An Experimental Investigation Towards Improvement of Thermoelectric Properties of Strontium Titanate Ceramics

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AN EXPERIMENTAL INVESTIGATION TOWARDS IMPROVEMENT OF THERMOELECTRIC PROPERTIES OF STRONTIUM TITANATE CERAMICS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Materials Science and Engineering

by
Arash Mehdizadeh Dehkordi
August 2014

Accepted by:
Dr. Terry M. Tritt, Committee Chair
Dr. John Ballato
Dr. Stephen Foulger
Dr. Gary Lickfield
Abstract

The direct energy conversion between heat and electricity based on thermoelectric effects is a topic of long-standing interest in condensed matter materials science. Experimental and theoretical investigations in order to understand the mechanisms involved and to improve the materials properties and conversion efficiency have been ongoing for more than half a century. While significant achievements have been accomplished in improving the properties of conventional heavy element based materials (such as Bi$_2$Te$_3$ and PbTe) as well as the discovery of new materials systems for the close-to-room temperature and intermediate temperatures, high-temperature applications of thermoelectrics is still limited to one materials system, namely SiGe. Recently, oxides have exhibited great potential to be investigated for high-temperature thermoelectric power generation.

The objective of this dissertation is to synthesize and investigate both electronic and thermal transport in strontium titanate (SrTiO$_3$) ceramics in order to experimentally realize its potential and to ultimately investigate the possibility of further improvement of the thermoelectric performance of this perovskite oxide for mid- to high temperature applications. Developing a synthesis strategy and tuning various synthesis parameters to benefit the thermoelectric transport form the foundation of this study. It is worth mentioning that the results of this study has been employed to prepare targets for pulsed-laser deposition (PLD) to study the thermoelectric properties of corresponding thin films and superlattice structures at Dr. Husam Alshareefs group at King Abdullah University of Science and Technology (KAUST), Saudi Arabia. Considering the broad range of functionality of SrTiO$_3$, the findings of this work will surely benefit other fields of research and application of this functional oxide such as photoluminescence, ferroelectricity or mixed-ionic electronic conductivity. This dissertation will ultimately attempt to answer the question, ”Is it possible to further improve the thermoelectric properties of SrTiO$_3$-based ceramics?”.

The organization of the dissertation is as follows: In Chapter 1, the fundamental concepts
in the thermoelectric theory is explained. Second, we briefly review the characteristics of "good" thermoelectric materials and highlight the differences exist between SrTiO$_3$ and conventional thermoelectric materials. In Chapter 2, SrTiO$_3$ is introduced and the electronic and thermal properties arising from its crystal structure are discussed. Chapter 3 is dedicated to the fundamentals of measurements of the electronic and thermal transport properties which are the backbone of the current work. Our experimental results are presented in Chapter 4 and 5. The synthesis and processing techniques to prepare doped SrTiO$_3$ powder and bulk polycrystalline ceramic are presented in Chapter 3. The optimizations of the synthesis and densification parameters involved are presented and discussed in this chapter as well. Significant improvement achieved in the thermoelectric figure of merit of Pr-doped SrTiO$_3$ and the studies performed to understand the results are presented in Chapter 5. Concluding remarks and future work are discussed in Chapter 6.
Dedication

To my parents, Ebi and Rezvan Mehdizadeh Dehkordi
My sister Aida Mehdizadeh Dehkordi
And my better half Sarah Parvini
Acknowledgments

First and foremost, I wish to express my sincere gratitude to my gracious advisor Prof. Terry M. Tritt who believed in me when I needed it the most. Joining his Complex and Advanced Materials Lab (CAML) was one of the best things that has happened to me. I also wish to express my gratitude to Dr. Sriparna Bhattacharya who mentored me as the postdoctoral associate of the group and a friend. I cherished our many conversations and discussions. I wish to acknowledge Dr. Jian He for many thoughtful discussions and conversations. I would also like to thank our group members, Dr. Jennifer Graff and Dr. Daniel Thompson in particular for their friendship. I acknowledge our collaborators from King-Abdullah University of Technology, Dr. Husam Alshareef in particular. I am very grateful for the financial support, which was provided by King-Abdullah University of Science and Technology (KAUST) through KAUST-Clemson Faculty Initiated Collaboration (FIC) Grant. I would also like to express my gratitude and appreciation to my committee members, Dr. John Ballato, Dr. Stephen Foulger and Dr. Gary Lickfield for their time. Finally, words cannot describe how grateful I am for my parents, Ebi and Rezvan Mehdizadeh Dehkordi. All that I am and all that I have would not have been possible without their love, support and sacrifice. Maman and Baba thank you!
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Chapter 1

Thermoelectric Materials:
Materials Physics and Recent Progress

Since the emergence of the energy crisis era, developing new technologies to produce sustainable energy has gained the attraction of scientific community and ground-breaking achievements have been accomplished. However, what limits the use of these new technologies to only a small fraction of the electricity produced is their relatively high cost/efficiency ratio. The overnight cost of these sustainable technologies still approaches $1/W. With almost 60% of all energy producing processes being wasted in the form of heat, this wasted heat is an untapped low-cost source of sustainable energy. Home heating, automotive exhaust and industrial processes are all considered as sources of sustainable energy for direct heat-to-electricity conversion. This fact gives rise to the importance of thermoelectric technology and drives the interest in finding novel cost-effective materials for waste heat recovery and electricity generation. [1,47]

Owing to their moderate energy conversion efficiency and relatively high cost, thermoelectric (TE) modules had been employed in niche applications such as radioisotope thermoelectric generator (RTG) for deep-space satellites and remote power generation for unmanned systems. However, recent ground-breaking discoveries over the past 15 years using nanostructuring and materials engineering techniques, significantly broadened the application landscape of thermoelectric technology. Novel
applications of TEs include aspects such as biothermal batteries and autonomous body sensors, enhanced performance of optoelectronics coupled with solid-state TE cooling, vehicle exhaust waste heat recovery, and wearable self-powered mobile electronics, which are actively being investigated. More recently, TEs have been investigated for their use in TE-solar hybrid systems to take advantage of the IR part of the solar spectrum and for TE-solar power generation. In addition to these applications, there is a huge potential for distributed power generation in poor countries. Many communities cannot afford the cost of power plants and the electricity grid. A small amount of electricity produced by thermoelectric modules in cooking stoves or solar thermal systems could improve the quality of life significantly. With such a huge potential, there is significant interest in improving the materials properties as well as reducing cost/efficiency ratio.

In this chapter, we start by briefly reviewing the fundamental effects related to thermoelectric power generation and refrigeration. The materials parameters involved and the thermoelectric figure of merit are discussed. Recent progress in materials engineering and the future prospect will be reviewed.

## 1.1 Thermoelectric Energy Conversion

### 1.1.1 Fundamental Thermoelectric Effects

Thermoelectric effects were discovered early in the 19th century, however, it was not until the second half of the 20th century that thermoelectric power generation became reasonably efficient and thermoelectric refrigeration became even practicable. The Seebeck effect, which is the cornerstone of thermoelectric power generation, is referred to the generation of a voltage ($\Delta V$) when two different conductors are joined together and the junctions were held at different temperature ($T$ and $T + \Delta T$). This phenomenon is now familiar to all scientists and engineers, as it has long been used to measure temperature using thermocouples. The ratio of the voltage developed to the temperature difference ($\Delta V/\Delta T$) is related to an intrinsic property of the materials termed the Seebeck coefficient ($\alpha$), or the thermopower. The thermoelectric power generation is gauged by the Seebeck coefficient for each material. This effect can be understood by applying a temperature gradient across a material; the more energetic electrons diffuse to a lower potential until an equilibrium electric field is established to impede the further flow of electrons. This potential difference can be used to power an external load. This is illustrated in Figure 1.1, which shows the establishment of
an electric field that is the opposite of that of the temperature gradient, $\nabla T$, given that the sign of $\alpha_n$ is negative for electrons,

$$E = \alpha_n \nabla T.$$  \hspace{1cm} (1.1)

The Seebeck coefficient is very low for metals (only a few microvolts per degree Kelvin) and is much higher for semiconductors (typically a few hundred microvolts per degree Kelvin). \[1\]

Figure 1.1: Schematic establishment of the thermoelectric effect when a material is subjected to an external temperature gradient and the system is in equilibrium. (a) Longer mean free path of the more energetic electrons. (b) Diffusion of the more energetic electrons (denoted by blue dots) to the cold side and the development of an electric field ($E$) to oppose any further diffusion. We define $x$ as increasing from the cold-side temperature $T_C$ to the hot-side temperature $T_H$, therefore defining the temperature gradient $\nabla T$ as shown. Because the electrons are negatively charged (and therefore $n$ is negative), an electric field is established that is the opposite of that of the temperature gradient to oppose further diffusion when the system is in equilibrium. \[1\]

The Peltier effect, which is the cornerstone of thermoelectric refrigeration, was discovered a few years after Seebeck’s observation and is referred to the heating or cooling (depending on the direction of current) of the junction between two conductors when an electric current passes through it. This effect is due largely to the difference in the Fermi energies of the two materials. For each material, the thermoelectric Peltier refrigeration is gauged by the Peltier coefficient that relates the heat carried by the charge carriers to the electrical current through $Q = \Pi \times I$. The Peltier and Seebeck effects are related through the Kelvin relation, $\Pi = \alpha T$, which is a consequence of Onsager’s reciprocity relation. Direct thermal energy conversion applications were realized in 1954 when Goldsmid and Douglas published a manuscript in The British Journal of Applied Physics demonstrating the possibility of cooling from ordinary ambient temperatures to below 0°C with a
thermocouple consisting of bismuth telluride, Bi$_2$Te$_3$. [52] This manuscript was the first successful discovery of the use of semiconductors for thermoelectric refrigeration.

