Fabrication and Characterization of Bulk Nanostructured Cobalt Antimonide based Skutterudites Materials for Thermoelectric Applications

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Fabrication and Characterization of Bulk Nanostructured Cobalt Antimonide based Skutterudites Materials for Thermoelectric Applications.

By
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Abstract

The increasing price of oil, global warming and rapid industrial growth has drawn much attention to renewable energy technologies over the last few decades. The total energy consumption is estimated to increase 1.4% per year globally. About 90% of this energy supply is generated through fossil fuel combustion with a typical efficiency of 30-40%. The remaining 60-70% of the energy is lost to the environment via automotive exhaust or industrial processes. It is highly desired to retrieve wasted heat to improve the overall efficiency of the energy conversion. Developing thermoelectric materials and devices is a potential solution to utilize waste heat as an energy source.

Skutterudites are known to be promising thermoelectric materials in the temperature range 600K to 900K. Novel nanoengineering approaches and filling of skutterudites structure can further improve the transport properties of the material. In this work, Cobalt Antimonide (Co$_4$Sb$_{12}$) based skutterudites were fabricated via mechanical milling and alloying. Rear earth material Ytterbium and Cerium are used as fillers to substitute the cages in the crystal lattice of these materials. Base material is synthesized via thermochemical reduction of the precursors under hydrogen. Further processing of the material is performed with ball milling and Spark Plasma Sintering (SPS). Ball milling parameters were optimized for nanostructuring of Co$_4$Sb$_{12}$. Grain size was significantly reduced after SPS compaction. Finally, Thermoelectric transport properties of the material is evaluated over the temperature range 300K to 900K for five different composition of the skutterudites materials. Significant reduction in materials thermal conductivity was achieved through nanostructuring.
Keywords: Thermoelectric, Bulk nanostructured, Skutterudites, Cobalt Antimonide, Ball milling, Spark Plasma Sintering.
# Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>TE</td>
<td>Thermoelectric</td>
</tr>
<tr>
<td>ZT</td>
<td>Thermoelectric Figure of Merit</td>
</tr>
<tr>
<td>S</td>
<td>Seebeck Coefficient</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Electrical Resistivity</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Electrical Conductivity</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>Thermal Conductivity</td>
</tr>
<tr>
<td>( \kappa_e )</td>
<td>Electronic Thermal Conductivity</td>
</tr>
<tr>
<td>( \kappa_l )</td>
<td>Lattice Thermal Conductivity</td>
</tr>
<tr>
<td>( S^2 \sigma )</td>
<td>Power Factor</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
</tr>
<tr>
<td>NS</td>
<td>Nanostructured</td>
</tr>
<tr>
<td>NM</td>
<td>Nanomaterial</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>BM</td>
<td>Ball Milling</td>
</tr>
<tr>
<td>PCA</td>
<td>Process Control Agent</td>
</tr>
<tr>
<td>SPS</td>
<td>Spark Plasma Sintering</td>
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<tr>
<td>PGEC</td>
<td>Phonon Glass Electron Crystal</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>PPMS</td>
<td>Physical Property Measurement System</td>
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1 Introduction

Due to massive industrial development and population growth over the 19th century, there is an enormous surge in the global demand for energy. To meet the energy deficiency in upcoming days a transition is required from natural energy resources to renewable and sustainable energy production. Thermoelectric materials are considered to be one of the potential solutions to tackle global energy crisis. Thermoelectric (TE) devices are environmentally friendly energy transforming unit that can convert waste heat into electricity. TE materials are fascinating for its small size, comparatively lower weight, scalability and high reproducibility.[1]

Despite all these advantages, TE devices are not widely in operation due to their low performing efficiency. Currently, they are only used in niche markets where reliability and simplicity are more important than the performance. Over the last two decades, intensive research took place globally demanding TE materials with improved energy conversion properties. The outcome so far achieved is very promising and appealing further attempts for the enhancement of the TE properties of materials to the next level.[2]

1.1 Thermoelectric Phenomenon

The thermoelectric effect is the direct conversion of heat into electrical energy and vice versa. A thermoelectric device creates electric voltage when there is a temperature difference (ΔT) on the two sides of the TE material. Conversely, when a voltage is applied to the material, it creates a temperature difference over the two sides of the material. At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side. This effect can be applied for generating electricity, measuring temperature or changing the temperature of objects. The term ‘Thermoelectric effect’ refers to three separately identified effects known as ‘Seebeck Effect’, ‘Peltier effect’ and ‘Thompson effect’.[3]

1.1.1 Seebeck Effect, Peltier Effect and Thompson Effect

In the early 1800s, German physicist Thomas Seebeck observed that if two dissimilar materials were joined together and the junctions were held at different Temperatures, then a voltage difference was developed which was proportional to the temperature difference.[4] The ratio of the voltage developed to the temperature difference is related to an intrinsic property of the materials termed as the Seebeck coefficient (S) or the Thermopower.
This effect can be observed by establishing a temperature gradient across a material while the more energetic electrons migrate to a lower potential until an electric field is established to slow down the further flow of electrons (Figure 1.1a). Seebeck effect is the basic theory behind TE Generators.

