P-type, Misfit Layered Structure Cobaltite for Thermoelectric Applications

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Table 10-1 Summary of experimentally-determined and refined structural parameters for ceramics of BSCO-0, BSCO-1, and BSCO-2 at room temperature. Structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters ($B_{\text{eq}}$), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parenthesis. Noted: $R_{\text{exp}}$ is R-expected and $R_{\text{wp}}$ is R-weighted pattern and $R_p$ is R-Pattern.

Table 10-2 Summary of experimentally-determined and refined structural parameters for ceramics of BSCO-0 at room temperature from the high resolution synchrotron source. Structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters ($B_{\text{eq}}$), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parenthesis.

Table 10-3 Refined room temperature structural parameters for BSCO-0, BSCO-1 and BSCO-2 ceramics prepared by SPS. Structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters ($B_{\text{eq}}$), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parenthesis.

Table 10-4 Summary of refined structural parameters for L-Bi-MO, L-MO and L-SPS ceramics at room temperature (structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters ($B_{\text{eq}}$), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parentheses.
Table 10-5 Summary of experimentally-determined and refined structural parameters for ceramics of CBCO-MO CBCO-SPS and CCO-SPS at room temperature; Structure type, lattice parameters, atomic positions, occupancies, Isotropic Thermal Parameters ($B_{eq}$), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parentheses. Note: $R_{\text{exp}}$ is R-expected and $R_{\text{wp}}$ is R-weighted pattern and $R_p$ is R-Pattern. .................................236

Table 10-6 Summary of experimentally-determined and refined structural parameters for ceramics of CCO-MO at room temperature using Synchrotron source. Structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters ($B_{eq}$), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parenthesis. Noted: $R_{\text{exp}}$ is R-expected and $R_{\text{wp}}$ is R-weighted pattern and $R_p$ is R-Pattern. .................................................................238

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Abstract

The thermoelectric properties and microstructure of two families of misfit type layered structure cobaltites were investigated for thermoelectric applications. Firstly, Bismuth strontium cobaltite ceramics with the formulations Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ ($x=0$, 0.1 and 0.2), Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_x$ and Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ were produced using solid-state reaction (MO) method. The same powders were also used to produce ceramics by Spark Plasma Sintering (SPS) fabrication technique. SEM, high resolution XRD and HRTEM techniques has been employed to characterise the microstructure and crystal structures of the ceramics. Figure of merit (ZT) was also determined from measurement of electrical resistivity, Seebeck coefficient and thermal conductivity. Together with the above, calcium cobaltite of formulation Ca$_{3}$Bi$_2$Co$_3$O$_9$ ($x=0$ and 0.3) was also produced via MO and SPS routes. The same characterisation techniques were used for characterisation of calcium cobaltite.

For Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ ceramics, it was found that SPS fabrication is essential to obtain high density samples. Excess bismuth has a major role in the adjustment of the microstructure and thermoelectric properties. The room temperature microstructure contains two minor phases with compositions of CoO and Bi$_{0.75}$Sr$_{0.25}$O$_{1.26}$. The crystal structure of the main phase was successfully indexed and refined as misfit type structure having monoclinic symmetry with $I2/a$ space group. A high ZT of 0.12 was achieved in both $x=0.1$ and 0.2 MO samples. For Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ ceramics, the microstructure contains only one minor phase, Bi$_{0.75}$Sr$_{0.25}$O$_{1.26}$. A high ZT of 0.16 was obtained at 900 K for this composition. For Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$, it was not possible to obtain high density ceramics by MO route and SPS fabrication was necessary. However, SPS sample showed a low ZT of 0.04 at 900 K.

For ceramics of formulation Ca$_{3-x}$Bi$_2$Co$_3$O$_9$ ($x=0$ and 0.3), it was difficult to obtain high density calcium cobaltite ceramics by MO route and SPS fabrication was found to be essential. In addition to improved density, SPS produced textured microstructure. Similar to bismuth strontium cobaltite, excess bismuth played a major role in microstructure development and thermoelectric properties. Single phase and high density Ca$_3$Co$_4$O$_9$ ceramics were obtained by SPS. A minor phase of Bi$_2$Ca$_2$Co$_2$O$_y$ was found in the microstructure of Ca$_3$Bi$_2$Co$_3$O$_4$ ($x=0.3$) samples. A high ZT of 0.25 was obtained for Ca$_3$Co$_4$O$_9$ SPS samples at 900 K through improvement of power factor.

In-situ synchrotron XRD in the temperature range of 300-1223 K was performed on both Bi$_2$Sr$_2$Co$_2$O$_y$ and Ca$_3$Co$_4$O$_9$ to obtain their high temperature structural characteristics. The crystal structure of both compounds remains unchanged till 1223 K. For, Bi$_2$Sr$_2$Co$_2$O$_y$ the CoO and Bi$_{0.75}$Sr$_{0.25}$O$_{1.26}$ minor phases disappear above 1073 K and a new minor phase containing (Bi-Sr-O) or (Bi-Co-O) starts forming. On heating, the lattice volume and coefficient of thermal expansion change linearly for both compounds. Thermal expansion coefficient was found to be 0.0000353-0.0000343 and 0.0000296-0.0000288 K$^{-1}$ over the temperature range of 300-1223 K for Bi$_2$Sr$_2$Co$_2$O$_y$ and Ca$_3$Co$_4$O$_9$ respectively.

Nuth Kulwongwit for Doctor of Philosophy at the University of Manchester

“P-type, Misfit Layered Structure Cobaltite Oxides for Thermoelectric Applications”
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1. Introduction

1.1 Overview and background

In the past two centuries, fossil fuels have been the primary energy source for cars, ships, and planes, and for generating electricity for cities. Energy consumption is projected to rise every year while our fossil reserves are expected to run out by 2100 [1], with new sources harder to reach, more expensive to extract and alarmingly detrimental to the environment. Combustion of fossil fuels releases a significant amount of CO$_2$ and other hydrocarbon molecules, some of which have been indicated as a cause of global climate change. Treaties and regulations have been imposed on CO$_2$ emissions which are an incentive to find cleaner and cheaper energy sources. Nuclear power has been used since the 1950s as a cleaner and more efficient energy source when compared to fossil fuels. The major drawback of widespread adoption of nuclear power, is how to manage the spent fuel rods which remain highly radioactive for many hundreds of years, and public concern over safety. Alternative solutions to cleaner energy sources such as nuclear fusion reactors, are required to meet energy demands as research into this technology is still ongoing.

Energy harvesting devices based on the recovery of waste heat using the Seebeck effects is one possible alternative energy source. Improving the efficiency of these devices is a priority to enable them to be modified and installed on energy production systems. Figure 1-1 shows the maximum efficiency of 70-80% is attained in machines which are governed by the Carnot law of thermodynamics [2]. The majority of power generation plants are on average between 30 to 50% efficient which means there is room for improvement.
Figure 1-1 A comparison of the figure of merit as a function of temperature for heat engine efficiency; black circles indicate the efficiency of non-thermoelectric energy sources, reproduced from Vinning [3].

Thermoelectric devices, composed of arrays of thermoelectric modules, are proposed as a method to increase the efficiency of power generation through the recovery of waste heat. This waste heat is converted to electrical energy which can be then supplied to the original system(s) or transferred to external systems [4]. The potentials of these devices are very promising given how much the energy is lost in our energy production consuming as showed in Figure 1-2.
Figure 1-2 Percentage of energy used and loss, reproduced from Science Daily [5].

Anywhere that there is heat generation, thermoelectric devices could potentially be used to act as modifiers/recyclers to improve overall energy yield. Thermoelectric devices use solid-state materials and having no moving parts means they do not vibrate. This is mechanically desirable as it will limit the damage to the thermoelectric devices or other attached components. The use of thermoelectric devices will not have a significant impact on the surrounding environment as there will be no noise generated by these devices and no radiation will be generated during its operational lifetime. The devices can also be scaled according to the application to optimise the recovery of waste heat.

Thermoelectric devices have been used in some limited long term, high-cost applications including space exploration craft in the years between 1950-60 [6], however since then there are many more prospective applications where thermoelectric could be put to good use. One of the primary targets is to integrate thermoelectric modules into automobiles [6] where concerns about rising fuel costs and environmental concerns are an incentive motivation to make them commercially available. Another example is to incorporate thermoelectric devices into household appliances such as heating systems, and in factories where there is a significant waste heat generated as a by-product of the systems. The example of a cooling application is the localised cooling of electronic components in computers, to enhance processing speed. They can also be used in critical hotspots, where the hotspots could lead to failure of the system or shorter lifespan, to limit detrimental effects of overheating [7].
Heavy metal alloys form the majority of traditional thermoelectric materials. Long accepted as a standard, against which other thermoelectric materials are often compared, is $\text{Bi}_2\text{Te}_3$ as it has a good efficiency. However, it has several drawbacks including poor thermal stability of telluride materials and high cost limiting the adoption of materials on a large scale. Therefore, many other candidates are have been researched to replace telluride materials [8].

In addition to the challenge of finding replacement materials for heavy metal thermoelectric, there are four major challenges that need to be addressed: First the efficiency: the highest efficiency of the devices are around 30% waste heat recovery, therefore, several research projects has been dedicated to seeking out and testing and developing high performance thermoelectric materials [9-18]. Secondly, stability and function at high temperature: thermoelectric devices should be able to function at high temperature with no loss of efficiency and also the stability of materials over their lifetime needs to be considered, as high temperatures are very detrimental to materials stability and might lead to failure. Thirdly, the economy of scale: in order to archive widespread usage, the materials need to be cheap enough through the mass production process, therefore, the materials should be easy to extract and process. Fourth, the impact on the environmental should be minimised, as some thermoelectric materials are based on heavy metals and the processing and disposal could potentially release some toxic substances into the environments.

In a direct response to above challenges, oxide materials are one possibility to address the problems presented. Oxides can address 3 out of 4 challenges above with the high stability of ceramic materials at high temperature, ease of manufacture by simple production route and the original materials are quite accessible and relatively cheap. The single major challenge is that of the performance as many oxides only achieve ~3-4% efficiency [19].
Figure 1-3 The thermoelectric figure of merit (ZT). A ZT of around 1 will mean a thermal efficiency of approximately 10%, adapted from Snyder et al. [16].

Many oxides are considered to exhibit promising thermoelectric properties [19-24]. Potential n-type candidates are perovskite structured materials including SrTiO$_3$, CaMnO$_3$, ZnO, and SnNb$_2$ (i.e. Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$-$d$, and on Ba$_{6-3x}$Nd$_{8+2x}$Ti$_{18}$O$_{54}$). Cobaltite ceramics including NaCoO$_2$, CaCo$_3$O$_4$, Bi$_2$Sr$_2$Co$_2$O$_y$, Bi$_2$Sr$_2$O$_y$, Bi$_2$Sr$_2$Co$_2$O$_y$, and Ca$_3$Co$_4$O$_9$ are considered promising candidates for use as p-type materials. One key challenge in oxides materials is to find a way to improve the efficiency. Understanding of the current materials at the microscopic and/or atomic level could lead to refinement and better processing of materials and design thus resulting in improvement of their efficiency. Bi$_2$Sr$_2$Co$_2$O$_y$ and Ca$_3$Co$_4$O$_9$ are oxides ceramic materials which have shown promising thermoelectric properties [25-27]. The Seebeck coefficient can reach around 160 μV/K at high temperature (800 K) with low resistivity of approximately 20-40 mΩ.cm demonstrated good electrical properties with an ability to modify layers of the structure by adjustment of the chemical composition. In addition, the starting powders are relatively abundant and cheap. The materials used in thermoelectric devices needs to withstand temperatures reaching 1000 K with no degradation of material properties.
1.2 Aims and objectives

In this study, $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ and $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics are investigated as potential candidates for thermoelectric materials due to their low thermal conductivity and high power factor. The primary objective of this study is to understand the factors that lead to the improvement of the thermoelectric figure of merit (ZT) of cobaltite family ceramics. In chapter 4, the effect of adding excess Bi is investigated with the aim of determining the effect of excess Bi on the microstructure and thermoelectric properties of bismuth strontium cobaltite. Spark plasma sintering (SPS) was used to improve the density. Chapter 5 aims to study the crystal structure, microstructure and the thermoelectric properties of deficient in cobalt variations of bismuth strontium cobaltite ceramics ($\text{Bi}_{1.74}\text{Sr}_{2}\text{Co}_{1.8}\text{O}_y$ ceramics and $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ ceramics). In chapter 6, $\text{Ca}_{3-x}\text{Bi}_x\text{Co}_4\text{O}_9$ with Bi-substituted was also investigated to complement the study of cobaltite family. The aim was to study the effect of Bi substitution on the microstructure and thermoelectric properties. Spark Plasma Sintering (SPS) was also used to increase the density of calcium cobaltite ceramics. In Chapter 8 Synchrotron X-ray diffraction will be used to investigate the structural properties as a function of temperature to 1223 K in both $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ and $\text{Ca}_3\text{Co}_4\text{O}_9$. 
2. Literature review

In this chapter, an overview of thermoelectric will be presented. This chapter is split into three sections: the first section describes the physical origin and principles of the thermoelectric properties of materials, while the second section describes their applications. In the final section, specific attention has been paid to a detailed literature review on the p-type oxide thermoelectric, highlighting the challenges of current research on this type of materials.

A combination of factors such as the depletion of the fossil fuel reserves, a rise in the demand for electricity and concerns for the environment due to rising CO\textsubscript{2} levels have driven a search for more environmentally friendly methods for the generation of electrical energy. Thermoelectric materials have been seen as one of the promising ways to recover or recycle waste heat generated by machines, such as waste engine heat or exhaust systems, for the purpose of producing electricity. They can also be operated in reverse by the application of a potential difference to generate a temperature difference across devices allowing them to cool down objects locally. This versatility allows thermoelectric materials to be considered as a promising class of materials with the potential to be used in many applications including automotive or home appliances.

2.1 Principles

2.1.1 Seebeck coefficient

T.J. Seebeck was the first to observe the deflection of a compass needle due to a potential difference resulting from a temperature gradient applied across two different solid materials [28]. Further observations have shown that the generated voltage (dV) is proportional to temperatures difference (dT) and the ratio dV/dT is known as the Seebeck coefficient (S).

\[ S = \frac{dV}{dT} \]  

S = Seebeck coefficient
V = electrical voltage (potential)
T = absolute temperature

The Seebeck and Peltier effects can also be regarded as thermos-physical phenomena as a result of charge carrier migration and the resistance faced by charge carriers to achieve equilibrium.
In the case of the Seebeck effect, the charge carriers migrate from the hot end to the cold end of the materials due to a driving force of the thermal gradient. While the charge carriers migration occurred in response to a thermal gradient, these charge carriers induced the heat propagation both through the lattice and the charge carriers themselves. Therefore, the migration of charge carriers is the natural respond to re-equilibrate the heat between both ends. The voltage generation is a by-product of such phenomena where the materials tried to reach thermal equilibrium (Figure 2-1). A typical value of S is of the order of few μV/K in metals and about 0.1 V/K in semiconductors [29]. The Seebeck coefficient can be considered as entropy per carrier or a determination of thermal energy needed to activate charge carrier movement from the hot end to the cold end.

In the case of the Peltier effect discovered by Peltier in 1834 [30], a similar theory can be applied. The power source generated by the voltage gradient between two ends of materials, therefore, creates a driving force for the charge carriers to try to rebalance themselves and causes migration, which in turn causes phonon propagation and thereby a thermal gradient between two ends, and thus active cooling.

![Figure 2-1 Configuration of thermoelectric in a refrigeration mode and power-generation mode [8].](image)

2.1.2 Theoretical calculation of Seebeck coefficient

The only factor that affects the Seebeck coefficient is how many valence electrons become mobile due to the thermal energy input into the system. In metals, the energy required for conduction of electrons is usually low leading to a very low Seebeck
coefficient (typically 1-10 μV/K)[31, 32] as can be seen from Equation 2. The Fermi energy is usually close to the conduction band; the energy needed to be supplied, in order for metals to become conductive is equal to the energy required to ionise the electrons from the valence band.

\[ S \approx \left( \frac{K_b}{e} \right) \frac{K_b T}{E_f} \]  

(2)

\( K_b \) = the Boltzmann constant
\( e \) = electronic charge
\( E_f \) = Fermi energy

In the case of semiconductors, the Fermi energy is much lower than the conduction band, in contrast to the case seen in metals (Figure 2-2).

Figure 2-2 Graphic demonstrated density of state for metal and semiconductor. \( E_F \) is the Fermi energy level. Upper band is conduction band and lower band is valence band, Adapted from Biswas et al [33].

The conduction bands in semiconductors are partially-filled, therefore it is necessary to supply enough energy for electrons to overcome the band gap and fill the conduction band for the material to become electrically conductive. Band gaps are dependent on the electronic configuration of each type of materials, and hence, controls the Seebeck
coefficient as seen in equation 3 [8]. It is believed that the bandgap limits the charge carrier concentration and subsequent flow of the charge carriers leading to a voltage gradient and high thermopower. Therefore, the thermopower of semiconductors is much larger than that of metals with typical values of 100 µV/K.

\[ S \approx \left( \frac{K_B}{e} \right) \frac{E_g}{K_B T} \]  

E\_g = band gap energy

Equations 2 and 3 use statistical mechanics to describe thermopower, in terms of electronic conduction alone. Further analysis of the equation 2 and 3 indicates that the first term is identical, hence the second term can be interpreted as the energy required by metals and semiconductor. However, for semiconductor materials, there is another expression that expresses thermopower in terms of carrier concentration, and is referred as the Heikes formula (with the aid of Stirling’s formula) as shown in equations 4 and 5

\[ S(T \to \infty) = -\frac{K_B}{e} \ln\left(\frac{1-c_e}{c_e}\right) \]  

Where \(c_e = n/N\), and \(n\) is the number of electrons and \(N\) is the number of available sites. The Heikes formula can also be defined relative to the hole concentration, \(c_h\), according to Equation 5 where \(c_h = 1 - c_e\) and \(c_h = p/N\), with \(p\) is the number of holes:

\[ S(T \to \infty) = +\frac{K_B}{e} \ln\left(\frac{1-c_h}{c_h}\right) \]  

**2.1.3 Peltier coefficient**

A Peltier coefficient is used to characterise the measurement corresponding to the Peltier effect, which states that when a current is applied across the junctions of two materials, there will be a temperature differential at the either junctions due to the Peltier effect as previously described. It can be seen from equations 6 and 7 that the Peltier coefficient is directly linked to the Seebeck coefficient and a further analysis of the equations indicated that thermoelectric materials can be used for devices that utilise both of the Seebeck and Peltier effects [11].

Peltier effect is defined as:
\[ \Pi = ST \]  \hspace{1cm} (6)

By applying current to Peltier materials, it was found that heat (Q) was generated

\[ Q = SIT \]  \hspace{1cm} (7)

\[ \Pi = \text{Peltier coefficient} \]
\[ Q = \text{heat per unit volume} \]
\[ I = \text{electrical current} \]

**2.1.4 Thompson effect**

The Thompson effect is a phenomenon which was first observed by Lord Kelvin in 1851 [34]. It is defined as the heating/cooling that occurs within semiconductors when they are subjected to thermal gradient and when current is applied. In a material where an electrical current is flowing, energy is lost in the form of heat produced due to the resistance to the flow of the current. The heat released as a result of the resistive losses produces a thermoelectric effect (equation 8).

\[ Q = \rho J^2 - \mu J \frac{dT}{dx} \]  \hspace{1cm} (8)

\[ J = \text{Current density} \]
\[ \rho = \text{Electrical resistivity} \]
\[ \mu = \text{Thomson coefficient} \]
\[ \frac{dT}{dx} = \text{Thermal gradient in one dimension} \]

The Thomson effect can be linked to the Peltier and Seebeck coefficients by equating Q. Where:

\[ \mu = T \frac{DS}{dT} \]  \hspace{1cm} (9)

\[ \frac{DS}{dT} = \text{Seebeck coefficient gradient to temperature.} \]

Together equations 7, 8, and 9 lead to the conclusion that the effects involve the transfer of energy between electricity and thermal power and vice versa.

**2.1.5 Figure of merit**

In addition to the thermopower, the thermal conductivity and electrical conductivity of a thermoelectric material are significant variables in materials selection. To aid the
ranking of thermoelectric materials, Altenkirch [35, 36] introduced a dimensionless term called ‘figure of merit’ which was later modified by Ioffe as [29];

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

It can be seen that for thermoelectric materials to have high ZT, they need to have high electrical conductivity (\(\sigma\)), a high Seebeck coefficient (S) and low thermal conductivity (\(\kappa\), where it contained both electron and phonon components). TE devices generally need to use both n and p-type thermoelectric materials. The \(ZT_{\text{eff}}\) is introduced to calculate average power of combined thermoelectric legs as stated in the equation 11 [37].

\[ ZT_{\text{eff}} = \frac{(S_p - S_n)^2 T}{\left[\frac{1}{(\rho_n \kappa_n)^2} + \frac{1}{(\rho_p \kappa_p)^2}\right]^2} \]  

\(\rho = \) electrical resistivity \\
\(n\) and \(p\) subscribe refer to \(n\)- and \(p\)-type materials respectively \\
Another way to compare thermoelectric materials is the power factor for cases when thermal conductivity data is not available. 

\[ \text{power factor} = \frac{S^2}{\rho} \]  

The power factor should not be used as the only property to rank the thermoelectric materials as a high power factor combined with a high thermal conductivity will result in poor ZT values (poor efficiency but high power).

\subsection*{2.1.6 Electrical resistivity}

Electrical resistivity is a property of materials, which can be expressed by a measurement of materials response to an electric field as proposed by Ohm’s law [38]. The classical approach to electrical resistivity is defined by equation 13:

\[ \rho = \frac{E}{J} \]  

\(E = \) magnitude of the electric field \\
\(J = \) magnitude of the current density \\
And electrical conductivity is defined and reciprocal of resistivity, i.e.
\[\sigma = \frac{1}{\rho}\]  

(14)

Materials can be divided into classes of metals, semiconductors, and insulators depending on the resistivity of the material with each type exhibiting a different response depending on the voltage applied. Metals and semiconductors are preferred for thermoelectric applications as insulators have very poor charge carrier’s concentration.

A definition of electrical conductivity is given by the following equation:

\[\sigma = ne\mu\]  

(15)

\(n\) = number of charge carriers  
\(\mu\) = electron mobility  

This electrical conductivity equation can be applied to all types of materials such as metals or semiconductor. The factor ‘\(\mu\)’ (electron mobility) depends on electrical conductivity mechanisms.

The electrical conductivity mechanisms in solid matters can be explained by band theory. Band theory states that solid matters become conductive when the electrons inside the materials reach a certain energy known as the Fermi energy level (materials dependant); it is also further stated that electrons prefer to configure themselves in lowest energy state until enough energy has been given for it to reach that conduction level. In the case of metals, however, the higher energy levels are partially filled due to the natural electronic state configuration. Therefore, metals can be easily excited and electrons are made available at the conduction band. The free electrons model was proposed by Drude [39], whereby free electrons are assumed to be mobile until there are interaction with electrons, phonons, or atoms and hence the conductivity can be roughly estimated as

\[\sigma = \frac{ne^2\tau}{m}\]  

(16)

\(\tau\) = collision time  
\(m\) = electron mass  

However, in the case of semiconductors, electrons need to be excited from the valence to conduction band in order for conduction to occur due to the different electronic
configuration from metals. Using statistical mechanics, the charge mobility can be described as a function of probability of electron to be excited to become conductivity where energy supplied must overcome the gap energy as shown in equation 17 [40].

\[
\mu = \mu \cdot \exp\left(\frac{E_g}{k_B T}\right)
\]  

\[17\]

By examining equations 16 and 17, it can be seen that in order to increase the conductivity, the charge carrier mobility can be improved either by modifying the electron state (band gap) or by supplying more energy to overcome the energy barrier. Another factor that should be considered is the carrier concentration that can be increased using chemical doping in order to generate more free electrons and improve electrical conductivity.

For metals, as the temperature increases, the interaction time \(\tau\) decreases which results in increased energy transfer to electrons. The additional energy leads to decreased charge carrier mobility which increases the probability of interactions with electrons, phonons, atoms, and boundaries which decrease electrical conductivity. In contrast, electrical conductivity in semiconductors increases with temperature due to thermal excitation of electrons across the band gap resulting in increased charge carrier concentration.

### 2.1.7 Thermal conductivity

Thermal conductivity is a measure of the rate of heat transfer through a material. In mathematical terms it can be described as[41]:

\[Q = -\kappa \nabla T\]

\[18\]

\(\nabla T\) = Temperature gradient

In solid state materials, \(\kappa\) can be separated into \(\kappa_{\text{phonon}}\) and \(\kappa_{\text{electric}}\) i.e.

\[\kappa = \kappa_{\text{phonon}} + \kappa_{\text{electric}}\]

\[19\]

Where \(\kappa_{\text{phonon}}\) is the thermal conductivity from phonon propagation (lattice vibrations) and \(\kappa_{\text{electric}}\) is a thermal conductivity from electrons movement. It can be seen from equation 19 that the thermal conductivity is linked to \(\kappa_{\text{electric}}\) and in turn the \(\kappa_{\text{electric}}\) links
to electrical conductivity, which can be described by Wiedemann-Franz law [42] as shown in equation 20. The law can be used to explain the relation between phonon and electron regards thermal conductivity. This variable cannot be reduced while increasing the electrical conductivity due to the fact that electrons are needed to conduct heat in addition to acting as charge carriers. Hence, lowering $\kappa_{\text{phonon}}$ remains the promising way to reduce overall thermal conductivity, which can be done in by reducing the mean free path of phonon.

$$\kappa_{\text{electric}} = \sigma LT$$

(20)

Where $L$ is the Lorenz number $= 2.44 \times 10^8 \text{ W} \Omega/\text{K}^2$

Thermal conductance is a random process [43], in which the heat does not flow unilaterally from one end to another, but in fact, it enters and propagates through the specimen in every direction and excited the atoms causing more vibration (phonon) which are in the materials. Due to the random nature of its propagation, the mean free path of a random walk is adopted to describe the thermal conductivity, using the classic kinetic theory of gas. This can be calculated from equation 21 [44].

$$\kappa = \frac{CL_{\text{phonon}}V_s}{3}$$

(21)

where $C$ is the heat capacity.

and $V_s$ is the average particle velocity.

$L_{\text{phonon}}$ is the mean free path of a particle between collisions.

$C$ and $V_s$ are usually material dependent parameters which cannot be altered. Only one parameter, the mean free path can be changed in order to modify the thermal conductivity. For thermoelectric materials, the mean free path should be minimised by crystal structure engineering to maximise phonon scattering.

2.1.7.1 Phonon scattering

Phonon scattering is a phenomenon where the phonon means free path through a material has been reduced; several factors can contribute to this effect. In the development of thermoelectric materials, there is a trade-off between the electrical and thermal conductivity [45]. Phonon scattering has therefore become a key method to reduce thermal conductivity without reducing the electrical conductivity.

There are four key methods of increasing phonon scattering in crystalline materials. Doping a material with elements to introduce lattice misfit and strain that increases phonon scattering without significant degradation of electrical conductivity. It also
alters the band structure and electron mobility which might be favourable to thermoelectric properties [29]. A second method to achieve phonon scattering is via ‘rattling’ crystal structures, where the crystal structure is engineered such that a dopant atom is surrounded by a ‘cage’ of atoms. The dopant- and cage atoms will have different vibrational frequencies at a given temperature leading to scattering of phonons [46]. Conventional microstructural engineering through the introduction of defects such as dislocations, high angle grain boundaries and reducing the grain size can reduce the thermal conductivity through boundary scattering of phonons. The creation of superstructures that increase the length of the lattice will lead to shorter mean free phonon paths [47]. Finally, the introduction of thin films or multi-layer structures is another way to scatter the phonons at the interface and this could be used to combine the strength of both materials of the naturally good thermopower, with a lower thermal conductivity of thin films [48].

The phonon-glass electron-crystal (PGEC) approach is a concept proposed by Slack in 1995 [49]. In order to establish the optimal thermoelectric material properties, it was hypothesised that the structure best suited for thermoelectric materials should comprise (a) phonon-glass region(s) with low thermal conductivity and an electron crystal with high electrical conductivity. Phonon-glasses are similar in nature to amorphous, glassy materials where there is no long-range crystal structure leading to scattering of phonons. An electron-crystal structure has high electron mobility leading to high electrical conductivity. The PGEC behaviour can be achieved by the introduction of point defects or by the formation of superlattice and misfit structures. Typical examples are Ruddelsden-Popper phase of SrTiO$_3$ [50, 51], superlattice ZnGaInO$_3$ materials [52, 53] and Cobaltite structures [21].

The idea of nano-engineering the materials to enhance their thermoelectric properties began when scientists predicted that introduction of defects at the nano level could interrupt the flow of phonon by selective-site scattering i.e. quantum dots and wire, which resulted in a decrease in thermal conductivity and lead to a higher figure of merit [54]. Furthermore, not only dispersed defects but also a layer of thin-film or a specific array of nanowires could be coated onto the thermoelectric material which could potentially alter its electronic state (Fermi energy level etc.) and lead to more favourable electrical characteristics [48]. Research literature suggests that nanomaterials have increased the figure of merit several folds [55, 56]. The concept of nano-materials has been widely used in thin film thermoelectric materials and in some
quantum dots [48, 54-60].

Figure 2-3 Illustration of materials of different levels of complexity and a comparison of ZT values [61].

2.1.8 Figure of merit and efficiency of materials

In this section, the relationship between conversion efficiency and figure of merit will be established. The conversion efficiency is widely used to determine how much heat (energy) input can be transferred into electricity. Therefore, the comparison between different kinds of power sources can be easily seen and achieved by linking the figure of merit to the conversion efficiency $\eta$.

A theoretical value of efficiency is defined as [2, 4]:

$$\eta = \frac{W_{\text{out}}}{W_{\text{in}}} \quad (22)$$

Where work generated ($W_{\text{out}}$) is divided by the amount of work put into the system ($W_{\text{in}}$). In the case of thermoelectric materials, the work output is electricity generated by the heat supplied as the work input [37].
\[ \eta = \frac{W}{Q_h} \]  
(23)

Where \( \eta \) is efficiency, \( W \) is work supplied to the system and \( Q_h \) is heat supplied. The heat supplied is ideally dependent on the Carnot cycle as explained in classical thermodynamics [43]. Therefore, in the case of thermoelectric materials, equation 22 can be reformulated as:

\[ \eta = \frac{(T_h - T_c)}{T_c} \eta_{couple} \]  
(24)

The overall efficiency equation combining traditional efficiency with ZT can be reformulated as [62]:

\[ \eta_{couple} = \eta \left[ \frac{(1 + ZT_{eff})^{0.5} - 1}{(1 + ZT_{eff})^{0.5} + (T_C/T_H)} \right] \]  
(25)

Where \( T_C \) = cold side temperature  
\( T_M \) = average temperature  
And \( T_H \) = hot side temperature  

On the other hand, the efficiency of thermoelectric couple can be roughly simplified and estimated as the following equation [8]:

\[ \eta_{couple} = (1 + ZT_{eff})^{0.5} \]  
(26)

Therefore, the \( \eta \) can be represented as a function of the figure of merit and temperature.

2.1.8.1 Charge carriers

In the optimisation of the properties of thermoelectric materials, there is a trade-off between the thermal conductivity, electrical conductivity and Seebeck coefficient. This is illustrated in Figure 2-4 which shows that despite a continuous increase in the electrical conductivity and thermal conductivity as a function of carrier concentration, the ZT reaches a maximum value when the carrier concentration is \( \sim 10^{19} \) carriers/cm\(^3\).
Although the electrical conductivity increases with charge carriers (equation 15), the ZT is ultimately limited by the Seebeck coefficient (represented by α in Figure 2-4) as the Seebeck coefficient decreases with increasing carrier concentration. As the charge carrier concentration increases, the probability of charge carriers becoming mobile is increased leading to a reduction of the voltage gradient, thermal gradient and subsequently the Seebeck coefficient. Therefore, optimisation of charge carrier concentration is required; the equation for thermopower in term of charge carrier concentration is stated in equation 27.

\[ S = \left( \frac{8\pi^2 k_B^2}{3e\hbar^2} \right) m^* T \left( \frac{\pi}{3n} \right)^{1.5} \]  

(27)

Where \( m^* \) is the effective mass of charge carriers and \( n \) is the charge carrier concentration

\( h = \) Planck’s constant
2.2 Applications

2.2.1 Overview

Thermoelectric devices can be operated to recover waste heat using the Seebeck effect or to cool objects using the Peltier effect. The wide variety of available thermoelectric materials in above-mentioned modes of operation, allows thermoelectric devices to be deployed in a wide variety of applications.

The primary focus of the thermoelectric research is the maximisation of ZT to achieve maximal device efficiency but in some applications the optimisation of power factor may take higher priority where high electrical supply is desirable. Easily accessible materials and/or ease of manufacture which leads to a reduction of overall cost by the economy of scale-up might be suitable for commercial applications over the state of the arts but expensive materials. For example: Tellurium is a rare-earth element which is hard to locate and process therefore has a very high price although it yields materials with a high ZT. The concern of waste management (of the tellurides) and its cost might also be a deciding factor in its use as well, since heavy metals are harder and costly to recycle. Other design factors such as mechanical aspects (strength of materials, joinability), environmental (thermal stress environment, and cyclic environment) and operating temperatures are also important when selecting materials.

Thermoelectric materials are generally employed in an array of couples called a module, with p-type and n-type materials, because of the low figure of merit and low voltage output in a single couple. Modules are normally connected in series for waste heat recovery or in parallel for Peltier cooling devices.

2.2.2 Historical review of materials and applications

Since the discovery of the Seebeck effect in 1821, many measurements of the ZT of metal alloys, semiconductors, and other materials have been made. Some heavy metal alloys and doped semiconductors are ideal materials for employment in thermoelectric applications due to their high Seebeck coefficient [12, 14]. Between 1940 and 1990, the maximum ZT was limited to values < 1. After 1990, there was renewed interest in raising the ZT value in order to provide alternative energy sources.
Figure 2.5 Development of ZT values of significant thermoelectric materials from 1940-1990. Note the lack of increase in ZT between 1970 and 1990 followed by a rapid increase to 2010 [63].

The first-generation materials were generally metal alloys in 1940-70 era. ZnSb with a ZT of 0.3 is an example of an early thermoelectric material and was included in Seebeck’s report on Seebeck effect [28]. Several publications have reported enhancement of the ZT of ZnSb with a notable work by Telkes in 1954 [64].

The Voyager and Pioneer space exploration programs used radioisotope thermoelectric generators (RTG) based on Telluride as a power source. RTGs use the heat generated by radioactive isotope (typically plutonium-238), which has a long decay lifetime for conversion of radiated heat to electrical energy. RTGs were designed to have a long life and to be reliable due to the long-term nature of space missions. The reliability of solid-state RTGs is in part due to the lack of moving components which are a common cause of mechanical failures.

Initially RTGs were manufactured using Telluride alloys i.e. Bi$_2$Te$_3$ and PbTe, which have ZT around 0.6-1.0, and usually yielded a 6-10% efficiency [9]. The first generation RTG was used on the Apollo program in the 1960s and had a minimum specific power of 1.3 W/kg and development of PBSnTe alloys lead to significant increases in the specific power to 2.7 W/kg for the Pioneer and Viking missions in the 1970s. Modern RTGs use SiGe alloys with an efficiency of approximately 8% and specific power of 4 W/kg leading to a reduction in the size of thermoelectric devices. Although these metal alloys provide excellent efficiency, power, and reliability, sources of tellurium are rare.
and consequently expensive. Tellurium is also mildly toxic; its alloys are difficult to recycle and are not stable when heated above temperatures of 400 °C leading to oxidation of metal and degradation of thermoelectric properties. The combination of these factors limits the use of tellurides in a wider range of thermoelectric applications.

2.2.3 Power generation mode

Thermoelectric devices can be used to generate electricity using the Seebeck effect by connecting the thermoelectric generator (TEG) to any electric resistor loads. The heat exchange in the generator leads to the diffusion of charge carriers in both the p-type and n-type materials and creates a voltage gradient, which could be used to drive a current through the electric resistor load. Efficiency is typically 6-10% for a ZT value of ~1 depending on the configuration of generators. The notable feature is that it requires no moving parts to generate electricity, unlike conventional methods where fans or turbines are used to induce electric potential.