1.1.2 Figure of Merit and Thermoelectric Performance

The potential of a material for thermoelectric applications, both power generation and refrigeration, is determined in large part by a measure of a material’s dimensionless figure of merit, $ZT$, 

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} = \frac{PF}{\kappa}$$  \hspace{1cm} (1.2) 

where $\alpha$ is the Seebeck coefficient, $\sigma$ the electrical conductivity, $\kappa$ the total thermal conductivity and $T$ the absolute temperature in Kelvin. Figure of merit, in essence, is a measure of the competition between electronic transport (i.e. power factor, herein defined as $PF = \alpha^2 \sigma T$) and thermal transport (i.e. total thermal conductivity) in a material.

It is common practice and convenient to use $ZT$ when one is searching for new thermoelectric materials for evaluation purposes, however, since an array of TE couples is utilized in a module; $ZT$ for a single material is somewhat meaningless. There are two materials in the TE couple, which is shown in Figure 1.2, an $n$-type and a $p$-type semiconductor. Ignoring parasitic contributions that reduce the device performance, such as contact resistance and radiation effects, the resulting figure of merit for the couple (based solely on the TE materials) is given by

$$ZT_{\text{couple}} = \frac{(\alpha_p - \alpha_n)^2 T}{\left(\left(\frac{\kappa_p}{\sigma_p}\right)^{1/2} + \left(\frac{\kappa_n}{\sigma_n}\right)^{1/2}\right)^2}$$  \hspace{1cm} (1.3) 

where the subscripts $n$ and $p$ refer to the $n$-type and $p$-type leg of the thermocouple. It is often happens that the figure of merit for a thermocouple is approximately equal to the average of the $ZT$ values for the two legs, however the reader should be warned that this is not always the case. [1,51]

Ioffe showed that the coefficient of performance ($\phi$) (refrigeration mode) and the TE efficiency ($\eta_{\text{TE}}$) (power generation mode) of the TE couple are both directly related to the $ZT$, as shown in Equation 1.4 for the efficiency. The efficiency ($\eta_{\text{TE}}$) of the TE couple is given by the power input to the load ($W$) over the net heat flow rate ($Q_H$), where $Q_H$ is positive for heat flow from the
source to the sink:

$$\eta_{TE} = \frac{W}{Q_H} = \frac{T_H - T_C}{T_H} \left( \frac{(1 + ZT_M)^{1/2} - 1}{(1 + ZT_M)^{1/2} + \frac{T_C}{T_H}} \right)$$  \hspace{1cm} (1.4)$$

where $T_H$ is the hot-side temperature, $T_C$ is the cold-side temperature, and $T_M$ is the average temperature. Thus, $\eta_{TE}$ is proportional to the Carnot efficiency ($\eta_C$):

$$\eta_C = \frac{T_H - T_C}{T_H}$$  \hspace{1cm} (1.5)$$

which we know from thermodynamics is the maximum efficiency of a heat engine operating between two temperatures, $T_H$ and $T_C$.

Figure 1.3 shows the relative efficiency ($\eta_{TE}/\eta_C$) as a function of $ZT$ for a thermoelectric heat engine operating between the temperatures of $T_H = 800$ K and $T_C = 300$K, which would yield a Carnot efficiency of 63%. This plot assumes no parasitic losses such as contact resistance or radiation effects and a constant $ZT$ between these two temperatures. Of course, these are not realistic assumptions, and the plot is used only to highlight the region where the greatest return in efficiency gain would be achieved per unit increase in $ZT$. The biggest return happens for a $ZT$ between 2 and 3. A $ZT \sim 2-3$ in stable, bulk TE n-type and p-type materials with low parasitic losses that can operate between these two temperatures is the ultimate goal of TE materials research. [1]
Figure 1.3: The ratio of thermoelectric efficiency to the Carnot efficiency ($\eta_{TE}/\eta_C$) as a function of the figure of merit, ZT. The maximum efficiency (i.e. Carnot efficiency) estimated from equation 1.4 is 63%. This plot assumes no parasitic losses such as contact resistance or radiation effects and that ZT is essentially constant between these two temperatures. [2]

1.2 Characteristics of Good Thermoelectrics

Over the course of the last 40 years, a series of guidelines for materials selection have been formalized to identify potential thermoelectric materials. Here, we briefly review these guidelines, as understanding them would highlight the intriguing properties of oxides which will be discussed in the following chapters. It should be noted that these are just general guiding principles that come in handy in identifying new potential materials for TE applications. As will be seen not all high-ZT materials follow these principles. As will also be discussed later, due to the inherent trade-off between electrical conductivity and Seebeck coefficient, many of these criteria are partially contradictory.

1.2.1 Optimum Electronic Transport

Ioffes observation in doped semiconductors highlighted the carrier concentration sweet spot of good thermoelectrics to be $n \sim 10^{18} - 10^{20} \text{ cm}^{-3}$, corresponding to degenerate semiconductors or semimetals. This follows the behavior of electronic transport in real-life materials as a function of carrier concentration. As the doping concentration increases, the electrical conductivity increases and the Seebeck coefficient decreases. Therefore there exists an optimum power factor versus doping concentration at relatively high doping concentrations and Fermi levels close to, or inside the conduction band (i.e. degenerate limit). The position of the optimum chemical potential depends
on the type of the material and on the operating temperature.

The intriguing question of "What is the best electronic band structure a thermoelectric can have?" has been the subject of theoretical studies and experimental exploration for more than 30 years. The connection between band structure calculations and electronic transport coefficients is made via kinetic (or Boltzmann) transport theory. [53] This approach is valid for diffusive transport (i.e. dimensions larger than carrier mean free path) when the semiclassical picture is valid (mean free path larger than atomic distances). The Bloch-Boltzmann expressions for electrical conductivity (along x direction) and Seebeck coefficient are given by [54]

\[
\sigma_x = e^2 \int_0^\infty g(E) v_x^2(E) \tau(E,T) \left( -\frac{\partial f(E)}{\partial E} \right) dE, \quad (1.6)
\]

\[
\alpha = -\frac{1}{eT} \left[ \int_0^\infty \frac{g(E) v_x^2(E) E \tau(E,T) \left( \frac{\partial f(E)}{\partial E} \right)}{g(E) v_x^2(E) \tau(E,T)} dE \right], \quad (1.7)
\]

where \( e \) is the electron charge, \( \tau(E) \) the momentum relaxation time for charge carriers, \( g(E) \) the total electronic density-of-states (DOS) and \( f(E) \) the energy distribution function. The Fermi window factor \( (-\partial f(E)/\partial E) \) is a bell-shaped function centered at \( E = E_F \) and has a width of \( \sim k_B T \). This factor is responsible for the fact that at a finite temperature only electrons near the Fermi surface contribute to the conduction process. It is observed that the Seebeck coefficient and electrical conductivity are connected through an energy-dependent function called the transport distribution function or differential conductivity, \( \sigma(E) \), defined as [47]

\[
\sigma(E) = e^2 g(E) v_x^2(E) \tau(E,T). \quad (1.8)
\]

\( \sigma(E) \) is a measure of the contribution of electrons with energy \( E \) to the total conductivity. It is observed that \( \sigma(E) \) contain two types of energy-dependent components, the band structure, which determines \( g(E) \) and \( v(E) \), and the scattering time \( \tau(E,T) \), which is not directly determined by the band structure alone. If the Fermi level is deep inside the band (degenerate limit, \( E_C - E_F > k_B T \)), i.e. for metals, the Seebeck coefficient in equation (3) could be approximated using Sommerfeld
expansion and is known as the Mott formula

\[ \alpha = \frac{\pi^2 k_B^2 T}{3e} \left. \frac{1}{\sigma(E)} \frac{d\sigma(E)}{dE} \right|_{E=E_F}. \] (1.9)

Typical values of the thermopower that are needed for good TE performance are on the order of 150–250 \( \mu V K^{-1} \) or greater, along with typical electrical conductivity values between 500 to 2000 S cm\(^{-1}\). During the past three decades, ideas were proposed to suppress the interplay between electrical conductivity and Seebeck coefficient, which provided several insights on ideal crystal and band structure that served as materials selection criteria.

