POWER FACTOR ENHANCEMENT OF THERMOELECTRIC OXIDE
COMPOSITES FOR HIGH TEMPERATURE APPLICATIONS

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ABSTRACT

POWER FACTOR ENHANCEMENT OF THERMOELECTRIC OXIDE COMPOSITES FOR HIGH TEMPERATURE APPLICATIONS

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In this work, we report a simultaneous increase in Seebeck coefficient and electrical conductivity, that results in increasing power factor, of Ca$_3$Co$_4$O$_9$ (C-349) ceramic by forming a composite system together with another promising oxyselenide; BiCuSeO (BCSO). Pristine C-349 and BCSO were synthesized using sol-gel and solid-state reaction methods, respectively and mixed by several ball-milling steps. We observed a remarkable increase in the power factor of, approximately 41% higher than the power factor of pristine C-349 at 900 K. The addition of BCSO phase results in slight decrease in carrier concentration and at the same time creates more porous structure. Both consequences have a positive impact on Seebeck coefficient. The reason for enhancement in electrical conductivity is related with high increase in hole mobility without significant decrease in carrier concentration. This study might inspire other researchers to explore the new concepts of developing high power factor thermoelectric (TE) materials. To our best knowledge, this is the first study on the TE properties of C-349/BCSO composites.

Keywords: Thermoelectric, Power factor, Hall effect, Ca$_3$Co$_4$O$_9$, BiCuSeO
ÖZ

YÜKSEK SICAKLIK UYGULAMALARI İÇİN TERMOELEKTRİK OKSİT KOMPOZİTLERİNİN GÜÇ FAKTORÜNÜN GELİŞTİRILMESİ

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Yüksek Lisans, Metalurji ve Malzeme Mühendisliği
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Bu çalışmada, Ca$_3$Co$_4$O$_9$ (C-349) seramiği ile bir diğer ümit vaat eden oksiselenit olan BiCuSeO kompozit sistem haline getirilmiş ve bu sayede Seebeck katsayısı ve elektriksel iletkenliği, dolayısıyla güç faktöründe artış gözlemlenmiştir. Saf haldeki C-349 ve BCSO, sol-jel ve katı-hal reaksiyon metodunu takiben gerçekleştirdiğimiz bilyalı öğütme aşamaları ile başarılı bir şekilde sentezlenmişdir. Seebeck katsayısı ve elektriksel iletkenlikteki paralel artış sayesinde %41 oranında güç faktörü artış elde edilmiştir. BCSO fazının eklenmesi, taşıyıcı konsantrasyonunda hafif bir düşüşe neden olur ve aynı zamanda daha gözenekli bir yapı oluşturur. Her iki sonuç da Seebeck katsayısı üzerinde olumlu bir etkiye şahittir. Elektriksel iletkenlikteki artışın nedeni, taşıyıcı konsantrasyonunda önemli bir azalma olmaksızın, deşik mobilitesinde yüksek artış ile ilgilidir. Bu çalışma daha yüksek güç faktörüne sahip malzemeler geliştirilmesine ışık tutacaktır. Bu çalışma bilgimiz dahilinde C-349/BCSO kompozit sisteminin termoelektrik özellikleri incelenmesinde ilki temsil etmektedir.

Anahtar Sözcükler: Termoelektrik, Güç faktörü, Hall etkisi, Ca$_3$Co$_4$O$_9$, BiCuSeO
To my family.
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<th>Definition</th>
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<tr>
<td>ZT</td>
<td>Dimensionless Figure of Merit</td>
</tr>
<tr>
<td>TE</td>
<td>Thermoelectric</td>
</tr>
<tr>
<td>TEG</td>
<td>Thermoelectric Generator</td>
</tr>
<tr>
<td>C-349</td>
<td>Ca$_3$Co$_4$O$_9$</td>
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<tr>
<td>BCSO</td>
<td>BiCuSeO</td>
</tr>
<tr>
<td>EMF</td>
<td>Electron Magnetic Force</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
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<tr>
<td>NP</td>
<td>Nanoparticle</td>
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<tr>
<td>SPS</td>
<td>Spark Plasma Sintering</td>
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<tr>
<td>VC</td>
<td>Vacuum Chamber</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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<tr>
<td>EMT</td>
<td>Effective Medium Theory</td>
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<tr>
<td>SD</td>
<td>Standard Deviation</td>
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LIST OF SYMBOLS

q \hspace{1em} \text{heat flux}
\alpha \hspace{1em} \text{Seebeck coefficient}
\pi \hspace{1em} \text{Peltier coefficient}
E \hspace{1em} \text{electric field}
J \hspace{1em} \text{current density}
I \hspace{1em} \text{electrical current}
\nabla \hspace{1em} \text{gradient}
T_H \hspace{1em} \text{hot side temperature}
T_C \hspace{1em} \text{cold side temperature}
E_f \hspace{1em} \text{the Fermi energy}
\mu \hspace{1em} \text{mobility}
n(E) \hspace{1em} \text{energy dependent carrier concentration}
\sigma \hspace{1em} \text{electrical conductivity}
Q_{\text{Peltier}} \hspace{1em} \text{Peltier heat}
Q_{\text{Thomson}} \hspace{1em} \text{Thomson heat}
\tau \hspace{1em} \text{Thomson coefficient}
k_B \hspace{1em} \text{Boltzmann constant}
h \hspace{1em} \text{Plank’s constant}
a \hspace{1em} \text{lattice parameter}
\rho \hspace{1em} \text{material density}
\gamma \hspace{1em} \text{the acoustic phonon Grüneisen parameter}
\Theta_D \hspace{1em} \text{Debye temperature}
\kappa \hspace{1em} \text{thermal conductivity}
\kappa_C \hspace{1em} \text{carrier part of thermal conductivity}
\kappa_{ph} \hspace{1em} \text{phonon part of thermal conductivity}
\eta \hspace{1em} \text{energy conversion efficiency}
CHAPTER 1

INTRODUCTION

In 1821-3, Thomas Johann Seebeck realized that the closed loop made from two
dissimilar conductors could change the compass needle when the junctions were
placed at different temperatures. However, incorrectly, Seebeck thought that the
reason was due to the magnetic field caused by the temperature difference between
equator and poles [1]. In 1834, Peltier observed temperature changes in the near of
junctions between two dissimilar conductors when a current passed [2]. However, he
could not relate this temperature change with Seebeck effect, although he used the
Seebeck effect in his experiments as a source of weak currents. Lenz explained the
true nature of Peltier effect in 1938 [3]. By applying current, he discovered that he
could melt the ice and change the direction of the current to freeze the water.

At the beginning of 1850s, the interest was focused on all forms of energy conversion
thanks to development in thermodynamics and as a result W. Thomson (Lord Kelvin)
discovered an interrelation between Seebeck and Peltier coefficients in 1851 and he
predicted 3\textsuperscript{rd} law of thermodynamics which is called Thomson effect. According to
Thomson effect, heat can be generated or absorbed in the presence of temperature
gradient by changing the direction of current flow [4].

The electricity generation concept by using thermoelectric principles was first
proposed by Rayleigh in 1885. However, the calculation of the efficiency of
thermoelectric generator was not correct. Altenkirch did the satisfactory
approximation to thermoelectric generation and refrigeration in 1906 [5] and 1911 [6],
respectively by using constant property model. According to this approach good
thermoelectric materials should have large Seebeck coefficient, low thermal conductivity to retain heat at the junction and high electric resistivity to minimize Joule heating. Altenkirch’s approach was embodied in dimensionless figure of merit (ZT) for a given material as $ZT = \frac{S^2 \sigma}{\kappa T}$ where $S$, $\sigma$, $\kappa$ and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively.

After ZT concept was constituted, the development process of thermoelectric had been continued during the World War II. The main objective was to provide cooling as well as power generation for military applications. However, due to the political issues, the information exchange between Eastern European and Western countries was highly restricted. In 1949 [7], Abram Fedorovich Ioffe had developed modern theory of thermoelectricity by using ZT concept and this was the first step for building up the first commercial thermoelectric generator. Ioffe also promoted the idea of making alloying and creating point defects to reduce the thermal conductivity. In 1954, H. Julian Goldsmid cooled a surface to 0 °C by using Peltier thermoelectric cooler which was made from Bi$_2$Te$_3$ [8]. Moreover, Goldsmid was one of the first who identified the importance of high mobility and effective mass combination with low lattice thermal conductivity in semiconductors for making good thermoelectric materials.

The reliability and simplicity of thermoelectricity makes it practical to generate power remotely. In 1968, NASA used the first radioisotope thermoelectric generator called SNAP-19 in spacecraft and after a decade, again NASA launched Voyagers 1 and 2 which have SiGe thermoelectric generator. Under the benefit of having no moving parts, Voyagers are still working.

Today, interest in thermoelectric materials started to renovate. Scientists are searching to find high-efficiency thermoelectric (TE) materials, since they are very important for power-generation devices which are designed to convert waste heat into electric energy. These materials can be used in electronic refrigeration and power generation, which shows a great possibility for developing alternative energy technologies [9,10].
On the other hand, the advantage of TE devices is their usability without moving parts. One can convert heat to electricity, or refrigerators that use electricity to pump heat from cold to hot, both work without any moving parts or bulk fluids [11,12].

Power generation applications are presently inspected by the automotive industry. The waste heat exists from the radiator and exhaust systems can be converted to electrical power for use in next-generation vehicles. Moreover, in refrigeration applications, TE materials can be used for seat coolers to create more comfort and electronic component cooling. More importantly, in small-scale computers, infrared detectors, electronics and optoelectronics, thermoelectric refrigeration becomes an “environmentally green” method. If compelling economical cooling can be accomplished, the following “cooling” could produce 30-200% speed gains in some computer processors [9]. On the other hand, for factories, power plants, incinerators, etc., thermoelectric materials that can operate at high temperatures should be used to reduce our dependence on fossil fuels and reduce greenhouse gas emission.

While investigating high temperature thermoelectric materials, researchers should consider materials’ properties like conversion efficiency, toxicity and thermal stability. These properties make the material as called “good”. However, for above-mentioned applications good thermoelectric materials have still not been created. Therefore, researchers should focus on developing high efficient, non-toxic and stable thermoelectric materials. High efficiency is related with low thermal conductivity and low electrical resistivity. Conventional thermoelectric materials are highly efficient, but they are not stable at high temperatures due to oxidation problems. Therefore, they can mainly be used in a strictly oxygen-free environment. Moreover, conventional TE materials generally made up of heavy elements like Sb, Pb and Te [13] that can create problems for health and environment. On the contrary, oxide-based thermoelectric materials are non-toxic, thermally and chemically stable at high temperatures, low cost and easily prepared. Moreover, they have a long service lifetime, which is very important for practical applications. Ca₃Co₄O₉ (C-349) is one of promising p-type
oxide-based thermoelectric materials. C-349 has low electrical resistivity and low thermal conductivity, which are very beneficial for high efficient TE materials. Moreover, thermodynamic stability, non-toxicity and easy fabrication make C-349 up and coming. However, the Seebeck coefficient of C-349 is low in comparison to state-of-art TE materials [14]. BiCuSeO (BCSO) is another encouraging oxyselenide compound with a layered ZrSiCuAs like structure. When compared with to the state of art lead tellurium, the lattice thermal conductivity of BCSO is much lower. Moreover, BCSO have a high Seebeck coefficient, which directly increases TE performance. Thermal stability, non-toxicity and low cost are the other crucial properties of BCSO. Nonetheless, pristine BCSO exhibits low electrical conductivity due to low number of charge carriers [15]. Therefore, it is significant to enhance both material efficiencies for regaining waste energy as electricity.