![Thermoelectric device in power generation mode](image)

*Figure 2-6 Thermoelectric device in power generation mode [65].*

2.2.3.1 Low power generator

Low power thermoelectric generators are used as power supplies for low power devices including mobile telephones, temperature sensors, cameras, avionics and in automotive applications where mobility is a higher priority than powering high electric load. Thermoelectric generators (TEGs) have superior durability compared to conventional
batteries and TEGs do not require replacement as often as batteries leading to a reduction in maintenance costs. All cars use the electrical energy from a battery pack to power the lighting, internal environment controls, and entertainment systems. The electrical energy generated from heat wasted from the engine, can be used to supply power to these secondary systems, potentially leading to an increase in the fuel efficiency. Only 20-30% of the fuel is used to accelerate and maintain the speed of the car and the remaining 70% is lost as waste heat. To address these issues, a redesign of cars and further research to optimise and integrate thermoelectric materials into automotive systems is an ongoing process [13]. The first automotive thermoelectric generator was constructed and evaluated by Neild et al. in 1963 [66]. This was followed by Birkholz in 1988 [67] where TEGs using FeSi₂ were installed on exhaust systems of Porsche model cars and a power generation of 10 W was reported. It was found by Matsubara in 2002 [68] that the thermoelectric materials of that time with a ZT of 1.0 could yield 6-8% efficiency with 266 W output and estimated that a ZT of 1.5 – 2.0 could potentially reach an efficiency of 10% or more in cars. A more recent study by Lagrandeur et al. [69] in 2007 confirmed Matsubara’s efficiency projections for thermoelectric materials such as skutterudites with ZT of ~1.5 and estimated power output to be as high as 750 W. In aerospace applications, thermoelectric devices can be used to power instruments and avionics or as backup auxiliary power units. While NASA has previously employed materials developed in the older generation, newer cheaper thermoelectric materials could potentially be put in commercial or in military aircraft. Passengers travelling on commercial airlines could see a benefit of thermoelectric blankets or small power generation to recharge mobile phones or internal/external entertainment systems. Thermoelectric devices can also be employed in many household appliances where heat is generated and can be salvaged/converted into electricity for use. The examples would include heaters, cooking appliances, and entertainment systems.

2.2.3.2 High power generation

Thermoelectric devices could be used as a principal enhancer in electrical energy generation as the running costs of thermoelectric devices are relatively low, as there are no associated fuel costs. This could lead to improvement of existing power plant efficiency by recovering waste heat and hence lower overall carbon emissions and lower the overall cost for manufacturing processes.
Power in the range of 15-550 W has been reported for commercially available devices with dimensions as small as 0.5x0.5x0.5 mm [70]. The price-performance review, over a 3 years period in early 1990 period collected from various source by Rowe [71], in waste heat generators, was reported to be comparable to conventional power generation sources. A thorough study of potential industry waste heat generations was conducted by Yodovard et al. [72] where information was collected from around 27000 factory sites in Thailand; it found that 20% of gas turbine waste heat and 10% from diesel cycle could be used to generate electricity.

Solar energy is also a source of clean alternative energy; however, its low heat to energy efficiency and high cost compared to fossil fuel has limited its widespread adoption. A typical single-crystal silicon solar cell has an efficiency of around 25%, and 20.7% for a polycrystalline silicon [73]. GaAs thin films have a higher conversion efficiency of 27.6%, however, they can generate with only 18.4% efficiency when polycrystalline materials are used. A multifunction device made of GalnP/GaAs/Ge yielded a higher efficiency of 32% [73]. In order to improve solar power systems, which have a lot of excess heat collected by the solar cells with average temperatures up to 1000 K, the solar panels could be used in conjunction with thermoelectric devices to increase the efficiency of energy conversion [74]. One junction system called a thermionic converter was reported to have a high conversion efficiency ~ 40% using graphite solar receiver enclosed by a molybdenum cup (Figure 2-7) [75].

![Figure 2-7 Schematic of thermionic converter system [75].](image)

### 2.2.4 Thermoelectric sensors

Several sensors can exploit the potential of thermoelectric devices, e.g. heat flux sensor where the sensitivity of 10 times higher than that of conventional sensors were reported
[76]. The function of these sensors is to detect heat dissipation in some area or can be adopted as heat lost detected handheld device. An ultrasonic intensity sensor is also considered a possibility as ultrasonic wavelengths also emit slight heat which can be detected by thermoelectric devices. Other notable examples of thermoelectric sensors include fluid flow and infrared radiation sensors [70].

### 2.2.5 Thermoelectric cooling

Thermoelectric cooling devices utilise the Peltier effect where the electrical current flow causes a thermal gradient across the material. As the electron charges concentration on the p-type side is lower than on the n-type side in the module as a result of charge movement; compensation by heat absorption/release is required in an attempt to rebalance the charges by the materials themselves.

There are two factors which hinder thermoelectric cooling: firstly, Joule heating where the resistance to the flow of an electric current generates heat within the materials. The Joule heating caused by the thermal gradient would generate a reverse current in the materials.

The cooling effects of thermoelectric devices have become promising as they can be employed locally and selectively. In many electrical components, such as computers or engines these are considered to be beneficial. It has been reported that cooling computers would allow them to operate more reliably and potentially at faster speeds [77]. Another possible application of cooling by thermoelectric devices is at hotspots, in order to prolong mechanical properties and life of materials [78]. Other small appliances could see the action of thermoelectric devices such as various refrigerators or coolers. The summary of potential applications is listed in Table 2-1.
Table 2-1 Potential applications where Peltier effect could be used, adapted from Riffat et al. [70].

<table>
<thead>
<tr>
<th>Category</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Military/aerospace</td>
<td>Electronic cooling; cooled personal garment; portable refrigerators; cooling</td>
</tr>
<tr>
<td></td>
<td>infrared sensors; cooling laser diodes</td>
</tr>
<tr>
<td>Consumer products</td>
<td>Recreational vehicle refrigerators; mobile home refrigerators; care refrigerators; portable picnic coolers; water coolers</td>
</tr>
<tr>
<td>Laboratory and scientific</td>
<td>Laser diode coolers; charge-coupled device coolers; Change induced device</td>
</tr>
<tr>
<td>Equipment</td>
<td>coolers; integrated circuit coolers; laboratory cold plates; stir coolers;</td>
</tr>
<tr>
<td></td>
<td>cold chambers; immersion coolers</td>
</tr>
<tr>
<td>Industrial-temperature</td>
<td>Harsh environment protection for critical components; PC computer</td>
</tr>
<tr>
<td>control</td>
<td>microprocessors; microprocessor and PCs in numerical control and robotics;</td>
</tr>
<tr>
<td></td>
<td>stabilising ink temperature in printers and copiers</td>
</tr>
<tr>
<td>Restaurant equipment</td>
<td>Cream dispensers; whipped cream dispensers; butter dispensers; individual</td>
</tr>
<tr>
<td></td>
<td>portion dispensers.</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>Pharmaceutical refrigerators-portable and stationary; hotel room refrigerators;</td>
</tr>
<tr>
<td></td>
<td>aircraft drinking water cooler; coach coolers; marine coolers van coolers and</td>
</tr>
<tr>
<td></td>
<td>refrigerators</td>
</tr>
</tbody>
</table>

2.2.6 Advantages of thermoelectric materials

There are several advantages of using thermoelectric materials. Firstly, they are solid state devices and involve no-moving-parts, which should result in less mechanical damage for the devices as they have no vibration in the device themselves, less wear and fatigue. Furthermore, they are also silent, compact and can be employed locally. Secondly, they are capable of recycling waste heat. Waste heat is a total loss with 0% efficiency as none of it can be used, but with thermoelectric devices, 7-10% of waste heat can be used. Thirdly, thermoelectric devices require no fuel in power generation; however, they might need to be replaced at the end of their lifetime due to thermal
electric properties degradation. Fourthly, they have a long lifetime with a capacity of exceeding $10^5$ hours. Fifthly, they are versatile, the same materials can be employed in two modes, electricity generation and cooling. It might be possible to employ them in processes, where cycling between heating and cooling is required. During heating, it can generate electricity and could save it for later use, in order to help the cooling stage. Sixthly, some manufacturing methods are quite cheap, readily available, and fast to produce a large batch of thermoelectric devices. Finally, they can be used in a wide range of temperatures and applications and they are generally lightweight with no pollution produced during power generation and precision temperature control within $\pm 0.1\%$ oC

2.2.7 Disadvantages of thermoelectric materials

There are some considered drawbacks of thermoelectric materials such as limited efficiency and potentially high cost. Second, they act as heat sink devices, which may accumulate heat and may affect other materials, and finally, the efficiency of the materials varies and depends on temperature ranges.

2.2.8 The challenge of mechanical properties

Thermoelectric materials need to be physically and chemically stable in their operating environment during operation. Several applications of thermoelectric devices require materials to maintain performance at elevated temperatures for extended periods of time. High temperatures and dissimilar materials used in thermoelectric devices lead to a high probability of diffusion of chemical species potentially leading to deterioration in electrical, mechanical, and thermal properties. Another challenge is that of corrosion between two materials especially the joints where a high temperature could accelerate the corrosion rate of metals electrode and thermoelectric materials. The thermal expansion of the two joined materials should also be considered because the difference between the thermal expansion coefficients will lead to thermal stresses and crack between the joints. Mechanical vibrations in some applications might cause fatigue in the materials. Furthermore, if deployed in space an extra criterion of extreme freezing and solar irradiation must also be considered. Lastly, most thermoelectric materials research has emphasised the efficiency (figure of merit) of the materials but there is little published research on how well these materials can withstand mechanical stresses [79].
Sublimation is another challenge for metal thermoelectric materials, which is a process where materials change phase from solids into gas without passing through a liquid phase [80]. It occurs at hot junctions and at interfaces of metallic thermoelectric devices and hence increases the resistivity of thermoelectric materials. This transition is considered as time-dependent due to the fact that supplied heat accelerates the process and supplies the driving forces for a change from one phase to another. The typical rate of loss is 5-10% reduction in cross-sectional area over ten years which results in a loss of efficiency of typically 10-20% depending on the materials [80].

2.2.9 The current goal for developing thermoelectric materials

The current goal for thermoelectric devices, is to achieve a higher efficiency (higher figure of merit values i.e.; ideally $ZT > 3$) for the temperature range of 250-1000 °C [16, 21, 22, 77, 81]. Secondly, to achieve a good performance with large-scale production; integrate and design into widely used applications.

2.3 Thermoelectric materials

From the first discovery of thermoelectric materials, the first way to the improve figure of merit is to test and find new materials which have a natural high figure of merit. Second consideration is to manipulate the microstructure of materials through various means. Much of the early work on thermoelectric materials was done on semiconductors as semiconductors give higher a Seebeck coefficient than metals. The goal of achieving a high figure of merit needs to be done by limiting charge carriers to optimised levels but with high electrical conductivity. This leads to optimised crystal structures such as zinc blende or diamond, with the need for a low Debye temperature and high harmonic lattice vibrations [56], as found in traditional intermetallic thermoelectric materials. A range of thermoelectric material families will be considered here: conventional thermoelectric materials, nano-complex oxides, bulk thermoelectric materials, nanostructures one-dimensional and composite thermoelectric materials, and the subject of this investigation cobaltite oxides.

2.3.1 Non-oxide thermoelectric materials

Several conventional thermoelectric materials consist mostly of metal alloys and semiconductors. These materials exhibit good thermal electric properties due to their complex structures or favourable electrical properties arising from the good electronic structure. Since 1950 people have been searching for new thermoelectric materials or ways to improve the thermoelectric properties by various ways. The most notable non-
oxide thermoelectric materials are Bi₂Te₃ the first widely used thermoelectric material, and PbTe which can be used as both p-type and n-type.

Figure 2-8 ZT values of various traditional thermoelectric materials [14].

Bi₂Te₃ is widely used and accepted as a standard for comparison of thermoelectric materials. It has a rhombohedral-hexagonal crystal structure with space group R̅3₃ with a Te-Bi-Te-Bi stacking along the c-axis and covalent bonds between tellurium and bismuth with Van der Waals forces between Te-Te on the different plane (Figure 2-9). The unit cell parameters are ‘a’ = 3.8 Å and ‘c’ = 30.5 Å. Figure of merit around 1 at 400 °C has been reported [37]. Bi₂Te₃ was used in last century in many thermoelectric applications; however, they are quite expensive due to the fact that tellurium is a rare element and mildly toxic [37].
2.3.2 Oxide Thermoelectrics

A carrier concentration of $10^{19}/\text{cm}^3$ was found to be the optimal point in achieving the highest power factor, regardless of materials according to classical semiconductor theories. If this optimal carrier concentration is reached, there are only other 2 possible parameters to achieve higher ZT. First is to increase the carrier mobility (higher $\sigma$ at fixed carrier concentration) and second is to decrease lattice thermal conductivity. Up until the 1990s, all conventional thermoelectric materials have been developed based on this principle. The materials that fit these criteria are usually intermetallic compounds with covalent bonds (for higher carrier mobility) and/or composed of heavy elements for lowering lattice thermal conductivity. The most notable materials are Bi$_2$Te$_3$, PbTe, and Si-Ge, which cover the temperature range of 25-1000 °C (Figure 2-8). However, these materials have many drawbacks such as oxidation at a high temperature in an air atmosphere, high cost of processing and extraction, high toxicity in some compound. All of which limited the adoptability and commercialisation of thermoelectric devices. Metal oxides are seen as an alternative and answer to the drawback of the metal compounds. The metal oxides are usually bonded by ionic force between metal cations.
and oxygen anions. The Coulombic interactions between cations and anions lead to highly-polarised materials. Furthermore, the size of atomic orbitals overlapping the atoms is smaller than those found in covalent bond compounds. These characteristics lead to the lower carrier mobility found in oxides materials, generally 2-3 magnitude lower than the covalent compounds. Moreover, high lattice thermal conductivity was commonly found since high velocity elastic wave can easily propagate through the oxide crystal lattice because of large ionic bonding energies and small oxygen atomic mass. All of these natural characteristics of metal oxides are in contrast to traditional principles and hence metal oxide have been disregarded in research and development for thermoelectric materials until 1997 when Terasaki et al. [82] discovered a high ZT of 1.0 for single crystal Na$_x$CoO$_2$. The discovery sparked interest in oxide thermoelectrics. The main advantages of oxides ceramics are that the starting materials are quite readily available as well as being cheap and fast to process. These materials themselves are generally non-toxic which, at the end of their life cycle, can be easily and cheaply disposed of. The flexibility of oxides materials can also mean that the structure can be freely designed, by means of adding/removing chemical compositions to modify the thermoelectric properties to suit each application needed in both $n$ and $p$ types. The ability to operate at high temperature means that they can be used at higher efficiency.

Due to current global warming and the need to reduce carbon dioxide emissions, oxide thermoelectric materials are becoming of more and more importance.

### 2.3.3 N-type oxides

Several $n$-type thermoelectric materials have been proposed. The most promising candidates are compounds with perovskite structures including SrTiO$_3$ [83-94] and CaMnO$_3$ [20, 22, 95-103] and perovskite-related compounds such as Ruddlesden-Popper [19, 22, 50, 51, 104] and Tungsten Bronze [105-110]. ZnO-based oxides also have shown promising thermoelectrics properties [21, 23, 52, 53, 58, 99, 104, 111-113]. In the following sections, the mentioned materials are reviewed.

#### 2.3.3.1 Strontium titanate

SrTiO$_3$ has a simple perovskite structure. The general chemical formula for perovskite compounds is ABX$_3$, where 'A' and 'B' are two different size cations, by convention ‘A’ atoms are, larger than ‘B’. The ‘A’ cations are located in corner positions of the cubic
unit. The ‘B’ cations are located in the middle of octahedral, surrounded by anion positions, the unit cell is shown in Figure 2-10 for SrTiO$_3$.

![Figure 2-10 Schematic presentation of the cubic structure for SrTiO$_3$ [83].](image)

Due to a high melting point of 2080 °C and absence of any phase transformation from ambient temperature to the melting point, it is one of the ideal candidates for thermoelectric materials. Pure SrTiO$_3$ is an insulator; the unmodified bandgap of SrTiO$_3$ is around 3.2 eV. The conduction band formed by of Ti 3d orbital (3d$_{xy}$, 3d$_{yz}$, 3d$_{xz}$) and valence band formed by O$_{2p}$ orbital which results in high electrical resistivity. High effective mass also leads to high thermopower of 650 µV/K at room temperature [20, 93]. However thermal conductivity is also high (~11 to 3.5 W/m.K) in the temperature range of 300 to 1000 K) [23, 87].

The potential of SrTiO$_3$ as a thermoelectric oxide was confirmed by Ohta et al. [88]. Single crystals of La- and Nb-doped SrTiO$_3$ were studied. The doping effectively changed the effective mass, due to free electrons introduced into the system, which led to a change in electrical conductivity and Seebeck coefficient with minimum effect on thermal conductivity compared to undoped samples. It was found that higher doping yielded higher ZT for both dopants. A ZT of 0.27 was achieved in high La-doped sample at 1073 K and 0.15 for high Nb-doped samples.

Doping of rare earth elements in polycrystalline SrTiO$_3$ was conducted by Muta et al. [87] in the form of Sr$_{0.9}$R$_{0.1}$TiO$_3$ (R=Y, La, Sm, Gd, Dy) using solid-state reaction. It was found that the electrical conductivity and Seebeck coefficients are not affected by different kind of lanthanides. However, the thermal conductivity decreases with atomic
mass and ionic radius of doping elements. The highest figure of merit of 0.22 at 573 K was achieved in Sr$_{0.9}$Dy$_{0.1}$TiO$_3$.

Further rare earth doping experiments were performed by Liu et al. [86]. Single and dual doping was carried out in form of Sr$_{0.9}$R$_{0.1}$TiO$_3$ (R= Er, Y, Dy, Gd, Sm, Nd), and Sr$_{0.8}$La$_{0.18}$Yb$_{0.02}$TiO$_3$ prepared by solid-state reaction. A similar finding to Muta et al., [87], concluded that ionic radius and an atomic mass of doping elements are the major factors on thermoelectric properties. The large rare earth ions gave large power factors, and the small ions did give low thermal conductivity. A combination of dual doped large and small ions elements in SrTiO$_3$ led to the higher figure of merit. The Sr$_{0.8}$La$_{0.18}$Yb$_{0.02}$TiO$_3$ had a ZT of 0.31 at 1023 K compared to single doped Sr$_{0.8}$La$_{0.2}$TiO$_3$ of 0.26. The thermoelectric data from their study are shown in Figure 2-11.

![Figure 2-11](image)

*Figure 2-11 Temperature dependence of thermoelectric properties of Sr$_{0.9}$RE$_{0.1}$TiO$_3$ ceramics (RE = La, Nd, Sm, Gd, Dy, Y, Er, Yb): a) resistivity, b) Seebeck coefficient, c) total thermal conductivity, and d) figure of merit reproduced from Liu et al. [86].*
Further attempts to modify SrTiO₃ by sintering in strongly reducing condition was carried out by Kovalevsky et al. [84]. Compositions Sr₀.₉R₀.₁TiO₃±δ (R = La, Ce, Pr, Nd, Sm, Gd, Dy, Y) were prepared by solid-state reactions and sintered in 10%H₂-90%N₂ atmosphere at 1773 K. The effect of cation size and unit cell on the thermoelectric properties reported previously [86] was again confirmed. The use of highly reducing conditions led to oxygen-deficient structures having a favourable effect on ZT, due to lower thermal conductivity resulted from phonon scattering from oxygen vacancies. A low thermal conductivity of 4-2 W/m.K between 300-1300 K and high ZT of 0.42 at 1190 K was achieved for Sr₀.₉Dy₀.₁TiO₃.

2.3.3.2. Ruddlesden-Popper Phases

Ruddlesden-Popper phases have a layered perovskite-like structure. Their general formula can be written as Aₙ₋₁A’₂BₙX₃n+₁ where A, A’ and B are cations, X is anion and n is the number of layers of octahedral in the perovskite-like stack. The structure for Srₙ₋₁Sr₂TinO₃n+₁ for n= 1, 3 and 6 is shown in Figure 2-12. The structure is built up of layers of rock salt SrO intercalated between SrTiO₃ perovskite layers.

![Figure 2-12 Schematic presentation of structure for Srₙ₋₁Sr₂TinO₃n+₁ for n= 1, 3 and 6 phases [114].](image)

Figure 2-12 Schematic presentation of structure for Srₙ₋₁Sr₂TinO₃n+₁ for n= 1, 3 and 6 phases [114].
The structure can be considered as a natural superlattice of two different phases having a rock salt layer between SrTiO$_3$ layers and thus may reduce the high thermal conductivity of SrTiO$_3$. Lee et al. [50] fabricated Ruddlesden-Popper type SrO(SrTiO$_3$)$_n$ ($n=1,2$) materials with different Nb doping levels (1%, 5%, 10%). Samples were manufactured by the mixed-oxide route followed by hot pressing. It was reported that for samples with $n=2$ doped with 20 % Nb, the thermal conductivity was reduced by 50% at room temperature and around 30% at 1000K compared to Nb-doped SrTiO$_3$ single crystal; lower thermal conductivity was attributed to phonon scattering by the superlattice structure. However, there was a decrease in electrical conductivity due to the SrO insulating layer compared to Nb-doped SrTiO$_3$. The Seebeck coefficient was found to be much lower than that of Nb-doped SrTiO$_3$. It was suggested that this reduction is due to distortion of TiO$_6$ octahedra in the Ruddlesden-Popper structure. Because of the reduction in both electrical conductivity and Seebeck coefficient, the highest ZT was only 0.15 in samples with $n=2$, doped with 5% Nb.

Wang et al. [51] carried out similar studies on $(Sr_{1-x}R_x)_n+1Ti_nO_{3n+1}$ ($n=1,2$) ($R= Nb$ La, $x= 0.05, 0.1$) compositions using the same preparation technique. The study confirmed previous findings [50] that the power factor and thermal conductivity of SrTiO$_3$ based Ruddlesden-Popper phase are lower than that of perovskite SrTiO$_3$.

Later Wang et al. [94] tried to eliminate the detrimental effect of distorted TiO$_6$ on thermopower in SrTiO$_3$ based Ruddlesden-Popper SrTiO$_3$, doped with Nb and rare-earth elements with different types of rare-earth elements. Two sets of electron-doped SrO(SrTiO$_3$)$_n$ ($n=1, 2$) compositions were selected: first, SrO(Sr$_1-x$Nb$_x$O$_3$)$_n$ ($x=0.05$-$0.2$), and second, $(Sr_{1-x}R_x)_{n+1}Ti_nO_{3n+1}$ ($x=0.05, 0.1$); R$= Gd^{3+}, Sm^{3+}, Nd^{3+},$ and La$^{3+}$. The results confirmed that Ruddlesden-Popper structures have a 60-30% lower thermal conductivity over 300-1000 K compared to SrTiO$_3$. The power factors of Nb-doped Ruddlesden-Popper phases were comparable with the results of Lee et al. [50] and similar explanations were given (i.e lower effective mass due to TiO$_6$ distortion). However, for the R-doped Ruddlesden-Popper phases, it was found that the TiO$_6$ octahedra were undistorted; this combined with the effect of increased O-Ti-O bond angle in the (100) plane, which created a triple 3d orbital degeneracy, resulted in higher effective mass and hence better power factor. A ZT of 0.24 was found in undistorted
TiO$_6$ Ruddlesden-Popper samples (5%-Gd$^{3+}$ doped) at 1000 K compared to 0.14 in Nb-doped compositions.

2.3.3.3 CaMnO$_3$

CaMnO$_3$ is another n-type material with a perovskite structure. Its space group has been identified as $Pnma$ orthorhombic with unit cell parameters $\sim\sqrt{2}a_p$, $\sim2a_p$, $\sim\sqrt{2}a_p$ ($a_p$ is unit cell length of ideal cubic perovskite) [98]. Two phase transition temperatures have been reported [98]: first, 896 °C from orthorhombic to tetragonal, and second, 913 °C from tetragonal to cubic. CaMnO$_3$ is a natural antiferromagnetic insulator at room temperature due to a lack of electrons in the valence band; due to this it has a comparatively low electrical conductivity of 10-100 S/m in temperature range of 300 to 1000 K. Thermal conductivity has also been found to be relatively high between 3.5-2.5 W/m.K in the same temperature range. It has a large room temperature thermopower of about -250 μV/K. Several studies reported that doping will change the charge of Mn from 4+ to 3+ and the difference in the radius of Mn will affect the effective mass and electrical properties [98]. Therefore, A-site substitution with different lanthanides or B-site substitution with hetero-valent cations (ie. Nb, Ta, W, Ru, and Mo) have been used to enhance the power factor of CaMnO$_3$.

Bocher et al. [95] studied the effect of preparation route on microstructure and thermoelectric properties of Nb-doped CaMnO$_3$. CaMn$_{1-x}$Nb$_x$O$_3$ ($x \leq 0.08$) compositions were manufactured by solid-state route and a chemical method. Chemically prepared samples showed higher ZT values compared to samples prepared by the mixed-oxide route. ZT of 0.3 at 1000 K was achieved in chemically prepared CaMn$_{0.98}$Nb$_{0.02}$O$_3$. The main difference was found to be the thermal conductivity, where the solid-state sample had values of around 2.8-1.5 W/m.K over the temperature range of 300-1000 K in comparison to 0.8 W/m.K found in chemically prepared samples.

Thiel et al. [103] also used a chemical route similar to Bocher et al. [95] to manufacture and investigate CaMn$_{1-x}$W$_x$O$_3$ ($x \leq 0.05$). The thermal conductivity of W-doped samples was slightly lower compared to Nd-doped samples but power factor was inferior. ZT was reported to be 0.15 at 1000 K and 0.25 at 1225 K. It was stated that increased ZT between 1200 and 1225 K was due to the creation of oxygen vacancies as a result of oxygen loss. Above 1225 K, ZT was found to be reducing; this was explained by a phase transition from orthorhombic to cubic.
Several simulation studies have been performed on the effect of oxygen contents on the crystal structure of CaMnO$_3$: Reller et al. [101] and Loashkareva et al. [97] suggested the formation of an ordered superstructure when oxygen vacancies were created. Using ab initio calculations, Molinari et al. [98] found that ordering of oxygen vacancies has a pronounced effect on thermoelectric properties of CaMnO$_3$. Seebeck coefficients were highly reduced and electrical resistivity was increased by increasing the oxygen vacancy content. As a summary, none of the computer studies showed a higher power factor or ZT values in oxygen deficient structure compared to stoichiometric CaMnO$_3$. Schrade et al. [115] have independently confirmed the simulation findings by experimental study and found that oxygen deficiency reduced the thermopower and increased the electrical resistivity.

Substitution of Mo for Mn was investigated by Pi et al. [100]. The results were found to be a reduction in both thermopower and electrical resistivity. The thermopower was found to be $110 \, \mu V/K$, the electrical resistivity $30 \, m\Omega cm$, the thermal conductivity $3.5 \, W/m.K$ at room temperature, and ZT of 0.01 for CaMn$_{0.96}$Mo$_{0.04}$O$_3$.

Computer modelling and experimental studies of the crystal structure and thermoelectric properties of Sr-Mo substituted CaMnO$_3$ were conducted by Srivastava et al. [102]. Samples with composition of Ca$_{(1-x)}$Sr$_x$Mn$_{(1-y)}$Mo$_y$O$_3$ with $x=0, 0.1, 0.3, 0.6$ and $y=0.02$ and 0.04 were prepared by the mixed-oxide route. Computer simulation was performed using ab initio method. A random distribution of Sr in the A-site of the perovskite structure was showed by analysis of atomically resolved imaging. A boundary structure of 90° rotational twin boundaries across 110 orthorhombic plane family, was observed from the analysis; the twin boundaries are suggested as a main phonon scattering source by molecular dynamics calculations, resulting in lower thermal conductivity. Increasing Sr substitution was found to reduce the Seebeck coefficient, however, the substitution helps to improve the densification which resulted in high power factor. Mo doping created additional charge carriers by the generation of Mn$^{3+}$ in the Mn$^{4+}$ matrix, which result in a reduction of electrical resistivity. The reduction in thermal conductivity was found to be the most important impact of Sr on thermoelectric behaviour, as demonstrated in experiments and simulation. The strontium doped ceramics showed ZT higher than 0.1 at temperatures above 850 K.
Ceramics of Ca$_{0.7}$Sr$_{0.3}$Mn$_{0.96}$Mo$_{0.04}$O$_3$ showed thermopower of $= -180$ $\mu$V/K, resistivity of $= 5 \times 10^{-5}$ $\Omega$ m, and thermal conductivity of 1.8 W/m K$^{-1}$ and $ZT \approx 0.11$ at 1000 K.

![Graphs showing thermoelectric properties](image)

**Figure 2-13** Thermoelectric properties of CaMn$_{0.96}$Mo$_{0.04}$O$_3$ (CMM4), Ca$_{0.9}$Sr$_{0.1}$Mn$_{0.98}$Mo$_{0.02}$O$_3$ (C9S1MM2), Ca$_{0.9}$Sr$_{0.1}$Mn$_{0.96}$Mo$_{0.04}$O$_3$ (C9S1MM4), Ca$_{0.7}$Sr$_{0.3}$Mn$_{0.96}$Mo$_{0.04}$O$_3$ (C7S3MM4), Ca$_{0.4}$Sr$_{0.6}$Mn$_{0.96}$Mo$_{0.04}$O$_3$ (C4S6MM4) as a function of temperature [102].

### 2.3.3.4 Tungsten bronze oxides

Recent studies [105-110] have shown that tungsten bronze oxides can be considered as $n$-type thermoelectrics. Work started by investigation of the thermoelectric properties of Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$; Lee et al. [108, 109] were the first to introduce tungsten bronze structured Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$-$\delta$ ($x \approx 0.61$) as thermoelectric materials. Non-textured and textured polycrystalline samples were manufactured by reactive sintering, then tape casting for texturing in c-direction, and annealing. It was found that annealing in higher reduction atmosphere led to a lower thermopower but better electrical conductivity; this resulted in a higher power factor than the lower reducing atmosphere. This change in electrical properties came from a change in carrier concentrations from the creation of oxygen vacancies, and free electrons from changing the Nb$^{4+}$/Nb$^{5+}$. Textured samples
showed a strong anisotropy towards the growth direction (c-axis), which had a higher Seebeck coefficient and electrical conductivity than in the a-b directions. However, both thermopower and electrical conductivity in the a-b direction in textured samples were comparable to non-textured samples. The large power factor in textured samples was attributed to crystal anisotropy and grain boundary density reduction from texturing. A power factor of ~5.8 μW/m.K was achieved at 500 K.

Li et al. [116] studied the effect of annealing conditions (atmosphere and temperature) on the microstructure development and thermoelectric response of Sr$_{0.61}$Ba$_{0.39}$Nb$_2$O$_6$ polycrystalline samples produced using solid-state reaction. It was found that the type of atmosphere and the annealing temperature had a major impact on Seebeck coefficient and electrical resistivity as well as thermal conductivity. The high degree of reduction (5% H$_2$ - 95%Ar at 1250°C) led to a high ZT of 0.19 at 1050 K.

![Figure 2-14 Thermoelectric properties of Sr$_{0.61}$Ba$_{0.39}$Nb$_2$O$_6$ (SBN61) as a function of temperature. “Ar” means 100% argon atmosphere and H is 5% hydrogen-95% argon atmosphere [116].](image-url)
Azough et al. [105] investigated the high temperature thermoelectric properties on \( \text{Ba}_{6-3x}\text{Nd}_{8+2x}\text{Ti}_{18}\text{O}_{54} \) \((x=0, 0.27, 0.85)\) tungsten bronze ceramic in conjunction with the atomistic simulations. Polycrystalline ceramics were synthesised by the solid-state reaction and followed by annealing in a reducing atmosphere. High Seebeck coefficient and moderately values of electrical conductivity were found in these ceramics. The ceramics also showed a low thermal conductivity with temperature stability over a wide range. \( \text{Ba}_{5.19}\text{Nd}_{8.54}\text{Ti}_{18}\text{O}_{54} \) exhibits promising thermoelectric characteristics: a Seebeck coefficient of 210 \( \mu \text{V/K} \), electrical conductivity of 60 S/cm and thermal conductivity of \( \approx 1.45 \text{ W/m.K} \) leading to a ZT value of 0.16 at 1000 K. It was stated that a direct relationship between the doping contents and thermoelectric properties could not be established as many crystal structural factors are involved such as the change in the \( \text{Ba}/\text{Nd} \) ratio, the variation of distribution of \( \text{Ba} \) and \( \text{Nd} \) cations in the lattice sites and change in the vacancy content by composition.

2.3.3.5 ZnO

ZnO is also one of the promising candidates for thermoelectric applications. It has high electron mobility with a wide band gap of 3.2 eV. The electric properties come from the polar covalent bond \( \text{Sp}^3 \) hybridisation orbital between Zn-O with a very strong ionic bond between them. It crystallises in hexagonal Wurtzite structure type with lattice parameters of \( a = 3.2496 \text{ Å} \) and \( c = 5.2042 \text{ Å} \). The tetrahedral sites are occupied by Zn surrounded by oxygen atoms. However, due to high symmetry of the Wurtzite structure, it also has high thermal conductivity. The thermoelectric properties were enhanced through doping by group 13 elements (Ga, Al, and In) [52, 53, 111, 112].

ZnO was first investigated as an oxide thermoelectric material by Ohtaki et al. [111]. Samples of \( (\text{Zn}_{1-x}\text{Al}_x)\text{O} \) \((x=0.0-0.1)\) were prepared from ZnO and \( \text{Al}_2\text{O}_3 \) precursors by solid-state reaction. It was found that samples consist of single phase \( \text{ZnO} \) when \( x<0.02 \), and a secondary spinel \( \text{ZnAl}_2\text{O}_4 \) phase was found for \( x \geq 0.02 \). Thermoelectric properties were measured over 25-1000 °C. The electrical conductivity of undoped samples were around 0.1-10 S/cm; however doping Al raised the room temperature conductivity values by 3 orders of magnitudes. The values were around 100, 200, 420, 400 S/cm for \( x= 0.005, 0.01, 0.02, 0.05 \) respectively. The Seebeck coefficients of doped samples \((x = 0.005-0.02)\) were found to be in the same range of 150-200 \( \mu \text{V/K} \). However, undoped samples had values of 300-450 \( \mu \text{V/K} \) in the same temperature range. The thermal conductivity of all samples was reported to be 5.0-40 W/m.K. The large thermal
conductivity values were attributed to the Wurtzite structure with simple hexagonal symmetry. A high figure of merit was observed in both $x=0.02$ and $x=0.05$ samples which were around 0.05-0.3 compared to values of 0-0.03 in undoped samples.

![Figure 2-15 Thermoelectric properties as a function of temperature for (Zn_{0.98}Al_{0.02})O [111]: a) thermal conductivity, b) power factor and ZT](image)

Tsubota et al. [113] investigated Zn$_{0.98}$M$_{0.02}$O; (M= Al, Ga, In). The samples were processed from ZnO, Al$_2$O$_3$, Ga$_2$O$_3$, and In$_2$O$_3$ powders by means of solid-state reaction. Doping of ZnO was found to significantly increase the electrical conductivity. The values of the doped samples were in this sequence: Al$>$Ga$>$In$>$undoped (420, 200, 100, and 30 S/cm at 1000 °C respectively). Thermopower of both Al and Ga-doped samples were around 100-180 μV/K, In-doped samples were around 200-250 μV/K in contrast to values of 350-450 μV/K for undoped samples. The power factor was significantly enhanced by any of the elements. The highest power factor belonged to Al-doped samples which varied around 70-17 mW/m.K$^2$. The increase of carrier concentration was indicated as the main cause of the increase in electrical conductivity; Hall measurements confirmed this to be the case. The thermal conductivity of all samples decreased as the temperature increased. Both Zn and Al-doped samples had similar values $\sim$40-50 W/m.K and gradually converged to 5 W/m.K in contrast to Ga and In doped samples of 20-5 W/m.K. The highest figure of merit was found to be for the Al-doped samples where the highest ZT of 0.25 was found at 1000 °C.
Dual doping of ZnO was also attempted by Ohtaki et al. [112] in the form of Zn$_{1-x-y}$Al$_x$Ga$_y$O. The solid-state reaction was used followed by sintering in N$_2$ atmosphere. It was found that doping by both Al and Ga caused a significant decrease in thermal conductivity to the range of 13-5 W/m.K in ZnAl$_{0.02}$Ga$_{0.02}$O compared to 40-8 W/m.K of single-doped ZnAl$_{0.02}$O over 25-1000 °C. A ZT of 0.03-0.7 was achieved in composition ZnAl$_{0.02}$Ga$_{0.02}$O.

