Figure 5.2. The patterns show identical diffraction peaks of copper selenide, as well as the Cu₃Se₂ phase was observed.

More detailed microstructural observations were performed by SEM analysis of the samples. The SEM images of group B samples at different magnifications were given in Figure 5.8. When SEM images of (a) C- Cu₂Se was analysed, the porous structure was observed. The porous structure can be due to evaporation of Se or Cu₂Se during heat treatment time[85].

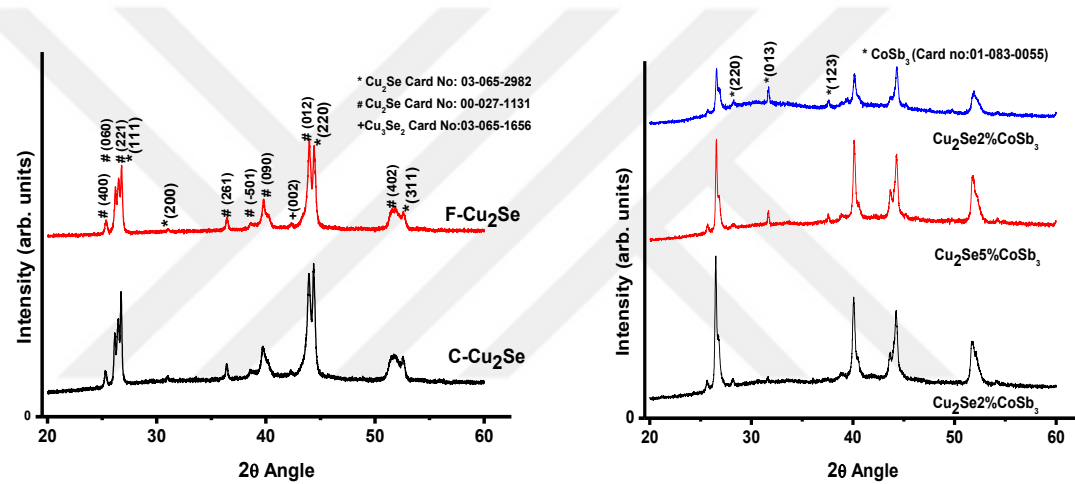
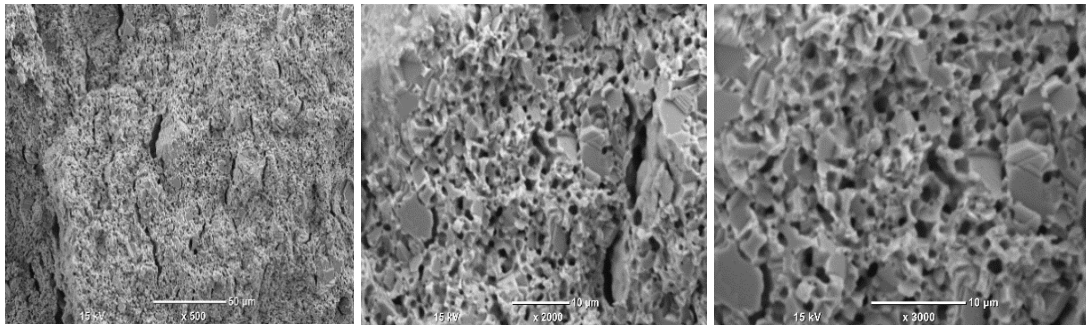
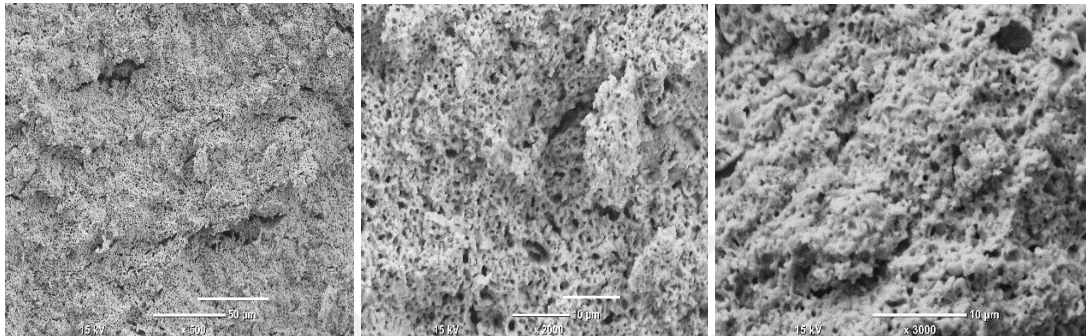


Figure 5. 7 : PXRD pattern of group B samples.

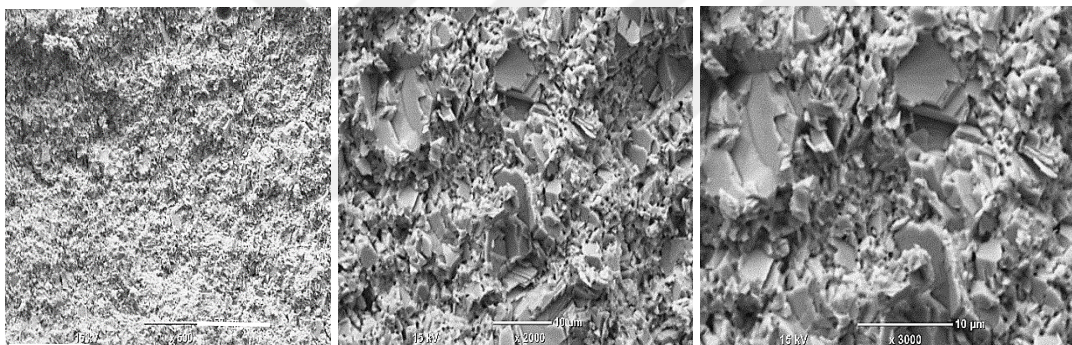
The grain size of this sample appears between 2 μm to 5 μm. The F- Cu₂Se sample was composed of tinier particle compared to the (a) C- Cu₂Se sample. The doped samples images were given in (c), (d) and (e). The addition of CoSb₃ led to the disappearance of the porous structure as well as crystallinity. Another point was that larger grains were observed for doped samples compared to the (a) C- Cu₂Se sample and (b) F- Cu₂Se sample.