The optimum band gap of a thermoelectric semiconductor was first investigated theoretically by Chasmar and Stratton for indirect gap semiconductors. [55] They found the best gap of \( 6k_B T \), where \( k_B \) is the Boltzmann constant and \( T \) the operating temperature of the thermoelectric device. Later Mahan did a similar study and found \( E_g \sim 10k_B T \) to be a more realistic optimum for indirect gap materials which is known as the "10\( k_B T \) rule". [56]

Another important feature of band structure, namely the density-of-states effective mass, \( m^* \), and its close relationship with the carrier mobility, were first investigated in detail by Goldsmid. [57] It was shown that the thermoelectric power factor, and hence \( ZT \), are dependent on \( \mu (m^*/m_e)^{3/2} \) (known as weighted mobility), where \( m_e \) is the free-electron mass. Therefore, ideally, it is desirable to maximize both \( m^* \) and \( \mu \). However, in practice, this is not quite simple due to their interplay. It is known that larger effective mass materials correspond to larger Seebeck values and so they are desirable for the thermoelectric applications. It is also known that generally large effective masses translate to low mobility values \( (\mu = e\tau/m^*) \). Therefore for a fixed doping density, the larger the Seebeck coefficient, the smaller the mobility of the charge carriers is and so again the trade-off appears. For heavy element-based highly doped thermoelectric materials with \( n \geq 10^{20} \text{cm}^{-3} \), mobility values of \( \leq 100 \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) is reported. The highest values are reported for PbTe-based thermoelectrics in both \( n- \) and \( p- \) type materials.

Mahan showed that in order to increase the density-of-states effective mass without sacrificing the mobility much, multivalley semiconductors with small inertial masses are desirable. For the most general case, the density-of-states effective mass is equal to \( N_v^{2/3}(m_1m_2m_3)^{1/3} \), where \( N_v \) is the number of equivalent valleys (band degeneracy) and \( m_{1,2,3} \) are inertial masses in each direction. Provided that intervalley scattering is minimized or absent, theory suggests that a multivalley semi-
conductor with small inertial masses would have the largest value of $\mu (m^*/m_e)^{3/2}$. This maximizes the thermoelectric power factor particularly through optimization of Seebeck coefficient over that of the single-valley counterpart. Mahan found the presence of at least four band minima is necessary for good thermoelectrics. [58] The number of equivalent conduction valleys for Bi$_2$Te$_3$, PbTe, and SiGe are 6, 4, and 6, respectively (excluding the spin degeneracy). [59] Compounds with a large number of equivalent valleys are typically those with high symmetry crystal structures. Figure 1.4 schematically shows this idea. [3]

Figure 1.4: Schematic diagram of the electronic band structure with a) single extremum and b) multiple extrema in the valence and conduction bands. When these systems are electron-doped (see $E_F$ level), more extrema (electron “pockets”) are populated in system (b) than in system (a). The power factor depends upon the number of populated extrema and therefore system (b) will have a higher power factor. [3]

Another idea is to take advantage of anisotropic band masses. This idea ties in with the idea of using multivalley band structures. In order to maximize the weighted mobility, while high mobility along the current flow direction is needed, high effective masses need not occur along the same crystallographic directions. Therefore, there should be good opportunities to optimize highly anisotropic structures. Carrier mobility should be high (small effective mass) along the direction of transport while there are many states (heavy mass) available in the transverse direction. A recent report on high $ZT$ of 2.6 along one crystallographic direction of the high temperature phase in SnSe, proves the potentials of anisotropic materials. [60] Even though the high $ZT$ is originated from ultralow thermal conductivity which is attributed to high anharmonicity of the chemical bonds, the electronic transport is still interesting. These single crystal samples possess 8 times larger carrier mobility at 300K along b-axis vs. a-axis for similar carrier concentration and Seebeck coefficient values, which leads to a 5-fold larger power factor in the direction of b-axis.
Electronegativity difference, $\langle \Delta \chi \rangle$, among constituent elements of a thermoelectric material (e.g. $\langle \Delta \chi \rangle = 0.3$ for Bi$_2$Te$_3$ and 0.53 for PbTe) was also found to be a powerful screening parameter for high carrier mobility materials, which was proposed by Slack. [61] Slack pointed out that materials with small electronegativity difference among their constituent atoms have high mobility values. Skutterudites were first identified as such by Slack, on the basis of this screening process based on electronegativity. Electronegativity difference is a measure of the covalency of the bonding in a material. Large $\langle \Delta \chi \rangle$ indicates ionic bonding and the scattering of carriers by polar optical phonons which reduce the carrier mobility significantly.

As it is seen in Equations 1.6 and 1.7, another band structure information which plays a crucial role in electronic transport is the density-of-states of charge carriers. Mahan and Sofo treated the problem of "What is the best electronic structure a thermoelectric can have?" as a problem in mathematics. They showed that the transport distribution function (or differential conductivity), $e^2g(E)v_x^2(E)\tau(E)$, that maximizes the power factor is delta function-shaped. Since the exact condition is not found in nature, they proposed the search for materials with narrow energy distribution of carriers but with high carrier velocity in the direction of transport. Optimal density of states for thermoelectric applications was suggested to possess sharp singularity in the vicinity of the Fermi energy as is shown schematically in Figure 1.5. [59] The natures closest approximation to delta function is observed in f-level rare-earth compounds. YbAl$_3$ and CeSn$_3$ are examples of such materials possessing the highest ever reported values of power factor of 5.4 and 3.0 Wm$^{-1}$K$^{-1}$ at 300K. It was suggested, but not proven, that this behavior holds true also for 3$d$ electrons in FeSb$_2$. [62]

Figure 1.5: Schematic illustration of density-of-state (DOS) possessing a) a large slope (i.e. large energy derivative of differential conductivity) and b) a small slope near $E_F$. [3]
1.2.2 Optimum Thermal Transport

Since the figure of merit is inversely proportional to thermal conductivity, Equation 1.2, it is clear that small values of thermal conductivity, approaching those of amorphous materials, are desired. However, yet again the inherent interplay between material properties, here electronic and thermal transport, makes it challenging. The thermal conductivity, $\kappa$, is related to the transfer of heat through a material by both electrons and phonons (quantized vibrations of the lattice) such that $\kappa = \kappa_L + \kappa_E$, where $\kappa_L$ is the heat transported by phonons (lattice vibrations) and $\kappa_E$ is the heat transported by charge carriers. The electrical and thermal conductivities, $\sigma$ and $\kappa$, are also interrelated: $\sigma$ is tied to $\kappa_E$ through the Wiedemann-Franz relationship given by [1]

$$\kappa_E = L\sigma T,$$

(1.10)

where $L$ is the Lorenz number, the value of which is $2.48 \times 10^8$ V$^2$ K$^{-2}$ for metals and is usually taken as $L = 2.0 \times 10^8$ V$^2$ K$^{-2}$ for degenerate, i.e., highly doped, semiconductors. In small-band gap semiconductors, contributions of the minority carriers (i.e. holes in an n-type material) can also contribute to thermal transport. This additional term is referred to as the bipolar thermal conduction, $\kappa_b$. As long as the band gap is $E_g > 10k_BT$ (which is the case for SrTiO$_3$ in this work), $\kappa_b$ can be ignored. [61]

Due to the correlation between the electrical and thermal conductivity, the reduction of lattice part of thermal conductivity, $\kappa_L$ has been focused as the main approach in order to improve the figure of merit. The classical kinetic theory provides a good approximation for the lattice thermal conductivity which is given by

$$\kappa_L = \frac{1}{3}v_s C_V l_{ph},$$

(1.11)

where $v_s$ is the velocity of sound, $C_V$ is the heat capacity at constant volume, and $l_{ph}$ is the mean free path of the phonons. At very low temperatures (under 40 K), the behavior of $\kappa_L$ is dominated by the Debye $T^3$ law for $C_V$. Phonon scattering is insignificant in this temperature range, because of the small number of excited phonons and their very long wavelength. However, at high temperatures ($T > \Theta_D$, where $\Theta_D$ is the Debye temperature which is above 300K for typical materials), the sound velocity and the heat capacity are essentially temperature-independent in typical materials.
and maybe regarded as constants. Therefore, it is safe to assume that the magnitude and the
temperature dependence of $\kappa_L$ are basically dictated by the mean free path of the phonons at higher
temperatures, $T > \Theta_D$.