Last decade, the number of studies about enhancing the TE properties of C-349 and BCSO has been increasing. Scientists have been trying various kinds of methods such as porosity approach, elemental substitution method and nanostructuring. However, there are very few studies related with the production of high efficient TE materials by composite engineering. In this study, the two aforesaid materials afforded to be combined. In other words, innovative TE materials were designed by completing the missing properties of each other. On the other hand, new physical concepts can be discovered by composite engineering. In this thesis, in accordance with the purpose of increasing thermoelectric conversion efficiencies of individual oxide materials, a multi-component system was created and TE properties were investigated. It is obvious that before starting to produce the composite system, the two C-349 and BCSO phases should to be obtained separately. C-349 was tried to be produced via sol-gel method. On the other side, BCSO was obtained by common two-step solid solution method.

The next section, TE materials’ mathematical and physical background was explained for better understanding. After background information, past, recent and future
applications related with TE concept were given. After that, application areas and comparison between conventional TE materials and oxides were explained. At the end of this section, properties of C-349 and BCSO and literature review about them were presented in more detail. In Chapter 3, physical and chemical preparation steps for C-349 and BCSO were described in detail. Sintering procedures for both materials were also mentioned. After the description of preparation steps and sintering operations, characterization methods and techniques were summarized. In results and discussion part, the structural characterization results were represented and discussed. Subsequently, the thermoelectric properties of pristine C-349, BCSO and their composites were demonstrated. At the end, all work done in this study was concluded, and further suggestions were offered.
CHAPTER 2

LITERATURE SURVEY

2.1. Thermoelectric Effects and Physical Background

A piece of matter is exposed to temperature difference when the heat flows automatically from the region of higher temperature, \( T_H \), to the region lower temperature, \( T_C \). Heat continues to flow until the thermal equilibrium \( (T_H = T_C = T) \) is developed or temperature gradient vanishes. In the case of temperature difference, the thermoelectric effect appears due to charge carriers’ movement to reach the equilibrium condition. Thermoelectric effect can be thought of a production of potential difference between two ends of a matter, which is an electromagnetic force (EMF). The creation of this phenomena is known as “Seebeck Effect”. On the other hand, if voltage difference is applied to matter, temperature gradient takes place and this phenomenon is known as “Peltier Effect”.

Figure 2.1 describes the TE effect when a material is exposed to external temperature gradient. The charge carriers in hot side of material have a higher kinetic energy, so have a longer mean free path than the electrons on cold side. Therefore, they supposed to diffuse to cold side. This mechanism is the first reason of Seebeck effect. The movement of charge carriers due to concentration gradient is the second mechanism which creates the TE effect. The number of particles on the cold side increases when the particles at hot side are initiated to diffuse to the cold side. After this accumulation, particles tend to migrate to hot side due to the concentration difference under the potential.
Figure 2.1 Description of TE effect when a material is exposed to external temperature gradient. a) More energetic particles have long mean free path. b) Energetic particles’ diffusion to cold side of material [16]

From the physical point of view, generally, a heat flux and electrical current are coupled due to phenomena of electron and phonon transport in conductors and semiconductors. Heat flux ($q$) is a linear function of the electric fields and the electrical current is directly proportional to the temperature gradient. These relations can be seen below: [17,18].

$$J = \sigma E = -\sigma \alpha \nabla T \quad \text{(2.1)}$$

$$q = \pi J = -\kappa \nabla T \quad \text{(2.2)}$$

where $J$, $E$ and $T$ is current density, electric field and temperature, respectively. The other notations; $\alpha$, $\pi$, $\kappa$ and $\sigma$ represent the Seebeck coefficient, Peltier coefficient, thermal conductivity, and the electrical conductivity, respectively. From equations
(2.1) and (2.2), it can be understood that the temperature gradient results in an electrical field. On the other hand, an electrical field creates temperature gradient.

### 2.1.1. Seebeck Effect

As mentioned in the introduction part, in 1821-3, Thomas Johann Seebeck realized that the closed loop made from two dissimilar conductors could change the compass needle when the junctions were placed at different temperatures. This is termed the Seebeck effect and is defined as follow:

\[
\alpha = \frac{E}{VT} \approx \frac{\Delta V}{\Delta T} \tag{2.3}
\]

Figure 2.2 represents a thermocouple, which consists of two different types of metals, is the best example for Seebeck effect. In equilibrium, no potential change is observed. However, in the case of one junction is heated, current starts to flow and this is called the Seebeck effect.

![Schematic description of Thermocouple](image)

**Figure 2.2** Schematic description of Thermocouple [20]

The conjugate of equation (2.3) can be written as follow:

\[
V = \alpha_{AB} \Delta T \tag{2.4}
\]
where $\Delta T = T_h - T_c$ and $\alpha_{AB} = \alpha_A - \alpha_B$. Seebeck coefficient is also called as thermopower which has a unit of $\mu$V/K. The sign of Seebeck coefficient depends on the type of the material due to properties of semiconductors, p-type or n-type. The sign is positive or negative when the excess charge distribution will result in positive or negative potential on the cold side, respectively [16].

2.1.2. Peltier Effect

In thermocouple circuit, when current is passing through a junction between two different wires, heat must be added or subtracted to keep the temperature constant. In other words, if current flows across, temperature gradient will occur and changes sign when the current is reversed. The description of the Peltier heat ($\dot{Q}_{\text{Peltier}}$) can be examined below.

$$\dot{Q}_{\text{Peltier}} = \pi_{AB} I \quad (2.5)$$

$\pi_{AB}(T)$ is Peltier coefficient with units of Watts per Ampere. As shown in Figure 2.3, the junction of wire where the current enters is heated, the sign of $\pi_{AB}$ becomes positive. Oppositely, the junction where current leaves becomes colder, the sign of $\pi_{AB}$ takes the negative value.

![Figure 2.3 Schematic for the Peltier effect and the Thomson effect [19].](image-url)
2.1.3. Thomson Effect

Due to Peltier effect, temperature gradient takes place at the junctions of wire A and B as explained above where it is assumed that the current flows in the direction described in Figure 2.3. While current flows in wire A, heat is absorbed due to negative temperature gradient. On the other hand, while flow in wire B takes place, heat is liberated due to positive temperature difference. This phenomenon explained experimentally by Amagai and Fujiki (2014) [20,21]. The Thomson heat ($\dot{Q}_{\text{Thomson}}$) is directly proportional to the electrical current ($I$) and the temperature gradient ($\Delta T$) as described below:

$$\dot{Q}_{\text{Thomson}} = \tau I \Delta T$$  \hspace{1cm} (2.6)

where $\tau$ is the Thomson coefficient and it is the only directly measurable coefficient between the three TE coefficients for an individual material. On the other hand, when the current passes through the wire, Joule heating occurs which is thermodynamically irreversible. However, this Joule heat is not the same as Thomson heat.

Lord Kelvin thermodynamically proved that the Seebeck and Peltier coefficients are dependent, and they are related to each other through the Kelvin’s second relation:

$$\alpha_{AB} = \frac{\pi_{AB}(T)}{T}$$  \hspace{1cm} (2.7)

This relation shows that Seebeck coefficient alone is sufficient for measuring thermoelectric properties of a material. Experimentally, it is difficult to measure the absolute value of the Seebeck coefficient of an individual material. This is because the measurement apparatus also suffers from the same temperature difference that is enforced to the material. However, it is still practical to obtain Seebeck coefficient since the most familiar conductive materials have imperceptible Seebeck coefficients.
2.1.4. Figure of Merit

The performance of thermoelectric devices is represented by figure of merit (Z) with unit of 1/K and described as follow:

\[ Z = \frac{\alpha^2 \sigma}{k} \]  

(2.8)

where \( \alpha \), \( \sigma \) and \( k \) are the Seebeck coefficient, electrical conductivity and thermal conductivity, respectively. The dimensionless figure of merit is defined by ZT where T is the absolute temperature. Moreover, \( \alpha^2 \sigma \) is called the power factor or thermoelectric power factor and to understand which physical properties affect ZT or power factor, more detailed description about the Seebeck coefficient is presented in equation 2.9 which is called as Mott relation [22].

\[ \alpha = \frac{\pi^2 \kappa_B}{3} \frac{\kappa_B T}{q} \left( \frac{1}{n} \frac{dn(E)}{dE} + \frac{1}{\mu} \frac{d\mu(E)}{dE} \right) \text{ at } E=E_F \]  

(2.9)

where \( n(E) \) is an energy dependent carrier concentration, \( \kappa_B \) is the Boltzmann constant, \( \mu(E) \) is the mobility, \( E_F \) is the Fermi energy, \( q \) and \( T \) represent an electronic charge and temperature, respectively. The Seebeck coefficient is directly affected by the absolute temperature, charge carrier concentration and crystal structure of the conductor. The change in the Seebeck coefficient with carrier concentration is plotted in Figure 2.4. From this plot, it can be interpreted that there is an optimum carrier concentration value for maximum power factor. Moreover, while electrical conductivity rises, the Seebeck coefficient decreases.

The second property that directly affects ZT is the electrical conductivity, \( \sigma \), which is a measure of charge carriers contributed by electrons and holes that has a unit of (\( \Omega \text{cm} \))\(^{-1}\). Carrier concentration \( n \) and mobility \( \mu \) directly contribute to electrical
conductivity as shown below:

\[ \sigma = ne\mu \quad (2.10) \]

Electrical conductivity is directly proportional with carrier concentration as shown in Figure 2.4. Metals have highest electrical conductivity, while insulators have the lowest and semiconductors have an intermediate value.