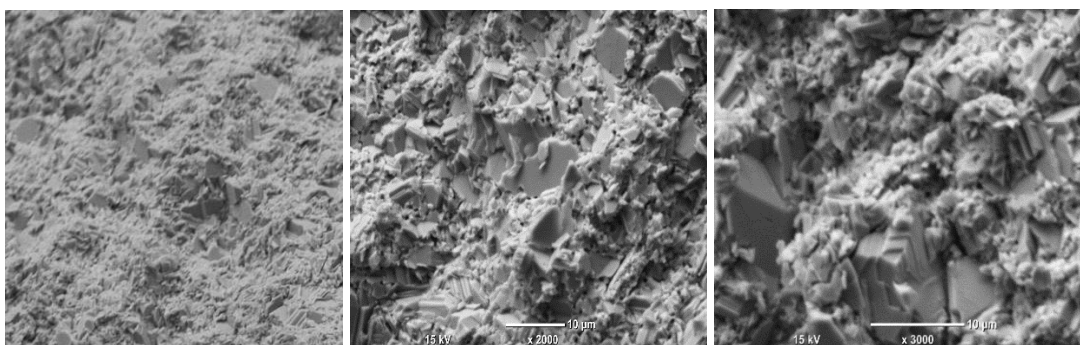
a)



b)



c)



d)

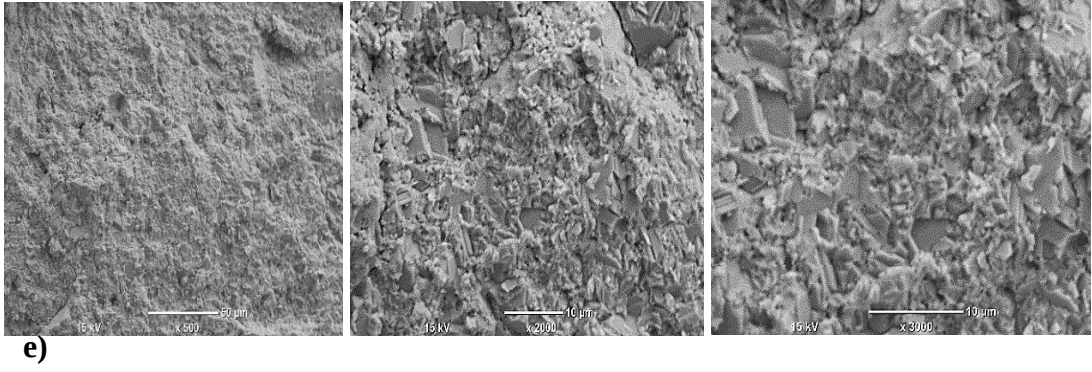
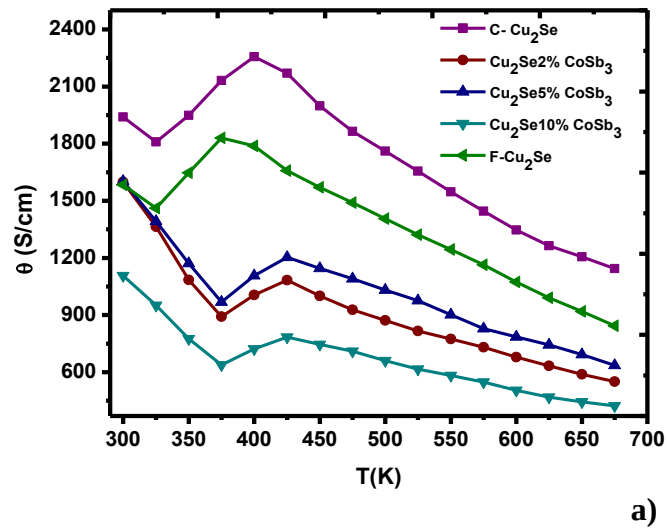


Figure 5. 8 : PXRD pattern of (a)C-Cu₂Se, (b) F-Cu₂Se, (c) Cu₂Se2% CoSb₃, (d) Cu₂Se5%CoSb₃ ,(e) Cu₂Se10% CoSb₃ respectively.

5.2.2. Transport data

5.2.2.1. Electrical conductivity and Seebeck coefficient

Figure 5.9 shows the plot of electrical conductivity and Seebeck coefficient as a function of temperature. As seen in the electrical conductivity vs temperature data (Figure 5.9a) all Group B samples behave as typical heavily doped semiconductors. The highest electrical conductivity value in the group samples was observed for the C-Cu₂Se sample. Due to decreasing in the concentration of charge carrier, the lowest electrical conductivity was found Cu₂Se 10% CoSb₃ sample. It was observed that all doped samples in the group has lower electrical conductivity than C- Cu₂Se and F-Cu₂Se.