Many of the guidelines for identifying materials with a low lattice thermal conductivity can
be understood from Equation 1.11. A key guideline is to look for materials with large atomic
masses. This rule originated from the fact that heavy atoms lead to small sound velocities and a
correspondingly low thermal conductivity. [63,64] Also, complex crystal structures with many atoms
per unit cell were found to tend to have low thermal conductivity values. This concept is not very
well-grounded theoretically, but nevertheless seems to be validated experimentally. Higher number
of defects, i.e. disorder, in larger unit cells and the possible break down of the concept of phonon
for large number of atoms in a cell might be the possible explanations for this idea. [64] A formula
obtained by Keyes, [65] which predicts the lattice thermal conductivity, quantifies these ideas and
can provide some useful insights.

$$\kappa_L T = \frac{R^{3/2}}{3\gamma^2 \epsilon^3 N_{A}^{1/3}} \frac{T_m^{3/2} \rho^{2/3}}{A^{7/6}},$$

(1.12)

where $T_m$ is the melting point, $A$ is the mean atomic weight, $\gamma$ is the Gruneisen parameter, $\epsilon$ is the
fractional amplitude of interatomic thermal vibration, $R$ is the ideal gas constant, $N_A$ is Avogadros
number, and $\rho$ is the density. This equation provides some useful insight into thermal conductivity:
(1) in the high temperature range $\kappa_L$ follows a $T^{-1}$ power law, (2) a low melting point can lead to a
low thermal conductivity, (3) $\kappa_L$ decreases with increasing atomic mass, and (4) the proportionality
to $\rho^{2/3}$ makes $\kappa_L$ small for crystals with large interatomic distances. [3,12] The advantage of Keyes
formula is that it involves the quantities $T_m, \rho,$ and $A$, which are known as soon as a new material is
synthesized, and a quantity $B = \frac{R^{3/2}}{3\gamma^2 \epsilon^3 N_{A}^{1/3}}$ that should not vary much from one substance to another
in a given system. [12]

Mass fluctuation scattering, which is the scattering of phonons by variations in the mass of
scattering centers (e.g. atoms in the lattice), can also be used to reduce lattice thermal conductivity.
Ioffe et al. first introduced and used the concept to reduce $\kappa_L$ in PbTe and Bi2Te3 by alloying
them with isomorphous elements (Sn and Sb, respectively) and the formation of respective solid
solutions. [51,66] The idea is that isovalent substitution (e.g. Si-Ge in SiGe alloys) will scatter
heat carrying phonons strongly because the wavelength of those phonons is about the same as the
distance between the scattering centers. Electrons, on the other hand, have a longer wavelength and will be scattered less. Therefore, carrier mobility is not going to be compromised much.

Another rule is an empirical relationship proposed by Spitzer (1970) based on the compilation of thermal conductivity data on more than 200 semiconductors that crystal structures in which the ions are highly coordinated tend to have lower thermal conductivities than crystal structures in which the ions have low coordination.

A guideline originally proposed by Slack [61] involves finding materials in which one or more atoms per unit cell are loosely bound and "rattle" in an oversized cage. Such rattlers resonantly scatter phonons and reduce the mean free path of the heat carrying phonons to dimensions comparable to the interatomic spacing which effect thermal conductivity dramatically, as was demonstrated in filled skutterudites and germanium clathrates. Use of atomic displacement parameter (formerly called thermal parameter), which is a measure of the mean-square displacement amplitude of an atom about its equilibrium position, was introduced by Sales et al. as a powerful experimental tool to investigate novel low thermal conductivity material. [64] Unusually large atomic displacement parameters (ADP) provide direct evidence of rattling in skutterudites and clathrates. Typical values of thermal conductivity for a good TE material are $\kappa < 2 \text{ Wm}^{-1}\text{K}^{-1}$.

1.3 Recent Progress in Thermoelectric Materials Research

Over the 3 decades from 1960 to 1990, only incremental gains were achieved in increasing ZT, with the (Bi$_{1-x}$Sb$_x$)$_2$(Se$_{1-y}$Te$_y$)$_3$ alloy family remaining the best commercial material with ZT values around 1. During this period, the field of thermoelectrics remained stagnant and received little attention from the scientific research community worldwide. However, the thermoelectrics industry grew slowly around niche applications for space missions, laboratory equipment, and medical applications, where cost and energy efficiency were not as important as energy availability, reliability, predictability, as well as the quiet operation of equipment. [67,68]

In the early 1990s, triggered by the renewed interest of US Department of Defense (DoD) in the field, the renaissance of thermoelectricity started with the predictions of Hicks and Dresselhaus, [68] which introduced the potentials of nanostructuring for thermoelectric materials. As a result of this stimulation, two different research approaches were adopted for developing the next generation of high-performance thermoelectric materials: (1) discovering and developing new families of advanced
bulk thermoelectric materials, and (2) low-dimensional materials systems. The so-called phonon-glass/electron-crystal (PGEC) materials[9] (such as the partially filled skutterudites based on alloys of CoSb$_3$)[10] are the most prominent of the new families of advanced thermoelectrics which have been developed since. [67] The guidelines which were discussed above served as useful tool for the materials selection in this approach. Regarding the low-dimensional materials approach, most efforts have been focused in two main directions: (i) the reduction of the lattice part of thermal conductivity through nanostructuring and the corresponding increased phonon scattering from the interfaces, and (ii) the enhancement of power factor, which was initially proposed via quantum-confinement effects. While groundbreaking success has been achieved through the former direction [28], progress has not developed as rapidly for the latter. Figure 1.6 shows the timeline of the evolution of thermoelectric figure of merit of conventional thermoelectric materials as well as the emergence of the new advanced families. [1]

![Figure 1.6: The figure of merit, ZT, as a function of the time frame of several key TE materials relative to their discovery year, thus showing many of the recent advancements in both thin-film and bulk thermoelectric materials. Abbreviations: LAST, PbAgSbTe compounds; QDSL, quantum dot superlattice; SL, superlattice. Blue markers represent thin films and Red ones indicate bulk samples. Updated and Reproduced from Reference [1].](image_url)

Some of the goals of current research efforts are to find new materials that either increase the current efficiency of TE devices (e.g., increase $ZT$) or have the capability of operating in new and broader temperature regimes, especially at lower temperatures ($T < 250$ K) and at higher temperatures ($T > 800$ K). High-temperature applications of thermoelectrics are limited to only one
candidate, SiGe alloys with maximum $ZT$ values around 800°C. Instability and dopant precipitation issues limit the use of SiGe to harvest higher temperature heat sources. Moreover, the search for earth-abundant thermoelectric materials remains an active area of research. Most of the high $ZT$ material systems are heavy-element based compounds which are facing abundance problems. During the recent years, oxide materials have shown to be of great potential to address these issues and to be promising candidates to investigate for new generation of high-temperature thermoelectric materials.

1.4 Oxide Thermoelectrics: Beyond Guiding Principles

In the view of the guidelines for choosing potential thermoelectric materials, oxides were believed to make poor thermoelectrics. They generally possess a large electronegativity difference among constituent elements (e.g. $\langle \Delta \chi \rangle = 2.2$ for SrTiO$_3$) which would lead to ionic bonding and the strong scattering of carriers by polar optical phonons. Hence, they have low carrier mobility ($\mu$), sometimes orders of magnitude smaller than that of the heavy element-based thermoelectrics. Moreover, the Seebeck coefficient is often found to be small for oxide semiconductors due to the cancellation between the electron and hole band contributions. Finally, the large bonding energy and the small mass of oxygen results in a high velocity of sound which would lead to a large lattice thermal conductivity. [4] However, after the report of Terasaki et al. [69] showed that $p$-type Na$_x$CoO$_2$ single crystal possesses higher room temperature power factor of $\sim 1.5 \text{ Wm}^{-1}\text{K}^{-1}$ than $\sim 1.2 \text{ Wm}^{-1}\text{K}^{-1}$ for Bi$_2$Te$_3$, exploration of thermoelectric properties of oxides began. Further investigations of oxide thermoelectrics highlighted layered alkali or alkaline earth cobaltite compounds (Na$_x$CoO$_2$, [70] and Ca$_3$Co$_4$O$_9$), [71] K$_x$RhO$_2$ [72] and recently BiCuSeO [73] as the most promising $p$-type oxide materials while SrTiO$_3$, CaMnO$_3$, [74] ZnO [75] and very recently (Sr$_x$Ba$_{1-x}$)Nb$_2$O$_6$ [76] were being investigated as potential $n$-type candidates among which we have studied the synthesis and thermoelectric transport properties of bulk polycrystalline SrTiO$_3$ in this work.