### 2.3.4 $P$-type oxides

One of the most promising $p$-type oxide thermoelectric materials are those based on metal-cobaltite compounds that form layered structures also referred as misfit oxide [117-119]. Three types of $p$-type cobaltites had been identified being Na$_x$CoO$_2$ [18, 120-126], Ca$_3$Co$_4$O$_9$ [19, 20, 22, 23, 90, 99, 104, 127-139] and various compositions in the (Bi-Sr-Co-O) system such as Bi$_2$Sr$_2$Co$_2$O$_y$ [25, 60, 128, 139-158] showing the most promising thermoelectric properties.

Cobaltite Misfit-layered (ML) structures can be described with formula, ‘[M$_m$A$_2$O$_{m+2}$]$_q$(CoO$_2$) (M=Co, Bi, Pb, Tl, etc.); A=Ca, Sr, Ba, etc.; m=0, 1, 2; q>0.5’ as purposed by Yamauchi et al. [119]. Two type of layer blocks: hexagonal (h) layer [CoO$_2$] and rock-salt (RS) layer [M$_m$A$_2$O$_{m+2}$] are stacked on each other forming a layer superstructure. The number of the cations is defined by m, and the misfit parameter ‘q= b$_H$/b$_RS$’ (b is defined as lattice parameter ‘b’ of respective layers along the perpendicular direction of stacking layer in the superstructure) is a ratio of mismatch between two layers. At q =0.5 (or 1.0), a distinct commensurate structure shows at this specific misfit ratio. The hexagonal [CoO$_2$] layer, which shares edges of CoO$_6$ polyhedra, is considered the basic common layer found in all multilayers. The structures of the three $p$-type cobaltites are shown in *Figure 2-16*.

![Figure 2-16](image)

*Figure 2-16 The stacking structures in Na$_x$CoO$_2$, Ca$_3$Co$_4$O$_9$, and Bi$_2$Sr$_2$Co$_2$O$_y$ [21].
The structure of Na$_x$CoO$_2$ consists of alternating Na ions and triangular CoO$_2$ layers with a $CdI_2$ type hexagonal structure [21]. In Ca$_3$Co$_4$O$_9$, the CoO$_2$ layers are stacked alternately with Ca$_2$CoO$_3$ layers having rock salt (RS) type structure [21]. Similarly, the second layer for Bi$_2$Sr$_2$Co$_2$O$_y$ has a RS type structure with the composition of Bi$_2$Sr$_2$O$_4$ [21, 150, 159]. In the cobaltites, the CoO$_2$ layers act as the conductive layers. The second layer acts as a non-conductive layer with low thermal conductivity. In addition to this, the large stacking misfit between the two structures creates a distorted interface which leads to an increase in phonon scattering, resulting in a reduced lattice thermal conductivity. Due to the nature of the misfit structure, highly anisotropic thermoelectric properties are expected.

### 2.3.4.1 Sodium cobaltite

Terasaki et al. [82] synthesised a single crystal of NaCo$_2$O$_4$ single crystals by NaCl flux technique using Na$_2$CO$_3$, Co$_3$O$_4$, NaCl as precursors and reported excellent room temperature thermoelectric properties comparable to that of Bi$_2$Te$_3$ as listed in Table 2-2. This discovery initiated interest in oxides for thermoelectric applications.

#### Table 2-2 Room temperature thermoelectric properties for NaCo$_2$O$_4$ single crystal and Bi$_2$Te$_3$ (after Terasaki et al. [82])

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>NaCo$_2$O$_4$</th>
<th>Bi$_2$Te$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical resistivity, $\rho$</td>
<td>m$\Omega$.cm</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>Seebeck coefficient, $S$</td>
<td>$\mu$V/K</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Power factor, P.F</td>
<td>$\mu$W/K$^2$Cm</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Charge mobility, $\mu$</td>
<td>Cm$^2$/Vs</td>
<td>13</td>
<td>150</td>
</tr>
</tbody>
</table>

The crystal structure of Na$_x$CoO$_2$ sodium cobaltite has been thoroughly investigated by Huang et al. [120] and Viciu et al. [124] using powder X-ray diffraction and neutron diffraction. Huang et al. [120] studied Na$_x$CoO$_2$ for ($x = 0.34, 0.56, 0.63, 0.71, 0.77, 0.76, 0.8, 1$) phases assuming a two-layer NaCoO$_2$. All the compositions showed misfit type structures consisting of triangular CoO$_2$ layers with Na ion in between. Two types of Na ions existed in the structures and the shape of the CoO$_6$ octahedra that make up the CoO$_2$ layers depend on the distribution of Na ions in the intervening layers. Viciu et al. [124] studied Na$_x$CoO$_2$ ($x=0.32, 0.51, 0.6, 0.75, 0.92$) phases assuming a three-layer NaCoO$_2$. The compositions were prepared from Na$_2$O and Co$_3$O$_4$ and sintered under O$_2$.
atmosphere. All the compositions showed a misfit type structure having triangular CoO$_2$ layers interleaved by sodium ions, with symmetry being dependent on the composition. The phases with highest and lowest Na content ($x = 0.92$ and $0.32$) showed triangular symmetry, with three CoO$_2$ layers per cell and octahedral Na ion coordination. The intermediate compositions were monoclinic. The composition $x = 0.75$ had one CoO$_2$ layer per unit cell with Na ions in octahedral coordination. The $x = 0.61$ and 0.51 phases also had one CoO$_2$ layer in the unit cell but Na ions were found in trigonal prismatic coordination.

Yakabe et al. [160] studied the thermoelectric properties of NaCo$_2$O$_4$ polycrystalline ceramics using conventional sintering and hot pressing. The powders were prepared from Na$_2$Co$_3$ and Co$_3$O$_4$ by means of solid-state reaction. The XRD spectra showed peaks of NaCo$_2$O$_4$ phase. It was stated that the peaks of hot pressed samples were sharper than conventionally sintered samples, implying a more crystalline structure. The thermoelectric properties were measured between 100 and 400 °C. The resistivity of conventionally sintered sample was in the range of 2.0-2.5 mΩ.cm compared to 1.1-1.6 mΩ.cm in the same temperature range in hot pressed samples. The Seebeck coefficients of two samples were almost identical over the temperature range, between 100 and 140 μV/K. It was suggested that thermopower was hardly affected by the degree of crystallinity of the samples prepared by different methods. Thermal conductivity values were around 1.5 W/m.K over the temperature range in conventional sintered sample and 1.8-2.0 W/m.K in hot-pressed samples. The ZT values were almost unchanged in the measured temperature range and highest figure of merit of 0.11 was achieved at 200 °C in hot pressed sample and 0.084 in conventionally sintered sample. The effect of 5mole% Ba or Bi substitution for Na, and 5 moles% Cu, Mn or Bi substitution was investigated. It was reported that 5 mole% Cu substitution greatly improved the thermoelectric properties, the maximum ZT value of 0.5 was achieved at 300 °C, with an electrical resistivity of 2 mΩ.cm, Seebeck coefficient of 147 μV/K and the thermal conductivity of 1.3 W/mK for hot-pressed samples.

2.3.4.2 Calcium cobaltite

Masset et al. [134] were amongst the first investigators to report the structure for Ca$_3$Co$_4$O$_9$. A mixture of CaO and Co$_3$O$_4$ was used to prepare polycrystalline Ca$_3$Co$_4$O$_9$ then single crystals were synthesised by flux method using K$_2$CoO$_3$ and Ca$_3$Co$_4$O$_9$ powders. It was reported that the compound is a misfit layered oxide consisting of two
monoclinic subsystems, CoO₂ and Ca₂CoO₃, with identical ‘a’ and ‘c’ but different ‘b’ parameters. The structural parameters for the two subsystems are shown in Table 2-3.

Table 2-3 Structural parameters for the two subsystems in Ca₃Co₄O₉ according to Masset et al. [134].

<table>
<thead>
<tr>
<th>System/Lattice parameters</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First subsystem, CoO₂</td>
<td>4.8376</td>
<td>2.82</td>
<td>10.833</td>
<td>98.06</td>
</tr>
<tr>
<td>Second subsystem, Ca₂CoO₃</td>
<td>4.8376</td>
<td>4.5565</td>
<td>10.833</td>
<td>98.06</td>
</tr>
</tbody>
</table>

In the same year, the structure of [Ca₂CoO₃]₀.₆₂CoO₂ was independently investigated and reported by Miyazaki et al. [135]. Solid-state reaction was used to prepare [Ca₂CoO₃]₀.₆₂CoO₂. Similar to findings of Masset et al. [134], it was reported that the compound consisted of two subsystems: Cdl₂-type CoO₂ (Co lattice also sharing an edge of the CoO₆ octahedra) and distorted layers of rock salt type Ca₂CoO₃. The two subsystems were alternately stacked in the c-direction with an incommensurate misfit relationship in the b-axis. The [Ca₂CoO₃]₀.₆₂CoO₂ structure without modulation (fundamental or average structure) was indexed and refined. Atomic positions and unit cell parameters are shown in Table 2-4.
Table 2-4 Structural parameters for the two subsystems in \([Ca_2CoO_3]_{0.62}CoO_2 = Ca_3Co_4O_9\) according to Miyazaki et al. [135].

<table>
<thead>
<tr>
<th>Subsystem1: [CoO_2]</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B (Å^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>O1</td>
<td>0.363(13)</td>
<td>0</td>
<td>0.084(5)</td>
<td>0.5</td>
</tr>
<tr>
<td>O2</td>
<td>0.636(13)</td>
<td>0</td>
<td>0.896(5)</td>
<td>0.5</td>
</tr>
<tr>
<td>Unit cell parameter</td>
<td>a=4.83 (Å)</td>
<td>b=2.82 (Å)</td>
<td>c=10.85 (Å)</td>
<td>β = 98.14 (°)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Subsystem1: [Ca_2CoO_3]</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B (Å^2)</th>
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<tbody>
<tr>
<td>Ca1</td>
<td>0.312(11)</td>
<td>0</td>
<td>0.727(5)</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca2</td>
<td>0.182(11)</td>
<td>0</td>
<td>0.281(6)</td>
<td>0.5</td>
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<tr>
<td>CaO2</td>
<td>0.702(11)</td>
<td>0</td>
<td>0.505(6)</td>
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</tr>
<tr>
<td>O3</td>
<td>0.183(11)</td>
<td>0</td>
<td>0.497(6)</td>
<td>0.5</td>
</tr>
<tr>
<td>O4</td>
<td>0.718(14)</td>
<td>0</td>
<td>0.338(7)</td>
<td>0.5</td>
</tr>
<tr>
<td>O5</td>
<td>0.837(13)</td>
<td>0</td>
<td>0.677(7)</td>
<td>0.5</td>
</tr>
<tr>
<td>Unit cell parameter</td>
<td>a=4.83 (Å)</td>
<td>b=4.55(Å)</td>
<td>c=10.85 (Å)</td>
<td>β = 98.14 (°)</td>
</tr>
</tbody>
</table>

The structure of \(Ca_3Co_4O_9\) also has been determined by Grebille et al. [117] using high resolution X-ray diffraction and Neutron diffraction techniques. The refined cell parameters from Neutron and synchrotron diffraction are shown in Table 2-5. Atomic positions and their site occupancies are shown in Table 2-6.
Table 2-5 Refined cell parameters for Ca$_3$Co$_4$O$_9$ ceramics from neutron and synchrotron diffraction data [117].

<table>
<thead>
<tr>
<th>Structural parameters</th>
<th>Neutron</th>
<th>Synchrotron</th>
</tr>
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<tbody>
<tr>
<td>a (Å)</td>
<td>4.8309 (1)</td>
<td>4.8270 (5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>4.5615 (2)</td>
<td>4.5615 (2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.8360 (4)</td>
<td>10.8300 (2)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>89.695 (4)</td>
</tr>
<tr>
<td>β (°)</td>
<td>98.134 (3)</td>
<td>98.136 (1)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90.133 (5)</td>
</tr>
<tr>
<td>δ = b1/b2</td>
<td>1.16180 (1)</td>
<td>1.6191 (1)</td>
</tr>
</tbody>
</table>

Table 2-6 Atomic positions and their site occupancies in Ca$_3$Co$_4$O$_9$ [117].

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Site Occupancies</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1</td>
<td>Ca 1.00</td>
<td>0.4295</td>
<td>0.0000</td>
<td>0.2762</td>
</tr>
<tr>
<td>Co1</td>
<td>Co 0.33</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Co2</td>
<td>Co 0.17</td>
<td>0.1030</td>
<td>0.0560</td>
<td>0.5000</td>
</tr>
<tr>
<td>O1</td>
<td>O 1.00</td>
<td>0.0543</td>
<td>0.0000</td>
<td>0.6647</td>
</tr>
<tr>
<td>O2</td>
<td>O 0.26</td>
<td>0.1000</td>
<td>0.5000</td>
<td>0.5000</td>
</tr>
<tr>
<td>O3</td>
<td>O 0.24</td>
<td>0.0000</td>
<td>0.5800</td>
<td>0.5000</td>
</tr>
</tbody>
</table>

The schematic presentations of the structure along the c- axis for one of the three major orientations ([010], [001] and [110]) is shown in Figure 2-17.
Figure 2-17 Schematic presentation for [010] orientation of $\text{Ca}_3\text{Co}_4\text{O}_9$ generated from the structural data of Grebille et al. [117].

Single crystals of $(\text{Ca}_2\text{CoO}_3)_{0.7}(\text{CoO}_2)$ were synthesised and studied by Shikano et al. [137]. The single crystals were grown by a modified strontium chloride flux technique using $\text{CaCo}_3$, $\text{Co}_3\text{O}_4$, $\text{CaCl}_2.2\text{H}_2\text{O}$, and $\text{SrCl}_2$ powders. EDS analysis confirmed the composition as $\text{Ca}_{3.2-3.4}\text{Co}_4\text{O}_y$ represented by mean composition as $(\text{Ca}_2\text{CoO}_3)_{0.7}(\text{CoO}_2)$. The X-ray analysis showed that $(\text{Ca}_2\text{CoO}_3)_{0.7}(\text{CoO}_2)$ single crystal had the structure of $\text{Ca}_3\text{Co}_4\text{O}_9$. Resistivity was reported to be around 2-2.3 m$\Omega$.cm over 300-1000 K, Seebeck coefficients were between 110-250 $\mu$V/K and thermal conductivity of 3.5-3 W/m.K over the measurement temperature range. The highest ZT was reported to be 0.9 at 1000 K for the single crystal.

Li et al. [161] were first to report the thermoelectric properties for $\text{Ca}_3\text{Co}_4\text{O}_9$ and the effect of Bi substitution for Ca. The ceramics with the composition $\text{Ca}_{3-x}\text{Bi}_x\text{Co}_4\text{O}_9$ (x=0.0-0.75) were prepared from $\text{CaCO}_3$, $\text{Bi}_2\text{O}_3$ and $\text{Co}_2\text{O}_3$ powders by solid-state reaction. The X-ray data was indexed using structural data for $\text{Ca}_2\text{Co}_2\text{O}_5$ phase due to similarity to structural data for the $\text{Na}_x\text{CoO}_2$ compound. It was reported that the ‘$a$’ and ‘$b$’ lattice parameters increased while ‘$c$’ decreased with the increase in Bi content. The largest cell volume was found in x=0.3 because the Bi$^{3+}$ atom is larger than Ca$^{2+}$. However, for
x>0.3 the cell volume decreased; it was suggested that this could be due to structural change or oxygen content which led to a decrease in cell volume. Several minor peaks were observed in samples where x>0.3 and they exhibited higher intensity with higher amounts of bismuth addition; therefore it was concluded that these minor peaks are from a secondary phase. EDS analysis showed that the composition of secondary phase to be Bi$_2$Ca$_2$Co$_5$O$_x$.

Figure 2-18 Thermoelectric properties as a function of temperature for Ca$_{3-x}$Bi$_x$Co$_4$O$_9$ (x= 0.0-0.75): a) electrical resistivity, b) thermopower, c) thermal conductivity, d) Figure of merit, adapted from Li et al.[161].

For undoped Ca$_3$O$_4$O$_9$, Seebeck coefficient of 80 μV/K, the resistivity of 12 mΩ.cm and thermal conductivity of 1.8 W/mK at room temperature were reported. However, substitution of Bi to Ca sites greatly improved the thermoelectric properties; compositions with x=0.5 showed a ZT value of 0.2 at 700 °C. The reason for the improvement of the thermoelectric properties was stated that the substitution of Bi for Ca led to an increase in carrier mobility, therefore, resulted in a rise of both thermopower and electrical conductivity. In addition, Bi$^{3+}$ is larger and heavier than Ca$^{2+}$ leading to higher phonon scattering, thus reducing the thermal conductivity.
The effect of texturing on the properties of calcium cobaltite was investigated by Hao et al. [131]. Two compositions, Ca₃Co₄O₉ and Ca₂.₇Bi₀.₃Co₄O₉, were prepared by a solid-state reaction using CaCO₃, Bi₂O₃, and Co₃O₄ as starting powders. The measured densities were typically 3.29 g/cm³ (71% of the theoretical density) and 4.34 g/cm³ (93% of the theoretical density) in Ca₃Co₄O₉ and Ca₂.₇Bi₀.₃Co₄O₉ respectively. The growth mechanism in Ca₂.₇Bi₀.₃Co₄O₉ was not very clearly understood however, the authors highlighted two important factors. Firstly, the presence of bismuth improved the diffusion and growth kinetics; it was found during experiments that bismuth-doped samples required a lower sintering temperature to prevent melting, 1273 K for Ca₂.₇Bi₀.₃Co₄O₉ instead of 1373 K for Ca₃Co₄O₉. Therefore, it was concluded that Bi decreased the melting point in calcium cobaltite and may form a liquid phase promoting stacking and sliding of plate-like grains during high temperature sintering. Comparison of the X-ray spectra of the two compositions showed higher intensity (00l) peaks for Ca₂.₇Bi₀.₃Co₄O₉ sample, an indication of the presence of texturing. The degree of texturing in Ca₂.₇Bi₀.₃Co₄O₉ was calculated based on Lotgering factor [162] and was found to be 86%. No texturing was observed for Ca₃Co₄O₉, therefore, it was concluded that bismuth had a pronounced effect on the grain alignment of Ca₃Co₄O₉. SEM showed that in powder samples of both bismuth-doped and bismuth-free samples, the grains exhibited a plate-like shape, several microns in size with no significant difference in the size and morphology of the grains between two samples. However, in bulk samples, the bismuth-doped samples had a larger grain size and also seemed to align homogeneously perpendicular to the direction of pressing compared to smaller and randomly orientated grains of the bismuth-free sample. The electrical conductivity and Seebeck coefficients were measured in both the a-b plane and along the c axis. It was found that the electrical conductivity was highly dependent on the lattice direction as shown in Figure 2-19a. The thermopower also exhibited small anisotropic dependence but to such a small degree it could not be considered different (Figure 2-19b). The highest power factor of 27.7 μW/m.K² at 1000 K was reported for the ab-plane of Ca₂.₇Bi₀.₃Co₄O₉ compared to 8.2 μW/m.K² in pure Ca₃Co₄O samples.
Figure 2-19 (a,b). The effect of Bi substitution and texturing on the resistivity and power factor of Ca$_3$Co$_4$O$_9$, adapted from Hao et al. [131].

Thermoelectric properties of Bi, Na and (Bi-Na) substituted Ca$_3$Co$_4$O$_9$ were studied by Xu et al.[138]. Ca$_3$Co$_4$O$_9$, Ca$_{2.7}$Na$_{0.3}$Co$_4$O$_9$, Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$, and Ca$_{2.4}$Bi$_{0.3}$Na$_{0.3}$Co$_4$O$_9$ were prepared using CaCo$_3$, Co$_3$O$_4$, Bi$_2$O$_3$ and Na$_2$Co$_3$ powders by the solid-state reaction then densified by hot pressing. X-ray analysis confirmed crystallised, single phase in all samples. The thermoelectric properties were measured from room temperature to 1000 K. The substitution of Na and Bi and double substitution enhanced the electrical conductivity values compared to pure Ca$_3$Co$_4$O$_9$. An increase in electrical conductivity values due to Na substitution was explained by an increase in carrier concentration (if other factors such as grain size and orientation were not considered). However, substitution of Bi$^{3+}$ for Ca$^{2+}$ would decrease hole concentration, therefore it would imply there is another factor to consider. The author stated one possibility that Bi substitution increased carrier mobility as well as microstructure factors contributing to a rise in electrical conductivity. Thermopower also showed a substantial increase by single and co-doping. The rise of thermopower in Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$ samples was attributed to a lower hole concentration due to Bi$^{3+}$ to Ca$^{2+}$ substitution and for co-doped Ca$_{2.4}$Bi$_{0.3}$Na$_{0.3}$Co$_4$O$_9$, it was suggested that the change in the energy dependence of mobility caused the increase in the thermopower. The thermal conductivity of Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$ was reported to be around 2 W/m.K over the temperature range of 300-1000 K in comparison to 1.8-1.7 W/m.K of Ca$_{2.4}$Bi$_{0.3}$Na$_{0.3}$Co$_4$O$_9$. The increase in the thermopower, electrical conductivity and reduction in the thermal conductivity led to a high ZT of 0.35 and 0.24 at 1000 K for compositions Ca$_{2.4}$Bi$_{0.3}$Na$_{0.3}$Co$_4$O$_9$ and Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$ respectively.
The electronic structure of misfit calcium cobaltite with the formula (Ca$_2$CoO$_3$)$_{4}$(CoO$_2$)$_6$ was studied by Asahi et al. [163] using ab initio density functional theory (DFT). The large thermopower at high temperature found in this composition was attributed to “the coexistence of degenerate Co$^{3+}$ and Co$^{4+}$ in the CoO$_2$ system”. It also supported the idea that the optimised structure should have distorted octahedra in both CoO$_2$ and RS subsystems (Ca$_2$CoO$_3$). Further electronic structure and thermoelectric property studies for the same composition, using the density functional theory-discreet variational method (DFT-DVM) method, were conducted by Min et al. [164]. The results showed that the RS layers were the primary contributor to thermopower. The CoO$_2$ layers, having high ionic and covalent bond strengths, led to high electrical conductivities. It was also indicated that the Ca atoms have interconnecting roles between the RS and CoO$_2$ layers, resulting in reducing the interlayer bond strengths, and therefore enhancing the thermopower in the structure. Soret et al. [165] investigated the electronic structure of [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] using ab initio methods. The results indicated that the Seebeck coefficient are strongly depend on cobalt’s $a_{1g}$ orbital at low temperature (<400K). It was also found that the modulations, naturally found in this cobaltite family are important to understanding the electronic properties. The large modulations led to Fermi electron localisation and thus changed the electronic structures within the materials (modulations were caused by a misfit between RS and CoO$_2$ layers). The authors, however, also stated that at high temperature the Seebeck coefficient would depend on the modulation alone not on the spin state change found in Co.

Baran et al. [127] used the coordinates of cations from Z-contrast images of Ca$_3$Co$_4$O$_9$ obtained in this study (this will be presented and discussed in Chapter 6) and using energy minimisation and DFT calculations studied the effect of chemical induced strain by substitution of Mg, Sr, and Ba for Ca sites on the thermoelectric properties. It was found that the substitution played a significant role in altering both electrical and thermal properties due to strain created in the system by lattice substitution misfit. By choosing different interlayer cations it was possible to alter the Seebeck coefficient; smaller ionic radius for the cation, which is equal to applying compressive strain to the system, increased Seebeck coefficient and vice versa. The power factor, however, is difficult to interpret as different electronic states are involved. The thermal conductivity was found to decrease with cation mass (less strain) leading to higher phonon scattering due to an increase of rattling modes. It was suggested that optimised thermoelectric
properties of misfit cobaltite could be achieved by mixing light and heavy interlayer alkaline earth cations.

To summarise, the crystal structure of calcium cobaltite was determined to be stacks of CoO\(_2\) layers with \(CdI_2\)-type structure and layers of distorted rock salt Ca\(_2\)CoO\(_3\) along the c-direction. The misfit ratio between 2 sub-structures was identified to be the source of high thermopower and low thermal conductivity. It is also found that the CoO\(_2\) layers were the conductive part of the structure promoting the low electrical resistivity. The typical thermoelectric properties in the temperature range of 300-1000 K are:

i. Seebeck coefficient is between 80-180 \(\mu\)V/K.

ii. electrical resistivity of 5-50 m\(\Omega\).cm.

iii. thermal conductivity of 0.75-2 W/m.K.

iv. highest ZT of 0.3 has been reported.

Several studies [128, 131, 138, 161, 166] have shown that substitution of 0.3 to 0.5 mole % Bi to Ca would lead to a better thermoelectric performance mole% and a ZT of 0.35 at 1000 K has been reported for Ca\(_{2.7}\)Bi\(_{0.3}\)Co\(_4\)O\(_9\).

### 2.3.4.3 Bismuth strontium cobaltite

Before reviewing the Bi-Sr-Co-O family of thermoelectrics, it is worth summarising the studies that have been performed on (SrO-CoO) binary systems. Nagai et al. [118] fabricated [Sr\(_2\)O\(_2\)]\(q\)CoO\(_2\) and using electron diffraction and high resolution TEM electron showed that the structures are a misfit type which could be expressed by the general formula for misfit cobaltites, [M\(_m\)A\(_2\)O\(_{m+2}\)]\(q\)[CoO\(_2\)] with m=0 and misfit parameter, q of 0.5; they are composed of two substructures: a CoO\(_2\) layer with a \(CdI_2\) structure and a SrO – SrO layer (two layers of SrO) with the rock salt structure. In this system, although the strontium gave a misfit structure with the \(p\)-type thermoelectric response it did not give a high ZT due to high thermal conductivity. However, the study proposed the idea of doping of bismuth into the structure.

Funahashi et al. [25] discovered and investigated thermoelectric properties of another cobaltite, Bi\(_2\)Sr\(_2\)Co\(_2\)O\(_y\) and its variants Bi\(_{1.8}\)Sr\(_2\)Co\(_2\)O\(_x\) and Bi\(_2\)Sr\(_{1.8}\)Co\(_2\)O\(_x\). It was reported that all thermoelectric properties are dependent on chemical composition as shown in Figure 2-20 (a, b, c, d).
Thermoelectric properties as a function of temperature for $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x$ (black rectangle), $\text{Bi}_{1.8}\text{Sr}_2\text{Co}_2\text{O}_x$ (black circle), and $\text{Bi}_2\text{Sr}_{1.8}\text{Co}_2\text{O}_x$ (black triangle) [25].

Figure 2-20a shows the temperature dependence of Seebeck coefficient for $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x$, $\text{Bi}_{1.8}\text{Sr}_2\text{Co}_2\text{O}_x$, and $\text{Bi}_2\text{Sr}_{1.8}\text{Co}_2\text{O}_x$. All the compositions showed p-type conducting behaviour. The Seebeck values reduced as the temperature increased to 673K but increased above this temperature. A transition in electrical resistivity was observed for $\text{Bi}_2\text{Sr}_{1.8}\text{Co}_2\text{O}_x$ and $\text{Bi}_{1.8}\text{Sr}_2\text{Co}_2\text{O}_x$ at around 750 K. They suggested that the change in Seebeck coefficient with temperature is due to change in conduction mechanism. It can be seen from Figure 2-20a that $\text{Bi}_{1.8}\text{Sr}_2\text{Co}_2\text{O}_x$ had the highest Seebeck coefficient. This was attributed to higher hole concentration compared to the other two compositions. The high Seebeck value of 150 μV/K at 973 K was obtained for $\text{Bi}_2\text{Sr}_{1.8}\text{Co}_2\text{O}_x$.

The $\rho$ values were reported to be in the range of 20-80 mΩ.cm across the compositions. The $\text{Bi}_2\text{Si}_3\text{Co}_2\text{O}_y$ showed semiconducting-like behaviour throughout the temperature
range of the measurement. However, the ρ initially increased with temperature with metallic-like behaviour in Bi$_{1.8}$Sr$_2$Co$_2$O$_x$ and Bi$_2$Sr$_{1.8}$Co$_2$O$_x$ samples at a temperature $<400$ K and $<500$ K respectively and at a temperature $>750$ K for both samples. The difference in conducting behaviour between Bi$_2$Sr$_2$ and the other cationic deficient samples was suggested to be due to the average valance state of Co, i.e the hole concentration.

*Figure 2-20c* shows the reported thermal conductivity values; all materials show progressively increasing thermal conductivity with increasing temperature which is typical for thermal conductivity where phonon transport is a dominant mechanism. The values are low, in the range of 0.8-1.8 W/m.K. The Bi$_2$Sr$_{1.8}$Co$_2$O$_x$ sample showed the lowest and almost temperature stable values of 0.8-0.9 W/m.K. This was suggested to be due to change of dominant thermal conductivity mode from phonons to electron transport.

The figure of merit data is shown in *Figure 2-20d*. The Bi$_2$Sr$_{1.8}$Co$_2$O$_x$ sample showed the highest ZT values for all the temperatures reaching the value of 0.2 at 1000K. By comparing the Seebeck coefficients, electrical resistivity, and thermal conductivity, it was suggested the low thermal conductivity of this composition had the main contribution to the improvement of the thermoelectric performance.

Fujii et al. [167] investigated the anisotropy of electrical conductivity for single crystals of Bi$_{2-x}$Pb$_x$Sr$_2$Co$_2$O$_y$ (x=0.0 to x=0.8). The single crystals were grown by travelling solvent floating zone (TSFZ) method. It was found that the Pb absorption was limited to x = 0.06. It was reported that the length of the samples in the c direction increased with increasing amount of Pb in contrast to the b direction where it shrank, the a direction was unchanged. TEM studies showed that where x=0, the structure is modulated, with a distinct satellite reflection along the oblique direction (tilted by 45 °). In x=0.4 the modulation disappeared. For electrical resistivity, anisotropy is reported; x=0.6 has almost no anisotropy and the lowest resistivity of 3 mΩ.cm at room temperature but x=0 has the strongest anisotropy and highest resistivity of 8 mΩ.cm at room temperature; all are attributed to doping of Pb in the materials. There is no distinct change in Seebeck coefficients in all composition, all values are around 120-140 µV/K at room temperature.
Figure 2-21 Electron diffraction patterns for Bi$_{2-x}$Pb$_x$Sr$_2$Co$_2$O$_y$ single crystals: a) $x = 0.0$, b) $x = 0.4$. [167].

A similar study by Funahashi et al. [141] investigated the high temperature properties of Pb and Ca-doped (Bi$_2$Sr$_2$O$_4$)$_x$CoO$_2$ whiskers. A high Seebeck coefficient of 180 $\mu$V/K around 800-1000 K was reported. The resistivity showed semiconductor-like behaviour around 4-7 m$\Omega$.cm across the temperature range (room temperature to 1000 K). The power factor was reported to be 0.9 at 1000 K. They reported the first TEM image for (Bi-Sr-Co-O)-based thermoelectric and identified Bi, Sr and Co layers in the structure (Figure 2-22).
Yamamoto et al. [156] investigated misfit layered Bi$_2$Pb$_x$Sr$_2$CoO$_y$ ($x=0.0$ to 0.8) produced by solid state reactions. The structure of the samples was analysed by X-ray and electron diffraction techniques. From X-ray data they suggested a C-centred monoclinic structure with ‘a’ = 4.92 Å, ‘b’ = 5.18 Å, ‘c’ = 15.07 Å and β angle = 92.7°. Furthermore, they suggested the crystal contains two sub-cells which have different b-axis lengths, but have a and c axes in common. This was confirmed by a study of [001] zone axis electron diffraction (Figure 2.23). A similar type of modulation was reported by Fujii [66, 1] for composition with $x=0.0$. The lattice parameters were unchanged in a and b directions by increasing the Pb content; however, the length of c axis increased with increasing Pb content. The β angle shrunk on increasing the Pb content. The room temperature resistivity reduced from 0.03 Ω.cm for composition with $x=0.0$ to 0.012 Ω.cm for composition with $x=0.8$. 

Figure 2-22 HRTEM image of (Bi$_2$Sr$_2$O$_4$)$_x$CoO$_2$ showing different stacking layers ($M=$ Sr, Ca and $M’=$Bi, Pb) [141].
Figure 2-23 [001] zone axis electron diffraction pattern for Bi$_{2-x}$Pb$_x$Sr$_2$Co$_2$O$_y$ (x=0.0). The electron diffraction was indexed based on two sub-lattices showing reflections around (020) reflections of Rock Salt structure [156].

Yin et al. [168] experimented with additives and their contribution to the thermoelectric properties for Bi$_2$Sr$_2$Co$_2$O$_y$ manufactured by the sol-gel method. Ag, Y, and Ca were substituted for Sr in the rock salt layer according to Bi$_2$Sr$_2$X$_{0.1}$Co$_2$O$_y$ formulation; Zr, Al, and Mo were substituted in Bi$_2$Sr$_2$Co$_{1.9}$X$_{0.1}$O$_y$ where X is an additive. The thermoelectric properties were tested from 10 K to room temperature. They reported that the substitution to rock salt layers is more beneficial compared to substitution to the CoO$_2$ layers. Bi$_2$Sr$_2$Co$_{1.9}$Ca$_{0.1}$O$_y$ was the most promising candidate with Seebeck coefficients of 105 μV/Km and resistivity in the magnitude of 10$^{-2}$ Ω.cm leading to a ZT of 0.012 at room temperature (Figure 2-24).
Figure 2-24 Figure of merit for $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$: a) Sr substituted with 5 mole% of Ag, Y or Ca, b) Co substituted with 5 mole % of Mo, Al, or Zr [168].

Wang et al. [169] examined the effect of the addition of Ag to $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ prepared by solid state reaction using $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ and Ag$_2$O powders as the precursors. Using X-ray diffraction and X-ray photoelectron spectroscopy, they showed that the Ag formed a thin film on top of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ surface instead of entering the $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ grains. Due to the Ag particles dispersed across the materials, the resistivity was found to reduce significantly. The pure $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ has a room temperature resistivity of 120 $\mu\Omega\cdot m$ compared to 75 $\mu\Omega\cdot m$ with 15wt% Ag additions. Seebeck coefficients were unaffected by silver particles and remained the same between 110 to 170 $\mu V/K$ across the temperature range of 300-1000 K. However, it was found that the room temperature thermal conductivity values remained unchanged up to 3 % of Ag additions (0.8 W/m.K) and increased to 1.0 W/m.K in 7% Al doping. Therefore, the optimised doped content was found to be 3wt%, and with that, a ZT of 0.26 was achieved at 973 K.

Combe et al. [140] investigated microstructure and thermal electric properties of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$. The composition was prepared by the solid-state reaction from $\text{Bi}_2\text{O}_3$, SrCO$_3$, and Co$_3$O$_4$ powders. Three different methods were used to produce the samples: conventional sintering at 910 °C, hot pressing (HP) at 800 °C and 850 °C; and partial melting at 923 °C and 940 °C. It was reported that the density was highly dependent on the preparation conditions. The HP process led to a high density of 94% theoretical compared to 90% in conventional sintering and 86% in the partial melting process. Using SEM, it was found that different pressing methods yielded different grain sizes whereby conventional sintering the average grain size was 7.6 $\mu$m in comparison to HP which it was in range 3.5 $\mu$m to 5.9 $\mu$m. The reason is attributed to the different
sintering temperatures and also because of the limitation of grain growth in hot pressing due to pressure applied. In the partial melting method, the average grain size was reported to be around 11 μm. It has been stated that the microstructure of the samples varied greatly as a result of the different processing temperatures. In the case of HP at 940 °C, secondary phases were present in the microstructures which were identified to be Co oxide and Bi-Sr phase. For XRD spectra, all the sample peaks were associated with bismuth strontium cobaltite main phase. There are also slight peak shifts identified in partial melting samples; this is attributed to differences in temperature of the processing conditions. The electrical resistivity exhibited a metallic-like behaviour in all the samples. The thermoelectric properties were also highly dependent on processing conditions. Partially melted samples at 923 °C showed the lowest resistivity 5 to 7 mΩ.cm in the temperature range of the measurement (25 °C to 723 °C). Samples prepared by the conventional sintering at 910 °C, hot pressed at 850 °C and partially melted at 940 °C showed higher resistivity values. The reason for the differences in the electrical resistivity was related to the different grain sizes and bulk densities. The Seebeck coefficients in all the compositions exhibited similar values ranging from around 100 μV/K to 160 μV/K across the temperature range of the measurement except the sample, hot pressed at 850 °C which showed Seebeck coefficients of 80 μV/K across the temperature range of the measurement. Thermal conductivity was reported to be highest in hot pressed samples and there is a clear link between higher thermal conductivity values and higher hot pressing temperature; values of 2.75 and 1.9 mW/m.K are reported for hot-pressing samples at 850 °C and 800 °C respectively in comparison to 1.3 mW/m.K for samples prepared by conventional sintering method and partial melting at 923 °C. In this study, the authors demonstrated the partial melting process is beneficial to the thermoelectric response. The highest ZT of 0.25 was achieved at 700 °C using the partial melting method at 923 °C in contrast to the conventional method of ZT of 0.07 and 0.05 by the hot pressing method.