![Thermoelectric Phenomena](image)

**Figure 1.1** Thermoelectric Phenomena (a) Seebeck Effect, (b) Peltier Effect

Few years after Seebeck’s observation, French physicist Jean Peltier introduced the opposite function of the Seebeck effect.[5] Peltier experimented that if an electrical current is passed through the junction of two dissimilar materials, heat is either absorbed or rejected at the junction, depending on the current’s direction (Figure 1.1b). This effect is due to the difference in the Fermi energies of the two materials. Peltier effect is the basic theory behind thermoelectric coolers or heaters. The Thompson effect deals with the heat transport within a single material unlike the Seebeck and Peltier effect.

### 1.2 TE Devices & Their Applications

Peltier effect is the basis for many modern-day TE refrigeration devices and Seebeck effect is the basis for TE power generation devices. The basic thermoelectric energy conversion unit composed of two different (a p-type and n-type) semiconducting materials connected together with a conducting material. A TE module or device consists of an array of these units, which are arranged electrically in series and thermally in parallel.[6]
Figure 1.2 Important Application areas for TEGs

In most of the sectors energy in the form of waste heat (65% of the energy invested) that would normally lost could be converted into electrical energy using a Thermoelectric Generator (TEG). TE material can be widely applicable in Automobile industries, airline industries, power plants and portable electronic devices (Figure 1.2).[7] The advantages of TE solid-state energy conversion are compactness, no moving parts and allow localized heating or cooling. TE materials are reliable for its reproducibility and scalability.

1.3 Figure of Merit (ZT)

TE properties of material is regulated by the trade-off between three fundamental characteristics which are often opposite in nature. These parameters defines the dimensionless Figure of merit (ZT) as

\[ ZT = \frac{S^2 \sigma}{\kappa} T \]

Which implies challenges to create efficient TE materials on achieving simultaneously high electrical conductivity (\(\sigma\)), High Seebeck coefficient or thermopower (\(S\)) and low thermal conductivity (\(\kappa\)), where \(T\) is the absolute Temperature. Also \(S^2 \sigma\) - is referred as the Power factor.[3]
1.4 Challenges in Thermoelectric Research

Improvement of TE materials performance requires critical engineering to deal with some conflicting inherited material characteristics. In order to increase $ZT$ simultaneously high $\sigma$, low $\kappa$ and a high $S$ are required in the same material. The fact that all these properties are strongly interdependent makes the enhancement of $ZT$ extremely difficult.[8] Novel approaches are required to achieve materials TE efficiency to its next level of improvement.

1.5 TE Materials of Interest

As there is no such material exists in nature that inherits good TE characteristics, materials needs to be engineered and designed for this purpose. But obviously selection of materials is based on the basic physical and chemical properties which propose a higher $ZT$.

![Figure 1.3 TE behavior of different classes of materials][9]

Figure 1.3 implies that depending on carrier concentration, among the four classes of materials doped Semiconductors and Semimetals are nominated as TE materials. Insulators are not a good candidate due to very low $\sigma$ and metals are excluded for very high $\kappa$ and low $S$. 

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[9] Figure 1.3 TE behavior of different classes of materials.
1.6 Strategies for Improving ZT

In 1995, a novel concept referred as the ‘Phonon Glass Electron Crystal’ (PGEC) approach was introduced by Slack and co-workers.[10] In the PGEC concept, a Glass-like \( \kappa \) can coexist with charge carriers of high mobility in the same material.

The PGEC approach has accelerated a significant amount of new research and has led to promising increment in TE conversion efficiency for several compounds such as the Skutterudites and Clathrates. ‘Skutterudites’ a very special group of materials compound that offers voids in its crystal structure as it was referred in the PGEC concept. Among the various combination of Skutterudites compounds, Cobalt Antimonide (Co\(_4\)Sb\(_{12}\)) based compounds have mostly attracted the researchers attention for its crystal structure.[11]

A PGEC materials features cages (voids) in its crystal structure. A relatively smaller atom than the cage could incorporate inside the cage and able to produce ‘rattling effect’ which can create dynamical disorders. This phenomenon produces a phonon damping effect that can result in dramatic reduction of the lattice thermal conductivity of the material.[12]

Various approaches have been taken so far to improve the overall efficiency of TE materials.[13] For achieving high \( \sigma \) and \( S \), doping or carrier concentration tuning is required.[14] Optimization of effective mass and band gap engineering taken into consideration for maintaining high \( S \).[15] For lowering \( \kappa \) in bulk TEs nanoengineering can offer significant improvement by phonon confinement and grain boundary scattering. Achieving low \( \kappa \) also contribute in enhancing materials \( S \).[16]