Although $ZT$ values reported for oxides are still lower than the current state-of-the-art TE materials, oxides possess several inherent advantages from fundamental and application points of view. First, they generally possess high chemical and thermal stability which allows for a large temperature gradient to be applied across the materials in air, therefore leading to a high Carnot efficiency in Equation 1.4 that somewhat compensates the low $ZT$. Second, novel nonlinear, nonlo-
cal thermoelectric effects (such as the Benedicks effect) might be induced by the large temperature gradient. Third, oxides are featured by their chemical versatility and structural intricacy, which offering a great flexibility of structural and compositional tailoring. Finally, oxides are decidedly advantageous in terms of the abundance and the cost of raw materials as well as the environmental friendliness, which are all major considerations for any large-scale application. Figure 1.7 compares the operating temperatures of various thermoelectric materials as well as the abundance of constituent elements in the earth crust. [4]
Chapter 2

SrTiO$_3$: Crystal Structure, Electronic and Vibrational Band Structures

Strontium titanate, an elegant model perovskite, has been studied extensively for technological applications as well as for basic science due to its many intriguing properties, such as superconductivity, [77] ferroelectricity, [78], giant dielectric permittivity, [79,80] photoluminescence, [81,82], interfacial two-dimensional electron gas, [83,84] as well as its chemical stability, and structural behavior. In this chapter we briefly review the main features of the crystal structure of SrTiO$_3$ followed by an overview of its electronic and vibrational (phononic) band structures.

2.1 Crystal Structure

At room temperature, SrTiO$_3$ crystallizes in a cubic perovskite structure (with a general formula of ABO$_3$) with Pm3m space group (#221) and a lattice parameter of $a = 0.3905$ nm (resulting in a theoretical density of 5.11 g cm$^{-3}$). In the perovskite structure, Sr$^{2+}$ as the larger cation (A-cation) occupies the corner position of the cube and is surrounded by twelve O$^{2-}$ located at the cube edge centers. The Ti$^{4+}$ as the smaller cation (B-cation) occupies the larger space in the center of the cube, which is surrounded by six O$^{2-}$ thus forming TiO$_6$ octahedral units. Figure
2.1 shows the cubic perovskite structure of SrTiO$_3$. The Wyckoff positions for the Pm3m cell are given in Table 2.1. At lower temperatures, SrTiO$_3$ undergoes an antiferrodistortive structural phase transition from cubic to I4/mcm tetragonal (at 110 K). This is a fascinating feature of the perovskite structure, in that it readily undergoes one (or more) structural phase transitions as the temperature is varied. It is interesting to note that K. A. Muller, who shared the 1987 Nobel Prize in Physics with J. G. Bednorz for their superconductivity discovery, studied this cubic-to-tetragonal phase transition by electron spin resonance for his PhD dissertation. Beside this nonferroelectric phase transition, additional phase transitions at 65 K (orthorhombic) and 35K (rhombohedral) have been claimed which are under controversy. The Goldschmidt tolerance factor, $t$, is often used to define regimes where the various structures are stable. Goldschmidt (1926) observed that the perovskite structure (ABO$_3$) is stable if a tolerance factor, $t$, defined by [85]

$$ t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} 
$$

lies in the range $0.7 < t < 1.0$, where R refers to the ionic radii of A, B and O atoms. If $t$ lies outside this limit other structures exist. Only compounds for which $t$ is close to unity adopt the cubic space group Pm3m (e.g. for SrTiO$_3$ $t = 1.002$). [85]

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>Coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Sr)</td>
<td>1a</td>
<td>(0, 0, 0)</td>
</tr>
<tr>
<td>B (Ti)</td>
<td>1b</td>
<td>($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)</td>
</tr>
<tr>
<td>O (O)</td>
<td>3c</td>
<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
</tr>
</tbody>
</table>

SrTiO$_3$ was first reported in 1935, [86] but it was not until 1946 that its structure was determined from X-ray powder diffraction studies to be of the ideal perovskite type. [87] Strontium titanate mineral was not discovered in nature until 1984. However, bulk synthetic SrTiO$_3$ crystals have been available for scientific study since 1951. The tricone Verneuil technique (also known as the flame-fusion method) provided the first useful SrTiO$_3$ single crystals. [88, 89] The method was originally developed for the growth of rutile TiO$_2$ by Merker and Lynd at the Commercial Crystals section of the National Lead Co. (now NL Industries, Inc.). [90] Prior to this development no large transparent crystals of this compound had ever been produced, nor have any been found in nature. Due to the optical similarity of SrTiO$_3$ with diamond (index of refraction 2.4, optical dispersion 0.1),
Figure 2.1: Two unit cells of the cubic perovskite lattice of SrTiO\(_3\). Ti atoms are inside the octahedra and were not shown.

National Lead Co. manufactured SrTiO\(_3\) in large quantities and marketed it as a diamond imitation (gemstone called fabulite) starting in 1955, replacing rutile. [91] The single crystal samples used for research during the next 20 years had also been mostly purchased from this company. Production is reduced to a very low level in 1970 when YAG was found to give a more superior diamond imitation (although less dispersive, it has a better overall visual match to diamond and also is much harder). YAG itself has in turn been replaced by cubic zirconia in the following years. [92]

Many techniques have been employed to synthesize SrTiO\(_3\) single crystals. In an excellent paper Nassau and Miller [92] reviewed a wide variety of SrTiO\(_3\) crystal growth techniques and the properties of the respective single crystals. Solution growth has been shown to produce much better crystal perfection than Verneuil growth. However, neither the solution growth technique nor any other melt-grown techniques have been brought to the point where multi-centimeter size crystals can be grown under reasonably controlled conditions at practical growth rates; certainly only the Verneuil grown products are available commercially. The very high melting point of SrTiO\(_3\) (ca. 2100\(^\circ\)C) would, in general, preclude the use of more conventional crystallization techniques involving the use of a container capable of withstanding the high temperature and corrosive attack of the melt. [93]
At the same time, it should be noted that the Verneuil growth is one of the most difficult and complicated of all crystal growth in terms of operator skill required and tricone modification, which has to be used for SrTiO₃. Later, Bednorz and Scheel reported the exact growth condition for reproducible production of optical grade SrTiO₃ single crystals. [91,94] It is interesting to note that the Masters thesis of J. G. Bednorz dealt with Veneuil growth of SrTiO₃. The single crystals used in the current work as a reference to compare our results for polycrystalline samples were also grown by Verneuil method and were purchased from MTI corp., USA.

Figure 2.2: SrO-TiO₂ phase diagram. [5]

Figure 2.2 shows the phase diagram of the SrO-TiO₂ system which includes three main intermediate compounds including the perovskite SrTiO₃, and the layer-structured Sr₂TiO₄ and Sr₃Ti₂O₇. [95–97] The perovskite melts congruently and the layered structures incongruently. [98] The Sr₂TiO₄ and Sr₃Ti₂O₇ both have tetragonal structures (space group I4/mmm) with a = 3.88 Å, c = 12.62 Å and a = 3.94 Å, c = 20.38 Å, respectively. The existing phase information for SrTiO₃ gives no indication of any solubility for excess TiO₂. On the other hand, increasing the strontium content of SrTiO₃ results in the formation of a series of compounds with alternating layers of SrO and TiO₂ with the generic formula SrO-nSrTiO₃ (known as the Ruddlesden and Popper phases) [99]. These structures consist of two-dimensional n-unit-cells-thick perovskite slabs, separated by single layers of excess SrO in a NaCl structure sequence. This behavior is a demonstration of the high
degree of energetic stability characteristic of the perovskite pattern. The systems try to retain as much of this pattern as possible, even when the composition deviates grossly from the ideal.