Shen et al. [170] examined the effect of doping by lanthanum in Bi$_2$Sr$_{2-x}$La$_x$Co$_2$O$_9$ (x = 0, 0.02, 0.04, and 0.08) synthesised by solid-state reaction using Bi$_2$O$_3$, SrCO$_3$, La$_2$O$_3$, Co$_3$O$_4$ powders as precursors. XRD data showed a misfit cobaltite structure with no shifting in peak positions for all the compositions. SEM showed plate-like grains typical for misfit cobaltite materials in all the compositions. It was found that the electrical conductivity decreased from 6800 S/m for undoped ceramic to 4500 S/m as the
lanthanum content increased to 0.08. It has been suggested that La\(^{3+}\) substitution reduces the negative charges in the lattice and leads to a reduction in hole concentration resulting in higher Fermi energy level for the lanthanum doped samples thus reducing the electrical conductivity. La doping was found to be effective in increasing the Seebeck coefficients. Bi\(_{2}\)Sr\(_{1.92}\)La\(_{0.08}\)Co\(_2\)O\(_9\) (x=0.08) showed higher Seebeck coefficients, as high as 180 \(\mu\)V/K at 750 K compared to 130 \(\mu\)V/K for undoped material. The thermal conductivity was not significantly different between the compositions (0.8 to 1.5 W/m.K in the temperature range 300K to 700K). It was reported that lanthanum can create point defects and that higher lanthanum content led to slightly lower thermal conductivity values. The optimised value for lanthanum doping is reported to be 0.04. In a trade-off between resistivity and thermal conductivity, the ZT value of 0.147 at 737 K was obtained for Bi\(_{2}\)Sr\(_{1.96}\)La\(_{0.04}\)Co\(_2\)O\(_9\) (x=0.04) in contrast to ZT value of 0.072 for the undoped ceramic.

Another composition in the (Bi-Sr-Co-O) system which has attracted attention as a thermoelectric is Bi\(_2\)Sr\(_2\)Co\(_{1.8}\)O\(_x\). Rubesová et al. [152] investigated the effect of compaction process on thermoelectric properties in Bi\(_2\)Sr\(_2\)Co\(_{1.8}\)O\(_x\). The powders were prepared by a chelating sol–gel route, and three different methods of pressing employed: cold uniaxial pressing, hot uniaxial pressing, and spark plasma sintering (SPS) followed by quenching or furnace cooling. The highest Seebeck of 190 \(\mu\)V/K at 300 °C was achieved using SPS followed by furnace cooling. The electrical resistivity and thermal conductivity values were not affected by the synthesis method used. The ZT of 0.024 at room temperature was reported for the sample prepared by SPS and cooling in the furnace.

An attempt to create a textured Bi\(_2\)Sr\(_2\)Co\(_{1.8}\)O\(_x\) by laser floating zone was made by Diez et al. [171]. The samples were prepared from Bi\(_2\)O\(_3\), SrCO\(_3\) and Co\(_2\)O\(_3\) using solid state reaction followed by a growth process to obtain textured sample using laser floating zone at growth rates of 15, 30 and 50 mm/h. SEM observation of longitudinally fractured surfaces of the samples showed textured microstructures. All the samples had platelet-like grains oriented with their a-b planes along the b axis. In the SEM study of the polished transversal surface of the samples, three distinct phases were identified: the main Bi–Sr–Co–O phase and two secondary phases of CoO and Sr\(_3\)Co\(_4\)O. The 15 mm/h sample showed two different main phases, grey and light grey in colour, identified as
Bi\textsubscript{2}Sr\textsubscript{2}Co\textsubscript{2}O\textsubscript{x} and Bi\textsubscript{2}Sr\textsubscript{2}Co\textsubscript{1.3}O\textsubscript{x}. The resistivity of all samples showed semiconducting-like behaviour. The resistivity values decreased when lower growth speeds were used; this was explained as a result of the better grain alignment and the larger grain sizes. The lowest values were reported to be 17 mΩ.cm at room temperature. The Seebeck coefficient also varied with the growth rate. The highest values of 140 μV/K at room temperature was achieved by the growth rate of 50mm/h in contrast to the values of around 120 μV/K for growth rates 30 and 15 mm/h. It was speculated that the high thermopower came from either alternate layers with different Co oxidation state in the CoO\textsubscript{2} layers or oxygen vacancies generated by laser floating method. The room temperature power factors of 0.10 mW/m.K\textsuperscript{2} and 0.06 mW/m.K\textsuperscript{2} were reported for growth rates of 15 mm/h and growth rates of 50 mm/h respectively.

In the later study by Diez et al. [172] on the same Bi\textsubscript{2}Sr\textsubscript{2}Co\textsubscript{1.8}O\textsubscript{x} and same manufacturing method, the effect of annealing was examined. The samples were prepared from Bi\textsubscript{2}O\textsubscript{3}, SrCO\textsubscript{3} and Co\textsubscript{2}O\textsubscript{3} using solid state reaction. The growth rate of 30 mm/h was selected. The samples were then subsequently annealed at 850 ºC for 0, 72, 192, 408, 504, 1008 hours. The X-ray spectra of all the samples showed Bi\textsubscript{2}Sr\textsubscript{2}Co\textsubscript{2}O\textsubscript{y} as the main phase with small amounts of two secondary phases being Bi\textsubscript{0.75}Sr\textsubscript{0.25}O\textsubscript{z} and Sr\textsubscript{6}Co\textsubscript{5}O\textsubscript{14.3}. However, under SEM observations it was found that the as-grown samples had 5 different phases: CoO, Sr\textsubscript{2}Co\textsubscript{1.8}O\textsubscript{a}, Bi\textsubscript{2}Sr\textsubscript{0.91}O\textsubscript{b}, Bi\textsubscript{2}Co\textsubscript{1.8}Sr\textsubscript{1.0}O\textsubscript{z} and Bi\textsubscript{2}Sr\textsubscript{2}Co\textsubscript{2}O\textsubscript{y}. A reduction in the type of the secondary phases was observed as a function of annealing time; samples annealed for 1008 hours showed Bi\textsubscript{2}Sr\textsubscript{1.8}Co\textsubscript{1.0}O\textsubscript{z} and Bi\textsubscript{2}Sr\textsubscript{2}Co\textsubscript{2}O\textsubscript{y} as the major phases with a small amount of CoO secondary phase. It was stated that the as-grown sample was in the non-equilibrium state and the annealing alleviated the state and led to the reduction in the type of the secondary phases. Thermoelectric properties were affected by the annealing time. The as-grown samples showed semiconducting-like behaviour in contrast to the annealed samples which all exhibited metallic-like behaviour and higher annealing times led to a lower resistivity. The value of 22 mΩ.cm at 300 K was obtained for the sample annealed for 480 hours in contrast to the value of 45 mΩ.cm in as-grown sample No significant difference in values for the longer annealing time of 1008 hours was observed. Thermopower also showed different trends and values between as-grown and annealed samples. The as-grown samples had values of 140 μV/K, which was unchanged over the temperature range of 25 to 650 ºC, whereas the annealed samples had values of 130 μV/K peaking at
around 220 μV/K at 650 °C for the 408 and 1008 hours. The highest power factor 0.18 mW/m.K² was achieved at 650 °C by samples annealed at or for longer than 408 hours in comparison to 0.12 mW/m.K² for samples annealed for 192 hours, and 0.05 mW/m.K² for the as-grown sample.

Sotelo et al. [173] investigated the effect of silver addition to (annealed-textured) Bi₂Sr₂Co₁₈Oₓ. Powders were prepared by a sol–gel chemical route using nitrates method from Bi(NO₃)₃·5H₂O, CaCO₃, Co(NO₃)₂·6H₂O, and metallic Ag (1 wt% and 2wt%). Textured samples were manufactured by the laser floating method [171]. It was found that additions of 1wt% or 3wt% Ag resulted in a significant reduction of electrical resistivity to 12 mΩ.cm where undoped sample had a value of 18 mΩ.cm at room temperature. The thermopower of both the 1 and 3wt% Ag-doped samples was found to be slightly lower across the temperature range of 25 to 650 °C compared to the undoped sample. The highest power factor of 0.27 mW/m.K² was reported for samples with 1wt% Ag compared to 0.17 mW/m.K² for undoped samples at 650°C.

Diez et al. [174] studied the effect of silver additions (0.1, 1, and 3 wt%) to Bi₁.₆Pb₀.₄Sr₂Co₁₈Oₓ. Powders were prepared by a sol–gel chemical route using nitrates. The addition of Ag increased the density and reduced the content of the secondary phase. The Seebeck coefficients were not affected by silver additions. However, it was found that the 3wt% Ag addition resulted in a significant reduction in the electrical resistivity. The room temperature electrical resistivity decreased from 13mΩ.cm for undoped sample to and 8 mΩ.cm for 3 wt% Ag-doped samples. The reduction in the electrical resistivity led to doubling of the power factor to 0.095 (mW/K²m) at about 950 K.

Rasekh et al. [175] investigated Bi₂Sr₂Co₁₈Oₓ comparing conventional sintering, growth by laser floating zone and annealing of laser floating zone products. The powder was prepared using polymer solution method route using Bi(CH₃CO₂), Sr(CH₃CO₂).2H₂O and Co(CH₃CO₂).24H₂O powders. The conventional sintering was made at 810 °C for 24 hours. Laser floating samples were made using 30mm/h growth rate and laser floated samples were annealed at 810 °C for 24 hours. The X-ray spectra showed three phases for the three production routes: bismuth strontium cobaltite thermoelectric phase, Bi₀.₇₅Sr₀.₂₅O₃, and Sr₆Co₅O₁₄.₃. There were lower peak intensities
for the secondary phases for laser floating method compared to conventional sintering and even lower in the annealed laser floating method samples. Grain sizes of the sintered samples were smaller with no texturing but high content of porosity. A higher content of the main bismuth strontium cobaltite phase was found in the annealed laser floating samples compared to the unannealed samples, while retain theirs prefer orientation microstructure. The electrical conductivity was lower in the laser floating method samples being 20 and 40 mΩ.cm for annealed samples and unannealed sample in contrast to 80 mΩ.cm for conventionally sintered samples. The thermopower showed a similar distinct trend for annealed samples and conventionally prepared samples having increasing values from around 120 to 200 μV/K over the range 25-650 °C. However, for the un-annealed laser floating samples the thermopower stayed around 140 μV/K over the temperature range; this was attributed to the nonequilibrium state of the samples prepared by laser floating method. The highest power factor of 0.2 mW/m.K² at 650 °C was obtained by annealing laser floating samples, in comparison to 0.05 mW/m.K² for samples prepared by the conventional sintering.

The structural determination of bismuth strontium cobaltite can be linked back to the related cuprate Bi₂Sr₂CaCu₂O₈ superconductors. In the very first reported study in 1989 on Bi₂Sr₂Cu₁₋ₓMₓO₇ (M=Co and Fe) and Bi₂M₃CoOy (M = Sr, Ca and Ba) systems by Tarascon et al. [176], it was suggested that the structure of Bi₂Sr₂CoO₉ and Bi₂Sr₂CoOₓ cobaltites are similar to that of Bi₂Sr₂CaCu₂O₈ superconductor.

Pelloquin et al. [177] synthesised a new cobaltite [SrCoO₃][CoO]₁₈. It was found that the structure type is similar to that of Ca₃Co₄O₉. The composition has two substructures of a SrO layer (Face Centered Cubic type) and CdI₂ of [CoO₂] layer. A substructure could be two monoclinic forms having a similar ‘a’, ‘c’ and β angle but with different lengths of ‘b’ parameter and hence this is a misfit type. A Seebeck value of 110 μV/K was reported at 300 K with resistivity as low as 20-30 mΩ.cm. This type of structure was found to be consistent with that in a study on [Sr₂O₂]₉[CoO₂] by Yamamuchi et al. [119] where he reported also a structure with 2 layers of SrO and CoO₂.

Pelloquin [178] prepared strontium-rich, Bi₁₋ₓSrₓCoO₀₋₆ (x=0.0 and -1.0) cobaltites using solid state method. Employing electron diffraction, HRTEM, and X-ray diffraction techniques the structure was determined to be a misfit type. It was suggested
that a superstructure comprised \([\text{Bi}_{0.5}\text{Sr}_{0.5}\text{O}]\) Rock Salt substructure along with \([\text{CoO}_2]\) with an alternative stacking of \([\text{CoO}_6]\) octahedral and \([\text{CoO}_3]\) pyramid. In addition to the preparation and structural determination of the (Bi-Sr-Co-O) family of cobaltites by Pelloquin et al. [179], Leligny et al. [150, 159] prepared another cobaltite with the composition of \([\text{Bi}_{0.87}\text{SrO}_2]_2[\text{CoO}_2]_{1.82} = \text{Bi}_{1.74}\text{Sr}_2\text{Co}_{1.82}\text{O}_{7.4}\). In a recent investigation of phase equilibrium in the Bi-Sr-Co-O system, Jankovsky et al. [146] confirmed the existence of \([\text{Bi}_{1.8}\text{Sr}_2\text{Co}_{1.8}\text{O}_x]\) as a single phase in the \([\text{Bi}_2\text{O}_3-\text{SrO-}\text{Co}_2\text{O}_3]\) ternary system and indeed this composition is the composition of the matrix phase of \([\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x]\) and \([\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x]\). As highlighted above, these two compositions have attracted considerable attention as promising \(p\)-type oxide thermoelectrics and detailed structural and thermoelectric property characterisation of them is one of the main objectives of the present investigation. Leligny et al. [150, 159] determined the structure of \([\text{Bi}_{0.87}\text{SrO}_2]_2[\text{CoO}_2]_{1.82} = \text{Bi}_{1.74}\text{Sr}_2\text{Co}_{1.82}\text{O}_{7.4}\) from single crystals using high resolution X-ray diffraction and TEM. The structure is intrinsically a modulated misfit type and was described “as an alteration along \(c\) axis of distorted rock–salt type slabs, formed from \([\text{BiO}]\) with Bi vacancies regularly distributed in the \([\text{BiO}]\) layers and \([\text{SrO}]\) layers (first subsystem), and of \([\text{CoO}_2]\) layers (second subsystem) displaying a distorted \(\text{CdI}_2\) – type structure”. The Refined cell parameters from neutron (N) and synchrotron (S) diffraction data and crystallographic parameters of the average structure are listed in Table 2-7 and Table 2-8 respectively.

Table 2-7 Refined lattice parameter of \([\text{Bi}_{0.87}\text{SrO}_2]_2[\text{CoO}_2]_{1.82} = \text{Bi}_{1.74}\text{Sr}_2\text{Co}_{1.82}\text{O}_{7.4}\) from neutron and synchrotron sources [150, 159].

<table>
<thead>
<tr>
<th>Cell parameters</th>
<th>Neutron</th>
<th>Synchrotron</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (Å)</td>
<td>4.8309 (1)</td>
<td>4.8270 (5)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>4.5615 (2)</td>
<td>4.5615 (2)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>10.8360 (4)</td>
<td>10.8300 (2)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>90</td>
<td>89.695 (4)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>98.134 (3)</td>
<td>98.136 (1)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>90</td>
<td>90.133 (5)</td>
</tr>
<tr>
<td>(q = b_1/b_2)</td>
<td>1.6180 (1)</td>
<td>1.6191 (1)</td>
</tr>
</tbody>
</table>
Table 2-8 Crystallographic parameters of the average structure of Bi$_{1.74}$Sr$_2$Co$_{1.82}$O$_{7.4}$ ceramics [159]

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Subsystem</th>
<th>Occupancies</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}/B_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>1</td>
<td>0.868(2)</td>
<td>0.0197(3)</td>
<td>0.2638(1)</td>
<td>0.05357(3)</td>
<td>0.0158(1)</td>
</tr>
<tr>
<td>Sr</td>
<td>1</td>
<td>1</td>
<td>0.0555(1)</td>
<td>-0.2514(1)</td>
<td>0.14851(2)</td>
<td>0.0116(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>1</td>
<td>1</td>
<td>0.0456(7)</td>
<td>0.2337(7)</td>
<td>0.1227(1)</td>
<td>0.0141(6)</td>
</tr>
<tr>
<td>O(2)</td>
<td>1</td>
<td>1</td>
<td>0.017(2)</td>
<td>0.6773(7)</td>
<td>0.0576(2)</td>
<td>0.026(1)</td>
</tr>
<tr>
<td>Co</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0.25</td>
<td>¼ = 0.25</td>
<td>0.0062(2)</td>
</tr>
<tr>
<td>O(3)</td>
<td>2</td>
<td>1</td>
<td>-0.1787(5)</td>
<td>0.75</td>
<td>0.21651(7)</td>
<td>0.0084(5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cell parameters</th>
<th>$a_1$</th>
<th>$b_1$</th>
<th>$c_1$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>First subsystem [Bi$_{0.872}$SrO$_2$]</td>
<td>4.905, 5.1120</td>
<td>29.857</td>
<td>93.45°</td>
<td></td>
</tr>
<tr>
<td>Second subsystem [CoO$_2$]</td>
<td>4.904, 2.8081</td>
<td>29.864</td>
<td>93.49°</td>
<td></td>
</tr>
</tbody>
</table>

Space group $I2/a$

$Z$ 4

The schematic representations of the three major orientations showing stacking of the layers of two structures along c direction produced from Leligny’s structural data [159] are shown in Figure 2-25.
Figure 2-25 Schematic representation of the structure of $\text{Bi}_{1.74}\text{Sr}_{2}\text{Co}_{1.82}\text{O}_{7.4}$ proposed by Leligny et al. [159]. [001], [010] and [110] projections are shown in Figure 2-25a, Figure 2-25b and Figure 2-25c respectively. Green circles are Sr, Purple circles are Bi and blue circles are Co. Oxygen ions are not shown for clarity of positions of cations in the lattice [159].

Jankovsky et al. [180] prepared $\text{Bi}_{1.85}\text{Sr}_{2}\text{Co}_{1.85}\text{O}_{7.7-δ}$ by both chemical and mixed-oxide methods. The study used the Rietveld analysis based on structural data of Leligny et al. [150]. By fixing the atomic positions as reported by Leligny et al. and refining background, lattice parameters, peak shape, preferred grain orientation and bi-occupancy a good fit with a factor of fit; $R=0.167$ was obtained. This is the only investigation where the authors had been able to refine their X-ray patterns using Leligny’s structural data.

Kobayashi et al. [149] extensively studied the effect of Ca, Sr and Ba substitution on the various misfit parameter, namely $b_1/b_2$, of 1.65, 1.8 and 1.98 for $[\text{Bi}_2\text{A}_2\text{O}_4][\text{CoO}_2]_{b_1b_2}$ single crystals from 10 K to ambient temperature. They reported that the Seebeck coefficients and power factor are highly dependent on the type of alkaline–earth element and the misfit parameter, as shown in Figure 2-26(a,b).
Kang et al. [181] studied the electronic structure of Bi$_{2-x}$Pb$_x$Sr$_2$Co$_2$O$_y$ (X= 0, 0.6) using photoemission and X-ray absorption methods. Similar conclusions to those for the Ca$_3$Co$_4$O$_9$ family were reached. The cobalt spin state of a$_{1g}$ and the ratio of Co$^{3+}$/Co$^{4+}$ were identified to have the crucial role in the electronic state controlling the thermopower.

![Thermopower and power factor as a function of the type of alkaline-earth elements the misfit parameter, reproduced from Kobayashi et al. [149].](image)

To summarise, the bismuth strontium cobaltite was identified to have a misfit type structure with hexagonal CoO$_2$ and (BiO, SrO) rock salt sub-substructures. The source of high thermopower was identified to be the rock salt layers and the misfit structure between the rock salt and hexagonal layers similar to that in calcium cobaltite. The misfit structure was also identified as a phonon scattering source, hence lowering the thermal conductivity. The hexagonal layers were found to be the conductive layers and resulted in low electrical resistivity, which was similar to that in calcium cobaltite. Compositions Bi$_2$Sr$_2$Co$_2$O$_y$ and Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ have been the subject of several investigations including doping, silver addition and different manufacturing techniques (crystal growth by laser floating zone technique, hot-pressing, SPS, chemical route and mixed-oxide route), which yielded different microstructures and thermoelectric properties for each processing condition. However, both compositions have similar thermoelectric properties when prepared by the mixed-oxide processing route, and the properties can be listed as: electrical resistivity of 20-40 mΩ.cm, thermopower of 100-160 μV/K and thermal conductivity of 1.5-3 W/m.K over the temperature range of 300-1000 K, which leads to ZT of 0.06-0.12 in the same temperature range.
2.4 Aims and objectives of this investigation

To recap, the aim of this investigation is to further study, understanding and advancing the knowledge for Bi$_2$Sr$_2$Co$_2$O$_y$ and Ca$_3$Co$_4$O$_9$ ceramics as potential thermoelectric materials. The primary purpose of this study is to understand the effects of structural and microstructure factors, produced by means of different dopants and processing techniques that lead to the improvements of the thermoelectric figure of merit (ZT) of cobaltite family ceramics.
3. Experimental Methodology

3.1 Introduction

The third chapter is dedicated to theories and procedures of characterisation and measuring techniques for the evaluation of the $p$-type cobaltite ceramics prepared by the mixed-oxide (MO) route, and densified by sintering in an air atmosphere and Spark Plasma Sintering (SPS). The crystal structures of the misfit layered-type phases were determined by X-ray diffraction (XRD). Scanning electron microscopy and transmission electron microscopy (SEM and TEM respectively) were used to study the microstructures of the synthesised oxides. Energy dispersive X-ray spectroscopy (EDS) was used to examine the chemical compositions of the constituent phases. In addition, atomic resolution Z-contrast imaging was performed in a dedicated scanning transmission electron microscope (STEM) for crystal structure evaluation. The electrical transport properties; (electrical resistivity and the Seebeck coefficient) and thermal transport properties (thermal conductivity) were measured over a temperature range of 300 K to 1000 K. The thermal conductivity was indirectly determined via the density measurement using Archimedes’ method, thermal diffusivity ($\alpha$) by laser flash method, and the specific heat capacity $C_p$ using differential scanning calorimetry (DSC). The compositions, objective of the study for each composition, and their fabrication routes are listed in Table 3-1.
Table 3-1 List of the compositions, the objectives of the study for each composition and their fabrication routes.

<table>
<thead>
<tr>
<th>Chapter number</th>
<th>Compositions</th>
<th>Objectives of the study to investigate:</th>
<th>Preparation routes</th>
</tr>
</thead>
</table>
| 4              | Bi_{2+x}Sr_2Co_2O_y  
(x = 0.0, 0.1and 0.2) | The effect of Bi stoichiometry and fabrication technique | Mixed-Oxide (MO)  
Spark Plasma Sintering (SPS) |
| 5              | Bi_{x}Sr_{2}Co_{1.8}O_y  
(x = 1.72, 2) | The effect of Bi stoichiometry and fabrication technique | MO, SPS |
| 6              | Ca_{3-x}Bi_{x}Co_{4}O_9  
(x= 0, 0.3) | The effect of Bi substitution and fabrication technique | MO, SPS |
| 7              | Bi_{2}Sr_{2}Co_{2}O_y  
and Ca_{3}Co_{4}O_9 | Thermal evolution and stability of phase | MO |

3.2 Raw materials

Samples in the (Bi-Sr-Co-O) system (the compositions are listed in the following section), Ca_{3}Co_{4}O_9 and Ca_{2.7}Bi_{0.3}Co_{4}O_9 were prepared from bismuth oxide, strontium carbonate, calcium carbonate and cobalt oxide.
Table 3-2 Details of raw materials used for the synthesis of the compositions listed in Table 3-1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds</th>
<th>Chemical Formula</th>
<th>Molecular weight (g/mol)</th>
<th>Purity</th>
<th>Supplier</th>
<th>CAS number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bismuth (III) oxides</td>
<td>Bi₂O₃</td>
<td>465.96</td>
<td>99.8%</td>
<td>Sigma – Aldrich</td>
<td>1304-76-3</td>
</tr>
<tr>
<td>2</td>
<td>Strontium carbonate</td>
<td>SrCO₃</td>
<td>147.63</td>
<td>99.9%</td>
<td>Solvay</td>
<td>1633 – 05 –02</td>
</tr>
<tr>
<td>3</td>
<td>Cobalt (III) oxides</td>
<td>Co₃O₄</td>
<td>165.86</td>
<td>99.5%</td>
<td>Sigma – Aldrich</td>
<td>1308-06-1</td>
</tr>
<tr>
<td>4</td>
<td>Propan-2-ol</td>
<td>C₃H₈O</td>
<td>60.11</td>
<td>99.5%</td>
<td>Sigma – Aldrich</td>
<td>67 – 63 – 01</td>
</tr>
<tr>
<td>5</td>
<td>Calcium Carbonate</td>
<td>CaCO₃</td>
<td>100.09</td>
<td>99.8%</td>
<td>Sigma – Aldrich</td>
<td>471-34-1</td>
</tr>
</tbody>
</table>

3.3 Processing of cobaltite thermoelectric

Samples of bismuth strontium cobaltite and calcium cobaltite based compositions with the batch size of 150 grams were prepared by mixed-oxide route.

Table 3-3 Powders required for samples for a batches of 150 grams.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Bi₂O₃ (g)</th>
<th>SrCO₃ (g)</th>
<th>Co₃O₄ (g)</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₁Sr₂Co₂O₇</td>
<td>83.30</td>
<td>52.78</td>
<td>28.70</td>
<td>BSCO-0</td>
</tr>
<tr>
<td>Bi₁₂Sr₂Co₂O₇</td>
<td>86.13</td>
<td>49.38</td>
<td>28.26</td>
<td>BSCO-1</td>
</tr>
<tr>
<td>Bi₁₂Sr₂Co₂O₇</td>
<td>86.81</td>
<td>35.1</td>
<td>28.092</td>
<td>BSCO-2</td>
</tr>
<tr>
<td>Bi₁Sr₂Co₁₈O₇</td>
<td>84.38</td>
<td>53.57</td>
<td>26.07</td>
<td>L-Bi</td>
</tr>
<tr>
<td>Bi₁₇₄Sr₂Co₁₈O₇</td>
<td>79.62</td>
<td>58.00</td>
<td>28.68</td>
<td>L</td>
</tr>
<tr>
<td>Compositions</td>
<td>Bi₂O₃ (g)</td>
<td>CaCO₃ (g)</td>
<td>Co₃O₄ (g)</td>
<td>Sample code</td>
</tr>
<tr>
<td>Ca₃Co₄O₉</td>
<td>-</td>
<td>50.47</td>
<td>99.53</td>
<td>CCO</td>
</tr>
<tr>
<td>Ca₂.₇Bi₂.₃Co₄O₉</td>
<td>18.95</td>
<td>73.31</td>
<td>87.1</td>
<td>CBCO</td>
</tr>
</tbody>
</table>
The required amount of powders to produce the compositions listed in Table 3-3 were weighed using Ohaus® model Adventurer Pro AV213 calibrated balance with an accuracy of 0.01 grams and loaded into a Polyethylene bottle. Zirconia milling media and Propan-2-ol were added to the bottle in a ratio of 1:1:1 to form a slurry for wet mixing in a vibratory mill for 24 hours. After mixing, the bottle was placed in an oven at 85 °C for 24 hours to allow a complete evaporation of the Propan-2-ol. The dried powder was separated from the zirconia milling media, and placed into an alumina crucible for calcination. This was undertaken in a Carbolite® C3 chamber furnace at 760-800 °C in an air atmosphere for 12 hours. The heating and cooling rates were set at 180 °C/hour. After calcination, the powder was wet milled for a further 24 hours and dried using the same conditions as above. Following this, 6 grams of powder was uniaxially pressed with 50 MPa pressure into pellets of 20 mm diameter. The samples were sintered at 880-910 °C for 8-12 hours in the air in the same furnace used for calcination. The heating and cooling rates were set at 180 °C/hour.

### 3.3.1 Spark plasma sintering (SPS)

A 25/1 GCT® SPS furnace at Queen Mary, University of London was used in this study with a set of graphite dies (20 mm in diameter) and punches from Erodex®. Graphite foil of 0.35 mm was used between die and punch to protect them from reaction and contamination with powders. Most of the compositions: BSCO-0, BSCO-1, BSCO-2, L, CCO, and CBCO were manufactured by spark plasma sintering route in addition to conventional solid state reaction. For BSCO-0, BSCO-1, BSCO-2, and L samples, the powders were sintered at 650 °C under pressure of 50 MPa for 5 mins; the CCO and CBCO samples were sintered at 750 °C under pressure of 50 MPa for 5 mins. The furnace was under a vacuum of ~5 Pascal.

### 3.4 Characterisation Techniques

After measuring the density of the sintered pellets, the samples were cut for thermoelectric properties and microstructure evaluations (Figure 3-1).
Figure 3-1 Diagram showing how the pellets were used for property measurement and analysis.

All electrical transport properties, SEM and XRD were investigated using the cross-sectional sides of the materials. Due to the difficulty of producing samples thick enough to be cut, the thermal diffusivity was then measured on the pressed surface. Heat capacity required no specific measuring direction as the heat transfer occurs in every direction. The direction of measurement in the samples is as shown in Figure 3-2 and this has been consistently used throughout the study.

Figure 3-2 The direction of measurement in the samples.
3.4.1 Density measurement

Both the geometric method and Archimedes method were employed to obtain the density of samples. In the geometric method, pellets were weighed three times to a precision of 0.001 g; dimensions were determined by micrometer to a precision of 0.01 mm. Density, \( \rho \), was determined from equation 28.

\[
\rho = \frac{m}{V}
\]  

(28)

where \( m \) is the mass of the sample in grams and \( V \) is the volume of the sample in \( \text{cm}^3 \).

Density measurements using the Archimedes method were carried out three times for each sample. First, the sample was weighed dry (\( w_{\text{dry}} \)) in air. The sample were then weight in deionised water (\( \rho_{\text{liquid}} = 1 \)) using a suspension set attached to the balance(\( w_{\text{sus}} \)), 15 minutes were given for the sample to reach weight equilibrium before reading the weight. The sample was taken out of water, patted dry with a paper towel and then reweighed (\( w_{\text{sat}} \)) in air. Sample density was determined from:

\[
\rho_{\text{bulk}} = \frac{w_{\text{dry}} \sum \rho_{\text{liquid}}}{w_{\text{sat}} - w_{\text{sus}}}
\]  

(29)

The calculated densities were compared to the theoretical density that can be calculated from equation 30,

\[
\rho_{\text{Theoretical}} = \frac{ZM}{V_N A}
\]  

(30)

\( Z \) = the number of atoms per formula unit
\( M \) = the molar mass
\( N_A \) = Avogadro’s number (6.023×10^{23} molecules/mole)

Where \( V \) is the volume of unit cell [182].

3.4.2 Phase identification by X-ray diffraction (XRD)

X-ray diffraction (XRD) techniques are widely used to acquire structural information of crystalline materials. X-ray data can be used to obtain information on the space group, crystal lattice parameters, compositions, residual stresses, crystallite size and strain, and texturing of materials. The XRD technique was developed by Debye & Scherrer working on the principal that randomly oriented crystallites will diffract a beam of short wavelength X-rays. By directing a beam of X-rays with known wavelength (\( \lambda \)) onto the surface of a crystalline sample, the beam will interact with atomic layers in the lattice. The Bragg law (illustrated in Figure 3-3) was used to describe the phenomenon that occurs when the beam interacts with the atomic layers and diffracts. When the incident
X-ray beams approach the atomic layers at an appropriate angle, which the Bragg condition is satisfied (Equation 31). The beams reflected will have a stronger signal (peak or intensity) captured by the detector due to constructive interference resulting from satisfying the Bragg angle.

\[ n\lambda = 2dsin\theta \]  \hspace{1cm} (31)

where ‘\(\lambda\)’ is the wavelength of the incident beam, ‘d’ is the distance between two atom planes in the crystal structure and ‘\(\theta\)’ is the average of the angles between the incident beam and reflected beam or the ‘Bragg angle’.

*Figure 3-3 Bragg diffraction: involving phase parallel electron beams interacting with lattice planes in a crystalline solid. Constructive interference happens when the distance travelled by the lower beam is equal to an integer multiple of the wavelength (equation 31), adapted from Cullity [183].*
The schematic representation of a Bragg spectrometer is shown in Figure 3-4.

![Figure 3-4](image)

**Figure 3-4** Schematic representation of a Bragg diffractometer [183]. X-ray tube (X-ray source). The X-ray sources typically composed of a specific metal element (i.e. Cu, Fe, and Co), which determined the wavelength and characteristic of an X-ray beam, were excited by electrons from applied electrical voltage, and hence generated an X-ray beam.

When the incident X-ray beam approached the samples, the X-ray’s electromagnetic cloud interacts with the electromagnetic cloud of the atoms within the sample. The result of these interactions leads to the scattering of the X-ray beam and the oscillation of the sample’s electrons (electron cloud). This oscillation causes a re-radiation of the X-ray beam and if the atoms are in a regular array the emitted X-ray beams will generate constructive interference (if the Bragg angle is satisfied). The atom nucleus is considered to be too large to be affected by the X-ray electromagnetic field, hence there is no change in its electromagnetic field characteristic. Therefore, the constructive wave (and hence signal/intensity) depends on the number of electrons of the sample. Higher atomic number (high Z) will generally generate more signal due to their larger electron cloud.

Furthermore, there are several other factors that could affect the intensity captured by the detector from the constructive wave: First and foremost, the intensity of the X-ray is affected by how the atoms are arranged within the structure (i.e. different crystal systems), as different arrangement of electrons affect how the electrons are scattered. To
account for the arrangement of atoms within the structure, the structure factor \( F_{hkl} \) was introduced to consider the total scattering intensity. The total scattering intensity is defined as a summation of scattering intensity from every atom in the unit cell and is given as:

\[
F_{hkl} = \sum f_n e^{2\pi i(hu_n + kv_n + lw_n)}
\]

(32)

Where \( f_n \) is the scattering factor of given atom \( n \). \( u_n, v_n, w_n \) are the fractional coordinates.

The intensity also depends on the following factors: \( L \), the Lorentz factor, \( P \), the polarisation factors, which considers how electrons behave when moving and oscillating, respectively, and \( T \) which is a temperature factor accounting for the atomic vibrations from their normal position due to thermal excitement. To sum all the factors the intensity of the X-ray peaks could be written as:

\[
I_{hkl} \approx F_{hkl}^2 \cdot P_{hkl} \cdot L P(2\theta) \cdot T \cdot F(2\theta)
\]

(33)

The ideal peak intensity captured by the detector from the constructive wave which satisfies the Bragg law in a perfect crystal should appear as a sharp single line. However, considering that the actual samples’ crystal arrangements are often distorted due to many reasons (i.e. defects, vacancies, and internal strains.), therefore, the peak intensity is usually shifted and/or broadened as a result of such imperfections. The graphic representation of how different crystal arrangements affect the intensity peak shape and position is shown in Figure 3-5.
Figure 3-5 Graphic representation of how crystal arrangements affect the peak intensity shape and position in a) a perfect lattice, b) a lattice with uniform strain, c) a lattice with non-uniform strain. Reproduced from Bennett [184].

3.4.2.1 Samples preparation and data collection

For each sample, the surface was ground with 1200 SiC paper prior to the examination. The samples were characterised using PANalytical X’pert Powder. The instrument parameters used are shown in Table 3-4.
Table 3-4 The parameters for x-ray powder diffraction instrumental setup (adapted).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diffractometer</strong></td>
<td>PANalytica X’Pert X-ray diffractometer</td>
</tr>
<tr>
<td><strong>Radiation source (wavelength):</strong></td>
<td>Copper $\text{k}<em>\alpha$ and $\text{k}</em>\beta$ ($\lambda_{\text{k}\alpha} = 1.5406 \text{ Å}, \lambda_{\text{k}\beta} = 1.5444 \text{ Å}$)</td>
</tr>
<tr>
<td><strong>Divergence slit:</strong></td>
<td>Fixed 5 mm</td>
</tr>
<tr>
<td><strong>Receiving slit:</strong></td>
<td>0.3 mm</td>
</tr>
<tr>
<td><strong>Generator voltage:</strong></td>
<td>45 kV</td>
</tr>
<tr>
<td><strong>Tube current:</strong></td>
<td>40 mA</td>
</tr>
<tr>
<td><strong>Scan angle (2$\theta$):</strong></td>
<td>$5^\circ$ – $80^\circ$</td>
</tr>
<tr>
<td><strong>Step size:</strong></td>
<td>0.05$^\circ$</td>
</tr>
<tr>
<td><strong>Step time:</strong></td>
<td>20 seconds for bulk samples, 4 seconds for powders</td>
</tr>
</tbody>
</table>

3.4.2.2 Synchrotron diffraction

In a synchrotron accelerator, charged particles are accelerated emitting high energy X-rays. In a typical synchrotron accelerator, high energy charged particles (typically electrons) are produced by means of a linear accelerator; bunches of high energy electrons are then injected into storage ring where they circulate until they accumulate enough kinetic energy and start emitting X-rays when changing directions as a result of relativistic speed changes. These high-energy X-ray can be used to characterise the phase of materials through the Bragg law as described in section 3.4.2. These high-energy X-rays high signal to noise ratio due to their high energy, and lower wavelength, which results in higher resolution (more accurate peak positions). This creates an almost parallel X-ray beam, which compared to the divergent laboratory X-ray beam produced sharper diffracted peaks that further allow us to distinguish between overlapping peaks.