![Figure 2.4](image)

**Figure 2.4** Electrical properties of TE materials as a function of carrier concentration [23].

The relation between electrical conductivity and the Seebeck coefficient is quite interesting. This relation can be interpreted by understanding density of states (DOS) studies [24]. When the Fermi energy closer to conduction band, maximum ZT can be obtained. In other words, when the degeneracy is not so strong, or charge carriers are highly asymmetric in terms of their DOS, maximum Seebeck coefficient can be obtained [25]. Doping moves the Fermi level deeper into the band of 3D-crystal which means increment in carrier concentration.
Thermal conductivity is the third important parameter which designates the value of ZT. In semiconductors, not only electrons and holes, but also phonons (lattice) contribute to thermal conductivity. When one type of charge carrier is dominant for transportation, the thermal conductivity can be defined as follows:

\[ \kappa = \kappa_C + \kappa_{ph} \]  

(2.11)

where \( \kappa_C \) and \( \kappa_{ph} \) represent carrier and phonon contribution part to thermal conductivity, respectively. \( \kappa_C \) which is defined by Lorentz factor (L) is equivalent to 2.4 \( \times 10^{-8} \) J/K^2c^2 for metals and 2.0 \( \times 10^{-8} \) J/K^2c^2 for semiconductors [16].

\[ \kappa_C = L \sigma T = n\mu LT \]  

(2.12)

On the other hand, phonon transportation has a strong effect on thermal conductivity. Lattice vibrations generate phonons and therefore crystal structure and lattice parameters of materials have a crucial role in thermal conductivity. In addition, density and anharmonic lattice vibrations have an effect on thermal conductivity, according to equation 2.13.

\[ \kappa_{ph} = \frac{k_B}{h^3} \frac{a^4 \rho \Theta_D^3}{\gamma^2 T} \]  

(2.13)

where \( k_B \), \( h \), \( a \), \( \rho \), \( \gamma \), and \( \Theta_D \) are Boltzmann constant, Planck’s constant, lattice parameter, material density, the acoustic phonon Grüneisen parameter (measure of anharmonic nature of lattice vibrations) and Debye temperature, respectively. For example, the production of alloys can result in tuning the lattice parameter which can let the scientist to enhance thermoelectric performance of materials by decreasing phonon thermal conductivity. To understand the importance of lattice structure, effect of doping (alloying) should be examined. The works of Yanzhong Pei and et al. [26]
and Chi Yu and et al. [27] are good examples for where doping method was used to enhance TE properties.

2.1.5. Thermoelectric Module and Power Conversion Efficiency

The Seebeck coefficients of n-type and p-type materials have an opposite sign to each other due to the properties of semiconductors. Therefore, a thermoelectric module consists of two semiconductor materials which is connected electrically in series and thermally in parallel as shown in Figure 2.5. By applying a heat source on one side and cooler heat sink to the other side of material, electrical power is produced, and this power can be converted to heating or cooling by changing the direction of current [28].

The maximum conversion efficiency of thermoelectric device can be expressed as below:

$$
\eta = \frac{\Delta T}{T_{hot}} \frac{\sqrt{1+ZT} \cdot 1}{\sqrt{1+ZT} + \frac{T_{cold}}{T_{hot}}} \quad (2.14)
$$

where $\frac{\Delta T}{T_{hot}}$ defined as Carnot efficiency. $T_{hot}$ and $T_{cold}$ denote hot end and cold end temperatures, respectively. The product of Carnot efficiency and ZT dependent quantity gives the conversion efficiency. Basically ZT>1 condition for a thermoelectric material can described as a good thermoelectric material since the conversion efficiency can be increased up to 10-15%. The further information about the effect of ZT on conversion efficiency is plotted in Figure 2.7 [30].
**Figure 2.5** Schematic representation of a thermoelectric module [28].

**Figure 2.6** Power generation and refrigeration modes for traditional thermoelectric engines [29].
2.2. Methods for Enhancement of Figure of Merit and Power Factor

Conversion efficiencies of conventional thermoelectric materials can reach up to 5-20% due to low ZT value of TE materials. However, scientist have been started to search on new ways to enhance ZT and power factor value which can be obtained by increasing electrical conductivity and Seebeck coefficient while decreasing thermal conductivity of material. The ZT value can be enhanced with useful strategies such as doping, alloying, nanostructuring, manufacturing thin films and creating superlattices, nanocomposites and composites.
2.2.1. Doping

In literature, doping is the most preferred way to create high performance thermoelectric materials. Appropriate doping element can modify the electronic band structure, which results in increase in carrier concentration. To obtain high power factor, elemental doping like modulation should be carried out. Heavy doped materials show greater power factor against undoped equivalents [31-33]. On the other hand, electron mobility can be increased and impurity scattering can be decreased by uniform doping. Moreover, electronic bands can converge in the bulk material so that the valence and conduction bands also converge. Therefore, both Seebeck coefficient and electrical conductivity have an ability to increase [32,34]. In some cases, doping elements can diffuse to band of matrix material and results in generation of resonant energy levels. This resonance can force DOS close to Fermi level so without changing carrier concentration, effective mass of the carriers can be increased. By changing doping concentration Seebeck coefficient can also be increased due to resonant energy levels [35].

2.2.2. Alloying

Alloying is an alternative way to increase thermoelectric performance of the material. However, different from doping, alloying is responsible of decreasing the thermal conductivity. Basically, alloying elements behave like scattering barriers for phonons and at the same time create a path for charge carriers that increase the electrical conductivity. Alloying with heavy atoms makes a rattling action that creates strain field effect and results in atomic disorder. This phenomenon reduces the phonon (lattice) thermal conductivity [36].

2.2.3. Nanostructuring

In physical background part, it was mentioned that the electrical conductivity and thermal conductivity are connected to each other since both carried out by charge
carriers. Nanostructuring approach enables scientists to break this connection. Due to quantum confinement effect, DOS near Fermi level can be enhanced and leading the increase of thermopower. On the other hand, if the size of particles smaller than the mean free path of phonons, thermal resistivity can be increased without decreasing the electrical conductivity. However, the size of particles should be larger than the mean free path of electrons at the same time. This way, phonon scattering at boundaries increase without affecting the electrical transport properties [37].

1D thermoelectric materials are represented by nanowires and theoretical studies predict that the large ZT and high-power factor in these 1D materials can be obtained due to additional quantum confinement effect and phonon scattering. There have been many reports on increasing thermoelectric properties by developing 1D materials [38,39]. 2D materials are another nanostructured material tried to be produced for thermoelectric applications [40-42]. Again, due to quantum confinement effect, scientists can develop high-power factor TE materials.

2.2.4. Composite and Nanocomposite Engineering

By nanocomposite engineering, electron and phonon transport properties can be developed. Since the mean free paths (mfp) of phonons are from several nanometers to few nanometers in length where mfp of charge carriers are up to few nanometers, phonon scattering could take place so that decrement in thermal conductivity can be achieved. Nano sized grains behave like phonon scattering barriers so that high efficient TE materials can further be developed by increasing the power factor. Scientists are mostly working on producing nanocomposite materials using state of art TE materials like BiTe [43], PbTe [44] and SiGe [45].

Composite engineering is based on discovering new properties or improving the existing properties in a multi-component system. Increasing the power factor of bulk TE materials is the ultimate goal of this approach. For instance, the Seebeck coefficient increases and thermal conductivity decrements can be achieved due to carrier
scattering effect [46]. However, the increase in Seebeck coefficient is not enough for the enhancement of power factor. Most importantly, the effective power factor of composite materials can be greater than the power factors of each component which is theoretically explained by Bergman and Fel [47] and experimentally showed by Heremans and Jaworski [48]. This behavior requires minimum or no drop in the Seebeck coefficient of the component having the highest value when the maximum decrease in electrical resistivity is desired. Schematic of composite system, the expected electrical improvement for the composite and the conductivities of individual components, and the temperature dependent Seebeck coefficient for the same composite system can be examined in Figure 2.8 [49]. High-yielding TE materials can be developed by the discovery of new properties and physical concepts in composite systems. Therefore, compounding two different TE materials having a feature complementary to one another is an important step towards developing materials with improved thermoelectric properties.
2.3. Classification of Thermoelectric Materials

All thermoelectric materials have a complex band structure and represented by degenerate semiconductors. These materials are commonly classified as intermetallics, rare earth chalcogenides, skutterudites, clathrates and oxides. On the other hand, thermoelectric materials can be classified according to their working temperature range. In Figure 2.9 and 2.10, some of n-type and p-type TE materials which spread out to their working temperature ranges are illustrated.
Figure 2.9 ZT versus n-type TE materials according to their working temperature range [50].

Figure 2.10 ZT versus p-type TE materials according to their working temperature range [50].
2.4. Production Methods of Thermoelectric Materials

Thermoelectric materials can both be produced by physical and chemical routes. The selection of a route is crucial for completing thermoelectric properties. Particle size and distribution are controlled more easily using chemical routes while large production range is possible with physical methods. All the processes have their own advantages and disadvantages.

2.4.1. Mechanical Alloying

Mechanical alloying process at the same time is called as solid-state reaction route. Stoichiometric amount of powders is mixed by hand or ball-milling. After obtaining finer particles, they are generally cold or hot pressed followed by sintering operations. By mechanical alloying processes, alloying or doping strategies can be easily achieved to obtain high quality thermoelectric materials.

2.4.2. Levitation or Arc Melting

Levitation is a special melting process to prepare high temperature materials like intermetallics. By levitation melting processes, contamination from the container can be avoided and unwanted inhomogeneous nucleation could be minimized in the solution [51]. After melting, materials are further exposed to spark plasma sintering (SPS) or hot pressing to obtain more dense materials. Both levitation and SPS are beneficial to yield homogeneous products within a short time duration.

2.4.3. Microwave Synthesis

Microwave synthesis of thermoelectric materials is a rapid and steady way. By this method nanocrystals with 15-100 nm sizes can be manufactured. A precursor first sealed in a vacuumed quartz tube and then exposed to microwave radiation. For example, Zhao et al. [52] obtained different size and morphology of lead sulfide (PbS)
nanocrystals by using ethanol, distilled water, ethylene glycol and polyethylene glycol-200 as solvents.

2.4.4. Sol-gel Synthesis

As a chemical reaction, the sol-gel method starts from ion or molecular compound and generates a 3D network through the oxygen bond formation between the ions [53]. Dispersed colloidal particles or polymers in a liquid called as sol and a gel is interconnected, rigid network with pores and polymeric bonds [54]. The sol-gel process is a favorite technique to produce nanocomposites that are basically organic and inorganic system in one material, which reinforced by nano-scale materials. There are several advantages that make the sol-gel process preferable. The low operating temperature, easy control of size and distribution of particles in early stages of production, homogeneity in atomic level are some benefits of sol-gel process.

2.4.5. Other Methods

Single-crystal growth, hydrothermal or solvothermal and low-temperature aqueous chemical routes are the other methods, which have been followed by scientists in the purpose of developing thermoelectric materials.

2.5. Conventional and Oxide-based Thermoelectric Materials

Recently, several works have been focused on conventional thermoelectric materials such as Bi$_2$Te$_3$ [55], MnSi [56], SiGe [57], Mg$_2$Si [58] due to their high ZT values compared to other materials. In 2014, Zhao et al. have obtained SnSe single crystal, which has a ZT value around 2.66 at 973 K along the b-axis. This is the highest ZT value for bulk thermoelectric materials until now [59].
Even though the conversion efficiencies of alloys are very impressive, they have some critical disadvantages as follows:

- Usually toxic,
- Thermal and chemically instable,
- Low in abundance as natural resources,
- Mainly be used in a strict oxygen-free environment.

On the contrary, oxide-based thermoelectric materials are

- Non-toxic,
- Thermally and chemically stable at high temperatures leading to a high Carnot efficiency in that somewhat compensates the low ZT,
- Low cost and easily prepared,
- Long service lifetime, which is very important for practical applications.