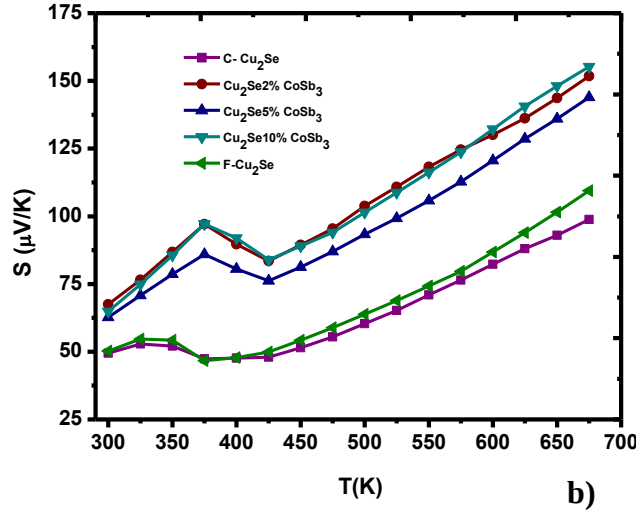


Figure 5. 9 : Electrical conductivity (a) and the Seebeck coefficient (b) of all group b samples.

Figure 5.9-b indicates the Seebeck coefficient of samples vs temperature. The positive sign of Seebeck coefficient shows dominance of holes in conductivity. The inverse relation between electrical conductivity and Seebeck coefficient obviously seen from graph.

Cu_2Se show a phase transition at around 400 K. This behaviour affects the transport properties. It was observed that the electrical conductivity of doped samples in the group decreased at the transition temperature, while C- Cu_2Se and F- Cu_2Se samples increase. The opposite relationship was seen for the Seebeck coefficient. While the Seebeck coefficient of all doped samples in the group increased at transition temperature, it was seen decreasing for Cu_2Se and F- Cu_2Se samples. The highest Seebeck coefficient value was observed for the Cu_2Se 10% CoSb_3 sample nearly 160 $\mu\text{V/K}$ at 675 K.

5.2.2.2. Thermal conductivity

The thermal conductivity of all Group B samples is given Figure 5.10. While thermal conductivity of Cu_2Se 10% CoSb_3 is $\sim 1.76 \text{ W/(m-K)}$ at phase transition temperature, decreases to 1.22 W/(m-K) at 675 K. Samples that doped 2% and 5% show nearly same thermal conductivity value 1.17 W/(m-K) and 1.16 W/(m-K) respectively. It is clearly seen from the thermal conductivity graph that all doped samples have lower thermal conductivity than F- Cu_2Se and C- Cu_2Se .

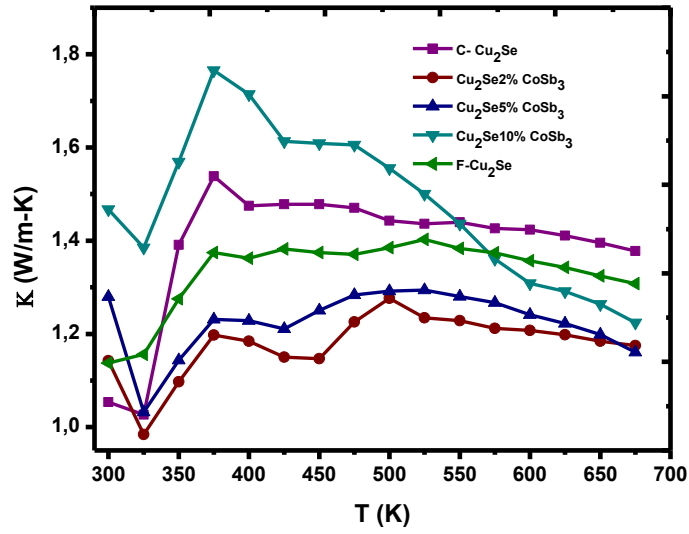
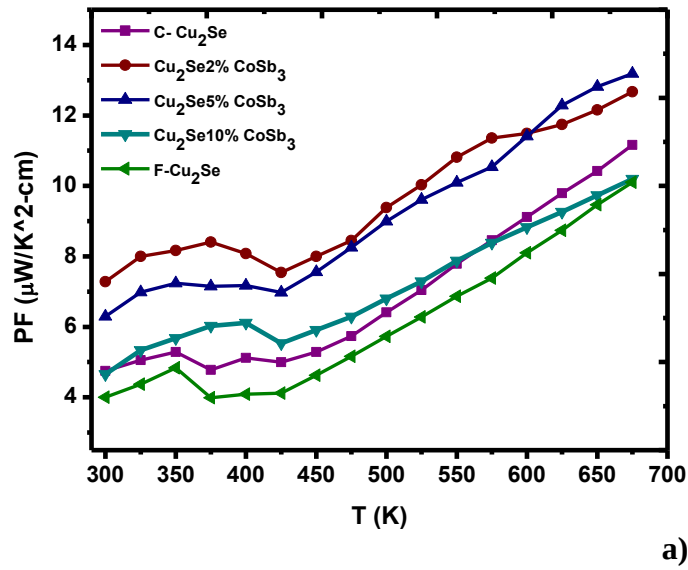


Figure 5. 10 : Total thermal conductivity of all group B samples.

5.2.2.3. Power factor and ZT

The power factor (PF) and figure of merit (ZT) value of all samples versus the temperature are given in Figure 5.11-(a) and (b), respectively.