Typical synchrotron machines consist of mainly four components: the linac (linear accelerator), the booster synchrotron, the storage ring, and the beamlines. The electrons are generated in the electron guns with very low energy through a thermionic emission process (similar to laboratory XRDs). Then, the electrons are transferred to the linac which boosts the energy of electrons close to several hundred MeV level. High energy
electrons are subsequently accelerated again to energy levels close to 1-10 GeV by a booster synchrotron, and then injected into the storage ring where they keep circulating under controlling magnetic poles, to control the speed and direction. The beamline sections, where the electrons from the storage ring can be directed to, are designed to fit different type of research and purposes.

In this thesis, the Diamond Light Source synchrotron was used, where the electrons can be accelerated up to energy level of 3 GeV. The beamline I11 was chosen as it is designed to function as a high-resolution power X-ray. The advantages of I11 are the capability of the system to work at high temperatures (>1500 K) with high signal to noise ratio and accurate peak position. Therefore, it is suitable to study the crystal structure of complex materials and their high temperature structural evolution, similar to the one presented in this thesis.

For data collection, pieces of MO prepared BSCO-0 and CCO-MO ceramics were crushed and ground into powders using a pestle and mortar. The powders were then loaded into 0.5 mm in diameter capillaries. A capillary furnace (298 – 1500 K) was used to control the temperature and environmental conditions of the test. A heating rate of 5 K/min was used, and 60 seconds was allowed for temperature equilibration at each collection point. A calibrated wavelength of 0.825634 Å was used in the experiment. The total scan time for collecting the diffraction patterns was 30 minutes with 0.001° step size. The scan angle is 0-150°. A photon energy of 25 keV was used to limit the absorption effect in samples. Multiple Analyser Crystal (MAC) detectors were selected to record the X-ray spectra. The spectra were analysed by Rietveld refinement method using the Bruker® Topas 5. Leligny’s [159] and Grebille’s [2] structural data were used as a initial structural files for the Rietveld refinement of BSCO-0 and CCO-MO respectively. Philips® X’Pert HighScore Plus software was used to identify the minor phases.

3.4.2.3 Structural refinement: the Rietveld method

The X-ray diffraction patterns can be analysed to obtain information on the crystal structure of materials (lattice parameters, coordinates, and site occupancies). However, it is difficult to fit the peaks manually and to determine the structural information due to overlapping of peaks arising from different phases. To overcome this, the Rietveld refinement technique was devised by Hugo Rietveld [185] to aid in analysing X-ray data and characterisation of crystalline materials. The mathematical regression of least
squares method (minimised function) was used to calculate and simulate “fitting line” profiles, in an attempt to achieve the best match to the measured profiles. The minimised function for each data point is given in following formula:

$$\sum_i (Y_i(\text{obs}) - Y_i(\text{Calc}))^2$$ (34)

where: $Y(\text{obs})$ is a set of observation values, and $Y(\text{Calc})$ is the calculated values from Rietveld refinement structural model.

$Y$ can be derived from the square of structural factor, $F^2$, or the total intensity of whole pattern reflections, in case of a single crystal data and powder diffraction, respectively. The $Y$ parameter therefore could be substituted by intensity term ($I$) which can be calculated by the following mathematical function:

$$I(\text{Calc}) = c_{hkl}L(2\theta)P(2\theta)A(2\theta)F^2(\text{hkl})$$ (35)

where $c$ is a scale factor (compensation for data instrumental acquisition correction parameters), $j$ is multiplicity factor (space group symmetry), $L$ is Lorentz correction, $P$ is polarisation correction, and $A$ is absorption correction.

Substituting equation 35 into 34, the new minimisation formula in term of intensity can be re-written as:

$$\sum_n (I_n(\text{obs}) - I_n(\text{Calc}))^2$$ (36)

However, due to the nature of the X-ray data collection, the area of the peaks could be better described by peak shape functions, to help the mathematical fitting, therefore, several peak shape functions were introduced in order to better fit the X-ray profiles: First, The Gaussian function, which is one of the commonly used function to describe symmetric peak shape. Gaussian type peak can be defined as:

$$I(2\theta) = I_{\text{max}} \exp\left(-\pi(2\theta - 2\theta_0)^2/\beta^2\right)$$ (37)

Where $I_{\text{max}}$ is the peak intensity, $2\theta_0$ is the position of the highest intensity peak, and $\beta=0.5H(\pi/\log_e2)^{1/2}$, where $H$ is a full width half maximum (FWHM) peak width.

The Gaussian peak function has the advantage of being easy to calculate and fit symmetric peaks reasonably well.

Second is the Lorentzian peak type, defined as:
\[ I(2\theta) = \frac{w^2}{w^2+(2\theta+2\theta_0)^2} \]  
\[ w = 0.5H. \] Lorentzian peak function is easy to calculate, and emphasises fitting the tail of the peaks. A modified Lorentz function, the Pearson VII, is better suited to accommodate a different shape of peaks tails. The formula can be written as:

\[ I(2\theta) = I_{\text{max}} \frac{w^2}{[w^2+(2^m-1)(2\theta-2\theta_0)^2]^m} \]  
\[ m \geq 1 \]  

Lastly, the pseudo-Voigt function is given as:

\[ I(2\theta) = l_{hkl}(\eta L(2\theta - 2\theta_0) + (1 - \eta)G(2\theta - 2\theta_0)) \]  

Where, \( L(2\theta - 2\theta_0) \) and \( G(2\theta - 2\theta_0) \) are the Lorentz function and Gaussian function respectively, and \( \eta \) is the Lorentz fraction.

It can easily be seen from equation 40 that the pseudo-Voigt function is a weight fraction combination of both Lorentz and Gaussian functions. By exploiting the advantage of both functions, the pseudo-Voigt function can model specific peak shapes. In this project, the Pearson VII peak function was chosen for refinement due to its advantage of dealing with peak tails seen in the X-ray data.

Preferred orientation is one of the factors that can also affect the peak intensity. If all the crystals in polycrystalline samples were aligned in the same plane, it would give a higher constructive signal (more intensity) in one diffracted peak than in the rest; therefore, two further correction factors have been introduced in order to compensate for higher intensity: First, the March doll model [186]:

\[ O_{ph} = \frac{1}{M_p} \sum_{j=1}^{M_p} (r_0^2 \cos^2 A_j + \frac{\sin^2 A_j}{r_0})^{-3/2} \]  

Where \( O_{ph} \) is the multiplier in intensity and the \( M_p \) are symmetrically equivalent reflections. \( R \) are refineable parameters in Rietveld analysis, \( A_j \) is the angle between the preferred orientation vector and the normal to the plane generating diffraction peaks. The March doll model introduces a preferred orientation method that assumes that the
texturing should be a result of deformation processes, therefore should have “the preferred orientation plane (HKL) the prominent planar surface for platy crystallites and the plane normal to the prominent elongation axis for rod-shaped crystallite” [186].

The second correction model, the spherical harmonic expansion method [187], is based on a concept that the texture could be described by mapping the probability occurrence of crystal orientation with respect to co-ordination (orientation distribution function). The concept of orientation distribution function is based on the assumption that the crystal is axial symmetric, and therefore, the co-ordinates could be described based on the axial symmetry. The equation of the spherical harmonic to correction function (A) can be given as:

\[
A(\varphi, \beta, \psi, \gamma) = 1 + \sum_{l=2}^{L} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} C_l^m k_l^m(\varphi, \beta) k_l^n(\psi, \gamma) \tag{42}
\]

Where \( k_l^m(\varphi, \beta) \), and \( k_l^n(\psi, \gamma) \) are harmonic terms, used to describe reflection coordinates and the sample coordinates respectively. \( C_l^m \) is an harmonic coefficient, and \( L \) is the maximum order of spherical harmonic. In this project both bismuth strontium cobaltite and calcium cobaltite were refined using spherical harmonic model to account for preferred orientation. However, apart from texturing and peaks profile functions, it has been observed from the refinement that the minimisation function considering the \( I \) alone are not sufficient enough, as the intensity in the collected profile are also affected by other factors (i.e. instrumental parameters, background fitting, etc.), therefore Rietveld had introduced a correction factor \( w_i \), which is defined as:

\[
w_i = \frac{1}{Y_i(obs)} \tag{43}
\]

By applying the correction factor to the original minimisation function (equation 34), the final formula for Rietveld minimisation formula can be given as:

\[
\sum_i w_i[Y_i(obs) - Y_i(Calc)]^2 \tag{44}
\]

Having modified the minimisation formula, the first standard terms in Rietveld refinement \( R_{wp} \) (weighted profile R-factor) showing the number for calculated pattern can be written as:
The second term, the expected profile residual factor ($R_{exp}$) which indicated the quality of data (derived from signal to noise ratio) can be formulated as:

$$R_{exp} = \left[ \frac{N-P+C}{\sum w_i(y_i)^2} \right]^{1/2} \quad (46)$$

Where $N$ is the total number of observation, $P$ is the number of parameter refine, and $C$ is the number of constraints.

From equation 46, it can be seen that high signal to noise ratio is necessary to obtain low $R_{exp}$. The last term, the goodness of fit, indicating the overall fitting quality is given as:

$$GOF^2 = \frac{R_{wp}^2}{R_{exp}^2} \quad (47)$$

Estimate standard deviation (ESD) in the Rietveld refinement could be estimate using the following formula:

$$ESD = [GOF^2A^{-1}_{jj}]^{1/2} \quad (48)$$

Where $A^{-1}_{jj}$ is an inverse normal equation matrix. The Rietveld method is accepted as a standard whole pattern fitting technique, as it could handle complicated peaks profiles including multiple overlapping peaks.

To improve the fit of measured profile to calculated spectrum, the lattice parameters, atomic positions, site occupancies, and temperature factors are refined along with instrument factors. The best possible fit is that which could be achieved by the minimisation of the R-factors (variables that define the effectiveness of fitting) such as, $R_p$ and $R_{wp}$ which corresponds to the residual of the least square pattern and of the weighted pattern respectively. The goodness of Fit (GOF) of around 2 or under is considered to be a good fit between simulated and experimental spectra [188]. Rietveld refinements were performed using the Bruker TOPAS® 5 program. The Stephens corrections [189] were used for peak shape corrections due to misfit (strain) in the crystal structure.
3.4.3 SEM characterisation

3.4.3.1 Scanning electron microscopy (SEM):

The scanning electron microscope is one of the most prevalent and useful characterisation techniques in the field of materials science. SEM was used to observe and investigate the microstructure of materials, which could be related to processing conditions and material properties. The main advantages of SEM are simplified image formation for investigating samples combined with very good magnification capability, high resolution and excellent depth of field.

SEM can provide much useful information including grain size, morphology, surface topography, phase differences/distribution, crystal orientation and defects. With the add-on instrument, energy dispersive X-ray spectrometer (EDS), SEM can determine and quantify elemental composition of each phase. Furthermore, additional characterisation is possible in the SEM using electron backscatter diffraction (EBSD) to examine the crystal orientation of constituent phases or energy dispersive x-ray spectrometer (EDS) for chemical analysis of constituent phases.

Inelastic interactions at the surface layer (Figure 3-6) of the samples are usually generating low energy secondary electron (~2 to 5 eV). The secondary word refers to the process of creation of these electrons, which takes place by knocking the outer shell electrons as the energy is transferred from an electron beam into sample surface.

Backscattered electrons (BSE) are generated from elastic interactions of electron beam (Figure 3-6) and the sample. Here the electron beam is scattered by the nucleus at high angles. These BSE electrons are highly energetic in nature and contribute to the majority of the signal from the samples. The depth of penetration within the sample, from where BSE signals are generated is usually about one-fifth of the overall interaction volume. However, this is dependent on the beam energy and specimen type. The backscattered image signal intensity greatly depends on the average atomic number of the samples, where samples with higher atomic number result in stronger BSE signal and vice versa. This signal is hence, very helpful to distinguish between different phases in the samples. In this case, phases which have higher atomic number will have a higher signal (brighter) than that of the lower average atomic number.
Figure 3-6 Schematic diagram of interaction effects (inelastic interactions at surface layer generated SE and elastic interactions at deeper level generated BSE) of the incident beam with the sample, reproduced from Australian Microscopy & Microanalysis Research Facility’s Scanning electron microscopy training module [190].

Samples were examined in a Philip® XL 30 FEGSEM (Field Emission Gun Scanning Electron Microscope) equipped with Bruker® EDS analysis facility.

Average grain size was calculated using the linear intercept method developed by Abrams et al. [191] where a number of lines typically 5 to 10 are superimposed on a SEM micrograph and the number of intercepts with grain boundaries are counted. Abrams’s method was later modified by Mendelson [192] for polycrystalline ceramics by accounting for a log-normal distribution of grain sizes with a truncated octahedral shape generally associated with ceramic grains. The formula is:

$$\bar{D} = 1.57 \frac{C}{MN}$$  \hspace{1cm} (49)

where $\bar{D}$ is the average grain size, $C$ is the length of the line used, $M$ is the magnification of the micrograph, and $N$ is the number of grain boundaries that intercept the line.
3.4.3.2 Scanning electron microscopy sample preparation

Cross-sections of the samples selected for SEM study (Figure 3.1) were cold mounted in epoxy resin then ground on SiC papers of grade P1200, P2500, and P4000. Care was taken to ensure that the surface after each grinding paper was removed before moving to the next grinding step. Samples were washed between each grinding step to ensure any remaining abrasive materials are removed from the sample surface. After grinding, the samples were polished using 1 micron and ¼ micron diamond pastes, and washed with detergent and industrial methylated spirit between each stage. The last step was to use oxide polishing suspension (OPS) to ensure a scratch free surface and to reveal surface features of samples. Samples were carbon coated to prevent the build-up of charge during SEM analysis. Carbon coatings were deposited using a Gatan® 682 Precision Etching Coating System (PECS); the settings were an acceleration voltage of 10 kV for two minutes per sample to ensure the optimised thickness on the surface of the samples.

3.4.4 Transmission electron microscopy (TEM)

A Transmission electron microscope is a powerful tool for the characterisation of crystal structure and chemistry with sub-nanometer resolution and is widely used in the characterisation of oxides.

*Figure 3-7* illustrates the optics of a TEM. An electron gun usually located at the top of the microscope emits electrons which travel through vacuumed column of the microscope. A condensed beam can be created by adjusting the electromagnetic lenses (condenser lens) to focus the travelling electrons down the column. The electron beam then interacts with a thin specimen. Upon interaction and diffraction of electrons in the sample, the transmitted beam forms an image when it reaches an image plane where it is detected by a sensitive material such as a fluorescent film or a charge-coupled device (CCD). A diffraction pattern can also be generated, by projection back focal plane, instead of imaging plane, into imaging detector using magnetic lenses.

High resolution transmission electron microscopy (HRTEM) is an imaging mode of the TEM that by using aberration corrected hardware, images with resolution in Angstrom level can be achieved enabling the determination of atomic positions in the lattice.
In this study, the microstructure and crystal structure of the phases in bismuth strontium cobalt and calcium cobalt compositions were investigated using FEI® Tecnai G2 T20 and FEI® Tecnai G2 F30. The images and electron diffraction patterns were recorded digitally and processed by Gatan® Digital Micrograph software.

### 3.4.5 Scanning Transmission Electron Microscopy (STEM)

In scanning transmission electron microscopy (STEM), a focused beam of electrons is scanned in a raster pattern across the specimen, similar to SEM. Secondary electrons, backscatter electrons, and other particles are detected and collected from the interaction and emissions of the interaction volume of the specimen generated by the electron beam in raster scan mode. The detected particles can be used to create images similar to SEM. (*Figure 3-8a*). TEM images can also be generated normally from the electrons that are transmitted through the specimen. Scattered transmitted electrons can be collected by an annular detector to form images consisting of incoherent spots with different intensities, where the intensity of the spots is directly related to the Z-number.
of the constituent elements of the sample.

Atomic resolution Z-contrast imaging is an ideal tool for crystal structure observation of materials [193]. The crystal structure observations of bismuth strontium cobaltite and calcium cobaltite compositions were performed on an aberration-corrected scanning transmission electron microscope instrument (Figure 3-8b). The microscope is a Nion® UltraSTEM100, operating at 100 kV using a cold field emission emitter. Up to fifth order spherical aberration is corrected by using a series of quadrupoles and octupoles, producing a focused probe achieving a sub-angstrom resolution.

*Figure 3-8 a) Schematic diagram showing the principles of STEM with three available detectors (BF, DF, and HAADF-detectors), adapted from Bocher [194]., b) SuperSTEM2, UltraSTEM-100 Nion Co, adapted from SuperSTEM Laboratory, Daresbury, UK.*

**3.4.6 TEM sample preparation**

There are several methods to prepare TEM samples, i.e. crushing, ion beam milling and focused ion beam (FIB). Each method has its own advantage and disadvantages; therefore, it is necessary to use the technique that is most suitable to the sample and the objectives of observation.

In this investigation, the TEM samples were prepared by the crushing method. Small pieces of the selected samples were cut and then ground in a pestle and mortar to obtain a homogenised fine powder. The resulting powder was then dispersed in chloroform and
dispensed dropwise onto a copper-finder-grid. The grid was then carefully dried and then samples were observed under optical microscopy to verify the uniform particle distribution on the grid. The SuperSTEM images were collected by Dr. F. Azough (University of Manchester)

3.5 Measurement of electrical resistivity

Electrical resistivity was measured using the 4-probe method as depicted in Figure 3-9 [195]. The 4-probe method is widely used and conventionally has been accepted as one of the techniques to reliably measure the resistivity.

The probes were set up to make a contact with the sample; then the current was applied to the two outermost probes using a Keithley® 6221 DC/AC current source. The voltage was measured using the inner probes using a Keithley® 2182 Nano-voltmeter. The resistivity is calculated from equation 50.

\[
\rho = \frac{Ra}{l} = \frac{Va}{Il}
\]

(50)

where ‘a’ is the cross-sectional area of the sample, R is the resistance and ‘l’ is the distance between two inner probes (Figure 3-9).

The samples were rectangular with dimensions of 12 x 4 x 4 mm. After measuring room temperature resistivity, the temperature dependence of the resistivity was measured in ULVAC® ZEM-3 as detailed in the following section.
3.6 Measurement of Seebeck coefficient

The Seebeck coefficient of a material is defined as a magnitude of the induced voltage over the temperature difference across the material i.e.:

\[ S = \frac{dV}{dT} \]  

(51)

The SI unit is V/K but commonly is expressed by μV/K. The Seebeck coefficient was measured by ULVAC® ZEM-3. The instrument measures the Seebeck coefficient and resistivity as a function of temperature simultaneously. The measurement is made in a Helium atmosphere with a pressure of 0.1 bar. The schematic representation of the instrument is shown in *Figure 3-10*.

![Figure 3-10 The schematic diagram of thermopower and resistivity measurement, adapted from ULVAC® ZEM-3 manual.](image)

To calculate the thermopower accurately, the precise recording of the temperature difference and change in voltage are required as part of the steady-state method where it is assumed that the current density is zero. This requires constant and stable ambient temperature as well as applied constant current as a baseline. After the stabilisation of the temperature, a small temperature gradient was established between both ends of the
sample and the difference in voltage was measured. The linear relation between voltage
gradient and temperature gradient were plotted and the thermopower can be determined
from the gradient of the graph. The samples were cut from the pellets and ground on
p1200 SiC paper into rectangular bars with a dimension of 3x3x8 mm (Figure 3-1). The
sample was put in between upper and lower holder in which the temperature gradient is
applied. The probes, which are 4 mm. apart, were brought into contact with the sample,
in order to measure the thermal electromotive force. Seebeck coefficient measurements
were made at room temperature and from 75 to 600 °C in steps of 75°C with a
temperature gradient ‘ΔT’ of 2, 3, and 4°C. The average Seebeck values of three
different temperatures were taken as a representative of the measuring temperature. A
current of 10 mA was selected to ensure a linear voltage to the current plot.

3.7 Determination of Thermal conductivity

Thermal conductivity (κ with the unit W/m.K) describes the transport of heat energy,
through a material toward a temperature gradient. The thermal conductivity of bulk
materials is obtaining from three parameters: the density ρ, heat capacity C_p, and
thermal diffusivity, α and can be calculated from the equation 52.

\[
κ = αρC_p
\]

Both C_p and α are temperature-dependent therefore thermal conductivity also changes
with temperature.

3.7.1 Measurement of thermal diffusivity

Thermal diffusivity is a measure of the ability of a material to dissipate the heat energy
relative to its ability to retain thermal energy. The common and accepted method to
measure thermal diffusivity is by means of laser flash apparatus (LFA). The principals
of LFA method of measuring thermal diffusivity were first described by Parker et al.
[197]. Its concept is based on deriving thermal diffusivity from the thermal response of
the rear side of an adiabatically insulated infinite plate whose front side was exposed to
a short pulse of radiant energy. The temperature different between the two end of the
samples is collected and then the thermal diffusivity values can be calculated from the
temperature-rise-versus-time data. According to this concept, the thermal diffusivity can
be calculated from equation 53.
where $L$ is the thickness of the sample, and $t_{0.5}$ is the time taken for the mean temperature to reduce to $\frac{1}{2}$ of its original value rear side due to the short laser pulse. The SI unit of $\alpha$ is $m^2/s$. Parker [197] assumed that no heat loss occurred in the system; however, there was actual heat loss occurring in the system due to the thermal contact from the sample and finite pulse time effect. This effect was subsequently modified by Cowan and later Taylor [198, 199] and they introduced the correct calibration and corrections to the convergence method and the instrument respectively.

In this project, the laser flash apparatus used was developed in-house at the University of Manchester by Taylor in 1980 [199]. The schematic diagram of laser flash apparatus is shown in Figure 3-11 [200]. The instrument contains a class 4 Nd:YAG laser of 100 J power with 1064 nm wavelength, and 10 mm beam diameter. Samples with 10 mm diameter with flat and parallel faces were held in a graphite holder so that the surface of the sample faces the high-energy laser; the samples were aligned closely to the centre of the laser beam using a Helium-Neon laser, then the chamber was secured, evacuated and filled with Argon gas to avoid any chemical reactions or oxidation on heating. The internal chamber atmosphere was heated by a Huttinger® Electronic Induction furnace MF 3000 series.

The laser was fired at the sample by reflecting with a prism and through a hole with 10 mm diameter with a short pulse of 0.67 ms, which heated the sample; the temperature was measured by a thermocouple attached to the rear face of the sample. The radiation from the rear of the sample passes through a lens and is reflected by a mirror out of the chamber through an optical system. The radiation is then detected by an InSb detector. The signal read from InSb detector was then transmitted, converted from analogue to digital, amplified and recorded. The software for this computer was developed in-house for the purpose of reading and recording the signal from the laser flash apparatus. The Cowan [198] method has been implemented in this software to gain better convergence reading and correction of any losses.
3.7.2 Heat capacity measurement

Heat capacity is defined as the ratio of heat energy supplied to solid matters in response to different in temperature in response to the heat given. It can be expressed as:

\[ C(T) \equiv \frac{\delta Q}{dT} \]  

The SI unit of heat capacity is Joules per Kelvin (J/K). Differential Scanning Calorimetry (DSC) is used in the determination of the heat capacity and requires measuring the amount of heat required to increase the temperature of the material. This reflects the difference between the amounts of heat required to increase the temperature of a sample and a standard. In order to calculate the heat capacity of the sample (\( C_{\text{sample}} \)) from the DSC curves measured, the ratio method is used [201]. This takes the ratio of the DSC curve of the sample (DSC_{sample}) to the DSC curve of the sapphire standard (DSC_{standard}) and multiplies the result by the known heat capacity of the standard (\( C_{\text{standard}} \)):

\[ C_{\text{Sample}} = \frac{dH_{\text{Sample-baseline}}}{dH_{\text{Standard-baseline}}} \times C_{\text{standard}} \]  

Figure 3-11 Schematic diagram of laser flash apparatus, reproduced from Casalegno et al. [200].
By taking the ratio of the DSC curves the uncertainty in the heat capacity comes only from the noise from in the data, and that can be minimised by averaging the data over several measurements.

The heat capacity of samples was measured using a Netzsch STA 449 C Jupiter® differential scanning calorimeter. Three runs were required for each sample: Baseline, Sapphire as the standard, and the sample. Successive runs have the same procedure as the baseline run. The platinum crucibles (baseline) with 0.7 mm diameter were heated to 50 °C with a heating rate of 5 °C/s and left to stabilise for 15 minutes; after that 20 °C/s heating rate was used to 600 °C under air atmosphere. The sapphire standard (0.5 mm disk-shaped) had an approximate mass of 85.5 mg. The samples were cut and ground to match the weight of the sapphire standard with a tolerance of ±10%. The Netzsch Proteus® software was used to extract the $C_p$, based on comparison and extrapolation of measured profiles [201, 202].
4. The effect of Bi content and fabrication route on the microstructure and thermoelectric properties of Bi$_{2+x}$Sr$_2$Co$_2$O$_y$

4.1 Introduction

In this chapter, the effect of Bi-stoichiometry and preparation route (MO and SPS), on the structural characteristics and thermoelectric properties of Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ compositions with $x = 0$, 0.1, and 0.2 denoted as (BSCO-0, BSCO-1, and BSCO-2 respectively) is presented and discussed.

In the year 2000 for the first time Funahashi et al. [25] reported the thermoelectric properties for bismuth strontium cobaltite, Bi$_2$Sr$_2$Co$_2$O$_y$ with Seebeck coefficient around 110-160 $\mu$V/K, and resistivity of 20-40 m$\Omega$ cm over the temperature range of 25-600 $^\circ$C. A ZT of 0.1 at 700 K was reported. This makes it a promising candidate for thermoelectric applications. Several methods have been applied to increase the ZT such as substitution at the Bismuth site with Pb by Yamamoto et al. [156]; the result showed that substitution of Pb led to change in lattice parameter of rock salt layers and the electronic properties. Yin et al. [168] also investigated substitution of Sr and Co site with various elements in the form of Bi$_2$Sr$_{1.9}$M$_{0.1}$Co$_2$O$_y$ (M=Ag, Ca, and Y) and X=Zr, Al, and MO), resulting in a change in band gap and electronic properties. Combe et al. [140] investigated three different fabrication processes; mixed-oxide, hot pressing, and partial melting of Bi$_2$Sr$_2$Co$_2$O$_y$ and compared the properties of each process. The ZT values of 0.25, 0.07 and 0.068 were reported for partial melting method, hot pressing method, and air sintering methods respectively. The results indicated that altering the manufacturing route could yield new phases and different properties.

There are many possible advantages in SPS processing as it generally yields high density materials which are desirable, and they may exhibit superior thermoelectric properties. This is the main reason to perform SPS on the calcined powders of BSCO-0, BSCO-1, and BSCO-2.

In this chapter, the comparison between the processing routes of SPS and MO as well as the effect of Bi content have been investigated. Several sources have indicated that the SPS fabrication could yield dense samples and better thermoelectric properties such as...
in the case of Ca$_3$CO$_4$O$_9$ by Zhang et al. [203] and in Bi$_2$Sr$_2$Co$_{1.8}$O$_{y}$ by Rubesova et al. [152] with ZT of 0.025 at 300 K by post SPS annealing in an air atmosphere.

Furthermore, a thorough study by Janvorsky et al. [180], who constructed a phase diagram of the Bi-Sr-Co-O system, found that by altering the Bi-Sr ratio, different phases with different compositions could be formed. These phases have been reported to have different crystal structures and properties [180]. These new phases could be beneficial to adjust the thermoelectric properties by lowering electrical resistivity and lowering thermal conductivity by phonon scattering at the phase boundary. Therefore, it is the aim to see the effect of these phases on the thermoelectric properties.

4.2 The structure and thermoelectric properties of Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ processed by MO method

4.2.1 Bulk physical properties
All the samples were visibly dark grey in colour. Both fabrication techniques produced crack–free, dense and uniform in shape samples. The values of the measured density are illustrated in Figure 4-1. The SPS route yielded highly dense samples with almost 100% relative density. This was independent of the Bi content in the composition. The densities of the samples prepared by the MO route were dependent on the Bi content varying between 81 to 90 % of the theoretical value. It can be seen that the samples obtained through SPS are of higher density.
4.2.2 X-ray diffraction analysis

X-ray diffraction (XRD) pattern of ceramic BSCO-0, BSCO-1, and BSCO-2 are shown in Figure 4-2. The observed XRD spectrum for BSCO-1 is in good agreement with reported XRD patterns [152, 170]. The majority of the peaks can be indexed as a misfit structure with monoclinic symmetry and $I2/a$ as space group based on Leligny study of the $\text{Bi}_{1.74}\text{Sr}_2\text{Co}_{1.8}\text{O}_{7.64}$ [159] phase. There are no established studies on the nature of crystal structure of $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ in the literature; published data on this composition [152, 170] only show indexed XRD spectra without providing the exact structural data. The only one Rietveld refinement published data available in literature is for the $\text{Bi}_{1.85}\text{Sr}_2\text{Co}_{1.85}\text{O}_{7.7}$ composition [180]; this was performed using the structural data proposed by Leligny for the $\text{Bi}_{1.74}\text{Sr}_2\text{Co}_{1.8}\text{O}_{7.64}$ [159] composition. Consistent with the reported data, low-intensity diffraction peaks arising from the two minor phases were also detected in all the three samples [172, 173]. The first minor phase was observed at $2\theta = 36.7$ degrees in all compositions with all having similar intensity. This peak was suggested by the literature [140] to be CoO and can be indexed using ICSD reference number 00-048-1719. A similar phase was also observed in the microstructure of the
samples as discussed in section 4.2.3. The second minor phase was clearly visible in the XRD spectrum of BSCO-2 only, however, there is an indication of peak formation for BSCO-1 but absent in BSCO-0 spectrum. The chemical composition and crystal structure of the second minor phase have been determined by HRTEM, electron diffraction pattern, and EDS techniques and will be reported in the section 4.2.3.

![XRD Spectra for BSCO-0, BSCO-1, and BSCO-2 ceramics.](image)

*Figure 4-2 XRD Spectra for BSCO-0, BSCO-1, and BSCO-2 ceramics. The spectra show the evolution of secondary phases with the amount of the bismuth content. Peaks for the main phase are marked with black circles, peaks for minor phase 1 and minor phase 2 are marked as a dark-blue triangle and red square respectively.*

*Figure 4-3* shows Rietveld refinement of the crystal structure for BSCO-1. The crystal structure was refined using Leligny’s average structure [159] for composition Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_{7.64}$ [150, 159]. It can be seen from *Figure 4-3* that there is a good fit ($R_{WP}$ 9.1) between the observed and the calculated data. These findings also hold true for the other two BSCO-0 and BSCO-1 samples with their R-values and GOF listed in Table 4-1. However, some of (0 0 l) family of reflections especially the (0 0 10) do not fully match the experimental intensity. The cause of this is thought to be very high aspect ratio (a-b/c) planes found naturally in this type of materials which causes high-intensity sharp peaks beyond the scope of mathematical compensation.
Figure 4-3 Rietveld refinement of BSCO-1 processed by mixed-oxide route. Experimental data is in black and the calculated fit is in red, the grey line shows the difference between the original and refined data. The black square is a reflection from the minor phase 2.

Table 4-1 R-values and goodness of fit (GOF) values from Rietveld refinement of mixed-oxide samples. The GoF values are artificially high because of the \( R_{\text{exp}} \) obtained on XRD.

<table>
<thead>
<tr>
<th></th>
<th>( R_{\text{exp}} )</th>
<th>( R_{\text{wp}} )</th>
<th>( R_{p} )</th>
<th>GoF</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSCO-0</td>
<td>2.09</td>
<td>11.06</td>
<td>7.69</td>
<td>5.3</td>
</tr>
<tr>
<td>BSCO-1</td>
<td>2.23</td>
<td>9.1</td>
<td>6.42</td>
<td>4.09</td>
</tr>
<tr>
<td>BSCO-2</td>
<td>2.22</td>
<td>10.28</td>
<td>6.88</td>
<td>4.62</td>
</tr>
</tbody>
</table>

Although, having only a limited number of low-intensity peaks in the XRD pattern an attempt was made to unambiguously identify the minor phases. The peaks of minor phase 2 can be indexed and refined as a \( \text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375} \) rhombohedral type phase using crystallographic information files from Mercurio et al. [204]. The Rietveld refinement for this phase is shown in Figure 4-4. The structure of \( \text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375} \) was determined to be rhombohedral structure with a \( R\overline{3}m \) space group from the previous study. The phase was reported to strongly exhibit ionic conductivity [204]. There has been no report on electrical resistivity for this composition. However, a similar composition with the same structure, \( \text{Bi}_{0.844}\text{Sr}_{0.156}\text{O}_{1.42} \), was reported to have resistivity values of around 30 mΩ.cm at 723 K and expected to be lower at lower temperatures [204]. Supporting SEM-EDS and HRTEM studies will be presented in sections 4.2.3. The amount of this
secondary phase deduced from the refinement was around 5% for BSCO-2 sample. The BSCO-0 and BSCO-1 samples, however, did not have sufficiently high-intensity data to carry out the quantitative analysis. Hence, it could be deemed as below 5% for BSCO-1 and negligible for BSCO-0. The same argument applies to CoO phase having only one low-intensity peak, in all samples, which is unsuitable for quantitative phase analysis.

![Graph showing Rietveld refinement results for BSCO-2 sample]

**Figure 4-4** The Rietveld refinement of the rhombohedral type second minor phase \((\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375})\) indexed in a black number. The reflections from the main phase are indexed by purple colour (purple circle). Experimental data is in black and the calculated fit is in red, the grey line shows the difference between the original and refined data. The thick black line is refinement from the minor phase 2.

The refined structural parameters for BSCO-0, BSCO-1 and BSCO-2 are presented in Appendix A, Table 10-1; the refinement showed little change in lattice parameters but no significant change in atomic positions and atomic occupancy as a function of Bi content, being very similar to structural parameters used for refinement [159].

Refined lattice parameters for the three compositions are shown in **Figure 4-5**. All the lattice parameters show a different trend as a function of Bi content. The length of the a-axis is about the same as for BSCO-0, BSCO-1 and BSCO-2 (**Figure 4-5a**). The length of the b-axis shows a maximum value for BSCO-1 (**Figure 4-5b**), while there is a minimum value of the length of c-axis for BSCO-2 (**Figure 4-5c**). The monoclinic angle, \(\beta\), shows increased values for BSCO-1 and BSCO-2 compared to BSCO-0.
However, when the estimated standard deviations for all graphs are considered, it could be seen that there are no significant changes in all lattice parameters and the monoclinic angle as a function of bismuth content.

**Figure 4-5 Refined crystal structural parameters as a function of bismuth content:** a) length of a-axis, b) length of b-axis, c) length of c-axis, d) value for β angle.

Refined cell volumes of all 3 compositions are displayed in **Figure 4-6**. There is no clear indication of a trend as a function of bismuth content. The BSCO-1 cell volume is the largest, however, it could be inferred from the graph, with consideration of the uncertainty of refinement, that there are no significant differences in cell volume. Therefore, it can be inferred that the main crystal structure should be the same in all 3 compositions.
Figure 4-6 Refined cell volume for Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ samples as a function of bismuth content.