Some of common oxide-based materials that have been studied in recent years are ZnO [61], CaMnO₃[62], SrTiO₃ [63], NiO [64], In₂O₃ [65]. These materials show great advantage against alloys as mentioned above; however, their low thermoelectric conversion efficiencies can not meet the requirements for practical applications. Thus, researchers should focus creating high ZT oxide based thermoelectric materials or on increasing the ZT of those oxide-based thermoelectric materials by different strategies.
Figure 2.11 a) Schematic comparison of conventional thermoelectric materials in terms of the temperature range and environmental friendliness of constituent elements. (b) Comparison of the abundance of elements [60]

2.6. Ca₃Co₄O₉ Oxide Thermoelectrics

At the end of 20th century, Terasaki et al. [66] measured and analyzed the transport properties of single-crystal NaCo₂O₄, which is a metallic transition-metal oxide consisting of a two-dimensional triangle lattice of Co. According to their report, this single crystal has a Seebeck coefficient around 100 μV/K at room temperature, which
was attention grabbing. This result can be understood by examining the structure of NaCo$_2$O$_4$. The crystal structure of NaCo$_2$O$_4$ consists of an alternate stacks with a highly vacant Na$^+$ layer and a CdI$_2$-type CoO$_2$ conducting sheet parallel to the c-axis. Ca$_3$Co$_4$O$_9$ has the same crystal structure with NaCo$_2$O$_4$. In 2002, by using super space group approach, Miyazaki et al. [67] determined crystal structure of the composite crystal [Ca$_2$CoO$_3$]$_{0.62}$CoO$_2$ which is actually known as Calcium Cobaltate (Ca$_3$Co$_4$O$_9$). The structure is illustrated in Figure 2.12. In this structure, two of CdI2-typed CoO$_2$ layers along the c axis surround the Ca$_2$CoO$_3$ layer.

![Figure 2.12 Schematic illustration of the crystal structure of C-349 oxide [68].](image)

Hexagonal CoO$_2$ layers are subject to the Seebeck coefficient and electrical conductivity as the carriers’ providers. Rock-salt type block Ca$_2$CoO$_3$ layer is an insulating layer since oxygen anions had attached to calcium and cobalt by ionic bond. Such an anisotropic structure is believed to show low thermal conductivity, high electrical conductivity and Seebeck coefficient. Different techniques have been used to increase power factor of C-349 material. The literature review can be examined in Table 2.1. Thermoelectric properties described in this table represents the maximum values that could be obtained.
<table>
<thead>
<tr>
<th>Author</th>
<th>Material</th>
<th>Precursors</th>
<th>Method</th>
<th>T (K)</th>
<th>S (µV/K)</th>
<th>κ (W/mK)</th>
<th>R (mΩ.cm)</th>
<th>PF (µW/mK²)</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. Gunes and M. Ozenbas [69]</td>
<td>Ca₃Co₄O₉</td>
<td>Ca(NO₃)₂·4H₂O and Co(NO₃)₂·6H₂O PEG 400 and citric acid</td>
<td>Sol-gel</td>
<td>1000</td>
<td>140</td>
<td>0.32</td>
<td>29</td>
<td>100</td>
<td>0.3</td>
</tr>
<tr>
<td>G. Constantinescu et al. [70]</td>
<td>Ca₃₋ₓSrₓCo₄O₉</td>
<td>CaCO₃, SrC₀₃ and Co₂O₃ powders</td>
<td>Conventional solid-state route</td>
<td>1073</td>
<td>220</td>
<td>-</td>
<td>-</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td>J.C. Diez et al. [71]</td>
<td>Ca₃Co₄₋ₓCrₓO₉</td>
<td>CaCO₃, CrC₀₃ and Co₂O₃ powders</td>
<td>Conventional solid-state route</td>
<td>1073</td>
<td>210</td>
<td>-</td>
<td>18</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>Driss Kenfaui et al. [72]</td>
<td>Ca₃Co₄O₉</td>
<td>CaCO₃, CoO₄</td>
<td>Hot-pressing</td>
<td>1000</td>
<td>175</td>
<td>1</td>
<td>10</td>
<td>600</td>
<td>0.16</td>
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Table 2.1 (cont’d) Thermoelectric properties of C-349 samples from the literature.

<table>
<thead>
<tr>
<th>Author</th>
<th>Material</th>
<th>Precursors</th>
<th>Method</th>
<th>T (K)</th>
<th>S (μV/K)</th>
<th>κ (W/mK)</th>
<th>R (mΩ·cm)</th>
<th>PF (μW/mK²)</th>
<th>ZT</th>
</tr>
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<tr>
<td>Weirong Zhang et al. [73]</td>
<td>Ca₃Co₄O₉</td>
<td>Ca(NO₃)₂·4H₂O and Co(NO₃)₂·6H₂O and ethyl alcohol, ethylene glycol</td>
<td>Sol-gel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Su et al. [74]</td>
<td>Ca₃₋ₓBiₓCo₄O₉</td>
<td>Ca(NO₃)₂·4H₂O, Co(NO₃)₂·6H₂O, Bi(NO₃)₃·5H₂O and citric acid</td>
<td>Solid state</td>
<td>973</td>
<td>190</td>
<td>20</td>
<td>0.65</td>
<td>-</td>
<td>0.27</td>
</tr>
<tr>
<td>Yinong Yin et al. [75]</td>
<td>Ca₃Co₄O₉ with wood powders</td>
<td>Results: x=0.3 CaO and Co₃O₄</td>
<td>Self-ignition</td>
<td>800</td>
<td>300</td>
<td>1.5</td>
<td>0.04</td>
<td>275</td>
<td>0.20</td>
</tr>
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<td>Nong et al. [76]</td>
<td>Ca₃₋ₓLnₓCo₄O₉₊φ</td>
<td>CaCO₃, Co₃O₄ and Ln₂O₃</td>
<td>Solid state</td>
<td>1073</td>
<td>190</td>
<td>1.2</td>
<td>9.5</td>
<td>380</td>
<td>0.36</td>
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</table>

Other TE properties than thermal conductivity were not measured in this work. κ alters from 2 to 1 (W/mK).
<table>
<thead>
<tr>
<th>Author</th>
<th>Material</th>
<th>Precursors</th>
<th>Method</th>
<th>T (K)</th>
<th>S (µV/K)</th>
<th>µ (W/mK)</th>
<th>R (mΩ.cm)</th>
<th>PF (µW/mK²)</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yunzhi Lina et al. [77]</td>
<td>Ca₃Co₄O₉ with Ag NPs Results: Ag 2 vol%</td>
<td>CaCO₃ and Co₃O₄ powders Silver Nitrate</td>
<td>Solid state</td>
<td>700</td>
<td>160</td>
<td>1.6</td>
<td>11</td>
<td>-</td>
<td>0.10</td>
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<tr>
<td>Raj Kumar Gupta et al. [78]</td>
<td>Ca₃Co₄O₉ with ZrO₂ Results: ZrO₂ 8% weight ratio</td>
<td>CaCO₃, Co₃O₄ and ZrO₂ powders</td>
<td>Solid state</td>
<td>550</td>
<td>160</td>
<td>-</td>
<td>13</td>
<td>210</td>
<td>-</td>
</tr>
<tr>
<td>M. Presečnik and S. Bernik [79]</td>
<td>Ca₃Co₄₋ₓWₓO₉ Results: x=0</td>
<td>CaCO₃, Co₃O and WO₃ powders</td>
<td>Solid state</td>
<td>600</td>
<td>148</td>
<td>1.09</td>
<td>32</td>
<td>-</td>
<td>0.06</td>
</tr>
</tbody>
</table>
2.7. BiCuSeO Oxide Thermoelectrics

BiCuSeO oxyselenide compound with a layered ZrSiCuAs like structure was reported as a promising p-type TE material. It is comprised of \((\text{Bi}_2\text{O}_2)^{2+}\) layers alternately stacked with \((\text{Cu}_2\text{Se}_2)^{2-}\) layers along the c-axis as seen in Figure 2.13.

![Crystal structure of BiCuSeO oxyselenide with a layered ZrSiCuAs like structure](image)

**Figure 2.13** Crystal structure of BiCuSeO oxyselenide with a layered ZrSiCuAs like structure [80].

\((\text{Bi}_2\text{O}_2)^{2+}\) layers behave like charge reservoir and the \((\text{Cu}_2\text{Se}_2)^{2-}\) layers create conduction pathway for carrier transportation. When compared with the state-of-art lead tellurium, the lattice thermal conductivity of BiCuSeO is much lower. On the other hand, the electrical resistivity is much higher than the thermoelectric alloys in the entire temperature range [12]. For example, it is about 1.12 S cm\(^{-1}\) at room temperature. The low electrical conductivity is related with the low carrier concentration and mobility. Although the thermal conductivity of BiCuSeO is much lower, the power factor is much lower than the state of art TE materials.
Table 2.2 Thermoelectric properties of BCSO samples from the literature.