The power factor was calculated with electrical conductivity combined with Seebeck coefficient, achieves $13 \mu\text{W}/(\text{m}\cdot\text{K}^2)$ at 675 K for Cu_2Se 5% CoSb_3 . However, when all samples were examined, the PF value of doped sample was found to be equal to or higher than the C- Cu_2Se and F- Cu_2Se samples.



a)

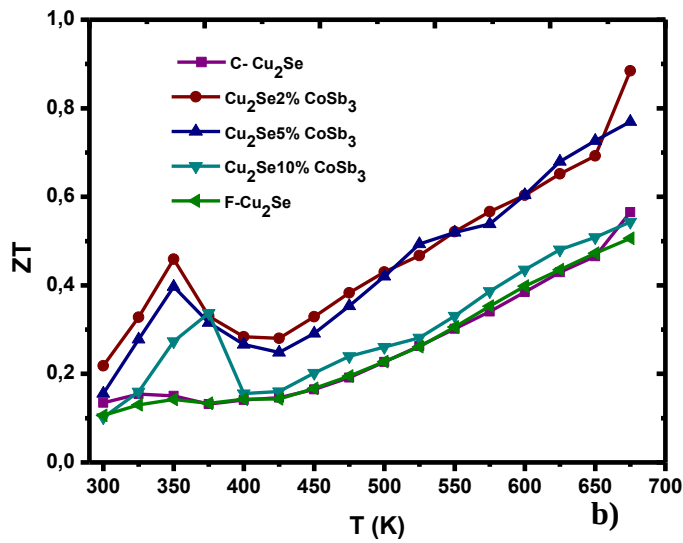


Figure 5. 11 : Power factor (a) and ZT value (b) of Group B samples.

When the ZT value of the samples are examined, doped samples show higher ZT value than the C- Cu₂Se and F- Cu₂Se samples. Though the 2 % and 5% doped samples show nearly same power factor value, but 2 % doped sample shows higher ZT value of 0,9 at 675 K because of its lower thermal conductivity in compare to 5%. The finding results is consistent with literature data for ZT value of C- Cu₂Se at 675 K[85], [97].

5.3. Nano Copper Selenide with Nano FeCoSb (Group C)

5.3.1. Structural analysis

Figure 5.12 shows the PXRD patterns of Group C samples. Figure 5.12-(a) indicates the pattern of nano FeCoSb that is doped material. Diffraction peaks are consistent with main the structure of CoSb₃ (card no: 00-065-1791). As is seen in Figure 5.12(b) and (c), nano Cu_{1.8}Se has monoclinic, while nano Cu₂Se has orthorhombic crystal structure. There were not observed different any other major peaks rather than Cu_{1.8}Se and Cu₂Se samples. Figure 5.12(d) indicates the pattern of Cu₂Se with 5% nano FeCoSb. The same spectrum was obtained for Cu₂Se with 2% nano FeCoSb structure (not shown in here).

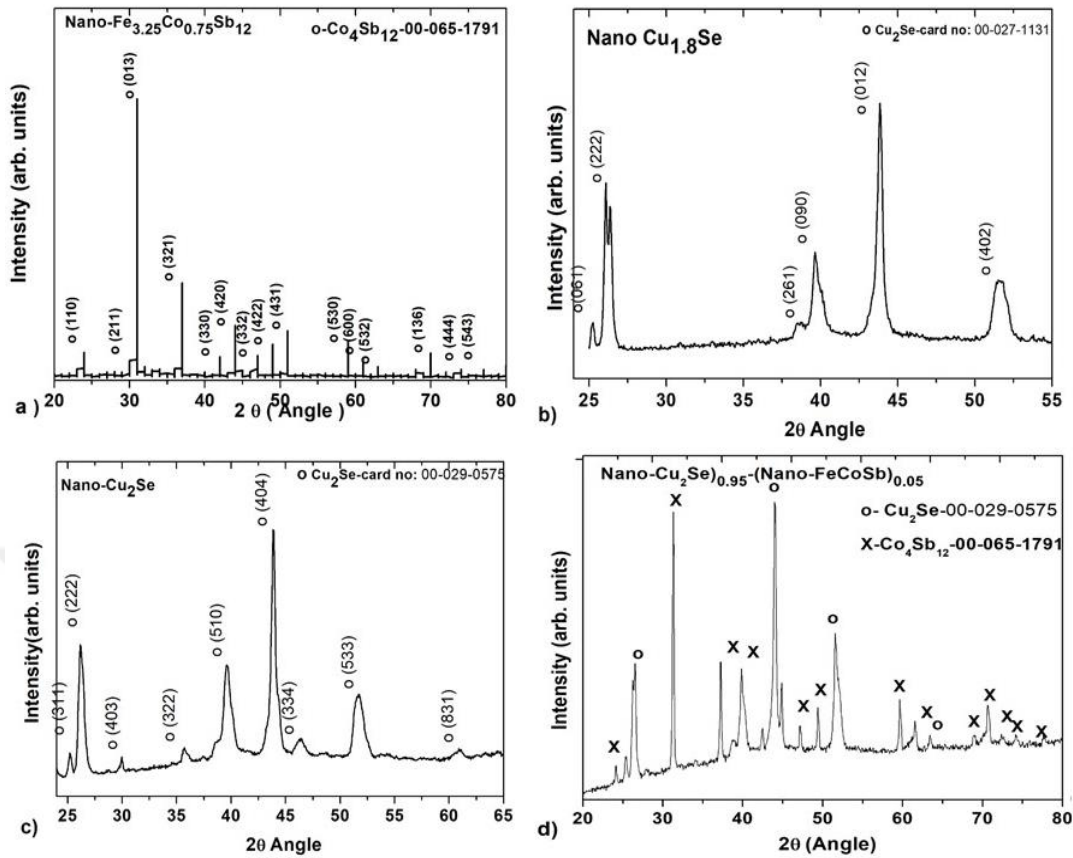


Figure 5. 12 : PXRD patterns of (a) nano FeCoSb, (b) nano- $\text{Cu}_{1.8}\text{Se}$, (c) nano- Cu_2Se and (d) nano- Cu_2Se -%5 nano FeCoSb.