1.6.1 Optimization of Thermal Conductivity

A primary requirement for an efficient TE material is to have low thermal conductivity. Overall thermal conductivity is contributed by two different means of thermal transport, which is referred in Weidemann-Franz law as below:

\[
\kappa = \kappa_e + \kappa_l
\]

\( \kappa \) represents the overall thermal conductivity, \( \kappa_e \) represents electronic part of the thermal conductivity and \( \kappa_l \) represents the lattice vibration contribution to the overall thermal conductivity.[10]

\( \kappa_e \) is the heat transported via electrons and holes. This part depends on materials carrier concentration or in other words directly proportional to materials \( \sigma \).
But as a good TE material requires high $\sigma$, so scientifically scope to optimize electronic part of the is limited.

TE materials research basically focuses on reducing $\kappa_l$. It is not dependent upon carrier concentration. The lattice thermal conductivity is expressed as;

$$\kappa_l = \frac{1}{3} v_s C_v L_{ph}$$

Where $v_s$ is the velocity of sound, $C_v$ is the heat capacity at constant volume and $L_{ph}$ is the mean free path of phonons.[17] At high temperatures (T>300K), the velocity of sound and heat capacity are essentially temperature independent in typical materials. Therefore, the magnitude of $\kappa_l$ is basically determined by the mean free path of phonons at higher temperatures. Phonons are effective at transporting heat through a material. Thus, $\kappa_l$ can be reduced by scattering or reducing their pathways and motion.[18]

Nanostructuring can facilitate the mechanism required for reducing $\kappa_l$ by effectively scattering phonons. Phonons will have shorter mean free paths due to reduced grain size.[19, 20]

1.6.2 Optimization of power factor

The least understood problems in current TE research are how to increase the power factor ($S^2\sigma$) of a material. The fact is the $\sigma$ and $S$ change in opposite directions with elemental doping. So, there is a compromised set of values for each material that must be achieved. Thus, semiconductors with optimum carrier concentration (between $10^{19}$ carriers/cm$^3$ to $10^{21}$ carriers/cm$^3$) can generate maximum power factor.[6, 14, 17]

However, other important parameters such as band gaps, effective mass and crystal structure are also crucial for the optimization of power factor. In principle, for cooling application small band gap materials are efficient whereas for high temperature power generation large gaps are required. The higher the band gap, the higher the temperature at which the maximum in $ZT$ will be reached before it declines. Effective mass of the charge carrier provides another conflict as large effective masses produce high $S$ but low $\sigma$. The actual dependency between the effective mass and carrier mobility is complex and depends on electronic structure, scattering mechanism and anisotropy. Good TE materials can be found within a wide range of effective masses.[21]
1.7 Promising TE Materials
In recent years, extensive research have been performed to find efficient TE materials.[22] TE materials can be categorized on the basis of temperature range offering highest $ZT$ for a particular composition of materials. Obviously, application areas of particular TE materials are also determined by this classification.

![Diagram of TE materials with optimum operating temperatures.](image)

According to Figure 1.4 few materials are appropriate for low temperature applications (4 to 250 K).[23] Cesium Bismuth telluride (CsBi$_4$Te$_6$) showed good characteristics in low temperature range.[1]

From 200 to 500K Bismuth telluride (Bi$_2$Te$_3$) showed decent performance for both n and p type dopants[24]. In the middle temperature range from 500 to 900K, Skutterudites, clathrates, silicides and chalcogenides based materials have shown the best TE performance. Co$_4$Sb$_{12}$ based materials have demonstrated the best $ZT$ values in the temperature range 300 to 900 K.[23] For higher temperature range 800 to 1100 K some Oxides and Silicon Germanium based materials have shown promising $ZT$ values.[25] Skutterudites are potential for further improvements as the parameters could be optimized to achieve higher $ZT$. 
1.8 Skutterudites

Skutterudites are potential candidates as efficient TE materials for future. These are special class of compounds that offer voids in its crystal structure, which increased researcher’s attentions.

Figure 1.5 Skutterudites crystal structure

Figure 1.5 shows that the crystal structure of skutterudites. Binary skutterudites composition is represented as M₄X₁₂, where M is a metal atom (Co, Rh or Ir) and X is a Pnicogen atom (P, As or Sb). [26] The lattice constant and voids radius increase with progressing from Phosphide to Arsenide to Antimonide skutterudites. Besides, the lattice constant increases with the heavier metal atom within the family of Skutterudites. So, among the groups of skutterudites Cobalt antimonide (Co₄Sb₁₂) are of more importance from the perspective of filling.