<table>
<thead>
<tr>
<th>Author</th>
<th>Material</th>
<th>Precursors</th>
<th>Method</th>
<th>T (K)</th>
<th>S (µV/K)</th>
<th>(\kappa) (W/mK)</th>
<th>(\sigma) (S/cm(^{-1}))</th>
<th>PF (µW/m K(^2))</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jing Li et al. [81]</td>
<td>Bi(_{1-x})Mg(_x)CuSeO (x=0.125)</td>
<td>Bi(_2)O(_3), Bi, Cu, Se and MgO powders</td>
<td>Two-step solid state reaction route 573 K for 8 h and 1023 K for 24 h in vacuum SPS at 973 K for 6 min at 50 MPa</td>
<td>923</td>
<td>254</td>
<td>0.34</td>
<td>32</td>
<td>240</td>
<td>0.67</td>
</tr>
<tr>
<td>Fu Li et al. [82]</td>
<td>BiCuSeO</td>
<td>Bi(_2)O(_3), Bi, Cu, Se powders</td>
<td>573 K for 8 h and 973 K for 24 h in vacuum Ball Milling followed by SPS</td>
<td>773</td>
<td>200</td>
<td>0.5</td>
<td>40</td>
<td>431</td>
<td>0.7</td>
</tr>
<tr>
<td>Jing Li et al. [83]</td>
<td>Bi(_{1-x})Ba(_x)CuSeO (x=0-0.15)</td>
<td>Bi(_2)O(_3), Bi, Cu, Se and BaO powders</td>
<td>Two-step solid state reaction route 573 K for 8 h and 1023 K for 24 h in vacuum SPS at 973 K for 6 min at 50 MPa</td>
<td>923</td>
<td>410</td>
<td>0.34</td>
<td>200</td>
<td>610</td>
<td>1.1</td>
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<tr>
<td>Author</td>
<td>Material</td>
<td>Precursors</td>
<td>Method</td>
<td>T (K)</td>
<td>S (µV/K)</td>
<td>$\kappa$ (W/mK)</td>
<td>$\sigma$ (Scm$^{-1}$)</td>
<td>PF ($\mu$W/mK$^2$)</td>
<td>ZT</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------------</td>
<td>-----------------------------</td>
<td>------------------------------------------------------------------------</td>
<td>-------</td>
<td>-----------</td>
<td>-----------------</td>
<td>---------------------</td>
<td>----------------------</td>
<td>-----</td>
</tr>
<tr>
<td>Jiehe Sui et al. [84]</td>
<td>$\text{Bi}<em>{0.87}\text{Ba}</em>{0.12}\text{CuSeO}$</td>
<td>$\text{Bi}_2\text{O}_3$, Bi, Cu, Se and BaO powders</td>
<td>573 K for 8 h and 1023 K for 24 h in vacuum Densified HPS 80 MPa in vacuum at 973 K for 30 min</td>
<td>923</td>
<td>187</td>
<td>0.6</td>
<td>210</td>
<td>810</td>
<td>1.4</td>
</tr>
<tr>
<td>Fu Li et al. [85]</td>
<td>$\text{Bi}_{1-x}\text{Ca}_x\text{CuSeO}$ ($x=0$-0.125)</td>
<td>$\text{Bi}_2\text{O}_3$, Bi, Cu, Se and CaO powders</td>
<td>2 step solid state reaction route SPS at 973 K for 5 min, 50 MPa</td>
<td>773</td>
<td>310</td>
<td>0.75</td>
<td>40</td>
<td>--</td>
<td>0.8</td>
</tr>
<tr>
<td>Son D. N. Luu and Paz Vaqueiro [86]</td>
<td>$\text{Bi}_{1-x}\text{Pb}_x\text{CuSeO}$ ($x=0$-0.2)</td>
<td>$\text{Bi}_2\text{O}_3$, Bi, Cu, Se and PbO$_2$ powders</td>
<td>Solid state 623 K for 20 h and 773 K for 10 h with a 2 Kmin$^{-1}$ ramp rate Annealing at 873 K for 7 h</td>
<td>673</td>
<td>300</td>
<td>1.5</td>
<td>--</td>
<td>830</td>
<td>0.6</td>
</tr>
<tr>
<td>Author</td>
<td>Material</td>
<td>Precursors</td>
<td>Method</td>
<td>T (K)</td>
<td>S (µV/K)</td>
<td>κ (W/mK)</td>
<td>σ (Scm⁻¹)</td>
<td>PF (µW/mK²)</td>
<td>ZT</td>
</tr>
<tr>
<td>------------------------</td>
<td>----------</td>
<td>-----------------------------------</td>
<td>------------------------------------------------------------------------</td>
<td>-------</td>
<td>----------</td>
<td>----------</td>
<td>-----------</td>
<td>-------------</td>
<td>----</td>
</tr>
<tr>
<td>Guang-Kun Ren et al. [87]</td>
<td>Bi₁₋ₓPbₓCuSeO</td>
<td>Bi₂O₃, Bi, Cu, Se and PbO powders</td>
<td>Cold pressed, torch flame SPS AT 973 K for 5 min.</td>
<td>873</td>
<td>300</td>
<td>0.85</td>
<td>250</td>
<td>780</td>
<td>0.9</td>
</tr>
<tr>
<td>Celine Barreteau et al. [88]</td>
<td>Bi₁₋ₓSrₓCuSeO (x=0-0.4)</td>
<td>Bi₂O₃, Cu, Se and SrO powders</td>
<td>Sealed under argon in silica ampules and annealed for 6 h at 573 K SPS at 950K for 10 min.</td>
<td>273</td>
<td>430</td>
<td>--</td>
<td>1000</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Yong Liu et al. [89]</td>
<td>BiCu₁₋ₓSeO (x=0-0.1)</td>
<td>Bi₂O₃, Bi, Cu, and Se powders</td>
<td>Solid state At 573 K 12 h sealed in silica tube At 973 K 8 h again Ball milled at 300 rpm for 4h</td>
<td>923</td>
<td>386</td>
<td>0.4</td>
<td>--</td>
<td>410</td>
<td>0.81</td>
</tr>
</tbody>
</table>
Table 2.2 (cont’d) Thermoelectric properties of BCSO samples from the literature.

<table>
<thead>
<tr>
<th>Author</th>
<th>Material</th>
<th>Precursors</th>
<th>Method</th>
<th>T (K)</th>
<th>S (μV/K)</th>
<th>κ (W/mK)</th>
<th>σ (S/cm⁻¹)</th>
<th>PF (μW/mK²)</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jin Wu et al. [90]</td>
<td>BiCuSeO</td>
<td>Bi, CuO, CaO, Se powders</td>
<td>Ball milled at 500 rpm for several min. SPS at 973 K for 5 min.</td>
<td>773</td>
<td>325</td>
<td>0.5</td>
<td>45</td>
<td>440</td>
<td>0.5</td>
</tr>
<tr>
<td>Yaochun Liu et al.</td>
<td>BiCuSeO</td>
<td>Bi₂O₃, Bi, Cu, and Se powders</td>
<td>Ball milling SPS at 823K for 30 min</td>
<td>773</td>
<td>275</td>
<td>0.53</td>
<td>60</td>
<td>270</td>
<td>0.3</td>
</tr>
</tbody>
</table>
CHAPTER 3

EXPERIMENTAL PART

In this chapter, physical and chemical preparation steps for C-349 and BCSO TE materials will be described in detail separately. Sintering procedures for both materials will also be mentioned. After the description of preparation steps and sintering operations, characterization methods and techniques will be summarized.

3.1. Chemical Synthesis of C-349

C-349 was synthesized by sol-gel route, which allows the production of fine grained powders with a uniform particle size distribution. Firstly, stoichiometric amounts of commercial nitrate salts are dissolved in aqueous pure water, which contains citric acid to obtain 0.1 M solution. The chemical formulas of salts are Ca(NO$_3$)$_2$·4H$_2$O and Co(NO$_3$)$_2$·6H$_2$O. After uniform solution was obtained by continuous stirring, some organics like PEG-400 was added. Citric acid and PEG-400 organics behave like dispersant and complexion agent for complexing metal ions in the solution. Moreover, agglomeration of particles is tried to be minimized due to the presence of these organics. After completing the chemical mixing of precursors as mentioned above, continuous mixing has been performed on hot plate which operated at 353 K. Reflux was also used for the protection of evaporation. Removing the reflux after 2 h mixing caused the gel formation. Before the last sintering operation, the violet color gel was dried at 353 K for 12 h and calcined at a ramp rate of 10°C/min in a programmable box furnace (Protherm) for 2 h at a temperature of 823 K. This operation lets the removal of residual organic compounds from the gel. After calcination, to obtain pure C-349 phase, post sintering was performed under air at 1123 K for 2 h. The sintering
procedure is illustrated in Figure 3.2. The violet gel formed just before sintering operations and the organic free black material after all sintering operations are illustrated in Figure 3.3. The low operating temperature, easy control of size and distribution in early stages of production, homogeneity in atomic level are some benefits of sol-gel process. The synthesis stages of the process and information about the chemicals used can be examined in Figure 3.1 and Table 3.1, respectively.

**Figure 3.1** Schematic representation of sol-gel process for C-349 [69].

**Figure 3.2** Illustration of sintering procedure.
Table 3.1 Detail information about the chemicals used in the synthesis process.

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Cobalt Nitrate</th>
<th>Calcium Nitrate</th>
<th>Citric Acid</th>
<th>PEG-400</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (g/mole)</td>
<td>Co(NO₃)₂·6H₂O</td>
<td>Ca(NO₃)₂·4H₂O</td>
<td>C₆H₈O₇H₂O</td>
<td>H(OC₂H₄)₆OH</td>
<td>H₂O</td>
</tr>
<tr>
<td>Amount used for 0.1 M solution</td>
<td>1.66 g</td>
<td>1.01 g</td>
<td>1 g</td>
<td>5 ml</td>
<td>100 ml</td>
</tr>
</tbody>
</table>

Figure 3.3 a) The violet gel formed just before sintering operations (with organics) and b) the organic free black material after all sintering operations.

3.2. Synthesis of BiCuSeO

Two state solid state reaction route was followed to obtain BCSO. First, the stoichiometric amount of commercial Bi₂O₃, Bi, Cu, and Se powders with high purity
were mixed. The amount of chemicals were used can be examined in Table 3.2. Solid mixture obtained was cold pressed under an axial compressive stress of 100 MPa for 5 min. Then, the disk-shaped samples of 13 mm diameter pellets were placed into a quartz tube with a ceramic boat and sealed under the positive pressure at 573 K for 8 h. Moreover, post sealing was completed at 973 K for 24 h. Sintering operation should be done in positive pressure, other than that, oxygen amount could not be controlled. The basic representation of sintering operation can be seen in Figure 3.5. The tube furnace and boat like ceramic used to place the pellets can be seen in Figure 3.4. Finally, to carry out Seebeck coefficient and electrical conductivity measurements, the disks were cut into a bar in 1*5*12 mm size to specify the heat flow direction and to make TE measurements in the same direction. Another experiment was followed to achieve BCSO powders. For that experiment, one additional step was carried out which include grinding and crashing the pellet to form powders in the agate mortar.

**Figure 3.4** a) The tube furnace where BCSO sintering operations was carried out and b) Boat with disk shaped pellets.
Figure 3.5 Illustration of sintering procedure.

Table 3.2 Details about precursor chemicals which is used for BCSO preparation.

<table>
<thead>
<tr>
<th></th>
<th>Bi$_2$O$_3$</th>
<th>Bi</th>
<th>Cu</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (g/mole)</td>
<td>466</td>
<td>209</td>
<td>64</td>
<td>79</td>
</tr>
<tr>
<td>Amount Used for 1 mmol Solid Solution</td>
<td>0.466 g</td>
<td>0.209 g</td>
<td>0.192 g</td>
<td>0.237 g</td>
</tr>
</tbody>
</table>

3.3. C-349 / BCSO Mixing Operation

After structural and thermoelectrical characterizations were completed for C-349 and BCSO materials, they mixed with each other. Mixing was performed by ball-milling at 400 rpm for 10 min. This mixing operation was repeated 3 times to obtain uniform solid-state mixture. The amount of TE materials that were mixed, designation of samples and brief schematic description of preparation can also be seen in Table 3.3 and Figure 3.6, respectively.
**Table 3.2** The amount of TE materials that were mixed and designation of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BiCuSeO Content</th>
<th>BiCuSeO Amount</th>
<th>Ca₃Co₄O₉ Amount / Composite Amount</th>
<th>Volume Fraction of C-349</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB-0</td>
<td>0 %</td>
<td>0 g</td>
<td>0.5 g / 0.5 g</td>
<td>100</td>
</tr>
<tr>
<td>CB-1</td>
<td>1 %</td>
<td>0.005 g</td>
<td>0.495 g / 0.5 g</td>
<td>99.5</td>
</tr>
<tr>
<td>CB-3</td>
<td>3 %</td>
<td>0.015 g</td>
<td>0.485 g / 0.5 g</td>
<td>98.4</td>
</tr>
<tr>
<td>CB-5</td>
<td>5 %</td>
<td>0.025 g</td>
<td>0.475 g / 0.5 g</td>
<td>97.3</td>
</tr>
</tbody>
</table>

**Figure 3.6** Brief schematic description for C-349 and BCSO production.
3.4. Characterization of Samples

Rigaku Ultima-IV powder diffractometer was used for recording X-ray diffractograms of samples at room temperature. CuKα radiation source is used in order to get information about the structure and phase compositions. Rigaku Qual Analysis software including ICDD PDF database [92] at METU METE X-ray Laboratory was used in order to analyze the phases and identify the peaks.