More detailed microstructural observations were performed by SEM analysis of the samples. Figure 5.13- shows the SEM image of the nano (a) ,nano Cu_2Se (b), Cu_2Se %2FeCoSb(c) and Cu_2Se %5FeCoSb (d) at different magnification. SEM images of nano $\text{Cu}_{1.8}\text{Se}$ shows, the sample has crystalline structure. The crystal size appears to around 500 nm and below. The SEM images of nano Cu_2Se shows (Figure 5.12-b), unlike nano $\text{Cu}_{1.8}\text{Se}$ sample, the crystal sizes are larger and appears around 1 μm and below. It can be said that both samples include irregular shape. As seen in SEM images of Cu_2Se %2FeCoSb (Figure 5.12(c)) and Cu_2Se %5FeCoSb (Figure 5.13(d)), there are two distinct phases in the samples that as marked Region 1 and Region 2. For both samples the grains size of Region 2 larger than the Region 1. It can be said, both samples do not have a certain orientation and regular shape.

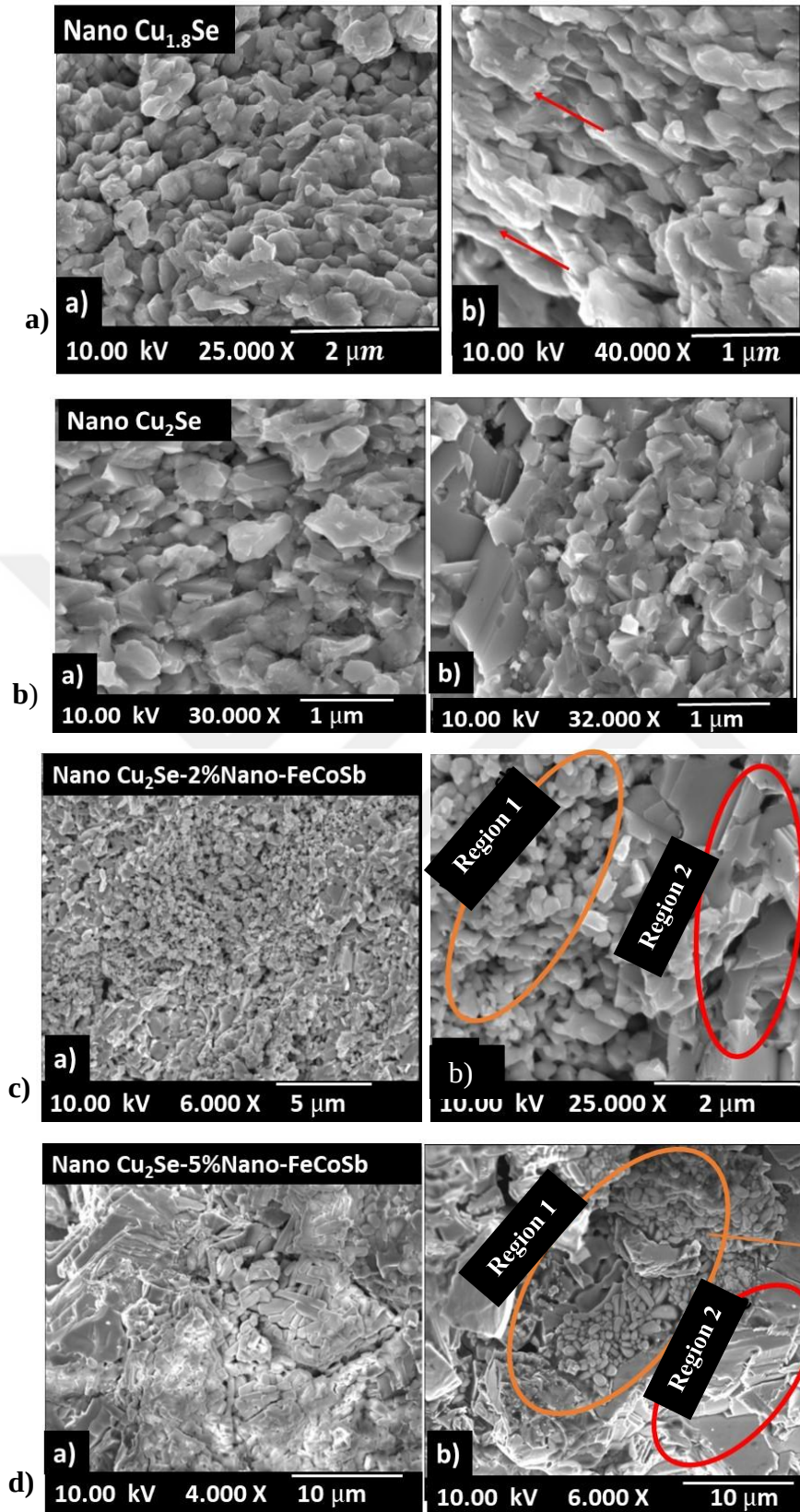


Figure 5. 13 : SEM images of (a) nano $\text{Cu}_{1.8}\text{Se}$, (b) nano- Cu_2Se , (c) nano Cu_2Se 2% FeCoSb and (d) nano- Cu_2Se -%5 FeCoSb.

5.3.2 Transport Data

5.3.2.1. Electrical conductivity and Seebeck coefficient

Figure 5.14 shows the plot of electrical conductivity-(a) and Seebeck coefficient-(b) as a function of temperature.

As seen in the electrical conductivity vs temperature data (Figure 14(a)), all samples behave as typical heavily doped semiconductors. The highest electrical conductivity value was observed for the nano $\text{Cu}_{1.8}\text{Se}$ sample. The doped samples in group C showed lower electrical conductivity than nano $\text{Cu}_{1.8}\text{Se}$ and nano Cu_2Se . So it can be said, the contribution of FeCoSb led to a decrease in electrical conductivity.