2.2 Electronic Band Structure

Stoichiometric SrTiO$_3$ with Ti$^{4+}$ ions has a $d^0$ electron configuration, and consequently is a band insulator (as opposed to a correlated Mott insulator) with an experimental indirect energy gap (R-Γ) of $E_g$ = 3.27 eV and a direct gap (Γ-Γ) of 3.46 eV. The nature and character of the conduction and valence bands in SrTiO$_3$ can be readily understood using the molecular orbital picture and the corresponding energy diagram of the TiO$_6$ cluster. These molecular orbitals are formed as a result of the overlap of Ti 3$d$ orbitals with the ligand 2$p$ orbitals of O. Due to the sixfold coordination of Ti ions by surrounding O octahedron, a crystal field splitting of the degenerated Ti-3$d$ states into separated states called Ti-3$d$ $t_{2g}$ and Ti-3$d$ $e_g$ appears (see Figure 3). As it is shown, the valence band in SrTiO$_3$ is formed predominantly by the oxygen 2$p$ state whereas the conduction band originates directly from the Ti-3$d$ $t_{2g}$ states. This suggests that the modification of Ti-O interaction through Ti site doping and/or creation of oxygen vacancies could affect the band structure more significantly than Sr site doping. However, often the size of the dopant occupying the Sr site plays a crucial role in modifying the TiO$_6$ connectivity of the SrTiO$_3$ structure, and hence the electronic structure.

The electronic band structure of SrTiO$_3$, particularly the conduction band edge, has been the subject of experimental and theoretical studies for about 50 years. It is now known that the valence band maximum is located at $R_{15'}$ whereas the conduction band minimum is located at $Γ_{25'}$. In the absence of spin-orbit coupling, the conduction band minimum is threefold degenerate at $Γ$. Calculated band structure of stoichiometric SrTiO$_3$ is shown in Figure 2.4. The next lowest conduction band minimum is located at $X_3$ (only slightly higher, 0.18 eV, 0.15 eV, 0.13 eV). Favored as the global minimum in the early literature, this conduction minimum can contribute to multivalley conduction at high temperature or high doping concentrations.

The overlap between Ti 3$d$ orbitals and O 2$p$ give rise to narrow electronic bands (i.e. small bandwidths of ca. 3 and 4 eV for $t_{2g}$ and $e_g$ bands, respectively) which leads to large effective mass and consequently small carrier mobility, as discussed in Chapter 1. A variety of experiments have been performed to measure the effective mass for the conduction electrons in SrTiO$_3$. It should
Figure 2.3: (Top) overlap between Ti 3d and O 2p orbitals (bottom) schematic energy bands for TiO$_6$ octahedron in SrTiO$_3$. The d orbitals of Ti (right) under the octahedral crystal field. The energy bands divide into a set of $\sigma^*$ bands and a set of $\pi^*$ bands where the bands involve only the $e_g$ Ti 3d orbitals and the $p_\sigma$ O 2p orbitals while the bands involve only the $t_{2g}$ Ti 3d orbitals and the $p_\pi$ O 2p orbitals. Schematic was generated based on ideas in [6].

It be noted that these masses are not all equivalent since they include density of states masses, cyclotron masses and mobility masses. Moreover, their determination often depends on the assumption of a particular model for the conduction bands. [110] Nevertheless, a wide range of masses are reported for SrTiO$_3$. As we will see later, the electronic transport in the samples prepared in this work can be explained by a single parabolic band model with density-of-states effective masses of $m^* \sim 3.5 \, m_e$. 

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2.3 Vibrational Band Structure

There are five atoms per unit cell in SrTiO$_3$, each of which is located at a point of inversion symmetry. At the Brillouin zone center, the 15 degrees of freedom ($3 \times 5$ atoms) are made up of 3 acoustic branches (one $F_{1u}$ triply degenerate acoustic mode) and 12 optical branches (three $F_{1u}$ plus one $F_{2u}$ triply degenerate optical modes). Since SrTiO$_3$ is a polar (ionic) compound, several of the 12 optical branches have polar character originating from the perturbed dipole of cations and anions by lattice vibration. These polar optical phonons play an important role in both electronic and thermal transport in SrTiO$_3$.

The lattice dynamics and phonon spectra of SrTiO$_3$ single crystals have been extensively investigated experimentally using a variety of methods. Many of these studies have been performed primarily to investigate the unusual dielectric and ferroelectric behavior in SrTiO$_3$ single crystal as well as to understand its low temperature structural phase transition. Cowley has reported fairly complete data on the energy-wave vector dispersion curves of the vibrational branches in SrTiO$_3$ using neutron diffraction. [112] The lattice dynamics of SrTiO$_3$ have also been studied by infrared techniques. These measurements yield the energies of the polar transverse optical (TO) modes near the Brillouin zone center. Both Barker and Tinkham, [113] as well as Spitzer et al., [114] measured the energy of the three active polar TO modes. Similar phonon energies were reported for these
three modes (ca. 11, 22 and 67 meV at 300K) by different groups. [115,116] The highest frequency mode (546 cm$^{-1}$, corresponds to 67 meV) is associated with the vibration of TiO$_6$ octahedral. [114] Due to similar energies of electrons in doped SrTiO$_3$ to these polar phonons, strong electron-phonon coupling and scattering occur which significantly affect electrical properties of doped SrTiO$_3$. More recent and more extensive analysis of the infrared data has yielded quite accurate energies not only for the polar TO modes but also for the polar LO modes at the zone center. Figure 2.5 shows the phonon dispersion curves of SrTiO$_3$ single crystal. It is observed that the theoretical calculations are consistent with the reported experimental results from Raman spectroscopy, IR spectroscopy, and inelastic X-ray and neutron scatterings. The ionic nature of the crystal is the reason behind the splitting of the longitudinal and transverse optical branches at the center of the Brillouin zone, $q = 0$ (for long-wavelength optical phonons).

Figure 2.5: Phonon dispersion curves (phonon frequency vs. reduced wave vector coordinate) obtained from various reports. Open circles: $T = 90$ K, full circles: $T = 297$ K; crosses: $T = 90$ K; squares: $T = 120$ K; triangles: $T = 300$ K. [8]
Chapter 3

Electrical and Thermal Transport Measurements

Achieving reliable and accurate measurements of electrical and thermal transport properties are of utmost importance in thermoelectric materials research. This chapter is dedicated to a brief review of the transport measurement techniques which were used to measure electronic and thermal transport properties of SrTiO$_3$ ceramics in this work. All of the transport measurements in this work were performed at Prof. Terry M. Tritts Complex and Advanced Materials Laboratory (CAML), which is known for repeatable and reliable characterization of both electrical and thermal transport properties over a wide temperature range (30K $< T < 1000$K). Readers are encourage to consult several excellent papers and book chapters by Prof. Terry Tritt [10,12,117], and others [9] on more detailed discussions and issues related to accurate transport measurements.

The typical measurements that are necessary in order to fully characterize a thermoelectric material, which will be discussed in this chapter, are listed in Table 3.1.

The additional terms are defined as follows: $\mu$ is the carrier mobility, $n$ is the carrier concentration, $l_0$ is the length between the measuring leads on the sample, $A$ is the sample cross-sectional area, $e$ is the unit charge of the carrier (with $-$ sign for electrons and $+$ sign for holes). All the $Q$-terms relate to the rate of heat transfer or power related to that phenomenon, e.g. $Q_P$ is the rate of Peltier heating/cooling, $Q_J$ refers to Joule heating, and $Q_T$ is the heat transferred through thermal conduction.
3.1 Propagation of Measurement Uncertainty in Calculating ZT

Before discussing the measurements methodology, it is constructive to highlight the importance of accurate measurement of the specific transport properties, namely $\alpha$, $\sigma$, and $\kappa$ and its impact on the calculated figure of merit, ZT. This is elegantly highlighted by Tritt [117] using a simple example. Here we compare the calculation of the ZT of a material based on the real intrinsic values for each parameter involved with the calculation based on values which include reasonable estimates of measurement errors. Let us consider a material with intrinsic real materials parameters of $\alpha = 275 \, \mu V K^{-1}$, $\sigma = 1000 \, S \, cm^{-1}$, and $\kappa = 2 \, Wm^{-1}K^{-1}$ at $T = 300K$, which would result in a real ZT value of 1.13.