Figure 4-7 shows a Rietveld refinement of the crystal structure of the synchrotron data for BSCO-0. The experimental peaks are very sharp and well defined. The majority of the peaks belong to the main phase. Low-intensity reflections from the two secondary phases also appear in the spectrum. The refinement procedure was the same as that used in the refinement of the mixed-oxide data. The R-values and GOF are listed in Appendix A, Table 10-2. GOF values of 1.48 demonstrated a very good fitting between the experimental and refinement. However, similar to the refinement of the data for the MO samples, some of (0 0 l) family of reflections especially the (0 0 10) do not fully match the experimental intensity as highlighted before. This is thought to be due to the very high degree of anisotropy in the grains. The same anisotropy was also noted and encountered by Leligny et al. [150, 159] who reported lamellae shaped grains systematically orientated along (001) [150, 159]. The refined atomic positions are also shown in Table 10-2, which are in good agreement with MO data presented in Table 10-1.
Figure 4-7 Rietveld refinement of the synchrotron data for BSCO-0 processed by mixed-oxide route. Experimental data is in black and the calculated fit is in red, the grey line shows the different between the original and refined data.

It can be seen from Table 10-2, that the refinement of the synchrotron data gave similar lattice parameters, cell volume, atomic position and atomic occupancy to those of the Cu-radiation source. The low $R_{\text{exp}}$ values indicated that the synchrotron source is a high-quality data and more accurate than the Cu-source X-ray. The GOF value, was also much lower showing a much better refinement. Comparing data from Cu radiation source and I11 synchrotron data, it can be seen that there are slight differences in lattice parameters. These slight variations, however, are very small and hence it could be concluded that the Cu radiation refinement was consistent with synchrotron data.

4.2.3 Microstructure analysis

The secondary electron (SE) and backscattered electron (BSE) images for BSCO-0, BSCO-1 and BSCO-2 samples prepared by the MO route are presented in Figure 4-8. The images show dense samples with a small amount of intergranular pores. The presence of small amount of pores could serve as a confirmation of density values presented in Figure 4-1.

Figure 4-8a is a SE image for BSCO-1 sample. In the SE mode, the main phase and a localised minor phase (inside ellipsoids) can be seen. A second minor phase, bright in colour (shown by red arrows), can be observed in BSE mode image as shown in Figure 4-8(b,d). In the BSE images, the second phase shown in in Figure 4-8a appears as black areas (inside ellipsoids). The first minor phase appears black in colour in the BSE images and could be mistaken for porosity; therefore, both SE and BSE images from the
same area were collected. BSE images for BSCO-0 and BSCO-2 are shown in Figure 4-8(c, d). They have similar microstructure to BSCO-1. The amount of the second minor phase increases as the Bi content increased in the composition. The main phase could be seen as plate-shaped grains with a preferred elongation in one direction. It can be seen from the BSE images that plate-shaped grains are formed from the stacking of thinner plates. Grain size analysis was also performed on the main phase. The calculated averaged surface area values are: 11.0 μm, for BSCO-0; 13.5 μm for BSCO-1 and 17.4 μm for BSCO-2.

![SEM micrographs of polished surfaces of Bi₂+ₓSr₂Co₂O₅ samples prepared by mixed-oxide route: a) SE image of BSCO-1, b) BSE Image of BSCO-1 in the same area as a), c) BSE image of BSCO-0, d) BSE image of BSCO-2.](image)

EDS area mapping was performed on the area containing primary phase, Bi-rich secondary phase, and Co-rich phase. A clear difference in the chemical composition between various phases was observed in BSE images as presented in Figure 4-9. The main phase contains Bi, Sr, and Co, while the second minor phase, which, appears as bright colour in the BSE images, contains Bi and Sr. The second minor phase, black in colour in BSE images, contains Co element.
Figure 4-9 EDS mapping of a BSCO-1 sample: a) the region where the EDS mapping has been performed showing Bismuth (cyan), Strontium (blue), and Cobalt (green) distribution. Red ellipsoid indicates Bi-rich area, blue ellipsoid indicates Co-rich area.

In addition to the EDS area mapping, point EDS analysis was also performed on the main phase and two minor phases, complementing the EDS area mapping analysis for these phases. The quantitative elemental analysis of three different phases, main phase, bright phase (rhombohedral phase), and dark phase (CoO phase) in atomic percent are presented in Table 4-2. It was estimated that the ratio between Bi:Sr:Co was 1.14:1:1.04. This ratio corresponds to $\text{Bi}_{2.28}\text{Sr}_{2.08}\text{O}_y$ phase; however, it is the authors opinion that the composition should be $\text{Bi}_{1.74}\text{Sr}_{2}\text{Co}_{1.82}\text{O}_y$ in accordance with the TEM and XRD data. The white secondary phase has a ratio of 14:5:1 which might correspond to $\text{Bi}_{14}\text{Sr}_5\text{Co}_y$. However, in conjunction with TEM and XRD results, it was determined that this phase is more likely to be $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375}$. The 5% excess cobalt is well within the uncertainty range of EDS, and therefore it could be discarded. The black secondary phase was identified as almost pure Cobalt oxide in agreement with XRD results.
Table 4-2 EDS quantitative analysis in atomic percent of the main phase, minor phase 2 (rhombohedral phase) and minor phase 1 (CoO phase).

<table>
<thead>
<tr>
<th>Composition/Atomic%</th>
<th>Co</th>
<th>Sr</th>
<th>Bi</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main phase</strong></td>
<td>32.8</td>
<td>31.4</td>
<td>35.8</td>
<td>100</td>
</tr>
<tr>
<td><strong>White phase</strong></td>
<td>5.4</td>
<td>24.9</td>
<td>69.7</td>
<td>100</td>
</tr>
<tr>
<td>(rhombohedral phase)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Second minor phase</strong></td>
<td>99.7</td>
<td>0</td>
<td>0.3</td>
<td>100</td>
</tr>
<tr>
<td>(CoO phase)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To further confirm the nature of the second minor phase, selected area electron diffraction (SAED) and HRTEM imaging were conducted. A SAED pattern for the Bi-Sr second phase in BSCO-1 prepared by the MO route is shown in Figure 4-10a. The main reflections in the diffraction pattern can be indexed as [0001] zone axis of hexagonal symmetry with $a_1 \approx a_2 \approx a_3 \approx 4\text{Å}$. The diffraction pattern shows six pairs of superlattice reflections around the main reflections. The diffraction pattern is very similar to the diffraction pattern observed for rhombohedral type Bi$_2$O$_3$ – SrO and Bi$_2$O$_3$ – CaO binary systems [205]. The HRTEM image of the same grain is shown in Figure 4-10b. The image shows round regions with the size ranging from 50 Å to 70Å. These regions can be interpreted as ordered domains confirming the proposal by Withers et al. [206] and Sorokina et al. [205]. SAED and HRTEM imaging confirms our X-ray and SEM-EDS findings that the minor phase 2 is Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$. 
Figure 4-10 a) [0001] zone axis SAED for the (Bi – Sr) phase in BSCO-1 prepared by the MO route showing six pairs of satellite diffraction spots around the main reflections., b) Corresponding HRTEM image showing round shaped domains of the phase.

There are limited TEM studies for bismuth strontium cobaltite: Fujii et al. [167] and Yamamoto et al. [156] studied the structure of a single crystal of Bi$_{2-x}$Pb$_x$Sr$_2$Co$_2$O$_y$ (x=0, 0.4, 0.6, and 0.8). Both reported the presence of a modulation, superstructure, indicated by the presence of extra reflections in the [001] zone axis diffraction patterns. However, none of the studies reported the corresponding TEM images for this modulation, superstructure and the nature of the modulation, superstructure, was not discussed. In order to identify the nature of this modulation more detailed microstructural investigations were undertaken by HRTEM and HAADF-STEM.

Figure 4-11 shows the [001] orientation bright field (BF) TEM image of the main matrix phase of BSCO-1 and its corresponding diffraction pattern. The diffraction pattern is similar to the diffraction patterns previously reported by Fujii et al. [167], and Yamamoto et al. [156] (Figure 2-21, and Figure 2-23).
Figure 4-11 [001] BF-TEM image and the corresponding electron diffraction pattern for matrix phase of BSCO-1.

In order to further understand the nature of this modulation, HAADF and BF images were obtained using an aberration corrected STEM. Figure 4-12 shows [001] HAADF-BF images for BSCO-1. In the HAADF image, dark bands can be seen forming the modulation. Atomically-resolved HAADF images are presented in Figure 4-13. The modulation appears as dark bands in the image (black arrowed). In the atomically resolved HAADF image, the view shows the atomic columns in the crystal structure and the intensity of the spots, atomic columns, depends on the average atomic number of the elements in the columns. The presence of atomic columns with lower intensity, dark bands in the image, suggests that these atomic columns could be deficient in the constituent elements of the crystal structure; therefore, Bi deficiency in the structure is a possibility, being consistent with the proposed composition of the matrix phase by Leligny et al. [150, 159].
Figure 4-12 [001] HAADF and BF images for the main phase in BSCO-1. The corresponding Fourier transform (FFT) is shown in the top right of the BF Image.

Figure 4-13 [001] High magnification HAADF image for the main phase in BSCO-1 showing bands of atomic columns with lower intensity.
4.2.4 Summary for XRD, SEM, and TEM-STEM data

From XRD, SEM and TEM analysis, it was found that there are three phases in the microstructure; the two minor phases were determined to be Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ and CoO. The main phase was found to have a composition close to that proposed by Leligny et al. (i.e. Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_{7.64}$), which was, in fact, less than the nominal stoichiometry composition Bi$_2$Sr$_2$Co$_2$O$_y$. The main phase was therefore deemed to be a Bi-deficient phase. The TEM data and HAADF images further support the Bi-deficiency proposal for the matrix phase as evident by the Bi-deficient modulation bands.

There are two effects on the microstructure by excess bismuth doping. Excess bismuth helped increased the density and increased the grain size. Secondly, the amount minor second phase, Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$, was increased as a function of Bismuth content.

4.2.5 Electrical properties

The temperature dependence of the resistivity of three compositions is presented in Figure 4-14a). The BSCO-0, BSCO-1 and BSCO-2 samples showed increasing resistivity values over the temperature range of the measurement. It is evident that higher bismuth contents (BSCO-2) lead to lower resistivity possibly due to the contribution of the excess carrier generated by doping bismuth. However, this is unlikely as there was no significant change in Seebeck coefficients among the 3 compositions. The most probable reason is a number of secondary phases created which then altered the electronic properties of the whole material. BSCO-1 composition had higher resistivity compared to both BSCO-0 and BSCO-2, which, coincided with a slight change in the composition of the matrix phase as a result of excess Bi as discussed in X-ray data (section 4.2.2). From the evidence of a change in resistivity and cell volume, it could be argued that BSCO-1 had a change in the stoichiometry of the main matrix which resulted in such changes. The resistivity values of 15- 20 mΩ.cm of BSCO-2 are well within the lower limit of other reported values for Bi$_2$Sr$_2$Co$_2$O$_y$ [25, 168].

The temperature dependence of Seebeck coefficients are presented in Figure 4-14b). All the Seebeck values were positive, indicating that the compositions are $p$-type (hole conduction) thermoelectric materials. The Seebeck coefficient values in all samples increase steadily with temperature followed the prediction of Heikes formula [207]. The values for all three compositions are similar with no significant difference between
them. Therefore, it could be concluded that doping of bismuth cation into bismuth strontium cobaltite ceramic did not have an impact on Seebeck values. The Seebeck values of 110-160 $\mu$V/K over a temperature range of 300-900 K are comparable to other investigations [25, 26, 141, 152-154, 169, 171-173, 175, 208].

Power factor data over the temperature range is depicted in Figure 4-14c. The combined data of Seebeck values and resistivity showed a superior value of power factor of BSCO-2 especially at high temperature, where the power factor for BSCO-1 seemed to reduce abruptly due to higher resistivity values. Power factor values of 0.075 mW/m.K$^2$ to 0.15 mW/m.K$^2$ have been reported, including Bi$_2$Sr$_2$CoO$_y$ reported by Wang et al. [169] which are consistent with findings in this study.

![Figure 4-14 Thermoelectric properties of BSCO-0, BSCO-1, BSCO-2 prepared by MO route as a function of temperature: a) Electrical resistivity, b) Seebeck coefficient, c) Power factor.](image-url)

Power factor
4.2.6 Thermal properties

The heat capacity values for the samples as a function of temperature are illustrated in Figure 4-15a. The \( C_p \) values demonstrated a rise over the temperature range, which is typical for solid state materials where the \( C_p \) values gradually rise, reaching equilibrium at higher temperature [209]. The \( C_p \) of all three compositions were in the range of 0.17 to 0.35 J/g.K in the measured temperature range. Amongst the three compositions, it appeared that excess bismuth lowers the heat capacity for BSCO-1 and BSCO-2 compositions. Although there is no available \( C_p \) data for \( \text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375} \), it is believed that this decrease could be due to the contribution of extra minor phase 2 (\( \text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375} \)).

Thermal diffusivity of BSCO samples as a function of temperature are given in Figure 4-15b. The values decreased with increase in temperature. This is expected and could be attributed to increasing in phonon-phonon scattering on increasing the temperature. The BSCO-1 sample was found to have lowest thermal diffusivity. The presence of a small amount of \( \text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375} \) secondary phase could be a factor in enhancing the grain boundary scattering of phonons which results in lower thermal diffusivity of BSCO-1. However, as the secondary phase volume grew in the BSCO-2 samples, thermal diffusivity may decrease as a result of larger grain boundary volume and change of grain shape [210]. Another possible explanation is that a slight change in the composition stoichiometry, as evident in lattice parameters and X-ray data (section 4.2.2), could lead to enhancement of phonon scattering in the BSCO-2 sample.

Thermal conductivity data are presented in Figure 4-15c. The values have been calculated from density, heat capacity and thermal diffusivity. All samples exhibited a very low thermal conductivity values, i.e thermal conductivity < 1 W/m.K. These low values can be explained by the structure; the alternating layers between rock salt and hexagonal layers cause a scattering of phonons due to shorter mean free path as described by Funahashi et al [26]. The thermal conductivity values were lower than that observed by Shen et al. (between 1-1.5 W/m.K) for \( \text{Bi}_2\text{Sr}_2\text{La}_x\text{Co}_2\text{O}_9 \) (X=0.0, 0.02, 0.04, 0.08). Combe et al. also reported similar values of 0.8-1 W/m.K for air-sintered composition \( \text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y \). However, it was found that hot pressing of \( \text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y \) could raise the thermal conductivity to 1.5-2 W/m.K. Furthermore values from this
investigation are lower than the values reported by Funahashi et al. [26] for whisker crystals of Bi$_2$Sr$_2$Co$_2$O$_y$.

Figure 4-15. Thermal properties as a function of temperature for Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ composition prepared by MO: a) heat capacity, b) thermal diffusivity and c) thermal conductivity.

**4.2.7 Thermoelectric figure of merit (ZT)**

The Figure of merit for bismuth strontium cobaltite ceramics are presented in Figure 4-16. The values show an upward trend for all compositions. It can be seen that an increase in bismuth content on the composition of Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ resulted in a more favourable figure of merit. Both BSCO-1 and BSCO-2 had better ZT values than undoped BSCO-0 over the same temperature range. The highest value of 0.12 was obtained for BSCO-1 and BSCO-2 at 870 K. The figure of merit was almost doubled when compared to initially reported values of 0.06 in Bi$_2$Sr$_2$Co$_2$O$_y$ composition by Funahashi et al. and Yin et al. [25, 168]. However, it is still inferior to that for Ag-doped Bi$_2$Sr$_2$Co$_2$O$_y$ with a ZT of 0.23 reported by Wang et al. [169]. It is also lower than that of samples prepared by partial melting fabrication process of Bi$_2$Sr$_2$Co$_2$O$_y$ investigated by Comb et al. of 0.23[140]. Overall it could be considered that addition of Bi to Bi$_2$Sr$_2$Co$_2$O$_y$ resulted in an improvement of thermoelectric figure of merit as both
BSCO-1, and BSCO-2 have a superior thermoelectric figure of merit compared to BSCO-0.

![Figure 4-16 Figure of merit of Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ processed by MO as a function of temperature.](image)

4.2.8 Summary

From the results obtained, it can be concluded that doping of bismuth into bismuth strontium cobaltite ceramics, Bi$_2$Sr$_2$Co$_2$O$_y$, did have a major impact on thermoelectric properties. The BSCO-1 samples have a high figure of merit despite the lowest power factor due to a formation of new secondary phase which aids phonon scattering and has a detrimental effect on the electrical properties. These could be adapted for high efficiency thermoelectric applications. On the other hand, the BSCO-2 samples which have a comparable figure of merit to BSCO-1 but with highest power factor (which might be a result of excessive doping carriers available) could be suitable for higher energy-demanded applications.

In the following section, the effect of Bi content on the microstructure and thermoelectric properties of SPS sample will be discussed.
4.3 The structure and thermoelectric properties of $\text{Bi}_{2+x}\text{Sr}_2\text{Co}_2\text{O}_y$
processed by SPS method

4.3.1 Physical properties
The density of materials obtained by SPS method was displayed in Figure 4-1 in comparison to MO route, which shows high density materials (around 95 % theoretical) as expected from SPS processing.

4.3.2 X-ray diffraction analysis
X-ray diffraction (XRD) spectra of ceramic BSCO-0, BSCO-1, and BSCO-2 samples, processed by SPS method are shown in Figure 4-17. XRD spectra for SPS samples are similar to that of mixed-oxide samples shown in Figure 4-2 and the reported XRD patterns [152, 170]. The majority of the peaks can be indexed as a misfit structure with monoclinic symmetry and $I2/a$ as space group [150, 159]. Low-intensity diffraction peaks arising from the secondary phases were also detected in all three samples; however, there are some extra new peaks compared the mixed-oxide route. The first secondary phase peak was observed at 36.7 degrees in all compositions, having a similar intensity and belongs to CoO [140]. The new peaks marked as dark green stars in Figure 4-17 were visible in the X-ray spectrum of all three compositions. These peaks could also be indexed as the $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375}$ phase. Rietveld refinement using $\text{Bi}_{1.74}\text{Sr}_2\text{Co}_{1.8}\text{O}_{7.64}$ phase alone, and using $\text{Bi}_{1.74}\text{Sr}_2\text{Co}_{1.8}\text{O}_{7.64}$ phase in conjunction with $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375}$ phase was performed for all compositions.
Figure 4-17 XRD Spectra for BSCO-0, BSCO-1, and BSCO-2 ceramics manufactured by SPS method. The spectra show the evolution of secondary phases with the amount of the bismuth content. The main phase is marked with black circle identified as Bi$_2$Sr$_2$Co$_2$O$_y$. Secondary phases marked as red square and green stars found to be Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$. The blue triangle represents CoO.

Figure 4-18 shows a Rietveld refinement of the crystal structure for BSCO-1. The crystal structure was refined with the same structural file used for the mixed-oxide samples (BSCO-1). It can be seen that there is a good fit ($R_{wp}$ 9.53) between the observed and calculated data. Similar fit values were obtained for BSCO-0 and BSCO-2 compositions with their R-values and GOF listed in Table 4-3. Difficulty of refinement of (0 0 l) family peaks occurred as previously described in section 4.2.
Figure 4-18 Rietveld refinement of BSCO-1 prepared by SPS processing. Experimental data is in black and the calculated fit is in red, the grey line shows the difference between the original and refined data. The black square is a reflection from the second minor phase (Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$).

Table 4-3 R-values and goodness of fit (GOF) values from Rietveld refinement of SPS samples. The GoF values are artificially high because of the $R_{\text{exp}}$ obtained on XRD.

<table>
<thead>
<tr>
<th></th>
<th>$R_{\text{exp}}$ :</th>
<th>$R_{\text{wp}}$ :</th>
<th>$R_{p}$ :</th>
<th>GOF :</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSCO-0</td>
<td>1.98</td>
<td>9.54</td>
<td>6.76</td>
<td>4.81</td>
</tr>
<tr>
<td>BSCO-1</td>
<td>2.07</td>
<td>9.53</td>
<td>6.75</td>
<td>4.61</td>
</tr>
<tr>
<td>BSCO-2</td>
<td>2.04</td>
<td>12.04</td>
<td>8.38</td>
<td>5.89</td>
</tr>
</tbody>
</table>

The Rietveld refinement including minor phases in the refinement is displayed in Figure 4-19. The additional peaks previous marked by a black star in Figure 4-17 could be indexed as (0 0 3) and (0 0 6) peaks of Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ phase [204]. Thus, the three peaks were observed in all three compositions. With the presence of these three major peaks of Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ [204] in the X-ray spectra, it can be concluded that the minor second phase is Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$. 
Quantitative phase analysis by Rietveld analysis showed a higher amount of rhombohedral secondary phase in SPS samples than in mixed-oxide samples. The approximate quantities of secondary phase for BSCO-0, BSCO-1, BSCO-2 are 8.07%, 11.75%, and 15.31% respectively. The amount of the secondary phase seemed to be dependent on the bismuth content. This was in accordance with the discussion elaborated in the section 4.2.2. The amount of CoO phase was not quantified; however, it was expected to be negligible (i.e. less than 5%); it did have only one observed peak and reliable treatment and refinement for Rietveld analysis is not possible. The R-values and GOF values of all compositions are given in Table 4-4 and in Appendix A (Table 10-3) for refined structural parameters: i.e atomic position, lattice parameter, $B_{eq}$ of all compositions. It was also noted that there were no significant changes in structural parameters between refinement with or without secondary phases.
Table 4-4 R-values and goodness of fit (GOF) values from Rietveld refinement in each SPS sample with an inclusion of secondary phases. The GoF values are artificially high because of the R_{exp} obtained on XRD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R_{exp}</th>
<th>R_{wp}</th>
<th>R_{p}</th>
<th>GoF</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSCO-0</td>
<td>1.98</td>
<td>8.26</td>
<td>5.74</td>
<td>4.18</td>
</tr>
<tr>
<td>BSCO-1</td>
<td>2.03</td>
<td>7.2</td>
<td>5.41</td>
<td>3.55</td>
</tr>
<tr>
<td>BSCO-2</td>
<td>2.04</td>
<td>10.65</td>
<td>7.47</td>
<td>5.23</td>
</tr>
</tbody>
</table>

Plots of lattice parameters and monoclinic angle, β, versus bismuth content are shown in Figure 4-20. All the lattice parameters show a different trend as a function of bismuth content. The length of a-axis shows a peak value for BSCO-2 and slightly lower values for BSCO-0 and BSCO-1. For the length of b-axis, the BSCO-1 has the maximum value while BSCO-0 and BSCO-2 have about the same values (Figure 4-20b). The length of c-axis shows a minimum value for BSCO-1, a slightly higher value for BSCO-0 and the highest value was observed for BSCO-2 (Figure 4-20c). The monoclinic angle, β, shows increasing values as a function of bismuth content (Figure 4-20d). However, from the values of each graphs and their estimated standard deviation, it could be interpreted that there is no significant differences in both lattice parameters and the monoclinic angle with composition as the values are within one standard deviation from each other.
Refined crystal structural parameters as a function of bismuth contents for SPS samples:
a) length of a-axis, b) length of b-axis, c) length of c-axis, d) value for $\beta$ angle.

Refined cell volume of all three compositions are displayed in Figure 4-21. There is no clear trend as a function of bismuth contents. However, similar to MO samples, the difference in cell volume between the 3 compositions are not significant when considering the uncertainty. Therefore, it can be assumed that the crystal structure of the main phase should be the same in all 3 samples.

Comparing the structural parameters between MO and SPS data, the SPS data showed smaller lattice parameters and beta angle in all compositions. It could be then inferred that SPS composition might be slightly different than their mixed-oxide counterpart. The work of Rubesova et al. [152] supports the proposal and they suggested that different fabrication routes could yield slightly different phases as a result of pressure and powder compaction. The other plausible explanation is that because the SPS samples were sintered at lower temperatures for shorter times, that could result in smaller lattice parameters and $\beta$ angle and hence cell volume.
Figure 4.21  Refined cell volume of Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ samples as a function of bismuth content.

4.3.3 Microstructure

Secondary electron (SE) and Back Scattered electron (BSE) images for BSCO-0, BSCO-1 and BSCO-2 samples prepared by the SPS method are presented in Figure 4-22. The images show samples of high density with no visible intergranular pores which serve as a confirmation of density values presented in Figure 4-1. Figure 4-22a is a SE image for BSCO-1 sample showing the main phase and a secondary phase, minor phase 1, shown inside red ellipsoids. The minor phase 1 appears black in colour and another secondary phase (inside white ellipsoids), bright in colour, becomes visible as shown in Figure 4-22b. The BSE images for BSCO-0 and BSCO-2 are shown in Figure 4-22(c - d). They have similar microstructures to BSCO-1. The content of the bright secondary phase increases as the Bi content was increased in the composition. It is difficult to see the grain boundaries of the matrix phase due to smaller grain size compared to that of the MO samples. It was suggested by Combe et al. [140] that the high pressure fabrication could result in such interconnected grains. Grain size analysis was not performed on the main phase due to the reason previously described in section 4.2.2.
Figure 4-22 SEM micrographs of polished surfaces of samples prepared by SPS method: a) SE electron of BSCO-1, b) BSE Image of BSCO-1 in the same area as (a), c) BSE image of BSCO-0 d) BSE image of BSCO-2. Highlighted area (red ellipsoid) depicts the cobalt oxide phase.

Further microstructure studies were conducted by TEM, to further verify the nature of both main phase and secondary phase in SPS samples. Figure 4-23a shows an HRTEM images of minor phase 2 (Bi_{0.75}Sr_{0.25}O_{1.375}) observed in BSCO-2 SPS sample. The domain structure is identical to the one observed in the MO-samples, indicating that it has the same crystal structure (rhombohedral type). Figure 4-23b shows the [001] orientation bright field (BF) TEM image of main matrix phase of BSCO-1 and its corresponding diffraction pattern. The TEM data for the modulation of the superstructure is similar to those observed in the MO samples. It can be seen from TEM data that both SPS and MO have identical microstructures and different processing methods did not alter the crystal structure of the main phase in the compositions.
4.3.4 Electronic transport properties

The variation of electrical resistivity across the temperature range is illustrated in Figure 4-24a. All the samples exhibited a downward relationship over the temperature range and behaved as semiconductors. The BSCO-1 has the highest resistivity values and BSCO-2 has the lowest values being similar to that of materials produced by the mixed-oxide route. This trend may be related to the differences in cell volumes, where different stoichiometry could lead to such high resistivity as seen in BSCO-1. Although the denser materials should conduct electricity better [211, 212] this is not the case here, therefore, other factors come into consideration. Since the primary phase is consistent in all compositions (ascertained from XRD/EDS), the grain size and grain roughness may be a possible reason for higher resistivity compared to mixed-oxide samples. The change in oxidation state of cobalt/oxygen vacancies, or oxygen deficiency, might be a contributing factor. Work on calcium cobaltite [213-216] suggested that the change in oxidation state of cobalt/oxygen vacancies could lead to a change in carrier concentration resulting in an increased resistivity. The reducing conditions of the SPS process are believed to change the oxidation state of cobalt/oxygen content. Similar research conducted by Rubesova et al. [152] using SPS method on Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ reported change of oxygen vacancy concentration and high resistivity values in unannealed samples. The SPS samples were then annealed in air to recover the lost
oxygen. The result of such annealing led to much lower resistivity. The minimum resistivity values here were obtained for BSCO-2, which is in the range of 30-40 mΩ.cm and is in the upper boundary of reported Bi$_2$Sr$_2$Co$_2$O$_y$ values [25, 168]. However, other samples have higher resistivity values as in the case of BSCO-1 (55-60 mΩ.cm) which is considered very high for this family of cobaltites.

![Graphs showing resistivity, Seebeck coefficient, and power factor vs. temperature](image)

*Figure 4-24 Electronic transport properties of SPS processed samples: a) Electrical resistivity, b) Seebeck coefficient, c) Power factor.*

The temperature dependence of thermopower is given in Figure 4-24b. The thermopower showed an interesting trend. Although all compositions seemed to have roughly equal values across measured temperature range which increased with temperature, it can be seen that the SPS samples have at least 10 μV/k higher thermopower than their MO counterpart at corresponding temperatures. This could be explained by a reduction of charge carrier concentration from a change in oxidation state of cobalt/oxygen content as a result of SPS processing. The values of 130-180 μV/K are amongst the highest Seebeck coefficient values reported in the literature. Comparing between the MO route and SPS samples, it can be seen that the SPS samples have inferior performance. Although SPS generated higher Seebeck coefficient, it is still not enough to compensate for a significant rise in resistivity values.
4.3.5 Thermal properties

The thermal conductivity values are illustrated in Figure 4-25a. The thermal conductivity of all sample are much higher compared to MO counterparts (Figure 4-25b). The trends showed that the thermal conductivity for BSCO-1 is lower than BSCO-0 and is in agreement with the oxide data. The combination of high density plus the higher contents of secondary phase could be reasons for an increase in values. Similar high thermal conductivity values between 2 and 2.5 W/m.K at room temperature was observed by Rubesova et al. in a Bi$_2$SrCoO$_{1.8}$ SPS samples [152]. Funahashi reported Bi$_2$Sr$_2$Co$_2$O$_y$ whisker samples had thermal conductivity around 2.0 W/m.K [26]. Combe et al. partial melting samples of Bi$_2$Sr$_2$Co$_2$O$_y$ had values around 1.5-2 W/m.K [140].

![Figure 4-25 Thermal conductivity of Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ composition through SPS as a function of temperature: a) SPS samples, b) SPS and mixed-oxide samples.](image)

4.3.6 Dimensionless figure of merit (ZT)

The figure of merit of bismuth strontium cobaltite ceramics is shown in Figure 4-26. The ZT of all samples steadily increases with temperature. The low thermal conductivity in BSCO-1 is helping this composition achieve a superior figure of merit in spite of the higher resistivity. The highest ZT of 0.06 was achieved in BSCO-2 SPS samples around 900 K. The figure of merit was lower than that reported by Rubesova et al. [152] for SPS fabrication of Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ which achieved a ZT of 0.024 at room temperature. In comparison the Ca$_3$Co$_4$O$_9$ fabricated by SPS by Zhang et al. [217] reached 0.23 at 1000 K. Similar values were also reported by Wu et al. (0.24 at 1000
K) [218]. The top values for the present samples, BSCO-2 are 0.06 at 900 K; this is on the lower edge of values for this composition.

Comparing the two processing methods, it can be seen that the figure or merit is much lower for SPS samples than that for MO samples, (ZT of 0.06 in SPS to 0.12 by the MO route at 900 K for BSCO-2 sample). This is due to higher resistivity values in SPS samples by a factor of 2-3 times. Although the SPS samples had higher Seebeck coefficient it was not sufficient to compensate for the increase in electrical resistivity and resulted in much lower power factor.

Figure 4-26 Figure of merit of Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ ceramics processed by SPS method as a function of temperature.

4.4 Conclusions

The doping of bismuth into bismuth strontium cobaltite (Bi$_2$Sr$_2$Co$_2$O$_y$) ceramics was investigated. The ceramics were manufactured by two different techniques: MO and SPS. The samples were all crack free with a relatively high density (~85, ~95% for MO and SPS respectively).

The microstructures of ceramics consisted of three phases. The main phase Bi$_{1.74}$Sr$_{2.82}$O$_2$ phase, a secondary phase of Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ and lastly CoO phase. Using XRD and SEM – EDS and TEM – SADP, it was demonstrated that the minor second phase in all samples is a rhombohedral type phase with a composition of Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$. The quantity of minor second phase increases as the amount of bismuth
increased. SEM images showed another secondary phase identified as CoO. However, with only one X-ray peak suggesting CoO, the data is not enough to confirm it. TEM-STEM analysis and Rietveld analysis of the main phase suggested that the main phase is, in fact, a Bi-deficient phase. This finding supports the purpose of Leligny et al [150, 159] for the composition of the main phase.

The MO samples showed a variation in electrical and thermal properties as a function of bismuth contents. The study concludes that a number of secondary phases might be a reason for such change. The BSCO-1 which contained a minor secondary phase showed the poorest electrical resistivity. However, due to its low thermal conductivity, a superior figure of merit was obtained. The BSCO-2 which had the most secondary phase was shown to have highest power factor, although with highest thermal conductivity. The highest power factor achieved for BSCO-2 makes this composition potentially suitable for the higher energy-demanded application. In conclusion, the doping by Bismuth led to superior thermoelectric properties.

It is difficult to determine which are the key physical properties affecting the thermoelectric properties for the MO samples, as one variable affect many parameters. However, the following factors are considered to be crucial to explain observed properties: First, denser materials (due to higher secondary phase content) showed better transport properties (Figure 4-14, Figure 4-16) than less dense materials, therefore it could be assumed that density along with secondary phase formation are one of the key parameters controlling the thermoelectric properties in this system. Secondly, BSCO-1 compositions have smaller minor second phases compared to BSCO-2. It is believed that minor second phase with smaller grain size could be the reason for low thermal conductivity (Figure 4-15) observed for BSCO-1, as smaller secondary phase size could help scattering the phonon due to higher amount of grain boundary interfaces.

The spark plasma sintering method yielded very dense samples (>95% theoretical density). Physical observation revealed they are crack free. The X-ray and SEM analysis showed different microstructures both in terms of morphology, size, and quantity. Quantitative analysis by Rietveld refinement showed a significantly increased presence of minor second phase, Bi_{0.75}Sr_{0.25}O_{1.375}, in all compositions. It was estimated that the amount of this phase increased by at least 5 % compared to their mixed-oxide
counterparts. The electrical resistivity of SPS prepared samples was much higher than that out mixed-oxide prepared samples; however, all samples exhibited semi-conducting like behaviour. Seebeck coefficients for SPS samples are also higher than that of mixed-oxide samples. All of this could be explained by a change in oxidation state of cobalt/oxygen vacancies from SPS fabrication. The trend for thermal conductivity data is identical for SPS and MO samples, however, the SPS values show a slight increase which is in accordance with higher density obtained in SPS samples. Lower power factor and high thermal conductivity resulted in a poorer figure of merit performance of SPS samples over MO samples.

Similar to the MO samples, it is difficult to determine which are the key physical properties affecting the thermoelectric properties for the SPS samples. However, the following factors are considered to be particularly important: First, higher thermopower and electrical resistivity (*Figure 4-24a, b*) for SPS samples were observed compared to MO samples. Based on this observation it could be then inferred that there was a lower number of charge carriers, possibly due to a change in main phase chemistry (oxidation state of cobalt/oxygen vacancies) from the SPS processing concentration. Secondly, there was higher thermal conductivity (*Figure 4-25b*) for SPS samples compared to MO samples; these changes in properties are attributed to higher amount of minor second phase and higher density in the SPS samples. Moreover, it could be assumed that the increase in the amount of the minor second phase does not play any significant role in altering the electronic transport properties, because no significant changes were observed in the electronic transport properties (*Figure 4-24a, b*) with respect to the amount of second phase, as a function of bismuth content.

Even though the initial assumption that higher density samples should give superior thermoelectric performance, it was proved that SPS samples did indeed give much higher denser samples at the expenses of secondary phase formation and a change in oxidation state of cobalt/oxygen vacancies. This suggests that heat treatment of SPS samples in air might improve the thermoelectric properties.
The final conclusion is that BSCO-2 showed a superior figure of merit performance both in MO and SPS processed samples. The BSCO-2 samples also yielded the highest power factor. All of this showed that bismuth doping had a positive effect on thermoelectric properties of bismuth strontium cobaltite ceramics and the properties could be tailored to suit the needs of relevant applications.
5. Characterisation of Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$ and Bi$_2$Sr$_2$Co$_{1.8}$O$_y$

Cobaltites

5.1 Introduction

After the investigation of the microstructure, crystal structure and thermoelectric properties of Bi$_{2+x}$Sr$_2$Co$_2$O$_{y}$ (x=0.0, 0.1, and 0.2), as reported in Chapter 4, it was decided that characterisation of the other two compositions in the bismuth strontium cobalt system (as highlighted in the literature review section, Chapter 2) would enhance the understanding. The compositions (formulations) are: Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$ and Bi$_2$Sr$_2$Co$_{1.8}$O$_y$. The first was proposed by Leligny et al. [150, 159] as the composition of the main phase in the bismuth strontium cobalt system and the second; the same as the first composition, but with excess bismuth. Both mixed-oxide (MO) and SPS routes were employed in the fabrication of the ceramics. The formulations and fabrication routes are listed in Table 5-1.

*Table 5-1 Bismuth strontium cobaltite compositions and their processing conditions.*

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Sample ID</th>
<th>Fabrication method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_{1.74}$Sr$<em>2$Co$</em>{1.8}$O$_y$</td>
<td>L-MO</td>
<td>MO</td>
</tr>
<tr>
<td>Bi$_{1.74}$Sr$<em>2$Co$</em>{1.8}$O$_y$</td>
<td>L-SPS</td>
<td>SPS</td>
</tr>
<tr>
<td>Bi$_2$Sr$<em>2$Co$</em>{1.8}$O$_y$</td>
<td>L-Bi-MO</td>
<td>MO</td>
</tr>
</tbody>
</table>

5.2 Bulk physical properties

All the samples were crack-free, dark grey in colour and uniform in shape. Samples prepared by the MO route showed low density whereas SPS route yielded highly dense samples in concurrent with the finding in Chapter 4. The density values are illustrated in Figure 5-1.
Figure 5-1 The effect of bismuth content and fabrication route and composition on the density.