The void in skutterudites is large enough to accommodate large metal atom to form ‘filled skutterudites’. These phenomena theoretically led to the concept of ‘rattling effect’, which proposes that the guest atom can act as strong phonon-scattering centers to reduce the $\kappa_l$. [11] In principle, the smaller and heavier the ions in the voids, the larger the reduction in the $\kappa_l$. Besides the void-filling atoms can act as electron donors or acceptors, partially filling the void space of skutterudites could lead towards an optimum electron concentration. Mostly rare-earth ions are chosen as fillers because they are comparatively heavier. But the size of the atom is crucial for fitting into the cages of skutterudites. It requires high pressure or some specialized means of synthesis to obtain filled antimonide skutterudites with heavy rare-earth fillers.[12]
1.9 Objectives

The main objective of this thesis is to synthesize effective $\text{Co}_4\text{Sb}_{12}$ based skutterudites TE materials with improved performance.

The work is designed for:

- Fabrication of nanostructured (NS) bulk $\text{Co}_4\text{Sb}_{12}$ based materials fabrication via mechanical milling and alloying.
- Nanostructuring, filling and partial doping of skutterudites material using planetary ball-milling (BM).
- Optimization of BM parameters for this material through a wide range of experiments.
- Substitution doping and void filling in the skutterudites structure with rare earth metal atoms like Ytterbium (Yb) and Cerium (Ce) in two different concentrations.
- Consolidation of as-synthesized nanopowders using Spark plasma Sintering (SPS) with optimized fabrication conditions.
- Performing the thermoelectric evaluations of fabricated samples.
- The overall goal is to produce NS bulk TE material with improved figure of merit, $ZT$. 

2 Experimental Methods

2.1 Fabrication of Materials
In this work, Co₄Sb₁₂ powder was synthesized from a mixture of Cobalt (II) oxide (CoO₂) and Antimony trioxide (Sb₂O₃) powders with 99.995% purity purchased from Sigma Aldrich. Stoichiometric proportions of Co and Sb respectively (4:12) were mixed with the help of mortar. Base material Co₄Sb₁₂ powder was prepared after the oxide reduction with highly purified gas (Hydrogen 95% & Nitrogen 5%).

Co₄Sb₁₂ NS bulk material has been synthesized via mechanical milling and alloying approach (Figure 2.1). For achieving bulk nanostructured material Planetary BM and SPS is utilized in fabrication process.

![Figure 2.1 A schematic for synthesis of nanostructured Co₄Sb₁₂ materials in this thesis.](image-url)
2.1.1 Materials Synthesis

2.1.1. a Reduction

Oxide reduction with hydrogen been performed to produce Co$_4$Sb$_{12}$ in rotating furnace following the optimized reduction parameters as reported by Toprak et al.[19] Powder mixtures were reduced in rotating furnace at 773 K for 3 hours with 99% pure H$_2$ gas. After that cooling of the furnace was done by compressed air until it reached at room temperature. Dark grey color Co$_4$Sb$_{12}$ powder is extracted as final product. SEM and XRD been performed to investigate the quality of the Skutterudite material.

2.1.1. b Optimization of Planetary Ball Milling

Planetary BM offers fast and reproducible grinding down to the micro and sub-micron size of the bulk powders.[27] BM is also suitable for mechanical alloying. The centrifugal forces produced by the rotation movement of the sample and the grinding balls against the inner wall of the grinding jar, where size reduction takes place primarily by pressure and friction. The extremely high centrifugal forces of the planetary BM result in very high pulverization energy. The rotation speed, duration of milling and balls to powder ratio and milling environment is critical to perform high quality grinding.[28] All these parameters were carefully optimized during the experimental work for Co$_4$Sb$_{12}$ based materials with a wide range of experiments.

2.1.2 Processing of Materials

2.1.2.1 Spark Plasma Sintering

SPS is an advanced technique to consolidate metals and metal oxides powder, which offers sintering in very short time. In SPS, nano sized powders can be sintered without considerable grain growth which is hardly possible in other conventional sintering process such as hot press.

In SPS, a DC pulse is generated and directly passed through the graphite die that generates localized temperature within the sample for sintering. Materials conductivity is an important factor in the SPS experiments. Maximum densification can be achieved by optimizing critical SPS parameters such as heating rate, maximum temperature, holding time and applied pressure. Schematic of SPS setup is shown in the figure 2.2.
2.1.3 Sample Preparation for TE Evaluation

After consolidation the cylindrical sample was cut into (5 x 5 x 5) mm³ size cube using the wire saw. The actual size is maintained with high precision as this a requirement for the physical property measurement. Fractured Consolidated sample was collected for SEM and XRD characterization. After cutting the sample was polished using sand paper. A shiny cubic solid sample was obtained after polishing (Figure 2.3).
2.2 Material Characterization

All synthesized materials have been characterized at various stages of fabrication process by using several different techniques to identify the crystallite phases, determination of composition, analyzing microstructures and TE transport evaluations.

2.2.1 X-Ray Diffraction (XRD)

X-Ray Diffraction is an analytical tool to obtain crystallographic information of materials. It is a non-destructive, reproducible and fast characterization technique to identify crystalline phases and orientation, to determine structural properties such as crystallite size, lattice parameters, grain size, phase composition, atomic arrangement etc.