Now if we attempt to measure these parameters with some systematic errors in our measurement systems, we can see the effect of the uncertainty in each measurement on the calculation of ZT. We assume that the measured Seebeck coefficient will be 10% low leading to $\alpha' = 250 \, \mu V K^{-1}$. Poor thermal anchoring of the thermocouples to the samples or inaccurate calibration of the thermocouples could result in a 10% higher measured T than the real temperature gradient. The measured electrical conductivity will be taken 5% too high, $\sigma' = 1050 \, S \, cm^{-1}$, which could originate from inaccurate determination of the sample dimensions (3-4%), as is seen for the conductivity equation in Table 3.1, or determination of the current passing through the sample (ca. 1-2%). Assume the measured thermal conductivity to be 10% too high resulting in $\kappa' = 2.2 \, Wm^{-1}K^{-1}$, which could result from inaccurate determination of sample dimensions, uncertainty in T or errors in determination of the power input through the sample (possibly due to radiation losses in measurement). It should be noted that these values are all reasonable estimates of typical errors that can be made in these
measurements. Assuming that there will be no error in measurement of the sample temperature, i.e. $T' = 300$K, a $(ZT)'=0.89$ would be achieved which has an uncertainty of 21% from the real $ZT$ values of 1.13. It is then obvious that the accurate determination of these properties is very crucial. [117]

3.2 Electrical Transport Measurements

3.2.1 Electrical conductivity

For many materials the measurement of the electrical conductivity, $\sigma$, is straightforward. Typically, a four-probe (four-terminal) method is used in which the current, $I$, is injected through one set of current leads and the voltage, $V$, is measured using another set of voltage leads. This configuration, shown in Figure 3.1, eliminates the contribution of the leads or contacts to the measured sample voltage. Knowing the dimensions of the sample (cross-sectional area, $A$, the length between the voltage leads on the sample, electrical conductivity can be calculated using [9,117]

$$\sigma = \left(\frac{I}{V}\right) \times \left(\frac{l_0}{A}\right). \quad (3.1)$$

Despite its apparent simplicity, however, accurate measurement of conductivity in thermoelectric materials over a broad temperature range poses several significant challenges. Due to the semiconducting nature of many thermoelectric materials, contacts often form p-n junctions which can result in nonohmic voltages that lead to erroneous conductivity measurements. Formation of surface oxide layers, which are typically metal-semiconductor interfaces, also affects the electrical contact. [117]

Accurate determination of sample dimensions ($w$ and $l_0$) and current are very important factors as it is concluded from the equation (1). Accurate measurement of the current is typically achieved by measuring a voltage across a known precision resistor ($\sim 0.01$ to 0.1%) placed in series with the sample. The typical resistances measured in many thermoelectric samples are on the order of several m$\Omega$, which dictate the value of the precision resistor. More accurate measurement of $l_0$ can be accomplished by using several sets of voltage leads and averaging conductivity measurements (if the sample is sufficiently long). Positioning these voltage leads are of much importance in measuring electrical conductivity. It is important to locate the leads away from the current leads in order to
Figure 3.1: Principal arrangement of electrical conductivity measurement setup. [9]

assure uniform current flow through the sample at the points where the voltage is being measured. A good rule of thumb is to position the current and voltage leads in a way that \( l - l_0 \geq 2w \), where \( l \) and \( w \) are the total length and width of the sample, respectively. Therefore, long and relatively thin samples are ideal for electrical conductivity measurements. [117]

The presence of Peltier effect in thermoelectric materials is another source of significant error in conductivity measurements. Thermoelectric materials exhibit relatively large values of the Seebeck coefficient. This result in the total voltage measured across the sample, \( V \), to be the sum of the Seebeck voltage, \( V_{TE} \), plus the resistive (IR) voltage, \( V_{IR} \). [117]

\[
V = V_{TE} + V_{IR} = \alpha \Delta T + IR
\]

where \( R \) is the resistance of the sample. The Seebeck contribution is often comparable to the resistive component, i.e. \( V_{TE} \sim V_{IR} \). In order to minimize this effect, the measurement should be made relatively quickly (2-3 sec). Besides, by switching the current direction, the Seebeck voltage can be subtracted out using [117]

\[
V_{IR} = \frac{[V(I^+ + \alpha \Delta T) + V(I^-) + \alpha \Delta T]}{2}
\]

where \( I^+ \) is positive and \( I^- \) is negative. This suggests that the electrical conductivity of the ther-
moelectric materials should be measured using either AC or fact-switching DC current.

Figure 3.2: A diagram is shown of the setup for the measurement of the resistivity and Seebeck coefficient of bulk samples. A heater is attached to a small copper plate that is soldered to the top of the sample. Leads for the current ($I$), the upper Seebeck voltage lead, and one end of the thermocouple are attached to this copper. The other end of the sample is attached to a copper base that is heat sunk to the thermometer. Similar leads are attached to the copper base. Voltage leads for the resistivity measurements $V_R$ are attached to the sample as shown. Typical sample size is 2 to 3 mm for the width and/or thickness, and the total sample length is $< 10$ to 12 mm. [10]

Figure 3.2 shows a diagram of the setup for measuring the conductivity and Seebeck coefficient of bulk samples which is used in a custom-designed system at Prof. Terry Tritts Complex and Advanced Materials Lab at Clemson University for 30-300K measurements. The typical sample dimension is 2-3 mm in width and/or thickness by 10-12 mm, which is the total length of the sample. As it is shown, a heater is attached to a small copper block that is typically soldered to one end of the sample using a PbSn solder over Ni plating or in the case of SrTiO$_3$ samples attached using silver paste (Dupont: 4929N). Leads for the current ($I^+$) (Cu wire, O.D. = 0.004”), the upper Seebeck voltage lead ($V_{TE}^+$) and one end of the thermocouple are attached to this block. The other end of the sample is attached to a copper base that is heat sunk to the thermometer and the cooling stage. Similar leads are attached to the copper base. Voltage leads (Cu wire, O.D. = 0.003”) for the conductivity measurements are attached onto the samples as shown. For Seebeck coefficient measurements, the temperature gradient is measured using a thermocouple (3-mil Chromel-Au-Fe (0.7 at% Fe)-Chromel), the junctions of which are permanently embedded in the copper plates at the
ends of the sample where the thermoelectric voltage is measured. Kapp golden flux (for aluminum and aluminum to copper surfaces) and Ostalloy 244 (In 52%, Sn 48%) are used to achieve a low contact resistance (< 2 Ohms). The sample current is set to zero to measure the thermoelectric voltage. This configuration yields the most reliable and consistent conductivity and Seebeck coefficient measurements. As it was explained, the sample current is reversed for the conductivity measurements to eliminate the contributions of the thermoelectric voltage from Seebeck effect. [117–119]

For high temperature measurements (300K < T < 800K), a commercial ZEM-3 system (ULVAC Technologies, Inc.) was used to simultaneously measure the electrical conductivity and Seebeck coefficient under a helium atmosphere. The measurement setup is shown in Figure 3.3. Similar to the low-temperature setup, the electrical conductivity is measured using the four-terminal method.

Figure 3.3: Photograph of the ZEM3 high-temperature Seebeck coefficient/electrical conductivity measurement system at Complex and Advanced Materials Lab at Clemson University. (Inset) Schematic of Sample and probes arrangements inside the IR Furnace/Sample part of the system.
3.2.2 Seebeck coefficient

As was discussed earlier, the Seebeck coefficient is an intrinsic property of a material related to the materials electronic band structure. Measurement of the Seebeck coefficient as a function of temperature can mainly provide information about (i) the sign of the charge carriers (electrons or holes), (ii) the nature and width of the energy gap ($E_g$), and (iii) understanding of various physical phenomena (such as the scattering parameter or effective mass), in conjunction with other measurements. Since the Seebeck coefficient is not geometry specific, uncertainties related to measurement of sample dimensions are not present as is expected from $\alpha = \Delta V/\Delta T$. The common error here lies in the determination of temperature gradient. The Seebeck coefficient is given by the a measurement of the ratio of the sample voltage difference to the temperature difference along the sample, \[117\]

$$\alpha_{\text{measured}} = \alpha_{\text{sample}} - \alpha_{\text{lead}} = \frac{\Delta V_{TE}}{\Delta T} \quad (3.4)$$

where $\alpha_{\text{sample}}$ is the sample contribution to the measured Seebeck value and $\alpha_{\text{lead}}$ ($\alpha_{\text{Cu}}$ for our system) is the contribution from the voltage leads. Therefore the contribution from the lead, typically Au, Cu or Chromel, must be known and subtracted from each data point at each temperature. The Seebeck coefficient is conceptually the easiest of three parameters ($\sigma$, $\alpha$ and $\kappa$) to measure. However, there are a number of sources of error in practice including (i) wrong sign of the thermopower arising from inconsistent definition of the direction of the temperature gradient with respect to voltage measurement, (ii) uncertainty from temperature measurements resulting from the poor placement of the thermocouples with respect to the voltage leads, (iii) poor thermal anchoring. For the low temperature measurements, a constant temperature difference of 5K is applied across the sample (between the copper blocks) and the data is collected as the system cools to 30K and as it warms back to 300K with the cooling/heating rate (slewing temperature) of 0.25 K min$^{-1}$. This approach creates a quasi-steady-state where the change in temperature during each individual data point measurement (which takes approx. 1-2 sec) is very small. The system maintains a constant temperature difference of 5K between the copper blocks. \[10,117\]

For high temperature measurements ($300K < T < 800K$), the commercial ZEM-3 system (ULVAC Technologies, Inc.) was used. As it is shown in Figure 3.3, unlike the low-temperature setup, the Seebeck voltage is measured from the upper and lower "probe" thermocouples pressed against the side of the sample. These spring-loaded "probe" thermocouples (referred to as PTC in
ZEM catalogue) are thermocouples and voltage leads built together. This gives an advantage of both the temperature and the voltage being probed at the same point of contact. The probe separation is measured accurately using a microscope camera installed on the ZEM-3 setup.