5.3 X-ray diffraction analysis

X-ray diffraction (XRD) spectra for L-Bi-MO, L-MO, and L-SPS ceramics are shown in Figure 5-2. All the observed XRD spectra are in good agreement with the reported XRD spectra for similar compositions (Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ and Bi$_{1.76}$Sr$_2$Co$_{1.8}$O$_{7.64}$) [172, 173, 175, 180]. The majority of the peaks can be indexed as a misfit structure with monoclinic symmetry and $I2/a$ as space group. Consistent with the reported data, low-intensity diffraction peaks, arising from the Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ secondary phase, were detected in L-Bi-MO and L-SPS samples [172, 173]. However, in the spectra of L-MO, these peaks were absent. The intensity of the peaks for Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ secondary phase were the highest for L-SPS suggesting that the SPS fabrication method seemed to promote and enhance the formation of this minor phase. No peaks corresponding to CoO phase were detected in these samples, in contrast to the observation CoO phase in the compositions reported in Chapter 4.
Figure 5-2  XRD spectra for L-Bi-MO, L-MO and L-SPS ceramics. The XRD spectra show the formation of Bi$_{0.75}$Sr$_{0.25}$O$_{1.75}$ secondary phase in L-SPS samples marked by red stars. The peaks of the main phase are marked with black circles.

Figure 5-3 shows a Rietveld refinement of the crystal structure for L-MO. The crystal structure was refined using structural data from Leligny et al. [150, 159]. It can be seen from Figure 5-3 that there is a good fit ($R_{wp}$ 9.04) between the observed and calculated data. These finding also hold true with other two samples L-Bi-MO and L-SPS with their $R$-values and GOF listed in Appendix A (Table 10-4).

Similar to the observations in the refinements of the XRD data in Chapter 4, some of $(0 0 l)$ family reflections especially the $(0 0 10)$ do not fully match the experimental intensity data. Some sharp peaks could not be refined due to the high aspect ratio of (a-b/c) planes naturally occurring for the plate type grain shapes of the cobaltite materials. Similar difficulty regarding the plate shape and nature of crystal structure was also mentioned by Leligny et al. [150, 159] and Pelloquin et al. [178, 179], who were among the first to examine the crystal structure of bismuth strontium cobaltite compositions.
Figure 5-3 Rietveld refinement of L-MO sample. Experimental data is in black and the calculated fit is in red; the grey line shows the difference between the original and refined data. The black square is a reflection from the second minor phase.

The plot of refined lattice parameters for the three compositions is shown in Figure 5-4. All the lattice parameters show a different trend as a function of composition. No significant changes were observed in a-axis and the monoclinic angle, β, as a function of bismuth content (Figure 5-4a, and Figure 5-4d). The length of b-axis (Figure 5-4b) shows a decrease as Bi content increases for the MO compositions, whereas there is an increase in the length of c-axis (Figure 5-4c). Comparing the lattice parameters between L-MO and L-SPS samples, smaller structural parameters were observed for L-SPS samples in all samples (a-axis, and c-axis) except the b-axis and monoclinic angle ‘β’ which had larger values than its MO counterpart. However, when considering the uncertainty range, it can be seen that there are no significant differences between L-MO and L-Bi-MO for all the lattice parameters and monoclinic angle. Therefore, it could be argued that they both have similar crystal structures. All the lattice parameters values and the monoclinic angle for both L-MO and L-Bi-MO are in agreement with the results obtained in chapter 4; this further verified the conclusion that the samples in chapter 4 (BSCO-0, BSCO-1, and BSCO-2) and chapter 5 (L-MO and L-Bi-MO) have one common crystal structure.
Refined crystal structural parameters as a function of bismuth values: a) length of a-axis, b) length of b-axis, c) length of c-axis, d) value for $\beta$ angle.

Refined cell volume values for all 3 compositions are displayed in Figure 5-5. There is no clear indication of any trend as a function of Bi content, as L-MO and L-Bi-MO show similar cell volumes. However, comparing the L-MO and L-SPS samples, the SPS fabricated sample had a much smaller unit cell volume, similar to the result obtained in SPS section of the chapter 4. Similar unit cell volumes were obtained for all samples from chapter 4 and chapter 5, which is in accordance with the discussion in the lattice parameter section.
Figure 5-5 Refined cell volume of the samples as a function of the value of bismuth content.

5.4 Microstructure analysis

The (SE and BSE) SEM images for L-Bi-MO, L-MO, and L-SPS samples are presented in Figure 5-6. The images of both L-Bi-MO and L-SPS show dense samples with small amounts of intergranular pores. The presence of small amounts of pores support the density values presented in Figure 5-1.

Figure 5-6a is a SE image for L-MO sample. In the SE mode, only the main phase can be observed. The Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ phase, previously found in all other bismuth strontium cobalt compositions, was not observed in both SE, and BSE mode as shown in Figure 5-6b. The XRD and SEM data confirm that L-MO is single phase without the presence of any minor secondary phases (i.e. Leligny’s composition is a single phase if it is sintered in the air without pressure). BSE images for L-Bi-MO and L-SPS are shown in Figure 5-6(c, d). Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ was detected in both samples, albeit the amount of the phase seems to be not significant in both samples, which is in agreement with XRD analysis (lower than 5 volume %). No traces of CoO were observed in any of the samples. The appearance of dark phase seen in Figure 5-6d (arrowed) is thought to be residual carbon from the fabrication process. The main phase morphology observed is different in each sample. In L-MO sample, the main phase is seen as a flake-like structure rather than rectangular plate-shaped grains observed in L-Bi-MO. The
microstructure of L-Bi-MO also contains polygonal plate-shaped grains in addition to rectangular plate-shaped grains. It was difficult to define the grain morphology for L-SPS samples (Figure 5-6d). Grain size analysis was also performed on the main phase; however, due to non-uniform shape of the plates grain size was difficult. The calculated values are 7.4 μm for L-MO and 11.3 μm for L-Bi-MO.

![SEM micrographs: a) SE image of L-MO, b) BSE Image of L-MO in the same area as a); c) BSE image of L-Bi-MO, d) BSE image of L-SPS.](image)

**5.5 Electronic transport properties**

The temperature dependence of the resistivity of three compositions is presented in Figure 5-7a. L-Bi-MO and L-MO showed increasing resistivity values over the temperature range of the measurement in contrast to L-SPS which had a semiconducting like behaviour. This observation is in agreement with the findings for other compositions prepared using SPS fabrication method as reported in Chapter 4. It is evident from the resistivity data that the L-MO samples had a much higher resistivity, which could be a result of reduced density. The effect of density on electrical resistivity
of electroceramics has been explained by several authors [211, 212]. Figure 5-7a. shows that the higher bismuth value (L-Bi-MO) resulted in lower resistivity values.

Figure 5-7 Electronic transport properties of L-Bi-MO, L-MO and L-SPS ceramics as a function of temperature: a) electrical resistivity, b) Seebeck coefficient, c) power factor.

Comparing the resistivity data of this L-Bi-MO study with the literature data, Rasekh et al. [175] reported the resistivity to be around 80-90 mΩ.cm for air sintered samples and 30-45 mΩ.cm for laser melting technique samples over the temperature range of 300-1000 K. However, Sotelo et al., [173] using laser melting technique with addition of between 0-3 weight percent Ag, reported lower resistivity values of 18-20 mΩ.cm for the same composition and temperature range. Diez et al. [172] reported values of 27.5-45 mΩ.cm for the same composition using laser melting technique followed by annealing in air. In conclusion, the resistivity data from the present study for L-Bi-MO showed lower values than published samples processed by MO method, the values obtained in this study are comparable values to the samples manufactured by laser melting technique.
The temperature dependence of Seebeck coefficients is presented in Figure 5-7b. All the Seebeck values were positive, indicating that the compositions are p-type (hole conduction) thermoelectric material. The Seebeck coefficients for all samples increase steadily with temperature following the predictions of the Heikes formula [207]. The values for all three compositions are different from each other and there is a significant difference between them. The Seebeck coefficient was found to be strongly dependent on Bi content. In a collaborative study, the Seebeck coefficient values obtained by DFT calculations by Baran et al. [219] are in excellent agreement with these experimental data. The L-SPS sample had higher Seebeck coefficient (140-200 μV/K over 300-900 K) compared to that for the same composition prepared by the MO route. The change in Seebeck coefficient also coincided with the trend for the change in resistivity and suggested a change in concentration of charge carriers.

Comparing the Seebeck data of this L-Bi-MO study with the literature, Rebesova et al. [152] reported Seebeck values of 150-190 μV/K over 300-1000 K for cold pressed MO samples; values of 110-140 μV/K for hot pressed samples; and values of 140-190 μV/K for SPS samples. Rasekh et al. [175] reported Seebeck coefficients of 130-140 μV/K over a temperature range of 300-1000 K for air sintered MO sample; values of (120-200 μV/K) for samples prepared by laser melting technique. Diez et al. [172] reported Seebeck values of 130-140 μV/K over 300-1000K for samples prepared by the laser melting technique and annealed in air. However, Sotelo et al. [173] reported Seebeck values of 130-200 μV/K for Ag added Bi2Sr2Co1.8Oy composition using the same laser manufacturing technique over the same temperature range. Thus, these Seebeck data for L-Bi-MO lie in the same range as that of the published data.

Power factor data is presented in Figure 5-7c. The power factor values for L-Mo and L-SPS were similar and in the range of 0.00002-0.00004 W/m.K². However, L-Bi-MO sample showed the superior value of power factor for all measured temperatures (0.00009 W/m.K² to 0.00013 W/m.K²). Comparing this power factor data of this for L-Bi-MO, L-MO, and L-SPS with the literature; to the author’s best knowledge, there is no publication data regarding power factor for L-MO compositions. For L-Bi-MO, Diez et al. [172] reported values of 0.00004-0.00006 mW/m.K² for laser melting manufactured Bi2Sr2Co1.8Oy samples, Rasekh et al. [175] reported values of 0.00002-0.00005 mW/m.K² for air sintered samples, and 0.0001-0.0002 mW/m.K² for samples.
processed by laser melting technique. Sotelo et al. [173] reported values of 0.00010-0.00015 mW/m.K² for samples processed by laser melting technique. Therefore, our power factor values are a little higher than the published samples processed by laser melting technique.

5.6 Thermal properties

The heat capacity values for the samples as a function of temperature are illustrated in Figure 5-8a. As expected the $C_p$ values increased with temperature and were in the range of 0.35 to 0.5 J/g.K. Thermal diffusivity of the samples as a function of temperature is given in Figure 5-8b. The values showed a decreasing trend with increasing the temperature. This is expected and could be attributed to increasing phonon-phonon scattering on increasing the temperature. L-MO samples showed very low thermal conductivity values compared to L-Bi-MO values; the lower density could be the reason for this. Despite having a much higher density, L-SPS samples yielded a lower thermal diffusivity values. The cause of this is thought to be the difference in bismuth content which changes the charge carrier concentration, as described in the electronic transport section (section 5.5).

Thermal conductivity data are presented in Figure 5-8c. All samples exhibited very low thermal conductivity values of less than 1 W/m.K. No thermal conductivity data has been reported for these compositions and the values are similar to the thermal conductivity of BSCO-0 composition reported in Chapter 4. The electronic thermal conductivity was significantly less pronounced in both L and L-SPS samples due to their high resistivity suggesting that the phonon contribution to the thermal conductivity has the highest effect on the total thermal conductivity, not the electronic thermal conductivity. The electronic thermal conductivity was for L-Bi-MO was of the order of 0.1-0.05 W/m.K and 0.01-0.001 W/m.K for L and L-SPS. Compared to other literature, these values are lower than that reported by Shen et al. [170] for Bi$_2$Sr$_{2-x}$La$_x$Co$_2$O$_y$ (x = 0, 0.02, 0.04, 0.08) compositions. Combe et al. [140] also reported similar values of 0.8-1.0 W/m.K for air-sintered Bi$_2$Sr$_2$Co$_2$O$_y$. However, it was reported [140] that hot pressing Bi$_2$Sr$_2$Co$_2$O$_y$ could raise the thermal conductivity to 1.5- 2.0 W/m.K which is similar to values reported for Bi$_2$Sr$_2$Co$_2$O$_y$ whiskers [26].
Figure 5-8 Thermal properties of L-Bi-MO, L-MO and L-SPS ceramics as a function of temperature: a) heat capacity, b) thermal diffusivity, c) thermal conductivity.

5.7 Thermoelectric figure of merit (ZT)

The figure of merit for L-Bi-MO, L-MO, and L-SPS ceramics are presented in Figure 5-9. It can be seen that the increase in bismuth content on composition of L-Bi-MO resulted in an improved figure of merit, reaching 0.16 at 870 K. The figure of merit was almost doubled when compared to initially reported values of 0.06 in Bi$_2$Sr$_2$Co$_2$O$_y$ composition by Funahashi et al. [25] and Yin et al. [25, 168]. However, it is still inferior to that of Bi$_2$Sr$_2$Co$_2$O$_y$ doped with Ag, having a ZT of 0.23 [169]. It is also lower than that of Bi$_2$Sr$_2$Co$_2$O$_y$ samples prepared by partial melting fabrication process investigated by Comb et al. (ZT of 0.23) [140]. The figure of merit for L-MO composition has not been reported elsewhere, therefore, it is believed that this is the first time that the figure of merit for this particular composition has been reported. The low values of 0.01-0.02, over the temperature range of 300-1000 K, is the result of the low density. Although the SPS fabricated L-SPS sample, has similar ZT values to the L-MO, it is believed that
upon further annealing higher ZT values could be achieved due to the recovery of oxygen vacancies and/or a change in oxidation state of Co.

Figure 5-9 Figure of merit for L-Bi-MO, L-MO and L-SPS as a function of temperature.

5.8 Conclusions

The microstructure and thermoelectric properties of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ and $\text{Bi}_{1.74}\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ were examined. The presence of excess bismuth in L-Bi-MO helped to improve the density by the formation of $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375}$. The microstructure of L-Bi-MO is a mixture of rectangular and polygonal plate-shaped grains in contrast to the flake-like grains in L-MO. The improvement in density and microstructure resulted in higher power factor albeit increasing the thermal conductivity. As a result, a high ZT of 0.16 at 900 K was achieved, compared to 0.03 for L-MO samples.

The effect of the fabrication process on $\text{Bi}_{1.74}\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ was examined. The low density of L-MO samples (~60% theoretical density) was rectified by using SPS fabrication technique, achieving 95% of the theoretical density. It is believed that L-MO samples are single phase without any secondary phase when sintered in air without any applied pressure. However, in the L-SPS samples, traces of $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375}$ phase were detected.

The correlation between physical properties and thermoelectric properties may be established using the hypothesis that the following factors are crucial for the explanation
of observed properties: First, samples with excess Bi content (L-Bi-MO), which are denser compared to L-MO, show lower electrical resistivity (Figure 5-7a). Based on this result it can be assumed that the density is one of the key parameters that affect thermoelectric properties of this system. Second, the changes in oxidation state of cobalt/oxygen vacancies, which inherently affects the charge carrier concentration, can be used to explain the electronic transport properties (Figure 5-7a, b) of L-SPS compared to L-MO due to the increased electrical resistivity and thermopower observed in L-SPS samples, which is considered to have lower charge carrier concentration. Third, it is believed that the effect of minor second phase on transport properties can be neglected as L-Bi-MO, L-MO and L-SPS samples contain very limited amounts of second phase.

L-SPS samples exhibit superior Seebeck coefficients compared to L-MO and L-Bi-MO samples; however, L-SPS samples have high electrical resistivity and thermal conductivity resulting in a poor ZT of 0.04 at 900 K. It is believed that upon further annealing the ZT values of L-SPS samples could be improved significantly. Excess Bi-containing samples of L-Bi-MO showed the highest ZT of 0.16 at 900 K.
6. The effect of Bi substitution and fabrication technique of the microstructure and thermoelectric properties of calcium cobaltites (Ca$_{3-x}$Bi$_x$Co$_4$O$_9$) $x = 0.0$ and $0.3$

6.1 Introduction

The misfit calcium cobaltite oxides are one of the most effective $p$-type oxide materials for thermoelectric applications, and several experimental and computational studies have examined its properties and microstructure [19, 115, 127-130, 132, 134, 135, 139, 213, 216, 217]. Several reports have suggested that doping of bismuth is one way of improving the physical properties and thermoelectric performance of calcium cobaltite [131, 161]. Advanced processing techniques such as SPS also yield higher density in several ceramic materials [203, 217, 218]. In this chapter, the combined techniques of doping and SPS technique coupled with advanced microstructure characterisation technique have been employed. For comparison purposes, samples prepared by SPS have also been prepared by the MO route. The samples and their preparation methods are listed in Table 6-1.

*Table 6-1 Formulations and processing methods.*

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Fabrication method</th>
<th>Sample ID</th>
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<tr>
<td>Ca$_3$Co$_4$O$_9$</td>
<td>MO</td>
<td>CCO-MO</td>
</tr>
<tr>
<td>Ca$<em>{2.7}$Bi$</em>{0.3}$Co$_4$O$_9$</td>
<td>MO</td>
<td>CBCO-MO</td>
</tr>
<tr>
<td>Ca$_3$Co$_4$O$_9$</td>
<td>SPS</td>
<td>CCO-SPS</td>
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<tr>
<td>Ca$<em>{2.7}$Bi$</em>{0.3}$Co$_4$O$_9$</td>
<td>SPS</td>
<td>CBCO-SPS</td>
</tr>
</tbody>
</table>

6.2 Bulk physical property and density

All the samples were dark grey to black in colour, crack-free and uniform in shape. The density values are illustrated in *Figure 6-1*. The MO prepared CCO and CBCO samples showed very low density; pure calcium cobaltite manufactured through the mixed-oxide route has the low density of 3.30 g/cm$^3$ equivalent to 70 % of the theoretical density.
CCO-MO sample shows low mechanical strength due to its low density. Substitution with Bi increases the density of the samples prepared by the MO route to 4.01 g/cm³ equivalent to 85% of the theoretical density. However, the obtained densities are still well below the theoretical density of 4.68 g/cm³ [134]. These data are consistent with literature density data for calcium cobaltite ceramics prepared by the MO route [131, 161, 220]. Use of a chemical route or hot pressing route has been beneficial for high density calcium cobaltite ceramics [128, 132, 138]. In view of the low densities encountered for the CCO and CBCO samples prepared by the MO method, SPS sintering has been employed for both CCO and CBCO in this study. High densities of 4.49 and 4.65 g/cm³ were obtained for CCO and CBCO ceramics respectively, which corresponds to almost 100% theoretical density.

Figure 6-1  Density as a function of bismuth content $x$ for $\text{Ca}_{3-x}\text{Bi}_x\text{Co}_4\text{O}_9$ ceramics.

6.3 X-ray diffraction analysis

XRD spectra for CBCO-MO, CCO-SPS, and CBCO-SPS ceramics are shown in Figure 6-2. The XRD spectra for all three samples are in good agreement with the reported XRD spectra [117, 134, 135] and can be readily indexed. For all three samples, the majority of the peaks can be indexed as a misfit structure with monoclinic symmetry and $C12/m1$ as space group using structural data from Grebille et al. [117] (ICSD number 55458). In agreement with the reported data, a low-intensity diffraction peak
arising from a secondary phase was also detected in both CBCO-MO and CBCO-SPS samples. The peak for this secondary phase was observed at 15.9 degrees. Using XRD and EDS techniques Li et al. [161] deduced that this secondary phase is Bi\(_2\)Ca\(_2\)Co\(_2\)O\(_y\). The CCO-SPS samples appeared to be a single phase with no extra peaks from secondary phases.

High-Intensity peaks of the (00l) family were observed in spectra of both SPS samples, combined with low-intensity peaks in other directions. These indicated that both SPS samples were highly textured. The Lotgering factor [162], \(F = \frac{(p-p_0)}{(1-p_0)}\) where \(p = \frac{\Sigma I(00l)}{\Sigma I(hkl)}\) (\(\Sigma I = \) sum of the XRD peak intensity of sample), and \(p_0 = \frac{\Sigma I_0(00l)}{\Sigma I_0(hkl)}\) (\(\Sigma I_0 = \) sum of the XRD peak intensity of powder), was used to calculate the degree of orientation in SPS samples. It was found that the Lotgering factor for CBCO-SPS is 0.72 and 0.95 for CCO-SPS.

![Figure 6-2 XRD Spectra of CBCO-MO, CBCO-SPS, and CCO-SPS. The main phase is indexed, secondary phase is marked as a red square. Note: the absence of CCO-MO spectrum is due to its low mechanical strength as mentioned in density section (section 6.2)](image)

Figure 6-3 shows a Rietveld refinement for a CBCO-SPS spectrum. The crystal structure was refined using \(C12/m1\) space group. The refinement was based on Ca\(_3\)Co\(_{3.93}\)O\(_{9.36}\) composition [117]. It can be seen from the figure that there is a good fit (\(R_{WP} 3.16\)) between the observed and calculated data. These findings also hold true for
the other two samples, CBCO-MO and CCO-SPS with their R-values and GOF listed in Table 6-2. However, similar to observations for bismuth strontium cobaltite (Chapter 4 and 5) the intensities of some of the (0 0 1) family of reflections, especially the (0 0 2), do not fully match the refinement. The high aspect ratio grains common to cobaltite materials might be the cause of these high intensities peaks which cannot be properly be taken into account in the refinement.

Figure 6-3 Rietveld refinement of CBCO processed by SPS. Experimental data is in black and the calculated fit is in red, the grey line shows the difference between the original and refined data.

Table 6-2  R-values and goodness of fit (GOF) values from Rietveld refinement of SPS processed samples. The GoF values are artificially high because of the $R_{exp}$ obtained on XRD.

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<td>2.94</td>
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<td>CCO-SPS</td>
<td>1.13</td>
<td>3.16</td>
<td>1.95</td>
<td>2.8</td>
</tr>
</tbody>
</table>

The refined lattice parameters of CCO-SPS were similar to the lattice parameters of the original crystallographic data from Miyazaki et al. and Grebille et al. [117, 135] as can be seen in Appendix A, Table 10-5. For the CBCO-MO, there was an increase in the lattice length in both ‘b’ and ‘c’ directions compared to that for CCO-SPS; however smaller ‘a’ length and monoclinic angle, $\beta$, were observed. For CBCO-SPS, there is an increase in the ‘a’ and ‘c’ length, while there are a reduction in ‘b’ lattice length and
monoclinic angle, \( \beta \), compared to that for CCO-SPS. These results indicate that the change in lattice parameters was caused by bismuth doping and the different processing route. However, there were no significant changes in the atomic positions and their occupancies for all three compositions. The SPS sample also yielded smaller unit cell volumes, similar to results found in BSCO-0, BSCO-1 and BSCO-2 samples (chapter 4).

*Figure 6-4* shows a Rietveld refinement of the crystal structure of the synchrotron data (collected from I11 station) for CCO-MO. The experimental peaks are very sharp and well defined. All peaks observed belong to calcium cobaltite phase. The refinement procedure was the same as mentioned in the previous section (section 6.3). The \( R \)-values and GOF are listed in Appendix A, *Table 10-6*. GOF values of 2.38 demonstrated a very good fitting between the experimental and refinement curve. However, similar to the refinement of the data for the Cu-radiation sauce, some of \((001)\) family of reflections especially the \((002)\) did not fully match the experimental intensity due to a high degree of anisotropy in grains as highlighted before. The refined atomic positions are also shown in *Table 10-6*, which are well in agreement with Cu-radiation data presented in *Table 10-5*. 
6.4 Microstructure analysis

SEM images for CBCO-MO, CBCO-SPS and CCO-SPS are presented in Figure 6-5. The images show large amounts of intergranular pores in the CBCO-MO sample, in contrast to the highly dense samples of CBCO-SPS and CCO-SPS (Figure 6-5c and Figure 6-5d). The SEM data confirmed the density values presented in Figure 6-1.

In SE- and BSE-SEM images for CBCO-MO sample (Figure 6-5a, Figure 6-5b) only one main phase, with plate-shaped grains was observed. Figure 6-5c shows a BSE image of CBCO-SPS; the main phase and two minor secondary phases can be seen. One of the minor phases has a localised distribution and is slightly darker in colour compared to the main phase (red arrows). The second minor phase, bright in colour, appears as curved plate shapes (blue circle). In Figure 6-5c, it can be seen that the grains of the main phase have plate shape morphology and are aligned in a horizontal direction. A BSE image for CCO-SPS is shown in Figure 6-5d; the sample has similar microstructure to the CBCO-SPS sample without the presence of any minor second phase. This indicates that in the calcium cobaltite system, grain oriented microstructures can be achieved by SPS technique.
EDS analysis was performed on the CBCO-SPS Sample. Both bright and dark secondary phase were too small for reliable quantitative chemical analysis. However, EDS mapping (Figure 6-6) suggested that the bright phase is composed of Bi, Ca, Co, and O, and the dark phase composed of only Co and O. On the basis of EDS and XRD analysis it is likely that the bright phase is $\text{Bi}_2\text{Ca}_2\text{Co}_2\text{O}_y$, in agreement with the work of Li et al. [161].
Figure 6-6 EDS mapping of a CBCO-SPS sample: a) the region where the EDS mapping has been performed showing Calcium (red), Cobalt (cyan), and Bismuth (purple) distribution. Red ellipsoid indicates the Co-rich area, blue ellipsoid indicates Bi-rich area.

The presence of the Bi-containing secondary phase, in CBCO-SPS samples, could be a result of the effect of pressure during the fabrication process, or the solubility of Bi in Calcium cobaltite, which might be less than 0.3 as similar observation was reported by Li et al. [161]. Grain size analysis was also performed on the main phase; The calculated values are 18.1 μm, for CBCO-MO; 7.3 μm for CBCO-SPS and 12.5 μm for CCO-SPS.

A crystal structure investigation was conducted by TEM, to further verify the formation of the misfit structure of the CCO-MO sample. A selected area diffraction pattern (SADP) for CCO-MO sample is shown in Figure 6-7.

The reflections in the diffraction pattern can be indexed as [001] zone axis of a misfit type structure. The diffraction pattern consists of two district sets of diffraction spots arising from rock salt (white circles) and CoO$_2$ sub-structures (red circles). The
The diffraction pattern is very similar to the diffraction pattern observed by Seo et al. [221] for Ca$_3$Co$_4$O$_9$.

![Diffraction pattern image]

*Figure 6-7 [001] SADP for CCO-MO. The diffraction pattern can be indexed as a misfit type structure.*

Further crystal structure investigation was conducted by atomic resolution Z-contrast imaging using STEM (Figure 6-8). The contrast in the image is sensitive the Z-number of the atoms in the structure, therefore the bright atomic columns represent Co atoms ($Z_{Co}=27$) and darker atomic columns represent Ca atoms ($Z_{Ca}=20$). The image is characterised by regular and repeated structural sequence with separation of 10.8 Å representing the length of c-axis deduced by XRD study. Therefore, the image provides direct evidence of the formation the misfit type crystal structure.
Figure 6-8 [010] HAADF image for CCO-MO showing Co columns in CoO₂ layers; and Co and Ca atomic columns in rock salt layers in the misfit type structure, provided by F. Azough.

6.5 Electrical properties

The transport properties for CBCO-MO, CBCO-SPS, and CCO-SPS are presented in Figure 6-9. The CBCO, CBCO-SPS, and CCO-SPS showed resistivity values which reduced with increasing temperature, which is semi-conducting like over the temperature range of the measurement. It is evident from the resistivity data that the bismuth containing samples (CBCO-MO and CBCO-SPS) exhibit higher resistivity due to the contribution of the excess carriers generated by bismuth doping. Another possible contribution to the low resistivity is the high density of the CBCO-SPS samples. The SPS samples would, therefore, have much lower resistivity, as evident in both SPS samples compared to the MO samples. The change in oxidation state of cobalt/oxygen vacancy content as a result of SPS fabrication might also be a reason for a change in resistivity [220]. The resistivity values range between 6 - 15 mΩ.cm for all the samples. These are well within the range of other reported values for calcium cobaltite ceramics. However, the CCO-SPS samples were one of the lowest values reported in the literature [20, 90, 129, 132, 133, 161].
Figure 6-9 Thermoelectric properties of CBCO-MO, CBCO-SPS and CCO-SPS Ceramics as a function of temperature: a) electrical resistivity, b) Seebeck coefficient, c) power factor.

All the Seebeck values are positive (Figure 6-9b), indicating that the compositions are $p$-type (hole conduction) thermoelectric materials. The Seebeck coefficients increase steadily with temperature followed the Heikes formula [207]. It can be seen that the bismuth containing SPS samples have at least 10 $\mu$V/k higher thermopower (Figure 6-9b) than CCO-SPS counterpart at the corresponding temperature. This could be explained by reduced charge carriers found in the bismuth doping samples and/or a change in oxidation state of cobalt/oxygen vacancies as mentioned in the resistivity section. The change in oxidation state of cobalt/oxygen vacancies content could give rise to higher Seebeck coefficients at the expenses of resistivity.

Power factor data are depicted Figure 6-9c. The combined data of Seebeck and resistivity showed a superior value of power factor for CCOS-SPS ranging from 0.0002 W/m.K$^2$ at room temperature to 0.0004 W/m.K$^2$ at 850 K.
Comparing the results of this study with the published data, Li et al. [161] reported values of 0.00005-0.00006 W/m.K² for Ca₃Co₄O₉ and 0.00006-0.00015 W/m.K² for Ca₂₋₇Bi₀₋₃Co₄O₉ composition. Moser et al. [220] reported values of 0.00011-0.0002 W/m.K² in composition of Ca₃₋₃BiₓCo₄O₉ (x=0-0.2). Xu et al. [138] reported values of 0.00013-0.00016 W/m.K² and 0.00016-0.00025 W/m.K² in hot pressed Ca₃Co₄O₉, and Ca₂₋₇Bi₀₋₃Co₄O₉ samples respectively. The values of 0.00018-0.0027 W/m.K² were found by Zhange et al. [203] in Ca₃Co₄O₉ fabricated from SPS method. Hence, the values of power factor obtained in this study are higher than those reported in the literature both for the MO sample and SPS samples especially CCO-SPS due to better processing conditions.

6.6 Thermal properties

The heat capacity values for CBCO-MO, CBCO-SPS, and CCO-SPS are presented in Figure 6-10a. The Cₚ values demonstrated the expected increase over the temperature range, [209]. The Cₚ of all three materials were in the range of 0.5 to 0.8 J/g.K. Thermal diffusivity of all CCO ceramics samples as a function of temperature is given in Figure 6-10b. The values decrease with increasing temperature. This could be attributed to an increase in phonon-phonon scattering on increasing the temperature. Comparing the behaviour of CBCO-SPS and CCO-SPS samples, it suggested that the bismuth doping could lead to lower thermal diffusivity. The presence of a small amount of secondary phase could also be a factor in enhancing grain boundary scattering of phonons which results in lower thermal diffusivity of CBCO-SPS. In addition, thermal diffusivity may be affected by the change of grain shape [210]. CBCO-MO had a much lower thermal diffusivity than the CBCO-SPS sample. The difference in grain morphology and density between MO and SPS could result in such different values.
Thermal conductivity data are presented in Figure 6-10c. All samples exhibit very low thermal conductivity values of less than 2 W/m.K. These low values can be explained by the material structure, the alternating layers between rock salt and hexagonal structure can enhance phonon scattering as described by Funahashi et al. [26]. The unexpectedly low values observed in CBCO-MO samples are attributed to the low density of materials. The thermal conductivity values are in the range of 1.5-2 W/m.K in CBCO-SPS and CCO-SPS samples and around 1 W/m.K in CBCO-MO sample.

Comparing with the literature, values of 1-1.2 W/m.K for Ca$_3$Co$_4$O$_9$ and 1.75-2 W/m.K in Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$ were reported by Li et al. [161]. Xu et al. [138] reported similar values of 1.8-2 W/m.K in Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$ composition produced by hot-pressing. Shikano et al. [137] reported values of 3.5-3 W/m.K for single crystal Ca$_3$Co$_{3.638}$O$_{8.776}$. Moser et al. [220] reported values of 2-2.5 W/m.K in Ca$_3$Co$_4$O$_9$ and 1.4-1.5 W/m.K in Ca$_{2.95}$Bi$_{0.05}$Co$_4$O$_9$ composition. Values of 1.65-1.7 W/m.K were found for Ca$_3$Co$_4$O$_9$ fabricated by SPS method by Zhange et al. [203]. The values of thermal conductivity
obtained in this study for CBCO-MO are lower than the published data. However, the values for both the CCO-SPS and CBCO-SPS samples are in good agreement with values reported in the literature.

6.7 Summary of thermoelectric properties

From the results obtained, it can be concluded that substitution of bismuth into calcium cobaltite ceramics did have a major impact on thermoelectric properties. The Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$ (CBCO-MO) samples have improved power factor and thermal conductivity compared to Ca$_3$Co$_4$O$_9$ MO samples [20, 138, 161, 203, 217, 220]. The processing method also has an impact on thermoelectric properties. The power factor of the SPS samples, CBCO-SPS was much higher than that of samples produced by MO method despite their higher thermal conductivity. The post annealing of SPS samples in an oxygen rich atmosphere could have led to better thermoelectric properties [161]. However, due to limited access time to relevant facilities, it could not be carried out, but is recommended for further experimental work.

6.8 Figure of merit

The Figure of merit for calcium cobaltite ceramics are presented in Figure 6-11. The values increase with increasing temperature. CCO-SPS samples showed a superior figure of merit compared to CBCO-SPS samples due to superior power factor despite having higher thermal conductivity. The highest ZT value obtained was 0.25 for CBCO-SPS at 900 K. In comparison, Wang et al. [222, 223] reported a high ZT of 0.4 at 950 K for Ca$_{3-x}$M$_x$Co$_4$O$_9$+d (M= Dy, Eu x=0,0.15, 0.3,0.25) prepared by sol-gel powders and SPS. Li et al. [161] reported a ZT of 0.18 at 900 K for Ca$_{2.5}$Bi$_{0.5}$Co$_4$O$_9$ prepared by MO route and sintered under oxygen atmosphere. Shikano et al. [137] reported the highest ZT of 0.9 at 1000 K for a single crystal of Ca$_{3}$Co$_{3.638}$O$_{8.776}$. Xu et al. [138] reported a ZT of 0.25 and 0.32 for hot-pressed Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$ and Ca$_{2.4}$Bi$_{0.3}$Na$_{0.3}$Co$_4$O$_9$ at 900 K respectively. ZT of 0.2 at 9000 K was reported by Moser et al. [220] in Ca$_{2.8}$Bi$_{0.2}$Co$_4$O$_9$ composition. Zhang et al. [203] reported ZT values of 0.25-0.23 in Ca$_3$Co$_4$O$_9$ SPS samples. Whilst the highest ZT values obtained in this investigation is of 0.25 for CCO-SPS at 900 K, it is believed that additional annealing of SPS samples under oxygen [161] may lead to higher ZT values.
6.9 Conclusions

The substitution of bismuth had a major impact on the final densities of the calcium cobaltite ceramics. The power factor and figure of merit of bismuth doped samples (CBCO-MO) were higher than for pure \( C_{33}C_{04}O_{9} \) samples.

On the fabrication process, the SPS method yielded a superior density closer to 100% theoretical density. The polished microstructure of SPS samples revealed a preferred orientation growth in the microstructure. From the Lotgering calculation, it was found that CCO-SPS sample has a higher degree of preferred orientation than the CBCO-SPS. The secondary phase presents in CBCO-SPS samples might disturb the growth of preferred orientation structures. The resistivity data for both SPS samples are lower than the MO sample data, because of the SPS fabrication process (high density, preferred orientation microstructure). However, it was found out that CBCO-SPS sample has higher resistivity values than CCO-SPS; the latter is one of the lowest observed in cobaltite due to better processing technique. The presence of secondary phase was believed to be a cause of higher resistivity values and less anisotropy in CBCO-SPS. Seebeck coefficients in CBCO-SPS, which are amongst the highest values reported, were found to be superior to both CCO-SPS and CBCO-MO. In this instance, it believed that the doping of bismuth into the CBCO-SPS main phase and the SPS fabrication were the reason of higher Seebeck values. Figure of merit of SPS samples were found to be superior compared to that of the MO samples due to their much higher
power factor, one of the highest reported in cobaltites, despite higher thermal conductivity. The ZT of 0.25 was archived in CCO-SPS sample at 900 K.