Multi-point BET analysis were carried out for each sample to investigate surface area, pore volume and pore size of samples. Quantachrome Corporation Autosorb-6 under nitrogen gas atmosphere was used for that purpose at METU Central Laboratory.

To determine the density of specimens, gravimetric method of porosity measurement is used. True density of the samples is investigated by Quantachrome Ultrapycnometer 1000 Helium Pycnometer based on Archimedes’ principle at room temperature at METU Central Laboratory.

The electrical properties of samples were investigated by Hall effect measurements at room temperature. Lakeshore 7700A system were used with van der Pauw geometry between 0.15 and 1.5 T at ASELSAN.

Microstructures of sintered BCSO and C-349 pellets are investigated using scanning electron microscopy (FEI 430 NanoSEM) in Metallurgical and Materials Engineering Department of METU. Variable pressure mode and gold coatings are applied since conducting coating is a matter.
3.5. Thermoelectric Characterizations

TE measurement system consists of a vacuum chamber (VC), two micro heaters and a sample probe. Moreover, Lakeshore model 336 temperature controller, K2182 digital nanovoltmeter and K238 current source comprise the electronic part of the system. VC and electronic parts can be examined in Figure 3.7. Vacuum chamber has four KF25 gates in order to create entrance for vacuum or inert gas pumps. Moreover, thermocouples and heater wires connected to the system through these gates. In order to create complete insulation from non-controlled atmosphere, gate caps are coated with silicone. Sample probe is located in the vacuum chamber. The general cross-sectional view of the sample probe can be examined in Figure 3.8. Heaters and thermocouple cables are connected to temperature controller Lakeshore model 336. In order to measure voltage simultaneously, K2182 digital nanovoltmeter is used. Moreover, K238 current source provides current for resistivity measurements.

![Figure 3.7 TE measurement system.](image)
The following operations were carried out to obtain the Seebeck coefficient and the electrical conductivity of the samples.

- Before all measurements, calibration of thermocouples was completed by using liquid nitrogen. Measurements were performed via Labview 8.0 software.
- For Seebeck measurements, temperature difference is created between two edges of specimen by setting the Lakeshore model 336 temperature controller.
- dV/dT data were taken automatically. Linear fitting to dV/dT data gives the Seebeck coefficient at that measurement temperature. However, the Seebeck voltage of thermocouple is included in that value. Therefore, for all temperature values, the Seebeck coefficient of Chromel leg of k-type thermocouple was measured.
- For electrical resistivity measurements, four-probe method was used. Basically, a constant current was applied to the two probes and the voltage drop on the other two probes was measured.
• Labview code gives the resistance of the samples. The resistivity values then calculated by using:

\[ R = \rho \frac{l}{A} \] (3.1)

Where \( \rho \), \( l \) and \( A \) are resistivity, length and cross-sectional area of samples, respectively.

Measurement is very critical to obtain accurate results. There are some remarkable points that one should be careful while measuring the TE properties of samples, summarized as follows:

For Seebeck measurements:
• the temperature and voltage should be measured at the same location and at the same time;
• the voltage versus temperature gradient data should show linear behavior;
• the electrical and thermal contacts between probe and specimen should be very good;
• the acquisition of low voltages (microvolts) with minimal extraneous contributions;
• the temperature difference of the edges (material) should not be greater than 10 K. More accurate results can be obtained while the temperature difference lies between 3 K and 5 K.
• measurements should be repeated in order to ensure the minimum error and standard deviation.

For electrical conductivity measurements:
• the electrical and thermal contacts between probe and specimen should be very good;
• the temperature difference of the edges (material) should not be greater than 0.05 K.
RESULTS AND DISCUSSION

In this chapter the structural analysis results will be represented and discussed. After structure analysis, the thermoelectric properties of pristine C-349, BCSO and their composites will be demonstrated separately.

4.1. Structural Characterization

4.1.1. Structural Characterization of Pristine C-349

The results of TG-DTA analysis were used for the determination of correct annealing temperature to obtain pure C-349 phase [69]. In Figure 4.1, decomposition of excess citric acid and nitrate salts can be understood by examining the endothermic peaks at 533 and 560 K which show 12.3 % weight loss. Moreover, decomposition of the citrate complex into Co$_3$O$_4$ and CaCO$_3$ phases observed in the exothermic peaks around 633 and 684 K results in a weight loss around 16.1 %. The endothermic peak over the range of 1009-1040 K is associated with the decomposition of CaCo$_3$ to CaO-CaO reaction with Co$_3$O$_4$. According to these results, 1123 K was selected as sintering temperature to obtain pure C-349 phase.
The sintering temperature for BCSO was selected as 973 K which was decided by examining the studies in the literature.

Figure 4.2 represents the XRD pattern of pristine C-349 which is synthesized by citrate sol-gel method. The pure phases of C-349 match with the JCPDS 580661 card formed as the major phase with monoclinic symmetry. There are no other observable traces of extraneous phases or impurities detected which indicate that C-349 phase was obtained purely using sol-gel method.

Figure 4.3 represents SEM images of C-349 at high and low magnifications. The images were taken at the fracture surfaces. Minor amount of agglomeration of plate like particles can be observed in SEM images. The agglomeration is related with the formation of metallic or covalent bonds that cannot be easily disrupted in nanoscale. Moreover, by examining SEM images, it can be concluded that the average particle
size is below 1 μm. Figure 4.4 shows the EDS spectrum of pristine C-349. The atomic percentage value of Ca to Co is 0.73 as given in Table 4.1. These results match with the stoichiometry of C-349.

![EDS spectrum of C-349](image)

**Figure 4.2** The XRD pattern of C-349 compound.

![XRD pattern](image)

**Figure 4.3** a) FE-SEM image of C-349 in high magnification and b) FE-SEM image of C-349 in low magnification.
The particle size was tried to be obtained by BET analysis. The surface area of C-349 was found as 14.34 m²g⁻¹ by BET analysis. According to true density measurements, the density of pristine C-349 is 4.53 g cm⁻³. By using \( \frac{6000}{\text{(surface area in m}^2\text{/g)}} \times \text{(density in g/cm}^3\text{)} \) formula, the average particle diameter was calculated as 92 nm. Pore volume and sizes can be seen in Table 4.3. Scherrer equation could not be used in particle size calculation because of crystallites with greater than 100 nm, there is no measurable peak broadening of diffraction lines in XRD spectra.

4.1.2. Structural Characterization of Pristine BCSO

Figure 4.5 shows powder XRD pattern of pristine BCSO. All the major Bragg peaks exactly match with the JCPDS 450296 card and can be indexed in the ZrSiCuAs structure type. The only little minor phase observed belongs to Bi₂O₃ which can be seen at 2θ=28°. No other secondary phases were detected. The lattice parameters \( a \) and \( c \) were calculated as 3.945 Å and 8.794 Å, respectively, which shows good agreement with the literature. The lattice parameters were calculated using Eq (4.1)
and Eq (4.2) which are Bragg’s Law and lattice constants equation for tetragonal symmetry, respectively. In Bragg’s Law, \( \lambda \), \( d \) and \( \Theta \) represents wavelength, lattice spacing and the angle that gives maximum diffraction, respectively. In lattice constants equation, \( d \) is interplanar spacing, \( h, k, l \) are miller indices and \( a, c \) represents the lattice constants. FE-SEM images and elemental analysis of BCSO powders are illustrated in Figure 4.6 and Figure 4.7, respectively. Examination of as-prepared samples by electron microscope indicates that the as-prepared samples contain plate-like grains and micron size particles. Moreover, grain boundaries cannot be easily definable, and a typical powder structure can be seen. The elemental analysis data is coherent with the stoichiometry of BCSO. The atomic ratios can be seen in Table 4.2.

![XRD pattern of BCSO compound](image)

**Figure 4.5** The XRD pattern of BCSO compound.

\[
2d\sin\Theta = n\lambda \tag{4.1}
\]

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \tag{4.2}
\]
Table 4.1 Atomic percentage values of Ca/Co for Ca$_3$Co$_4$O$_9$ composition obtained through EDS analysis.

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>Ca$_3$Co$_4$O$_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/Co</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Table 4.2 Atomic percentage values of Bi/Cu, Bi/Se and Cu/Se for BiCuSeO composition obtained through EDS analysis.

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>BiCuSeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi/Cu</td>
<td>1.08</td>
</tr>
<tr>
<td>Bi/Se</td>
<td>0.93</td>
</tr>
<tr>
<td>Cu/Se</td>
<td>0.84</td>
</tr>
</tbody>
</table>

The average particle size of the BCSO powders was calculated using surface area measurements through multi point BET analysis and true density measurements. The surface area and density of BCSO was measured as 1.21 m$^2$g$^{-1}$ and 7.91 g/cm$^3$, respectively. Using 6000/(surface area in m$^2$/g)x(density in g/cm$^3$) formula, the average particle size was calculated as 0.62 µm. In this calculation, particles were assumed as spherical and agglomeration was neglected. The theoretical and measured densities, measured BET surface areas, pore volume and sizes, calculated average particle sizes from BET analysis can be seen in Table 4.3.
Figure 4.6 a) FE-SEM image of BCSO powders in high magnification. b) FE-SEM image of BCSO powders in low magnification.

Figure 4.7 EDS spectrum and elemental analysis of BCSO.
Table 4.3 Density, pore size and particle size analysis of C-349 and BCSO samples.

<table>
<thead>
<tr>
<th></th>
<th>C-349</th>
<th>BCSO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Theoretical density (g/cm³)</strong></td>
<td>4.68</td>
<td>8.90</td>
</tr>
<tr>
<td><strong>Measured density (g/cm³)</strong></td>
<td>4.53</td>
<td>7.91</td>
</tr>
<tr>
<td><strong>BET surface area (m²/g)</strong></td>
<td>1.21</td>
<td>14.34</td>
</tr>
<tr>
<td><strong>Pore Volume (g/cc)</strong></td>
<td>1121.0</td>
<td>246.3</td>
</tr>
<tr>
<td><strong>Pore Size (Å)</strong></td>
<td>74.81</td>
<td>74.00</td>
</tr>
<tr>
<td><strong>Calculated average particle size through BET measurements (μm)</strong></td>
<td>0.09</td>
<td>0.62</td>
</tr>
</tbody>
</table>

4.1.3. Structural Characterization of C-349/BCSO Composites

The XRD patterns of C-349 (CB-0) and composites (CB-1, CB-3 and CB-5) are illustrated in Figure 4.8. For CB-0, all the relative Bragg peaks match with the JCPDS 580661 card, which is for Ca₃Co₄O₉. Although there is a little difference in the intensities of relative peaks, no other extra phase is observed. Since XRD is only able to detect the secondary phases more than 5 wt%, BCSO peaks could not be observed. It can be concluded that the matrix cobaltite phase is protected.