The interaction of the incident beams with the sample produces diffracted beams that satisfies the Bragg’s law

\[ n\lambda = 2d \sin \theta \]

This equation relates the wavelength of electromagnetic radiation (\( \lambda \)) to the diffraction angle (\( \theta \)) and the lattice spacing in a crystalline sample (\( d \)). As illustrated in figure 2.4 by scanning the sample through a range of 2\( \theta \) angles, all possible diffraction patterns of the lattice is obtained due to the random orientation of the material. Diffracted X-ray beams are detected, processed and counted. By analyzing the position, shape and intensity of the diffraction peaks important atomic and molecular structure of the crystal can be obtained. Philips X’pert Pro
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and PW3710 diffractometer were used with Bragg-Brentano geometry and Cu K alpha source of 1.54Å wavelength.

2.2.2 Scanning Electron Microscopy (SEM)

SEM is a very convenient and dynamic characterization tool to obtain high-resolution microstructure images of desired materials. SEM utilizes electrons for imaging as they have much shorter wavelengths than light, enabling better resolution and magnification. SEM can be operated in various modes for analyzing surface morphology, elemental composition, microstructure studies, Surface contamination etc.

![Schematic diagram of a typical Scanning Electron Microscope](image)

**Figure 2.5** Schematic diagram of a typical Scanning Electron Microscope.[30]

The basic working principle of SEM is- a beam of incident electrons, which is generated in an electron column above the sample chamber (presented in Figure 2.5). Depending on the evaluation objectives the energy of the incident electrons may vary from 100eV up to 30 keV. The electrons generated are focused into a small beam by a series of electromagnetic lenses in the SEM column. Scanning coils near the bottom of the column direct and position the focused beam onto the sample surface. The incident electrons cause electrons to be emitted from the sample due to elastic and inelastic scattering from the sample’s surface and near-surface material. High energy electrons that are ejected by an elastic collision of an incident electron are referred to as backscattered electrons. Back scattered imaging mode provides image contrast as a function of elemental composition, as well as, surface topography. Emitted lower energy electrons resulting from inelastic scattering are referred as secondary electrons.
The SEM column and sample chamber are maintained at a moderate vacuum to allow the electrons to travel freely from the electron beam source to the sample and then to the detectors. Imaging of non-conductive, volatile, and vacuum-sensitive samples can be performed at higher pressures. Images were obtained via Zeiss FEG-SEM Ultra 55 and Sigma Zeiss FE-SEM.

### 2.2.3 Energy Dispersive X-ray Spectroscopy (EDS)

EDS is an analytical tool used for the elemental analysis or chemical composition of the materials. Backscattered electron images in the SEM shows compositional contrast that results from different atomic number elements and their distribution. Energy Dispersive Spectroscopy (EDS) allows to identify what those particular elements are and their relative proportions (Atomic % or weight %).

EDS relies upon X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. In principle, all elements from atomic number 4 (Be) to 92 (U) can be detected, though not all instruments are equipped for 'light' elements (Z < 10). Qualitative analysis (identification of the elements present) refers to the identification of the lines in the X-Ray spectrum. Quantitative analysis (measuring the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition.

### 2.2.4 TE Transport Evaluation

Since some of the best TE materials do have an anisotropic crystal structure and SPS is uniaxial, most or all samples produced by SPS should show to some extend anisotropy of the transport properties. In addition, inhomogeneity is also expected in SPS samples because the current density, the temperature field and pressure may not be homogeneous during the sintering process. Anisotropic and inhomogenic measurement of the transport properties of spark plasma sintered sample was developed at Fraunhofer-IPM. It enables the simultaneous measurement of the $\sigma$, $S$ and up to 900K of cubes at least (5 x 5 x 5) mm$^3$ in size. The advantage of this methodology over other techniques is that this approach do not lead to an overestimation of Figure of merit.[31]
**Figure 2.6** TE sample mounted on sample holder for PPMS.

Figure 2.6 shows a TE sample is mounted on sample holder for TE evaluation. PPMS sample mounting is very sensitive and critical to avoid experimental error during measurements.
3 Results and Discussions

In this thesis, the objective was to synthesize nanostructured filled and partially doped Co₄Sb₁₂ based skutterudites. The work was designed to fabricate bulk NS Co₄Sb₁₂ based materials via reduction reaction followed by BM and SPS processing steps. BM parameters were optimized by performing a wide range of experiments. Other experimental processes such as Oxide reduction from the precursors and parameters for SPS were previously optimized in earlier works in our group.

BM has been performed to produce NS filled and partially doped Co₄Sb₁₂ powder. Consolidations of powders have been performed by SPS. The parameters for sintering were optimized for this particular material in earlier published work of our group.