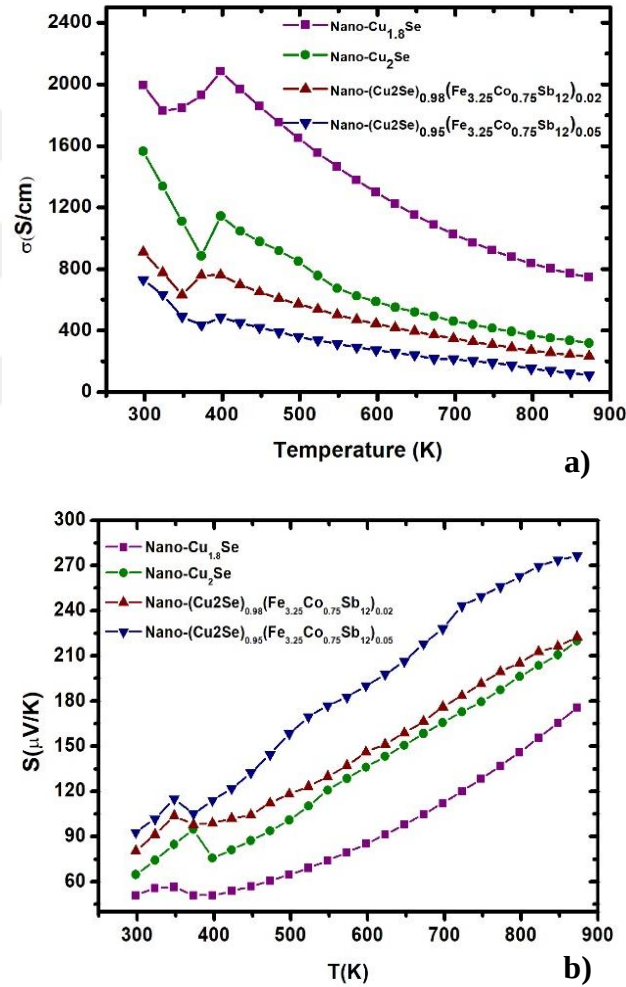


Figure 5. 14 : Electrical conductivity (a) and Seebeck coefficient (b) of group C samples.

Figure 5.14-(b) shows the Seebeck coefficient of group C samples as a function of temperature. The positive sign of the Seebeck coefficient shows the dominance of holes in the charge carrier transport. Also, the increase in Seebeck coefficient, due to

FeCoSb contribution, show that charge balance in structure is maintained. In other words, the increase in the Seebeck coefficient with the FeCoSb addition is due to the strongly charged carrier scatterings in samples. Since the temperature dependence of the Seebeck coefficient is generally opposite to the electrical conductivity. Because of this, the lowest and the highest Seebeck coefficient was found for the nano $\text{Cu}_{1.8}\text{Se}$ sample and the nano Cu_2Se 5% FeCoSb sample, respectively.

5.1.2.2. Thermal conductivity

The thermal conductivity of all sample is given in Figure 5.15-(a) and except $\text{Cu}_{1.8}\text{Se}$ in Figure 5.15-b. While thermal conductivity of nano $\text{Cu}_{1.8}\text{Se}$ is $\sim 3.5 \text{ W/(m-K)}$ at room temperature, decreases to 0.9 W/(m-K) at 900 K. This excessive decrease in thermal conductivity can be explained by micro structural properties of this sample.

As seen from the SEM image (Figure 5.13-a), this sample is composed of crystals of smaller size (vary between 500 nm and below). Thus, phonon scattering at grain boundaries more powerful than electron scattering. Therefore, phonon boundary scattering increases due to increasing phonon density with increasing temperature. The low thermal conductivity value of nano Cu_2Se sample is thought to be due to different sized structures (irregular shape) as is seen Figure 5.13-(b). In other words, since different size of nano crystals form interfaces and boundaries of different widths, this cause heat-carrying phonon scattering of different energy (having different wavelengths, leading to further thermal conductivity to fall [98]–[100]. The thermal conductivity behaviour of these samples was also similar to FeCoSb doped samples. If the homogeneous distribution in the samples had been achieved, it is possible to say that the phonon scattering would be more powerful than the charge carrier scattering, thus further reducing the thermal conductivity value.

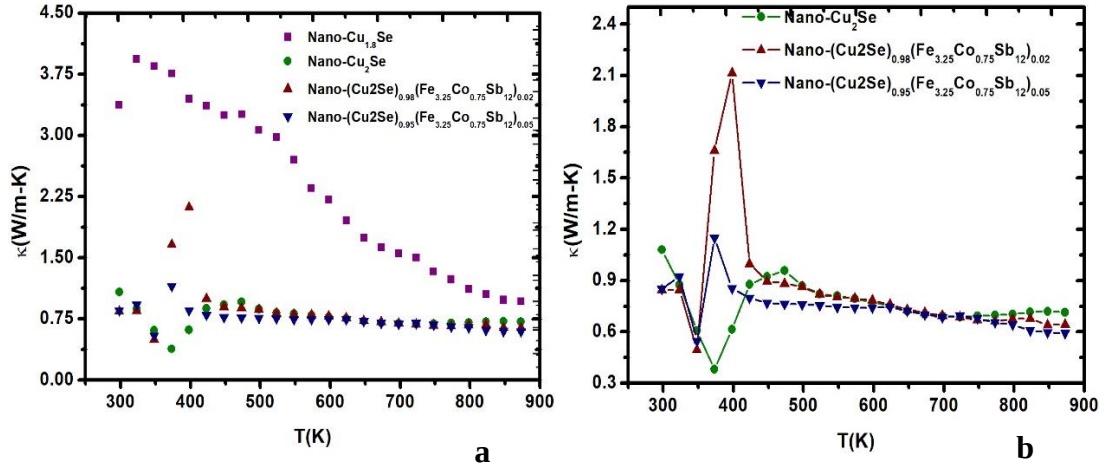


Figure 5. 15 : Thermal diffusivity (a), thermal conductivity (b) for all samples and thermal conductivity except nano $\text{Cu}_{1.8}\text{Se}$.