Microstructures of ball-milled oxide pellets were investigated using scanning electron microscopy (FEI Quanta 400F) at METU Central Laboratory. Figure 4.9 depicts the SEM images of pristine C-349, pristine BCSO and their composites. The results of the EDS analysis were consistent with the stoichiometry of C-349 and BCSO. For all samples, fresh fracture surfaces were investigated. Plate-like grains with different sizes and orientations can be observed which are typical microstructures of TE materials prepared by solid-state technique. The addition of BCSO has no effect on this plate-like microstructure. As can be seen from the SEM images, the particle size of BCSO
is in micron size where C-349 phase consists of sub-micron particles. Figure 4.10 shows the EDS mapping. In this figure, calcium is represented by purple, cobalt by turquois, bismuth by yellow, copper by green and selenium by blue colors. Mapping images showed that the BCSO material could be homogenously dispersed into C-349 matrix by successful ball-milling process. The partial accumulation of BCSO was observed as the amount increase. The accumulation can be examined in Figure 4.10 (h). The EDS analysis was performed to determine the increase in BCSO in matrix material C-349 that can be examined in Figure 4.11. There is a continuous increase in atomic ratios of Bi, Cu and Se between the samples of CB-0 and CB-5 that verifies the increase the amount of BCSO.

![XRD patterns](image.png)

**Figure 4.8** The XRD patterns of pristine C-349 (CB-0), CB-1, CB-3 and CB-5.
Table 4.4 Atomic percentage values of second phase elements of pristine C-349 and its composites

<table>
<thead>
<tr>
<th>Atomic Percentage Values Bi, Cu and Se</th>
<th>CB-0</th>
<th>CB-1</th>
<th>CB-3</th>
<th>CB-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0</td>
<td>0.68</td>
<td>1.08</td>
<td>1.31</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>0.15</td>
<td>0.42</td>
<td>0.90</td>
</tr>
<tr>
<td>Se</td>
<td>0</td>
<td>0.63</td>
<td>0.80</td>
<td>1.15</td>
</tr>
</tbody>
</table>

To investigate the particle sizes more clearly and to determine pore volume and size, multi point BET analysis were carried out. The obtained values are illustrated in Table 4.5. Addition of BCSO into C-349 phase results in decrease in pore size and increase in pore volume. The pore volume of CB-5 is nearly three times more than pristine C-349. Moreover, the increase in pore volume consistent with decrease in densities.

Table 4.5 Surface areas, pore volumes and pore sizes, measured densities and calculated particle sizes of all samples obtained by multi-point BET analysis.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (g/cc)</th>
<th>Pore Size (Å)</th>
<th>Measured Density (g/ cm³)</th>
<th>Calculated Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCSO</td>
<td>1.21</td>
<td>1121.0</td>
<td>74.00</td>
<td>7.91</td>
<td>626</td>
</tr>
<tr>
<td>C-349</td>
<td>14.34</td>
<td>246.3</td>
<td>74.81</td>
<td>4.53</td>
<td>92</td>
</tr>
<tr>
<td>CB-1</td>
<td>6.33</td>
<td>340.1</td>
<td>63.63</td>
<td>4.47</td>
<td>212</td>
</tr>
<tr>
<td>CB-3</td>
<td>5.67</td>
<td>465.1</td>
<td>59.38</td>
<td>4.32</td>
<td>245</td>
</tr>
<tr>
<td>CB-5</td>
<td>2.70</td>
<td>729.9</td>
<td>63.89</td>
<td>3.89</td>
<td>571</td>
</tr>
</tbody>
</table>
Figure 4.9 SEM images of a) BCSO b) CB-0 c) CB-1 d) CB-3 e) CB-5.
Figure 4.10 a) SEM image of CB-5 and quantitative maps of main constituents (b) oxygen, (c) calcium, (d) cobalt, (e) bismuth, (f) copper and (g) Ca,Co,O together and (h) Bi,Cu,Se together. Major phases are identifiable by comparing concentrations in the individual maps.
Figure 4.11 EDS spectra and elemental analysis of a) CB-0, b) CB-1, c) CB-3 and d) CB-5.

4.2. Electrical Properties

The electrical properties of samples with 0.05 cm thickness were investigated by Hall effect measurements at room temperature. Lakeshore 7700A system were used with van der Pauw geometry between 0.15 and 1.5 T at ASELSAN. Table 4.6
summarizes the results of Hall effect measurements. The electrical conductivity and resistivities are calculated from the following equation:

\[
\text{Conductivity} = \frac{\text{Sheet carrier density} \times 1.6 \times 10^{-19} \times \text{Mobility}}{\text{Sample thickness}} = \frac{1}{\text{Resistivity}} \quad (4.1)
\]

The carrier concentrations of BCSO and CB-0 were measured \(1.1 \times 10^{18}\) and \(1.3 \times 10^{20}\), respectively. Although the electron mobility of pristine BCSO is high, the conductivity is not sufficient for high efficient TE materials due to low carrier concentration. On the other hand, pristine C-349 (CB-0) shows low mobility, while the carrier concentration is optimum. From Hall effect measurements, it has been observed that as the BCSO content increase, there is no significant decrease in carrier concentration. Moreover, measured mobility of composites are varying but all have almost 3 times greater value than CB-0. The increase in mobility without any significant decrease in carrier concentration results in increase in electrical conductivity. In our experimental system, the resistivity decreased up to 9 m\(\Omega\).cm for CB-5.

**Table 4.6** Hall effect measurements results and calculated conductivity and resistivity values.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Sheet Hall coefficient (cm(^2)/C)</th>
<th>Sheet carrier density (1/cm(^2))</th>
<th>Mobility [cm(^2)/(V s)]</th>
<th>Resistivity ((\Omega).cm)</th>
<th>Conductivity (1/(\Omega).cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCSO</td>
<td>109.0</td>
<td>(5.7 \times 10^{16})</td>
<td>16.4</td>
<td>0.281</td>
<td>3.5</td>
</tr>
<tr>
<td>CB-0</td>
<td>7.2</td>
<td>(6.6 \times 10^{18})</td>
<td>1.8</td>
<td>0.026</td>
<td>38.4</td>
</tr>
<tr>
<td>CB-1</td>
<td>2.6</td>
<td>(3.1 \times 10^{18})</td>
<td>6.7</td>
<td>0.015</td>
<td>66.4</td>
</tr>
<tr>
<td>CB-3</td>
<td>5.6</td>
<td>(1.4 \times 10^{18})</td>
<td>22.9</td>
<td>0.001</td>
<td>102.6</td>
</tr>
<tr>
<td>CB-5</td>
<td>3.0</td>
<td>(1.2 \times 10^{18})</td>
<td>28.9</td>
<td>0.001</td>
<td>110.9</td>
</tr>
</tbody>
</table>

The temperature dependent Seebeck coefficient and electrical conductivity were investigated for both pristine and composite samples from 300 K to 900 K. Fig. 3a exhibits Seebeck coefficients of pristine BCSO. All the values of the Seebeck coefficient are positive, indicating p-type conduction. The origin of the p-type
conduction in pristine BCSO is possibly related to Cu vacancies [25]. The Seebeck coefficient measured at 300K around 320 µV/K and reached up to 369 µV/K at 900 K. The results are very compatible with early findings [26-28]. The measured values of pristine C-349 and composites can be seen in Fig. 3(b). The positive Seebeck coefficient of C-349 (CB-0) indicating that holes are dominant for conduction. The values of the Seebeck coefficient exhibit the same trends which slightly increase with the temperature for all the samples.

The properties such as Seebeck coefficient, electrical conductivity and power factor which determine thermoelectric characteristics were investigated for both pristine and composite samples. Temperature dependent Seebeck coefficient and electrical conductivity measurements were performed between 300 K and 900 K using the measurement system described in Chapter 3.

Table 4.7 Temperature dependent Seebeck coefficient of Chromel leg of k-type thermocouple.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Measured Seebeck coefficient (µV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>29.2</td>
</tr>
<tr>
<td>400</td>
<td>27.4</td>
</tr>
<tr>
<td>500</td>
<td>25.6</td>
</tr>
<tr>
<td>600</td>
<td>23.8</td>
</tr>
<tr>
<td>700</td>
<td>21.9</td>
</tr>
<tr>
<td>800</td>
<td>20.0</td>
</tr>
<tr>
<td>900</td>
<td>18.2</td>
</tr>
</tbody>
</table>

As mentioned in Chapter 3, Chromel leg of k-type thermocouple was placed in the system to measure the temperature simultaneously and voltage created between two edges of the specimen. Therefore, the Seebeck voltage of thermocouple is included
in all measurements. In order to find the correct voltage drop of the sample, for all temperature ranges, the Seebeck coefficient of Chromel leg of k-type thermocouple was calculated separately. The measurements of Chromel leg of k-type thermocouple can be seen in Table 4.7.

4.3. Thermoelectric Properties of Pristine C-349, Pristine BCSO and Their Composites

Seebeck coefficient, electrical conductivity and power factor were investigated for both pristine and composite samples. Temperature dependent Seebeck coefficient and electrical conductivity measurements were performed between 300 K and 900 K. Figure 4.12 exhibits the Seebeck coefficients of pristine BCSO. All the values of Seebeck coefficient are positive, indicating p-type conduction. The origin of the p-type conduction in pristine BCSO is possibly related with Cu vacancies since the holes are directly generated in conductive (Cu$_2$Se)$_2^-$ layers due to Cu vacancies [12]. The Seebeck coefficient is measured as 320 µV/K at 300K and reached up to 369 µV/K at 900 K. The results are very compatible with early findings [89, 90]. The measured Seebeck values of pristine C-349 and composites can be seen in Figure 4.13. The positive Seebeck coefficient of C-349 (CB-0) indicates that holes are the dominant carriers for conduction. For all the samples, the values of the Seebeck coefficient exhibit the same trend which gradually increase with the temperature. To obtain total errors of all Seebeck measurements, the samples were measured 11 times under the same condition. First, the standard deviations were calculated. Afterwards, by adding an instrumental uncertainty to standard deviation multiplied by 3 gives the total error. The obtained values, standard deviations and calculated total errors for all samples are illustrated in Table 4.8.

At room temperature, the absolute value of the Seebeck coefficient of CB-0 was measured as 119 µV/K and reaches the maximum value of 154 µV/K at 900 K. It is observed that the Seebeck coefficient increases while the BCSO content in C-349 matrix also increases. The maximum Seebeck coefficient measured was 167 µV/K
for CB-5 at 900 K. The increase in Seebeck coefficient with BCSO content can be explained as follow. First, the Seebeck coefficient of BCSO is higher than CB-0. Therefore, according to rule of mixture, it is normal to obtain higher Seebeck coefficient. Second, CB-5 sample has a more porous structure than CB-0 and this structural change will lead to increased carrier scattering at grain boundaries and results an enhancement in the Seebeck coefficient.