3.1 Synthesis of Co₄Sb₁₂ powder

Cobalt (II) Oxide (CoO₂) and Antimony trioxide (Sb₂O₃) powder with purity of 99.99% purchased from Sigma Aldrich. These precursors were firmly mixed in mortar with stoichiometric proportions. Oxide precursors of Co and Sb were reduced at 450°C for 3 Hours with 95% pure H₂ gas to produce Co₄Sb₁₂. Reduction reaction was performed in custom designed rotating furnace as reported By Toprak et al.[19] The furnace was cooled down with compressed air until it reached at room temperature. Dark grey Co₄Sb₁₂ powder was extracted as final product. Total approx. 50g of Co₄Sb₁₂ powder was successfully synthesized in two separate batches. However, the size of the batch was limited due to the capacity of the furnace and this process is easily scalable for larger batches. SEM and XRD were performed to investigate the quality of the as-synthesized skutterudite materials. In result, both batches have shown identical samples in the final product. This confirms the reproducibility of our base material via thermochemical reduction. Thermochemical synthesis of Co₄Sb₁₂ was completed as explained in the following chemical reactions.

$$\text{CoO}_2 (s) + 2\text{H}_2 (g) \xrightarrow{\Delta} \text{Co} (s) + 2\text{H}_2\text{O} (g)$$

$$2\text{Sb}_2\text{O}_3 (s) + 6\text{H}_2 (g) \xrightarrow{\Delta} \text{Sb}_4 (s) + 6\text{H}_2\text{O} (g)$$

$$4\text{Co} (s) + 3\text{Sb}_4 (s) \xrightarrow{\Delta} \text{Co}_4\text{Sb}_{12} (s)$$
At high temperature (500°C) H₂ gas reacted with Co and Sb oxides to form Co₄Sb₁₂ and released H₂O. During the experiment gas leakage was frequently checked to ensure purity. The base material Co₄Sb₁₂ was cooled down to room temperature (25°C) to avoid oxidation.

**Batch 1**

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<thead>
<tr>
<th>Precursors</th>
<th>Quantity (g)</th>
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<tr>
<td>Cobalt (II) oxide (CoO₂)</td>
<td>5.366</td>
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<tr>
<td>Antimony trioxide (Sb₂O₃)</td>
<td>27.505</td>
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<tr>
<td>Total amount of mixture</td>
<td>32.871</td>
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Amount of sample before reduction = 32.578 g  
Amount of sample collected after Reduction = 25.8 g

**Batch 2**

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Quantity (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt (II) oxide (CoO₂)</td>
<td>5.367</td>
</tr>
<tr>
<td>Antimony trioxide (Sb₂O₃)</td>
<td>27.527</td>
</tr>
<tr>
<td>Total amount of mixture</td>
<td>32.824</td>
</tr>
</tbody>
</table>

Amount of sample before Reduction = 32.463 g  
Amount of sample collected after Reduction = 25.86 g

Fine dark gray powder of Co₄Sb₁₂ was obtained and stored for further processing.

**3.2 Optimization of Ball milling**

A series of BM experiments were designed to optimize the process parameters such as the rotation speed, duration of milling and balls to powder ratio and milling environment to achieve desired nanostructures. Hexane is used as Process Control Agent (PCA). The PCA has a lubricating effect that minimizes the cold welding effect. Without the PCA, the powder being milled welds on the milling chamber vessel walls, resulting in only a fraction of the powder being retrieved. To avoid oxidation milling jar was filled with N₂. Zirconia milling jar and balls were used to avoid the contamination. Duration of milling was optimized by performing 8 to 72 hours of milling having the other parameters fixed for each sample. Samples are collected in every 8 hours of interval for grain size measurement in SEM & crystal structure analysis with XRD technique.
Table 3.1 BM processing parameters for optimization of Co₄Sb₁₂ powder

<table>
<thead>
<tr>
<th>Material Composition</th>
<th>Co₄Sb₁₂</th>
<th>Co₄Sb₁₂</th>
<th>Co₄Sb₁₂</th>
<th>Co₄Sb₁₂</th>
<th>Co₄Sb₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milling Duration (hours)</td>
<td>8</td>
<td>16</td>
<td>24</td>
<td>48</td>
<td>72</td>
</tr>
<tr>
<td>Speed (rpm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>350</td>
</tr>
<tr>
<td>Weight of sample (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>Type of PCA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hexane</td>
</tr>
<tr>
<td>Amount of PCA (ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Size of Jar (ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>250</td>
</tr>
<tr>
<td>Type of Jar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Zirconia</td>
</tr>
<tr>
<td>Size of ball (mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>No. of Balls</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Type of ball</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Zirconia</td>
</tr>
<tr>
<td>Weight of Balls (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>~30</td>
</tr>
<tr>
<td>Amount of PCA (ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5 ml</td>
</tr>
<tr>
<td>Milling environment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Balls to Powder ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3:1</td>
</tr>
</tbody>
</table>