5.2.1.3. Power factor and ZT

The power factor (PF) and figure of merit (ZT) value of all samples versus the temperature are given in Figure 5.16-(a) and (b), respectively.

The power factor was calculated with electrical conductivity combined with Seebeck coefficient, achieves $24 \mu\text{W}/(\text{m}\cdot\text{K}^2)$ at 900 K for $\text{Cu}_{1.8}\text{Se}$. Both doped samples in group C, However, when all samples are examined, the PF value obtained is found to be equal to or higher than the Cu_2Se samples.

When the ZT value of the samples are examined, except the 5% nano FeCoSb doped sample, the ZT value is higher than the micron Cu_2Se sample. Due to high power factor value of $\text{Cu}_{1.8}\text{Se}$ sample, $\text{ZT}=2.1$ is reached. This value is one of the highest ZT value obtained in this material group. The high ZT value in this sample is that nano particle are smaller in size, relatively uniform distribution causing less scattering of charge carrier particles but strong scattering of the heat carrying phonons. Therefore, high ZT value was obtained due to decrease in thermal conductivity value without shifting in electronic properties. The ZT value of nano Cu_2Se sample reached 1.9 and is very close to the literature data. Seeing the same ZT values in the same compound prepared by the same method at different times is important in terms of demonstrating that the preparation technique and characterization are reproducible. The existence of different sizes nano structures in this sample allowed the scattering of the wider spectrum of phonons at different energy, thus result in significant reduction in the thermal conductivity that come from the lattice contribution. The ZT value of FeCoSb doped

sample is lower than the nano $\text{Cu}_{1.8}\text{Se}$ and nano Cu_2Se . The main reason for this is the deterioration of the electrical properties due to FeCoSb contribution and so excessive decrease of the electrical conductivity.

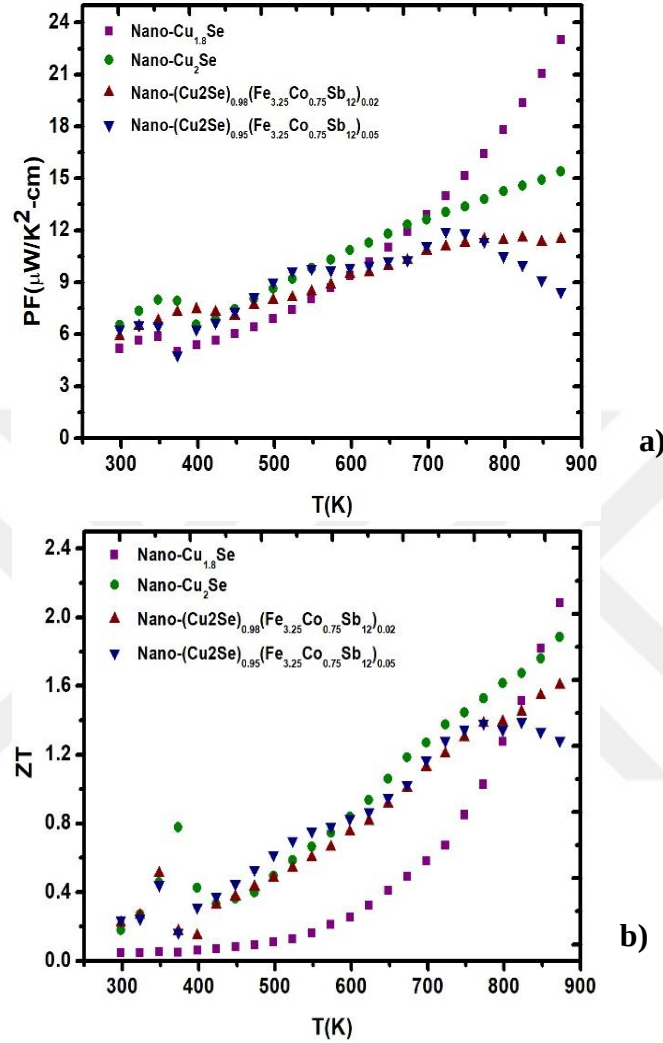


Figure 5. 16 : Power factor (a) and the ZT value (b) of Group C samples.

5.4.Discussion

As already mentioned, a good thermoelectric material should have high electrical conductivity, the high Seebeck coefficient, and low thermal conductivity. It can be achieved with more phonon scattering and less charge carriers particle scattering.

In group A, C- CoSb_3 and F- CoSb_3 , CoSb_3 with 2%, 5% and 10% Cu_2Se samples were synthesised.

The Seebeck coefficient found around 125 $\mu\text{V/K}$ and 145 $\mu\text{V/K}$ at 675 K for the C- CoSb_3 and F- CoSb_3 samples. However, there was not any significant change in the