The correlation between physical properties and thermoelectric properties of calcium cobaltite may be established using the hypothesis that the following factors, which are similar to the factors affecting the properties of bismuth strontium cobaltite ceramics, are crucial for the explanation of observed properties. Firstly, samples prepared by SPS show higher density compared to MO samples (Figure 6-1) and this results in reduced electrical resistivity. Therefore, the density of this type of cobaltite can be assumed to be the one of the most important parameter that affects the thermoelectric properties. Secondly, the observed electrical resistivity and thermopower values (Figure 6-9a, b) of samples prepared by SPS and MO suggest that it is difficult to identify the exact mechanism behind the improvement in properties as both Bi substitution and a change in oxidation state of cobalt/oxygen vacancies from the SPS processing can alter the carrier concentration. However, it is believed that thermal treatment of SPS samples in an oxygen rich atmosphere can be used to modify oxygen vacancy concentration, as suggested in literature [161], and hence to enhance the thermoelectric properties of SPS samples. Finally, the presence of a secondary phase has a detrimental effect on texturing by SPS, which is evident from Lotgering calculation in Section 6.3, although it can help to improve the densification of the samples by MO.
7. In-situ study of Bi$_2$Sr$_2$Co$_2$O$_y$ and Ca$_3$Co$_4$O$_9$ by high resolution synchrotron X-ray diffraction

7.1 Introduction

One major application area for oxide thermoelectric is in devices that are required to function in high temperature (~ 900 K) environments. The main criteria for the material are chemical stability, and sufficient mechanical strength to be able to operate in demanding environments. Also, it is important to know the coefficient of thermal expansion, which is an important parameter in the design of thermoelectric units. So far in this study, the crystal structure of bismuth strontium cobaltite ceramics at room temperature has been investigated and to the best of the authors' knowledge, there is no reported data in the literature on the high temperature structural characteristics of bismuth strontium cobaltite and calcium cobaltite. In this chapter, samples of BSCO-0 and CCO-MO were examined by high resolution powder diffraction at station I11 of Diamond Light Source, to investigate changes in the crystal structure and structural parameters in the 300-1200 K temperature range. The results could further advance the understanding of the BSCO-0 and the CCO-MO cobaltites regarding their crystal structural and phase evolution at high temperature and will enable us to obtain thermal expansion data at higher temperatures.

7.2 Analysis of Bi$_2$Sr$_2$Co$_2$O$_y$ ceramics

X-ray diffraction (XRD) spectra for BSCO-0 as a function of temperature, from 298 to 1173 K, is shown in Figure 7-1. Analysis of the diffraction spectra reveals that for all the temperatures, the main phase can be indexed and refined as a misfit type structure as described in detail in Chapter 4. Two secondary minor phases (i.e., Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$, and CoO) that were identified and characterised at room spectrum of BSCO-0 in Chapter 4 were observed at all the measured temperatures up to 1073 K. Qualitative phase analysis of CoO, and Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ secondary phases were not possible due to limited signal, as previously stated in Chapter 4. Their contents remained similar for all the measured temperatures up to 1073 K. However, it is believed that minor phase 1 (CoO) and 2 (Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$) start to disappear at 1073 K, coinciding with the formation of minor
phase 3 at high temperature (1073-1173 K). The Rietveld refinement for the main phase is reported, followed by the characterisation of the third minor phase.

Figure 7-1  High resolution X-ray spectra for BSCO-0 ceramics from 298 to 1173 K showing reflections from the main phase in the whole temperature range of measurement.

The XRD spectra for the main phase was successfully refined using Leligny’s structural data [150, 159] for all the measured temperatures. There is a good fit (R_{\text{wp}} 13.17, GOF 1.39) between the observed and calculated data at room temperature. Similar fit values, GOF between 1.4-1.7, were observed for BSCO-0 at all temperature, except at temperatures above 1073 K, where GOF increased to 1.91 at 1073 K and 2.29 at 1173 K. The refinement showed that there were changes in lattice parameter but no significant changes in atomic positions and atomic occupancies (Appendix A, Table 10-7). Therefore, it could be concluded that the main phase of BSCO-0 remained stable up to 1173 K.

After refinement of the main phase, attention was paid to the characterisation of the minor third phase evaluation, both its content and structure.

Figure 7-2 shows Rietveld refinement of the crystal structure for BSCO-0 at higher temperatures of 1073, 1123, and 1173 K associated with the formation of the minor
third phase. The peaks from the third minor phase are marked as red stars (Figure 7-2(b, c)). The new phase could not be unambiguously identified as there are insufficient reflection peaks. However, by matching the peaks of minor phase 3 using Philips® X’Pert HighScore Plus’s ICDD database, possible phases were identified as listed in Table 7-1.
Figure 7-2 XRD spectra and refinement information for BSCO-0 showing the evolution of the third minor phase: a) 1073 K, b) 1123 K, and c) 1173 K. Experimental data is in black and the calculated fit is in red, grey line shows the difference between the original and refined data. The red stars indicate peaks from an unidentified minor third phase.

From the list of candidates presented in Table 7-1, it is in the Author’s opinion that the most likely formulation for the minor phase 3 is Bi$_{12.71}$Co$_{0.3}$O$_{19.35}$. Due to the formation temperature of this phase coinciding with the dissolving of minor phase 1 and 2, then bismuth and cobalt element could diffuse into minor phase 3. The Rietveld refinement was performed, using CIF files for compositions Bi$_{12.71}$Co$_{0.3}$O$_{19.35}$ and Bi$_{12.22}$Sr$_{0.78}$O$_4$ (no CIF available for composition Bi$_{1.26}$Sr$_{0.74}$O$_{2.63}$). These high temperature phases did show a high GOF, therefore, a definite conclusion cannot be reached, as there are too many ambiguous peaks still left unrefined.
Table 7-1 Possible phases for high temperature minor phase 3. The ICSD number, formula, crystal system, and space group are included. The three strongest peaks with their corresponding hkl are also included.

<table>
<thead>
<tr>
<th>Structure and chemical information</th>
<th>Main (hkl) reflections</th>
<th>2Theta of the main peaks (°)</th>
<th>References</th>
</tr>
</thead>
<tbody>
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<td>Formula: Bi\textsubscript{12.71}Co\textsubscript{0.3}O\textsubscript{19.35}</td>
<td>310</td>
<td>27.1</td>
<td>ICSD Number: 81412</td>
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<tr>
<td>Crystal system: Cubic</td>
<td>321</td>
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<tr>
<td>Space group: \textit{I}2\textit{3}</td>
<td>134</td>
<td>52.4</td>
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</tr>
<tr>
<td>Formula: Bi\textsubscript{2.22}Sr\textsubscript{0.78}O\textsubscript{4}</td>
<td>012</td>
<td>26.645</td>
<td>ICSD Number: 15976</td>
</tr>
<tr>
<td>Crystal system: Rhombohedral</td>
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</tr>
<tr>
<td>Space group: \textit{R}\textbar{3}m</td>
<td>015</td>
<td>30.310</td>
<td></td>
</tr>
<tr>
<td>Formula: Bi\textsubscript{1.26}Sr\textsubscript{0.74}O\textsubscript{2.63}</td>
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<td>29.031</td>
<td>ICDD Number: 00-046-0484</td>
</tr>
<tr>
<td>Crystal system: Cubic</td>
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<td></td>
</tr>
<tr>
<td>Space group: \textit{Im}\textbar{3}m</td>
<td>211</td>
<td>51.451</td>
<td></td>
</tr>
</tbody>
</table>

Refined structural parameters for the BSCO-0 compositions are presented in Figure 7-3. All the lattice parameters show a clear trend as a function of temperature. The length of ‘a’, ‘b’ and ‘c’ axes increase in value with increasing the temperature, Figure 7-3(a-c), while the monoclinic angle, \( \beta \), is also increasing (Figure 7-3d). There is no discontinuity of values in any lattice parameters, suggesting that there was no significant change of the main phase. The rate of changes in the length of ‘a’, ‘c’ is linear. However, it was noticed that the length of the ‘b’ axis showed a distinct change in the rate between 823 and 873 K.
Figure 7-3 Refined crystal structural parameters as a function of temperature: a) length of a-axis, b) length of b-axis, c) length of c-axis, d) value for β angle.

The linear regression of all lattice parameter data (black solid line) are included in Figure 7-3(a, b, and c), the equations expressing the regression are also given. For the change in the length of ‘b’ axis, 2 sets of linear regression and equations were given to represent the change in gradient. It can be seen from the equations, which represent the rate of change in lattice parameter over the temperature, that the length of ‘a’ and ‘b’ have a similar rate of change up until 773-873 K. After 873 K, the rate of change in ‘a’ is unchanged whereas above that temperature, the rate of change for ‘b’ becomes 5 times more than that of ‘a’. The rate of change in ‘c’ was about ten times higher than that of ‘a’ at all temperature and at least 4 times higher than for ‘b’. The higher rate of change observed for ‘c’ supported the concept of the preferred growth in the c direction in this family of cobaltites, resulted in plate like structure as evident in Chapter 4. There are three anomalies in the data for the change of β angle (shown by black arrows in Figure 7-3d). There is no clear explanation for these anomalies but it seems that the sharp increase of the β angle at high temperatures (1073-1173 K) coincides with the formation of third minor phase. In addition, it seems that the change in the rate increase
in ‘b’ lattice parameter at 823-873 K, coincides with one of the anomalies in β angle. This could indicate some phase change or minor chemistry change at that temperature. Refined cell volume data for BSCO-0 are displayed in Figure 7-4, it can be seen that there is an increase in cell volume with increasing temperature. However, it could be seen that there is a change in trend line coinciding with the change in ‘b’ lattice parameter and β angle at around 873 K. The rapid increase in β angle at temperature > 1073 K could mean that the crystal structure become less symmetric at high temperature. BSCO-0 has a cell volume of 788.32 Å³ at room temperature as reported in Chapter 4. The value gradually increases linearly with temperature, reaching a value of around 816 Å³ at 1173 K.

Figure 7-4 Refined cell volume as a function of temperature for BSCO-0 ceramics.

The thermal expansion coefficient defined as \( \alpha = \frac{V}{V} \frac{dT}{dV} \) (V = volume, T = temperature), has been identified as a key design parameter for thermoelectric materials [224] because the mismatch stress generated during thermal expansion could cause serious damage to devices. The thermal expansion coefficient of BSCO-0 was calculated by finding a gradient of the plot of change in the cell volume using linear regression analysis (solid black line Figure 7-5a); the small variation in the rate of change at 873 K was ignored to simplified the equation, and hence, the thermal expansion coefficient as a function of temperature is plotted in Figure 7-5b. The thermal expansion coefficient decreases linearly with increasing temperature, ranging from 0.0000356 to 0.0000344 K⁻¹.
The abnormal changes in the thermal expansion coefficient of a solid were suggested by Broemme et al. [225] to be an indication of a change in electronic band gaps and hence the thermoelectric properties. The thermoelectric properties of BSCO-0 over the temperature of 300-900 K are given in Figure 7-6. In this investigation, however, there are no traces of sudden change in both thermal expansion coefficient and thermoelectric properties. Therefore, a simple relationship between them cannot be established. It was also considered that the structural parameters ‘a’, ‘b’, ‘c’ and β angle may also provide a link to the thermoelectric properties. However, there are no clear indications of any relationships between them.

Figure 7-6 Thermoelectric properties of BSCO-0 over the temperature range: a) electrical resistivity and Seebeck coefficient, b) thermal conductivity.
7.3 Analysis of Ca₃Co₄O₉ ceramics

The XRD spectra for CCO-MO as a function of temperature from 298 to 1223 K are shown in Figure 7-7. Analysis of the diffraction spectra reveals that for all the temperatures, the main phase can be indexed and refined as a misfit type structure as described in detail in Chapter 6. No secondary peaks were observed in all the spectra in the temperature range of measurement.

![X-ray spectra for CCO-MO ceramics](image)

*Figure 7-7 High resolution X-ray spectra for CCO-MO ceramics from 298 to 1223 K showing reflections from the main phase in the whole temperature range of measurement.*

The Rietveld refinement was successfully performed in the same manner as performed in Chapter 6 on the main phase, using structural data from Grebille et al. [117] for all temperatures. There is a good fit (RWP 17.42, GOF 2.42) between the observed and calculated data at room temperature. Similar fit values, GOF between 1.21-2.42 were observed for CCO-MO at all temperature. The refinement showed that there were only changes in lattice parameter but no significant changes in atomic positions and atomic occupancies (Appendix A, Table 10-8).

Refined structural parameters for CCO-MO are shown in Figure 7-8. All the lattice parameters show a clear trend as a function of temperature. The length of ‘a’, 'b' and ‘c’ axes show an increase with increasing temperature (Figure 7-8(a-c)), while the
monoclinic angle, $\beta$ (Figure 7-8d), remains stable throughout most of the temperature range. However, it can be seen that the $\beta$ angle decreases rapidly at temperatures above 1073 K (showed by an arrow in Figure 7-8d) coinciding with the exponential decrease of the length of ‘a’ axis. This could indicate a change in the crystal structure (becoming more symmetric) at temperatures beyond 1073 K. Between 300-1073 K, there is no discontinuity in the values of any of the lattice parameters, suggesting that there was no major phase change and the symmetry remains the same within this temperature range. The linear regression lines and their equations were calculated in the same manner as for BSCO-0 (section 7.3) and are shown in Figure 7-8(a, b, and c). The rate of change in the ‘b’ axis is slightly lower than that of the ‘a’ axis. However, the rate of change of the ‘c’ axis is about 2-3 times higher than ‘a and b’ axis. The highest rate of change in the ‘c’ axis, is, therefore, indicative of the presence of preferred growth in this direction, which resulted in plate-like microstructures (as seen in the microstructure, Chapter 6).

![Figure 7-8](image.png)

*Figure 7-8 Refined crystal structural parameters as a function of temperature: a) length of a-axis, b) length of b-axis, c) length of c-axis, d) value for $\beta$ angle.*

The refined cell volume data of CCO-MO is displayed in Figure 7-9. There is an increase in cell volume as the temperature increases, similar to that observed for
BSCO-0 ceramics. The CCO-0 had a cell volume of 236.31 Å³ at room temperature as reported in Chapter 6. The values gradually increase with temperature, reaching the value of around 244 Å³ at 1173 K.

Figure 7-9 Refined cell volume as a function of temperature for CCO-MO ceramics.

The thermal expansion coefficient for CCO-MO was calculated by the same procedure as that for BSCO-0 in section 7.3. The thermal expansion coefficient as a function of time is plotted in Figure 7-10b. The thermal expansion coefficient decreases with increasing temperature, ranging from 0.0000294 to 0.0000287 K⁻¹.

Figure 7-10 Thermal expansion coefficient plot: a) linear regression fitting of CCO-MO’s cell volume over the temperature range, b) calculated thermal expansion coefficient of CCO-MO as a function of temperature.
To try to establish a relationship between the structural parameters, the thermal expansion coefficient and the thermoelectric properties, the thermoelectric properties of CCO-SPS, were used instead of those for CCO-MO, as the latter were unavailable over the temperature of 300-900 K as described in Chapter 6. (Relevant data are presented in Figure 7-11). There is no sudden change or break in continuity in the structural parameters, thermal expansion coefficients or thermoelectric properties. Therefore, no direct relations between a, b, c, β and thermal expansion coefficient to thermal electric properties can be established.

![Figure 7-11 Thermoelectric properties of CCO-SPS over the temperature range: a) electrical resistivity and Seebeck coefficient, b) thermal conductivity.](image)

7.4 Conclusions

The crystal structures of BSCO-0 ceramics have been investigated using high temperature XRD analysis. Several key aspects have been found. First, the main phase of BSCO-0 and was found to remain up to 1173 K retaining the room temperature structure. Minor phase 1 and 2 (CoO and Bi$_{0.75}$Sr$_{0.25}$O$_{1.75}$) were found to remain up to 1073 K. In the temperature range 1073-1173 K, several new peaks have been detected, arising from a new phase (minor phase 3), which coincides with the disappearance of minor phase 1 and 2. This newly observed high temperature phase, yet to be conclusively identified, is thought to be a compound of (Bi-Sr) or (Bi-Co) oxides. Closer examination of the cell volume over the temperature range brought the stability of the Bi$_2$Sr$_2$Co$_2$O$_y$ at high temperature into question, as the cell volume increases rapidly with temperature, especially after the change of rate at 873 K. Therefore, a cautious conclusion could be that Bi$_2$Sr$_2$Co$_2$O$_y$ would remain stable up to 873 K.
Rietveld analysis of XRD data for BSCO-0 showed that the 3 lattice parameters ‘a’, ‘b’, and ‘c’ and also the monoclinic angle, β, increased as a function of temperature. The rate of change in the ‘c’ direction was found to be substantially higher (at least 4 times higher) than the ones in the ‘a’ and ‘b’ directions. The thermal expansion coefficient of BSCO-0 was determined to be in the range of 0.0000356 to 0.0000344 K⁻¹. This data could be important design consideration for thermoelectric devices.

The crystal structure of CCO-MO remains stable up to 1173 K with no indication of any extra peaks from secondary phase formation. Rietveld analysis showed that all the monoclinic structural parameters ‘a’, ‘b’, ‘c’ increased as a function of temperature while the monoclinic β angle remained stable throughout most of the temperature range, but decreased exponentially at temperature above 1073 K. The rate of change in the ‘c’ direction was found to be substantially higher (at least 2.5 times higher) than in the ‘a’ and ‘b’ directions. The thermal expansion coefficient of CCO-MO was determined to be in the range of 0.0000294 to 0.0000287 K⁻¹.
8. Conclusions and recommendations for further work

8.1 Conclusions

8.1.1 Effect of Bi content and fabrication route on the microstructure and thermoelectric properties of Bi$_{2+x}$Sr$_2$Co$_2$O$_y$

There is information in the literature about the crystal structure and thermoelectric properties of Bi$_2$Sr$_2$Co$_2$O$_y$ cobaltite. However, for the first time, the effect of excess bismuth doping on this formulation (Bi$_{2+x}$Sr$_2$Co$_2$O$_y$) was explored. The ceramics were initially prepared by mixed-oxide route in an air atmosphere. All the mixed-oxide prepared samples appeared crack-free and dark-grey in colour after sintering. The addition of excess bismuth oxide is vital in densifying this family of cobaltite. Densities of greater than of 87% of the theoretical density were achieved for samples with x=0.2. Examination of the microstructures of the polished cross-sectional surfaces of the samples by SE and BSE revealed plate-shaped grains for the main phase along with the presence of two minor secondary phases. XRD-Rietveld refinement of the data collected by laboratory Cu radiation source and synchrotron source, enabled the crystal structure of the main phase to be successfully refined as a misfit type structure with monoclinic symmetry in $I2/a$ space group. From the SEM-EDS, TEM, and XRD-Rietveld refinement, it can be concluded that the formulation of the main phase could be described as Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$. Using the same techniques, the first minor phase was identified to be CoO with the content of less than 5 volume%. It was established that the second minor phase is a rhombohedral type phase with a composition of Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$. The content of this phase increases with increasing the bismuth content. However, the content of this minor phase was less than 5 % even at the highest levels of Bi.

The electrical resistivity showed no indicative trend as a function of bismuth content. However, it was found that Bi$_{2.2}$Sr$_2$Co$_2$O$_y$ had the lowest electrical resistivity, suggesting that formation of the Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ phase could result in lower electrical resistivity. The low electrical resistivity values of 16-21 mΩ.cm for 300-900 K was achieved in the Bi$_{2.2}$Sr$_2$Co$_2$O$_y$ samples; this is one of the lowest values reported for bismuth strontium cobaltite samples prepared by mixed oxide route in an air atmosphere. No difference in Seebeck coefficients were observed as a function of bismuth content; all the samples exhibit similar values (110-160 μV/K) in the
temperature range of 300 to 900 K. The low resistivity values observed in Bi$_{2.2}$Sr$_2$Co$_2$O$_y$ samples led to the highest power factor of 0.12 mW/m.K$^2$ at 900 K. Trends in the thermal conductivity data indicate that doping of bismuth could lead to lower thermal conductivity. The lowest values, 0.6-0.7 W/m.K over the 300-900 K temperature range was attained in Bi$_{2.1}$Sr$_2$Co$_2$O$_y$, with a slight increase in Bi$_{2.2}$Sr$_2$Co$_2$O$_y$ samples. From these data, it can be concluded that bismuth doping is beneficial to electronic and thermal transport properties of Bi$_2$Sr$_2$Co$_2$O$_y$. The highest ZT, 0.12 at 900 K was obtained for both Bi$_{2.1}$Sr$_2$Co$_2$O$_y$ and Bi$_{2.2}$Sr$_2$Co$_2$O$_y$ due to lowest thermal conductivity, and electrical resistivity respectively.

The correlation between physical properties and thermoelectric properties may be established using a hypothesis based on the following factors: First, the density still plays a significant role in controlling resistivity and thermal conductivity, as inferred from the electrical resistivity graph; BSCO-2 has the lowest electrical resistivity and highest thermal conductivity due to its highest density. Second, the small grain size of minor second phase observed in the BSCO-1 sample could be the reason for lowest thermal conductivity as smaller secondary phase grains might promote more phonon scattering.

To further improve the density and to also assess the effect of SPS fabrication technique on the microstructure development and thermoelectric properties, the same mixed oxide prepared powders of Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ (x=0, 0.1, 0.2) were sintered by SPS method. The densities obtained in SPS samples were much higher, more than 95% of the theoretical density, significantly more than the air sintered samples. The SPS samples are dark-grey in colour and all appeared crack-free. XRD-Rietveld refinement confirmed the formation of the same misfit type structure as mixed oxide samples with monoclinic symmetry in I2/a space group. The XRD and SEM analysis revealed that the Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$ second phase is more prevalent in the SPS samples, with values between 5% in Bi$_2$Sr$_2$Co$_2$O$_y$ samples and 15% in Bi$_{2.2}$Sr$_2$Co$_2$O$_y$ samples.

The correlation between physical properties and thermoelectric properties may also be established using the following factors: For SPS samples, it was inferred that the oxidation state of cobalt/oxygen vacancies are one of the key factors for increasing the electrical resistivity, leading to more resistive SPS samples compared to MO samples.
despite higher density. It is the author’s opinion that the change in oxidation state of cobalt/oxygen vacancies changes the electronic structure and is the cause of lower ZT found in SPS samples. Higher density and higher content of minor phase 2 (Bi$_{0.75}$Sr$_{0.25}$O$_{1.375}$) compared to MO samples, were surmised to be the cause of higher thermal conductivity for SPS samples.

The electrical resistivity in SPS samples also showed no trend as a function of bismuth content; however, Bi$_{2.2}$Sr$_2$Co$_2$O$_y$ samples still achieved the lowest values. Despite the higher density values, the resistivity values of all SPS samples were higher than their mixed-oxide counterpart, ranging between 30-55 mΩ.cm for the same temperature range. Seebeck values in SPS samples are about 10% higher than for the mixed-oxide samples, in the range of 130-180 μV/K. The change in electronic transport properties was attributed to the change in oxidation state of cobalt/oxygen vacancies as a result of the SPS fabrication process. It is believed that further annealing of the SPS samples in air atmosphere could further reduce the resistivity values and yield higher power factors. A power factor of 0.0001 W/m.K$^2$ was obtained for in Bi$_{2.2}$Sr$_2$Co$_2$O$_y$ SPS samples at 900 K. The trend of values of thermal conductivity as a function of bismuth also suggested that doping of bismuth led to lower thermal conductivity, similar to mixed oxide samples, and the optimal doping bismuth content was found to be for x=0.1 where the thermal conductivity is lowest (1.4-1.5 W/m.K). The highest ZT of 0.06 at 900 K was recorded for Bi$_{2.2}$Sr$_2$Co$_2$O$_y$ SPS samples.

8.1.2 Characterisation of Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$ and Bi$_{2}$Sr$_2$Co$_{1.8}$O$_y$ cobaltites

In addition to Bi$_{2+x}$Sr$_2$Co$_2$O$_y$ (x=0.0, 0.1, 0.2), further compositional variations of bismuth strontium cobaltite were investigated. The first composition, Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$ was demonstrated by Leligny et al. to be the single-phase composition of this family. However, there is no report in the literature of the thermoelectric properties for this composition. The second composition, Bi$_2$Sr$_2$Co$_{1.8}$O$_y$, contains excess bismuth compared with the composition proposed by the Leligny et al.

Both compositions were made by mixed oxide route and sintered in air. Both sets of air sintered samples appeared black in colour and no external cracks were observed. Mixed-oxide prepared Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ samples had a density of 81% of the theoretical density. However, it was noticed that mixed-oxide prepared Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$ samples had a low density of only 60% of the theoretical density. To obtain higher density
samples, the SPS fabrication method was used and achieved 93% of the theoretical density.

For Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$, XRD analysis showed the absence of any reflections from secondary phases and the crystal structure was successfully refined as a misfit type structure with monoclinic symmetry in $I2/a$ space group. Further examination of the microstructure by SEM confirmed that Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$ is a single-phase material with no secondary phase in the microstructure. Thus, further evidence is provided in support of Leligny’s proposed composition. As expected, in the microstructure of Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ samples, the Bi$_{0.75}$Sr$_{0.25}$O$_{1.75}$, the secondary phase was observed. However, there was no CoO minor phase in the microstructure.

Further the correlation between physical properties and thermoelectric properties may be established through the following factors: First, the improved density achieved by the excess bismuth found in L-Bi-MO significantly lowered the electrical resistivity compared to L-MO, without diminishing Seebeck coefficient and resulting in improved power factor. Therefore, it could be surmised that density is one of the key parameters controlling the thermoelectric properties in this system. Second, the higher resistivity and higher thermopower observed in L-SPS compared to L-MO samples was inferred to be a result of lower charge carrier concentration, due to a change in oxidation state of cobalt/oxygen vacancies generation during the SPS processing.

The resistivity values for both mixed oxide and SPS prepared Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$ samples were relatively high, around 80-100 mΩ.cm in the temperature range of 300-900 K, in contrast to lower resistivity for Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ being 16-20 mΩ.cm for the same temperature range. However, high Seebeck values of 140-180 μV/K were obtained for SPS prepared Bi$_{1.74}$Sr$_2$Co$_{1.8}$O$_y$ samples being the highest value amongst the bismuth strontium cobaltite. The mixed-oxide prepared Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ samples have Seebeck coefficients ranging between 110-140 μV/K for the same temperature range. From the electrical transport property characterisation, it is evident that excess bismuth in the main composition is important in order to achieve higher power factors. The highest power factor of 0.00014 W/m.K at 900 K was obtained for Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ samples leading to a ZT of 0.16.
8.1.3 Effect of bismuth substitution and fabrication technique of the microstructure and thermoelectric properties of calcium cobaltite (Ca$_{3-x}$Bi$_x$Co$_4$O$_9$, $x = 0.0$ and 0.3)

Two compositions of Ca$_3$Co$_4$O$_9$ and Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$ were prepared by mixed-oxide and SPS for characterisation. All samples appeared black and crack free. Mixed-oxide prepared Ca$_3$Co$_4$O$_9$ showed a low density of 70% theoretical and exhibited low mechanical strength; further characterisation was not conducted. However, SPS prepared Ca$_3$Co$_4$O$_9$ samples had a high density of 95% theoretical. Bismuth substituted samples, Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$, showed improved densities of 85% and 99% theoretical when prepared by mixed oxide and SPS respectively.

BSE–SEM observations revealed highly orientated grains in SPS samples. All the samples were single phase except SPS prepared Ca$_{2.7}$Bi$_{0.3}$Co$_4$O$_9$, showing a small amount of one secondary phase, identified to be Bi$_2$Ca$_2$Co$_2$O$_y$.

SPS yielded lower electrical resistivity values than the mixed oxide route. In the Ca$_3$Co$_4$O$_9$ SPS samples, low values between 6-8 mΩ.cm in the temperature range of 300-900 K were achieved. These values are amongst lowest values reported for this composition. This is attributed to the high density achieved and no contribution of any second phase. For these samples, a high power factor of 0.00045 W/m.K$^2$ was obtained at 900 K. Bismuth-doped SPS samples have superior Seebeck values ranging from 145-170 μV/K, being amongst the highest values reported. The superior Seebeck values are attributed to bismuth substitution, where the substitution of Bi$^{3+}$ could lead to a change in carrier concentration and hence Seebeck values. Thermal conductivity measurement showed higher thermal conductivity values (1.5-2 W/m.K) for SPS samples compared to mixed-oxide samples (1-1.2 W/m.K). The highest ZT of 0.25 at 900 K was achieved in Ca$_3$Co$_4$O$_9$ - SPS samples due to the low resistivity despite showing high thermal conductivity.

Similarly, in this system the correlation between physical properties and thermoelectric properties of may be explored using the following factors: First the density is one of the most important factor in this family of cobaltite, as inferred from the SPS samples, which have higher density; they had better electrical resistivity values compared to MO samples. The observed electrical resistivity and thermopower values of samples
prepared by SPS and MO suggest that there is a change in charge carrier concentration. Further heat treatment in an oxygen rich atmosphere is expected to further optimise the charge carrier concentration, and hence should improve the thermoelectric properties for SPS samples as suggested in the literature [161]. Lastly, the presence of the secondary phase \((\text{Bi}_2\text{Ca}_2\text{Co}_2\text{O})\) although it helped to improve the densification of MO samples, it seemed to be detrimental to promoting the texturing for SPS samples.

**8.1.4 In-situ study of \(\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y\) and \(\text{Ca}_3\text{Co}_4\text{O}_9\) by high resolution synchrotron X-ray diffraction**

To investigate the structure and phase evolution of both \(\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y\) and \(\text{Ca}_3\text{Co}_4\text{O}_9\) as a function of temperature, in-situ high resolution synchrotron X-ray Diffraction was conducted at I11 station of the Diamond Light Source. It was found that the crystal structure of \(\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y\) was constant up to 1173 K, the minor phases (CoO and \(\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_{1.375}\)) were found to be stable up to 1073 K. Above this temperature they started to disappear, coinciding with the formation of a new phase. The third minor phase, thought to be a compound of (Bi-Sr) or (Bi-Co) oxide, appeared to increase in amount with temperature. However, the stability of the \(\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y\) at high temperature might be questionable as the cell volume increased rapidly, especially above 873 K. The cautious interpretation is that the \(\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y\) would remain stable up to 873 K. Rietveld analysis revealed that all the monoclinic lattice parameters \((‘a’, ‘b’, ‘c’)\) and cell volume increased linearly as a function of temperature. The rate of change in the ‘c’ direction was found to be at least 4 times higher than in the ‘a’ and ‘b’ directions. The thermal expansion coefficient, one of critical key design factors, was found to be in the range 0.0000356 to 0.0000344 K\(^{-1}\).

The crystal structure of \(\text{Ca}_3\text{Co}_4\text{O}_9\) was found to be a single-phase up to 1223 K. No trace of any secondary phase formation was detected. Similar to \(\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y\), the monoclinic lattice parameters \((‘a’, ‘b’, ‘c’)\) and cell volume were found to increase linearly as a function of temperature. The rate of change in the ‘c’ direction was also found to be at least 2.5 times higher than in the ‘a’ and ‘b’ directions. The thermal expansion coefficient was determined to be in range 0.0000294 to 0.0000287 K\(^{-1}\).
8.2 Recommendations for further work

1. The purity and controlling of phases in the microstructure of layered cobaltites are paramount important to their thermoelectric properties. Preparing the powders through chemical method could lead to more homogeneous powders and microstructure, which could be lead to better thermoelectric properties.

2. The SPS method yielded very high density samples. However, it did not yield a high figure of merit in the case of bismuth strontium cobaltite samples. Further optimisation and control of the microstructure through changing sintering conditions could lead to better thermoelectric properties. In addition, further annealing of the SPS samples in an oxidising environment, could bring about lower electrical resistivity and hence higher figures of merit.

3. Changing the the oxidation state of Co/oxygen stoichiometry was found to be one way of improving electrical conductivity and Seebeck coefficient; annealing of bismuth strontium cobaltite mixed-oxide samples in oxygen could improve the thermoelectric properties.

4. A systematic study of the oxygen content through neutron diffraction could lead to a greater understanding the effect of oxygen content and the thermoelectric properties. A further XRD analysis and Rietveld refinement could also be performed based on further oxygen positions analysis from neutron diffraction and the calculation/modelling of atomic bonds minimisation energy theory.

5. Through collaborative work using computer simulation, we showed that mechanical strain would improve the Seebeck values in calcium cobaltite. Proper and systematic experiments could be conducted to verify and establish a relationship between strain and performance.

6. The effect of texturing on both bismuth strontium cobaltite and calcium cobaltite should be further investigated to find a relationship between grains orientation and properties. Highly advanced techniques such as X-ray orientation distribution function (ODF) and SEM electron backscatter diffraction (EBSD) could be employed to further establish the relationships.
It could be useful to investigate thin film preparation of bismuth strontium cobaltite and calcium cobaltite samples for thermoelectric applications.
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10. **Appendix A: Rietveld refinement data**

*Table 10-1 Summary of experimentally-determined and refined structural parameters for ceramics of BSCO-0, BSCO-1, and BSCO-2 at room temperature. Structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters ($B_{eq}$), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parenthesis. Noted: $R_{exp}$ is R-expected and $R_{wp}$ is R-weighted pattern and $R_p$ is R-Pattern.*

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<th>BSCO-2</th>
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Table 10-2 Summary of experimentally-determined and refined structural parameters for ceramics of BSCO-0 at room temperature from the high resolution synchrotron source. Structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters \((B_{eq})\), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parenthesis.

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Table 10-3 Refined room temperature structural parameters for BSCO-0, BSCO-1 and BSCO-2 ceramics prepared by SPS. Structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters (B<sub>eq</sub>), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parenthesis.

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Table 10-4 Summary of refined structural parameters for L-Bi-MO, L-MO and L-SPS ceramics at room temperature (structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters (B\text{eq}), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parentheses.

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Table 10-5 Summary of experimentally-determined and refined structural parameters for ceramics of CBCO-MO CBCO-SPS and CCO-SPS at room temperature; Structure type, lattice parameters, atomic positions, occupancies, Isotropic Thermal Parameters ($B_{eq}$), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parentheses. Note: $R_{exp}$ is R-expected and $R_{wp}$ is R-weighted pattern and $R_p$ is R-Pattern. np is Number of position.

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Table 10-6 Summary of experimentally-determined and refined structural parameters for ceramics of CCO-MO at room temperature using Synchrotron source. Structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters ($B_{eq}$), $R$-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parenthesis. Noted: $R_{exp}$ is $R$-expected and $R_{wp}$ is $R$-weighted pattern and $R_p$ is R-Pattern.

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Table 10-7 Summary of experimentally-determined and refined structural parameters for ceramics of BSCO-0 at room temperature, 873, 1073, 1123 and 1173 K. Structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters \( (B_{eq}) \), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parenthesis. Note: \( R_{exp} \) is R-expected and \( R_{wp} \) is R-weighted pattern and \( R_p \) is R-Pattern.

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Table 10-8 Summary of experimentally-determined and refined structural parameters for ceramics of CCO-MO at room temperature, 873, 1123, 1173 and 1223 K. Structure type, lattice parameters, atomic positions, occupancies, isotropic thermal parameters (\(B_{eq}\)), R-values and goodness of fit (GOF). The standard deviation values for the atomic coordinates are shown inside the parenthesis. Note: \(R_{exp}\) is R-expected and \(R_{wp}\) is R-weighted pattern and \(R_p\) is R-Pattern.

<table>
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<th>Parameters/temperature</th>
<th>298 K</th>
<th>873 K</th>
<th>1123 K</th>
<th>1173 K</th>
<th>1223 K</th>
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<td>C(12/m1)</td>
<td>C(12/m1)</td>
<td>C(12/m1)</td>
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<td>4.9087(3)</td>
<td>4.9045(3)</td>
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<tr>
<td>b (Å)</td>
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<td>4.5776(2)</td>
<td>4.58289(16)</td>
<td>4.58447(12)</td>
<td>4.58533(13)</td>
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<td>10.9681(4)</td>
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<td>98.870(6)</td>
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<td>-0.007</td>
<td>-0.007</td>
<td>-0.007</td>
<td>-0.007</td>
</tr>
<tr>
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<td>0.184(8)</td>
<td>0.036(4)</td>
<td>0.017(5)</td>
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<td>( 0.2745 ) (4)</td>
<td>( 0.22827 ) (17)</td>
<td>( 0.22770 ) (16)</td>
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11. Appendix B: Published papers and presentations