Table 4.8 Seebeck coefficient measurements for total error calculation.

<table>
<thead>
<tr>
<th>Number of measurements</th>
<th>BCSO</th>
<th>CB-0</th>
<th>CB-1</th>
<th>CB-3</th>
<th>CB-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>320.2</td>
<td>119.1</td>
<td>121.3</td>
<td>132.4</td>
<td>139.4</td>
</tr>
<tr>
<td>2</td>
<td>316.5</td>
<td>121.2</td>
<td>120.3</td>
<td>130.3</td>
<td>140.3</td>
</tr>
<tr>
<td>3</td>
<td>323.4</td>
<td>124.6</td>
<td>122.2</td>
<td>131.1</td>
<td>140.6</td>
</tr>
<tr>
<td>4</td>
<td>316.2</td>
<td>118.4</td>
<td>122.9</td>
<td>131.8</td>
<td>142.7</td>
</tr>
<tr>
<td>5</td>
<td>318.8</td>
<td>120.3</td>
<td>125.5</td>
<td>133.6</td>
<td>138.3</td>
</tr>
<tr>
<td>6</td>
<td>315.9</td>
<td>123.5</td>
<td>117.4</td>
<td>130.9</td>
<td>139.4</td>
</tr>
<tr>
<td>7</td>
<td>321.4</td>
<td>120.3</td>
<td>119.4</td>
<td>134.1</td>
<td>139.0</td>
</tr>
<tr>
<td>8</td>
<td>314.4</td>
<td>119.7</td>
<td>120.8</td>
<td>129.3</td>
<td>142.3</td>
</tr>
<tr>
<td>9</td>
<td>319.1</td>
<td>120.8</td>
<td>121.7</td>
<td>130.2</td>
<td>143.2</td>
</tr>
<tr>
<td>10</td>
<td>320.0</td>
<td>123.7</td>
<td>123.9</td>
<td>129.9</td>
<td>137.4</td>
</tr>
<tr>
<td>11</td>
<td>324.7</td>
<td>118.6</td>
<td>122.6</td>
<td>131.6</td>
<td>144.2</td>
</tr>
</tbody>
</table>

Average: 318.9 120.1 121.6 131.3 140.6

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Deviation</td>
<td>3.71</td>
<td>1.87</td>
<td>2.09</td>
<td>1.46</td>
<td>2.09</td>
</tr>
<tr>
<td>3*Standard Deviation</td>
<td>9.32</td>
<td>5.61</td>
<td>6.2958</td>
<td>4.40</td>
<td>6.27</td>
</tr>
<tr>
<td>Instrumental Uncertainty (± 0.29 μV)</td>
<td>0.29</td>
<td>0.29</td>
<td>0.29</td>
<td>0.29</td>
<td>0.29</td>
</tr>
</tbody>
</table>

**Total Error (μV/K)**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>9.61</td>
<td>5.90</td>
<td>6.58</td>
<td>4.69</td>
<td>6.56</td>
</tr>
</tbody>
</table>
Figure 4.12 Temperature dependent Seebeck coefficient of pristine BCSO.

Figure 4.13 Temperature dependent Seebeck coefficients of CB-0, CB-1, CB-3 and CB-5.
The temperature dependent electrical conductivity measurements were performed by four-probe technique. Results of pristine BCSO can be examined in Figure 4.14. The electrical conductivity of pristine BCSO is 0.98 S/cm at 300 K that is very similar with the findings in the literature [12]. The electrical conductivity is almost doubled from RT to 600 K. On the other hand, after 600 K, the increment gets faster and reached up to 10.3 S/cm at 900 K. The continuous increase in conductivity with temperature indicates the semiconductor transport behavior. However, the conductivity of BCSO is relatively low compared to other TE oxides. The low conductivity is related with low carrier concentration, which is about $1 \times 10^{18}$ cm$^{-3}$ [12]. The measured conductivity in this work is rather low compared to literature values [85,90]. The reason can be related with very minor amount of Bi$_2$O$_3$ phase that can be seen in XRD pattern. The temperature dependence of the electrical resistivity of pristine C-349 and composites between 300 and 900 K is shown in Figure 4.15. While the BCSO quantity increases, the resistivity of composites decreases. The most conductive sample is CB-5 with a resistivity 16.2 mΩ.cm at 900 K.

![Figure 4.14 Temperature dependent electrical conductivity of BCSO.](image)
As described in Chapter 2, the power factor of material equal to the square of Seebeck coefficient times the electrical conductivity. The calculated power factors (PF) of samples are illustrated in Figure 4.16. As expected, BCSO has a low PF at low temperatures due to having an insufficient electrical conductivity. However, at high temperatures, although the electrical conductivity is still low, BCSO shows high PF due to the relatively high Seebeck coefficient. The sample with the highest power factor is CB-5 with 0.17 mW/mK² at 900 K. It can be concluded that the significant power factor enhancement of C-349 was achieved in composite sample, approximately 41% higher than pristine C-349 at 900 K.

![Temperature dependent electrical resistivity of CB-0, CB-1, CB-3 and CB-5 samples.](image)

**Figure 4.15** Temperature dependent electrical resistivity of CB-0, CB-1, CB-3 and CB-5 samples.
Figure 4.16 Temperature dependent power factors of BCSO, CB-0, CB-1, CB-3 and CB-5.

Table 4.9 Maximum TE properties of all samples. All values represent the measurements at 900 K.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Seebeck Coefficient (µV/K)</th>
<th>Seebeck Coefficient from Rule of Mixture (µV/K)</th>
<th>Electrical Resistivity (mΩ.cm)</th>
<th>Power Factor (mW/K²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCSO</td>
<td>367.2</td>
<td>367.3</td>
<td>94.3</td>
<td>0.143</td>
</tr>
<tr>
<td>CB-0</td>
<td>155.1</td>
<td>155.6</td>
<td>19.9</td>
<td>0.120</td>
</tr>
<tr>
<td>CB-1</td>
<td>158.7</td>
<td>156.1</td>
<td>18.4</td>
<td>0.135</td>
</tr>
<tr>
<td>CB-3</td>
<td>163.4</td>
<td>158.4</td>
<td>17.3</td>
<td>0.153</td>
</tr>
<tr>
<td>CB-5</td>
<td>167.2</td>
<td>160.7</td>
<td>16.2</td>
<td>0.172</td>
</tr>
</tbody>
</table>

Power factor enhancement is caused by the simultaneous increase in Seebeck coefficient and electrical conductivity. Explanation and comments should be
carried out by evaluating the reasons of the increase in Seebeck coefficient and electrical conductivity separately. There are two main reasons for the increase in the Seebeck coefficient value in parallel with the BCSO ratio in the composite. According to Hall effect measurements, the addition of BCSO into C-349 phase cause a decrease in total carrier concentration and this decrement leads the Seebeck coefficient to increase. Moreover, multi-point BET analysis shows that CB-5 has a more porous structure than CB-0 and this porous structure will lead more carrier scattering at grain boundaries and results in the enhancement of the Seebeck coefficient [93]. The enhancement in electrical conductivity is related with carrier mobility increase without any significant decrease in carrier concentration. The addition of BCSO phase cause increase in product of carrier concentration and mobility. The same behavior has been observed by Yang Du et al. [95] for Na_{0.77}CoO_2/Ca_3Co_4O_9 composites. However, in their work, the Hall effect measurements were not been carried out. In literature, most work intent to reduce thermal conductivity and therefore the carrier transportation mechanisms related with electrical conductivity are somehow skipped. This work provides important information about transportation mechanisms, but to get more information, suggestions should be taken to account in the following section.
CHAPTER 5

SUMMARY, CONCLUSION AND SUGGESTIONS

In this study, the production and development of high temperature TE oxide and their composites has been accomplished. Successful preparation was carried out for pristine C-349 and BCSO by sol-gel and solid-state reaction route respectively. In structural characterization, no second phase was observed for C-349. For BCSO, only second phase was Bi$_2$O$_3$ and it probably caused by the excess oxygen in sintering operation. After complete structural characterization of each pristine material, C-349/BCSO bulk composites as pellets have been prepared and thermoelectric properties have been investigated.

As the BCSO content increased, the electrical conductivity and the Seebeck coefficient simultaneously increased. The highest power factor was obtained as 0.17 mW/mK$^2$ in the composite containing 5 wt% of BCSO. This value represents nearly 41% improvement in PF of C-349. These results prove that composite engineering technology will provide a tremendous advantage in developing TE materials with higher efficiency. In this work, it is observed that slight decrease in carrier concentration and obtaining more porous structure cause an increase in Seebeck coefficient. The electrical conductivity enhancement based on significant mobility increase. It was proved that increasing electrical properties has a crucial role in obtaining highly efficient TE materials. However, in literature, most work carried out about composite engineering to this time indent to reduce the thermal conductivity. Therefore, there is a huge potential for further experimental studies on power factor enhancement under the purpose of obtaining high TE materials.
It will be useful to consider the following suggestions in the studies that will be the continuation of this study.

- The matrix material can be exchanged with BCSO and TE properties of new composite system can be reinvestigated. While this suggestion will be considered, the additional amount of second phase should be same with the first system in order make appropriate comparison.
- The amount of second phase will be increased to more than 5% so that the effect of addition on structure will be further investigated.
- Measuring temperature dependent thermal conductivities of all samples can give an important information about the carrier transportation mechanisms.
REFERENCES


[19] Lee HoSung “Thermoelectric Design and Materials” Western Michigan University, USA, 2017

a thin-wire metal” Precision Electromagnetic Measurements (CPEM 2014), 52–53, 2014


53, 2016


[84] Jiehe Sui, Jing Li, Jiaqing He, Yan-Ling Pei, David Berardan, Haijun Wu, Nita Dragoe, Wei Cai and Li-Dong Zhao, “Texturation boosts the thermoelectric performance of BiCuSeO oxyselenides”, Energy and Environmental Science 6:2916-2920, 2013


[87] Guang-Kun Ren, Jin-le Lan, Sajid Butt, Kyle J. Ventura, Yuan-Hua Lin and Ce-Wen Nan “Enhanced thermoelectric properties in Pb-doped BiCuSeO
oxyselenides prepared by ultrafast synthesis”, RSC Advances 5:69878-69885, 2015


[89] Yong Liu, Li-Dong Zhao, Yaochun Liu, Jinle Lan, Wei Xu, Fu Li, Bo-Ping Zhang, David Berardan, Nita Dragoe, Yuan-Hua Lin, Ce-Wen Nan, Jing-Feng Li, and Hongmin Zhu, “Remarkable Enhancement in Thermoelectric Performance of BiCuSeO by Cu Deficiencies” Journal of American Chemical Society 133:20112–20115, 2011