Seebeck coefficient at room temperature to 675 K for both samples. Addition of Cu_2Se resulted in a change in conductivity type. It was observed n-type electrical conductivity up to 450 K for 5% and 10% doped samples and 475K for 2% sample. In other words, electrons are the dominant charge carriers up to this temperature. This situation can be explained with the phase transition of Cu_2Se around 400K. If examined the Seebeck coefficient graph given in Figure 5.4-b, the highest Seebeck coefficient was observed for the CoSb_3 2% Cu_2Se with 367 $\mu\text{V/K}$ at room temperature. The Seebeck coefficient decreased with increase in the amount of Cu_2Se . Also, it was found 294 $\mu\text{V/K}$ and 88 $\mu\text{V/K}$ at room temperature for the CoSb_3 5% Cu_2Se and CoSb_3 10% Cu_2Se samples. Doped samples in group A show nearly the same Seebeck coefficient that of C- CoSb_3 and F- CoSb_3 samples at 675 K. Therefore, it can be said that the lower thermal conductivity and higher electrical conductivity determines the ZT parameter. When examined ZT graph in Figure 5.6-b the highest ZT value was observed for the F- CoSb_3 sample with 0.08, nearly three times of C- CoSb_3 sample with 0.03 at 675 K. The difference between these samples, it can be seen from SEM image in Figure 5.3- (a) and (b) was particle size. One can be said, this situation affects the TE properties. Because of the preparation method of the sample determines the structural properties, applying a different method can result in different TE properties. The ZT value of CoSb_3 was found 0.035 at 650 K with arc melting method by Kawaharada et al. The study conducted by Zhang et al. examined the effect of sintering temperature, sintering time, ball milling time and particle size that of on the single-phase polycrystal CoSb_3 synthesised with solid-state reaction following by SPS system. The ZT value of this sample was found 0.095 at 673 K with grain size around 100 nm. Thanks to low thermal conductivity, all doped samples in group A showed higher ZT value than C- CoSb_3 . It observed that the ZT value of CoSb_3 2% Cu_2Se and CoSb_3 5% Cu_2Se samples were 0,057 at 675 K and this value two times ZT value of C- CoSb_3 sample with 0,03 at 675K [101], [102].

In group B, C- Cu_2Se , F- Cu_2Se , Cu_2Se with 2%,5% and 10% CoSb_3 samples were synthesised.

SEM images of group B samples were given in Figure 5.8. The addition of CoSb_3 led to crystalline structure and disappearance of the porous structure. The aim of the addition of CoSb_3 , it was mentioned before, is that doped samples result in more phonon scattering and therefore, low thermal conductivity. The thermal conductivity

of all group B samples was given in Figure 5.10. While the thermal conductivity of Cu_2Se 10% CoSb_3 $\sim 1.76 \text{ W/(m-K)}$ at the phase transition temperature, decreases to 1.22 W/(m-K) at 675 K. This excessive decrease in thermal conductivity can be explained by microstructural properties of this sample. As seen from the SEM images (Figure 5.8-e), this sample includes smaller grain size contribution than other that of doped samples. Thus, phonon scattering at grain boundaries can be more powerful than electron scattering. Samples that doped 2% and 5% show nearly the same thermal conductivity value 1.17 W/(m-K) and 1.16 W/(m-K) respectively. It is seen from the thermal conductivity graph that all doped samples have lower thermal conductivity than C- Cu_2Se and F- Cu_2Se samples. When the ZT value of the samples was examined, CoSb_3 doped samples shows the ZT value is higher than the C- Cu_2Se and F- Cu_2Se samples. Though the 2 % and 5% doped samples nearly same power factor value, thanks to the lower thermal conductivity of 2 % doped sample have higher ZT with 0.9 at 675 K. The study conducted by Liu et al. the ZT value of Cu_2Se found nearly 0.6 at 650 K with melting followed by SPS method. Another study conducted by Shi et al. examined the effect of sintering temperature and time on the Cu_2Se that synthesised with the solid-state sintering following cold pressing. It found that 0.5 at 675 K for the samples sintered at 973 K-2 hours and 1173K-20 hour, while sintered at 1173 K 20-hour was 0.7 [11], [85].

In group C, thermoelectric behaviour of nano $\text{Cu}_{1.8}\text{Se}$, nano Cu_2Se , nano Cu_2Se with 2% and 5% FeCoSb analysed. SEM analysis indicates that nano $\text{Cu}_{1.8}\text{Se}$ has smaller grain size, homogeneous distribution in structure. The contribution of FeCoSb led to more phonon scattering as well as two distinct phases (Region 1 and Region 2) result more charge carrier scattering so low electrical conductivity. The study conducted by Mohsen et al. found that the ZT value of nano copper selenide synthesised with the microwave-assisted method and consolidated by SPS was 2 at 900 K. In group the ZT value of $\text{Cu}_{1.8}\text{Se}$ sample found 2.1 at 900 K [86].

6. CONCLUSIONS

Investigation TE properties of CoSb_3 and Cu_2Se was aimed in this thesis. Within this scope, The TE behaviours of three group sample were examined.

- ✓ Group A sample include C- CoSb_3 , F- CoSb_3 , CoSb_3 with 2%, 5% and 10% Cu_2Se . While C- CoSb_3 and F- CoSb_3 show p-type conductivity, the addition of Cu_2Se led to a change in conductivity type up to phase transition temperature of Cu_2Se . The amount of contribution determined the Seebeck coefficient because the increase in contribution resulted in lower Seebeck coefficient at low temperature. Beyond the phase transition temperature, all samples showed p-type conductivity and nearly same Seebeck coefficient.
- ✓ The ZT value of all doped sample with Cu_2Se in Group A was higher than the C- CoSb_3 , however, the highest ZT value was observed for the F- CoSb_3 . It can be said the grain size of the sample more affect the TE properties accordance to the C- CoSb_3 .
- ✓ The Group B samples include C- Cu_2Se , F- Cu_2Se , Cu_2Se with 2%, 5% and 10% CoSb_3 . The addition of CoSb_3 to sample led to a decrease in thermal conductivity. Besides, the addition of CoSb_3 with 2% resulted in improvement ZT value nearly 80% compared to the undoped samples. The highest ZT value was observed for the CoSb_3 2% Cu_2Se sample with 0.9 at 675 K. One can say that the crystal mismatch results in improvement for the Thermoelectricity in group B.
- ✓ In Group C the TE properties of nano $\text{Cu}_{1.8}\text{Se}$, nano Cu_2Se and nano Cu_2Se with 2% and 5% FeCoSb were analysed. It was found the ZT value 2.1 at 675 K for $\text{Cu}_{1.8}\text{Se}$ sample.



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