Scanning electron microscopy (SEM) analysis was performed to visualize the morphology and size of the nanoparticles. Dried nanopowders of BM samples were prepared on carbon tape. Figure 3.1 (a-f) is taken from the reduced Co₄Sb₁₂ powder. Particle size varies from 400 nm to submicron range. Average particle size of the Co₄Sb₁₂ powders was calculated using the software image J for the samples.
Figure 3.1 (a-f) SEM micrographs of Co₄Sb₁₂ after 0, 8, 16, 24 & 72 hours milling time. According to the SEM micrographs of the Co₄Sb₁₂ powders significant reduction of particle size is obtained after increasing milling time. Agglomeration is also observed because of wet milling, but overall particle size reduces with longer milling time.
Table 3.2 Average particle size of Co$_4$Sb$_{12}$ powders with different milling time.

<table>
<thead>
<tr>
<th>BM duration (Hours)</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>~ 540</td>
</tr>
<tr>
<td>8</td>
<td>~ 460</td>
</tr>
<tr>
<td>16</td>
<td>~ 390</td>
</tr>
<tr>
<td>24</td>
<td>~ 270</td>
</tr>
<tr>
<td>48</td>
<td>~ 160</td>
</tr>
<tr>
<td>72</td>
<td>~ 140</td>
</tr>
</tbody>
</table>

XRD was performed to investigate phase identification and quantitative analysis of the nanopowders. In Figure 3.2 it was observed that XRD peaks for all the samples are identical. Which implies no additional phase of the material is formed through the experiments. The intensity peaks getting broaden with BM milling duration which is a sign of particle size got smaller over time.

Figure 3.2 XRD patterns of BM Co$_4$Sb$_{12}$ samples
3.3 Spark Plasma Sintering
Co₄Sb₁₂ nanopowder is consolidated by SPS. Important parameters to achieve a uniform porosity and maximum densification with undesired grain growth are sintering temperature, heating rate, holding time and applied pressure. These parameters were optimized in the previous master’s thesis work in our group.[33] The study demonstrated that the maximum densification of approx. 95% and uniform porosity can be achieved with the SPS conditions mentioned in the table below:

Table 3.3 Optimized SPS Parameters for Co₄Sb₁₂ nanopowders.[33]

<table>
<thead>
<tr>
<th>SPS Conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Die Size (mm)</td>
<td>12</td>
</tr>
<tr>
<td>Amount of Sample (g)</td>
<td>4</td>
</tr>
<tr>
<td>Maximum Temperature (°C)</td>
<td>500</td>
</tr>
<tr>
<td>Heating Rate (°C/min)</td>
<td>75</td>
</tr>
<tr>
<td>Holding Time (min)</td>
<td>3</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>75</td>
</tr>
</tbody>
</table>
In Figure 3.3 (a-f) SEM images shows plate-like morphology with an average grain size of 150nm in consolidated samples. Limited grain growth is encountered during the SPS. Approx. 95% densification achieved compared the theoretical density of the Co$_4$Sb$_{12}$ materials.

![Powder SEM images](image1)

![Sintered SEM images](image2)

**Figure 3.3 (a-f) SEM images different powders and sintered sample**
Figure 3.4 (a-d) shows SEM images of Ce₅Co₄Sb₁₂ powders and sintered sample. Grain growth during the SPS is in acceptable range. Like the Yb doped or partially filled samples approx. 95% densification achieved compared the theoretical density of the Co₄Sb₁₂ materials.

Figure 3.4 (a-d) SEM images of Ce₅Co₄Sb₁₂ powders and sintered sample
XRD was performed to investigate phase identification and quantitative analysis of the nanopowders and sintered samples. According to figure 3.5 no extra phase of the materials was identified on the XRD patterns, which confirmed materials purity. It was also observed that excessive free amorphous Sb crystallizes after sintering. Intensity of the peak increases after sintering due to heating. Furthermore, filling of rare earth atoms may take place during SPS. XRD with higher resolution or other characterization technique is required to provide evidence for filling skutterudites materials.

![XRD patterns of skutterudites powder and sintered samples of various compositions](image)

**Figure 3.5** XRD patterns of skutterudites powder and sintered samples of various compositions
3.4 Physical Property Measurement

The transport properties of the Co$_4$Sb$_{12}$ Bulk NS sample were evaluated by measuring the $S$, $\sigma$ & $\kappa$ in the temperature range 300 to 900 K and results are reported in Figure 3.6(a-d). TE transport evaluation showed positive $S$ value, which implies the p-type behavior of the Co$_4$Sb$_{12}$ sample. $S$ reached a maximum value of 140$\mu$V/K at 520 K. Nolas et al showed that a high carrier concentration yields a low $S$ and high $\sigma$. [22] For this sample, we can assume that carrier concentration is low, as it is showing a high $S$ and low $\sigma$. Maximum $\sigma$ of 210 S/cm is obtained at 830K. $\kappa$ of the sample is between 2.2 to 2.8 W/m.K. which is two times lower than the previous work in our group.[32] Low $\kappa$ is achieved with high concentration of grain boundaries due to nanostructuring. Highest ZT value of 0.035 achieved for the sample at 610K with an average grain size of 170 nm.

![Figure 3.6](image)

**Figure 3.6** TE evaluation of Co$_4$Sb$_{12}$ Bulk NS sample. (a) Seebeck Coefficient ($S$), (b) Electrical Conductivity ($\sigma$), (c) Thermal Conductivity ($\kappa$) & (d) Figure of Merit (ZT)
In Figure 3.7(a-d) presents the transport properties of the Yb$_x$Co$_4$Sb$_{12}$ (x=0.125 and 0.250) bulk NS samples in the temperature range 300 to 900 K. TE transport evaluation showed both negative and positive $S$ value, which implies up to 350K the samples have n-type characteristics, with increase in temperature it is turning to p-type. $S$ reached a maximum value of 100 $\mu$V/K at 610 K for Yb$_{0.250}$Co$_4$Sb$_{12}$ sample. For both samples $\sigma$ is highest at 800K. $\kappa$ value for both samples lies between 2.2 to 3.0 W/m.K. which is comparatively lower than the $\kappa$ reported by Nolas et.al for Yb filled Co$_4$Sb$_{12}$ material.[34]. Both the sample showed highest ZT value of 0.035 at 610 K.

![Figure 3.7](image.png)

**Figure 3.7** TE evaluation of Yb$_x$Co$_4$Sb$_{12}$ Bulk NS sample. (a) Seebeck Coefficient ($S$), (b)Electrical Conductivity ($\sigma$), (c)Thermal Conductivity ($\kappa$) & (d) Figure of Merit(ZT)
Figure 3.8(a-d) presents the transport properties of the Ce$_x$Co$_4$Sb$_{12}$ ($x=0.125$ and 0.250) bulk NS samples in the temperature range 300 to 900 K. TE transport evaluation showed positive $S$ value. $S$ reached a maximum value of 180$\mu$V/K at 540K for Ce$_{0.250}$Co$_4$Sb$_{12}$ sample. For both samples $\sigma$ is highest at 800K. $\kappa$ of the samples are between 4.5 to 3.0 W/m.K, which is close to the lowest $\kappa$ reported for Ce filled Co$_4$Sb$_{12}$ material.[35] Ce filled or partially doped samples have shown better $S$ and $\sigma$ than our Yb$_x$Co$_4$Sb$_{12}$ samples. But Yb filled or partially doped samples have better $\kappa$ than Ce$_x$Co$_4$Sb$_{12}$ samples. The reason could be Yb atoms are heavier than Ce atoms. So Yb atoms are more effective in generating phonons. Both the sample showed highest ZT value at 610 K.

![Figure 3.8](image.png)

**Figure 3.8** TE evaluation of Ce$_x$Co$_4$Sb$_{12}$ Bulk NS sample. (a) Seebeck Coefficient ($S$), (b) Electrical Conductivity ($\sigma$), (c) Thermal Conductivity ($\kappa$) & (d) Figure of Merit (ZT)

Though the overall ZT is not high, significant reduction in materials $\kappa$ is achieved through nanostructuring. Optimum carrier concentration can lead to improve materials $S$ and $\sigma$. Some alteration during chemical treatments like, processing of materials in glove box and drying nanopowders in room temperature have also the possibility to improve the purity the material.
4 Conclusions

In this thesis, we have fabricated bulk nanostructured $\text{Co}_4\text{Sb}_{12}$ based skutterudites material via chemical reduction of metal oxides followed by mechanical milling and alloying. Synthesis of base skutterudite material is produced via high temperature ($500 \degree\text{C}$) reduction reaction under hydrogen gas. BM was used for reducing particle size from micron to nanostructures. Filling or partially doping with rare earth material were done during BM. SPS was performed for consolidation of nanopowder preserving nanosize grains. Cutting and polishing was performed for TE property evaluation.

From Physical property measurements of the samples p-type and n-type behavior identified. $S$ and $\sigma$ seems to be very low in the samples. However, significant reduction in $\kappa$ is achieved due to nanostructuring.

5 Future works

In further investigations, Hall measurement can be performed to determine the carrier concentration and mobility in our samples. Carrier concentration can be optimized with doping to increase the $\sigma$ and improve the $S$. Chemical treatments during the experiments can be altered for avoiding oxidation of nanopowders. To provide evidence for filling of rare earth atoms inside the skutterudites structure, synchrotron based nanocharacterization technique can be studied.
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I would like to express my deep gratitude to my examiner, Prof. Muhammet Toprak for providing me the opportunity for performing my Master thesis work at Functional Nanomaterials Division, KTH. All the work has been done with his guidance and support. I am really honored by becoming a member of his group.

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References