### 3.2.3 Hall coefficient, carrier concentration and mobility

As it was discussed in Chapter 2, the appropriate optimization of the band structure and electronic transport requires the knowledge of the carrier concentration, \( n \), of a thermoelectric material which is determined by the Hall effect measurement. Other than carrier concentration, information on carrier type (electron or hole) and mobility is obtained from this measurement. Hall voltage is the quantity which is measured following (for a single-carrier system)

\[
V_H = \frac{BIw}{neA} = \frac{R_H BI}{t}
\]  

where \( V_H \) is the Hall voltage, \( R_H \) the Hall coefficient, \( B \) the magnetic field intensity, \( I \) the current injected through the sample, \( A \) the area which equals thickness \( (t) \times \) width \( (w) \), \( n \) the carrier concentration and \( e \) the electron charge. The parameters \( I, B \) and \( V_H \) are all perpendicular to each other. It is observed that the Hall coefficient is given by \( R_H = \frac{1}{ne} \) for a single-carrier system (such as SrTiO\(_3\)) and is much more complicated for a two-carrier system where both electrons and hole contribute to the transport. The electrical conductivity is then related to carrier mobility through \( \mu = R_H \sigma \) (or \( \sigma = ne\mu \)). The Hall voltage is created as a result of the Lorentz force \( (F_m = ev \times B) \) acting on a charged particle moving with a velocity, \( v \), in a magnetic field \( B \) being balanced out by the created electrostatic force \( (F_e = eE = eV/w) \). The electrostatic force arises from the electrons deflected by the magnetic field building up on one side of the material. Sources of errors that must be considered here are mainly (i) misalignment of the leads (IR leads), (ii) misalignment of the magnetic field, and (iii) unwanted temperature gradients (which might lead to thermoelectric voltages). In practice, four measured Hall voltages are averaged to account for thermal, thermoelectric, and Nerst contributions. \[117\]

In this work, the Hall voltage was measured on each sample with a Quantum Design Physical Properties Measurement System (QD PPMS) using a five-probe configuration under reversible low (0.5T) and high (3T) magnetic fields using AC current. This configuration uses three Hall voltage leads that are balanced with a bridge at a zero magnetic field to eliminate any resistive contributions.
Samples, typically 8 mm × 4 mm × 0.5 -1 mm in size, were mounted on a QD PPMS puck for measurement.

3.3 Thermal Transport Measurements

Thermal conductivity measurements are the most difficult to make of all three properties (σ, α and κ) with relatively high accuracy (5%). Very low thermal conductivity of good thermoelectric materials (typically κ < 2 Wm⁻¹K⁻¹) makes the measurement even more difficult, since the heat will flow through other paths of higher thermal conductivity (e.g. down lead wires or conduction by any gases or air flow around the sample). These result in an uncertainty in determination of the power input into the sample (QT). Therefore, of critical importance is the calculation of the heat loss corrections and the proper thermal shielding techniques to minimize these corrections and radiations effects. Thermal conductivity for a typical steady-state method, which is used for the low temperature (T < 300K) measurements performed in this work, is given by [12]

\[ \kappa = \frac{Q_T l_0}{A \Delta T} \]  

where QT is the heating power through the sample, l0 the length between the thermocouple leads, A the cross-sectional area and ΔT the measured temperature difference. A typical sample mounted on a removable sample mount (puck) is shown in Figure 3.4 along with the schematic of the leads configuration.

A small strain gauge heater is placed on top of the sample for which the heating power is given by I²R through the heater. Small copper flags (#38 gauge) are attached to the sample with thermal epoxy (Stycast 2850FT) and small Cu-Cr thermocouples (0.001” diameter) are attached to these flags to measure the temperature gradient. The base temperature is stabilized using a temperature controller. The power then sweeps at fixed temperatures yielding a QT vs. ΔT curve from which the slope is calculated, yielding the thermal conductance of the sample. Combining this with the dimension measurements, thermal conductivity of the sample at a given temperature is determined. [12]

As it was mentioned in the beginning of this section, the accurate measurement of thermal conductivity lies within the accurate calculation of the heat loss corrections and determination of QT. In the most general form, the power through the sample is the input power (I²R) applied to
one end of the sample minus the $Q_{\text{loss}}$, which is the power lost to radiation, heat conduction through gases or the connection leads, or losses due to heat convection currents.

\[ Q_T = I^2 R - Q_{\text{loss}}. \]  

(3.7)

These losses cannot be completely eliminated, but an appropriate experimental design would include design considerations to minimize or sufficiently account for each loss term. Choice of thermocouple and lead wires materials and diameters are examples of such design considerations to minimize the power lost to heat conduction through the leads. Corrections related to convection or radiation losses can be more substantial and difficult to minimize. The radiation loss, which is important for $T > 150\text{K}$, is given by \cite{12,118}

\[ Q_{\text{radiation}} = \epsilon \sigma_{SB} A (T_{\text{sample}}^4 - T_{\text{surroundings}}^4), \]  

(3.8)

where $T_{\text{sample}}$ and $T_{\text{surroundings}}$ are the temperatures of the sample and surroundings, $\sigma_{SB}$ the Stephan-Boltzmann constant $\sigma_{SB} = 5.7 \times 10^{-8}$ Wm$^2$K$^4$, and $\epsilon$ ($0 < \epsilon < 1$) the emissivity. One of the disadvantages of steady-state method for temperature above 150K is the relatively serious issue of radiation loss which needs to be dealt with effectively. If the heat conduction and radiation losses have been minimized with the appropriate measurement system design, then radiation losses should
be very small below 150K. One approach to account for the radiation loss corrections is to: [12,117]

1. calculate the lattice thermal conductivity, $\kappa_L$, from the measure $\kappa$ using $\kappa = \kappa_L + \sigma LT$, where the electronic contribution is extracted using the previously measure electrical conductivity,
2. mathematically fit the distinct temperature-dependence of lattice thermal conductivity observed between 5-150K (typically $\kappa_L \sim 1/T$ for crystalline materials) and extrapolate to $T = 300K$,
3. calculate the difference between the extrapolated $L$ and the measured $L$, i.e. $\Delta \kappa_L$,
4. if $\Delta \kappa_L$ displays a $T^3$ temperature-dependence, it generally be attributed to the radiation loss. $T^3$ is the typical temperature dependence of the radiation loss estimated from the Taylor expansion of $Q_{\text{radiation}}$ equation, Equation 3.8, taking the $T_{\text{sample}} = T_{\text{surroundings}} + \Delta T$, where $T_{\text{surroundings}}$ is the base temperature in the diagram in Figure 3.4. This is illustrated in Figure 3.5 for a AlPdMn quasicrystal. Typically as long as the radiation term is not greater than 15% of the total thermal conductivity, this correction to the data can be perform as described by Pope et al. [120]

![Figure 3.5: Temperature-dependence of thermal conductivity and its electronic and thermal components for a AlPdMn quasicrystal sample. The radiation-corrected total thermal conductivity (corrected $\kappa_{TOT}$) and lattice thermal conductivity (corrected $L$) are shown. (Inset) The difference between the extrapolated or corrected and measured lattice thermal conductivity, $\Delta \kappa_L$, is plotted as a function of $T^3$, illustrating losses due to radiation effects.][1]

For high temperature region ($T > 300K$), thermal conductivity was obtained from the measurements of thermal diffusivity ($d$), specific heat ($C_V$) and geometrical density ($\rho$) of the sample
using

\[ \kappa = d \rho C_V. \]  

(3.9)

The thermal diffusivity, \( d \), is measured using the transient (vs. steady-state) laser-flash technique by a Netzsch LFA 457 MicroFlash system. Parallel-faced samples with different sizes and shapes (e.g. round discs 12.7 mm in diameter or square 10 × 10 mm\(^2\) disks) and thicknesses between 0.5 and 5 mm can be measured. In the lase-flash thermal diffusivity technique, one face of the sample is irradiated by a short (\( \leq 1\)ms) laser pulse and the temperature rise on the opposite face is recorded by an IR detector. The thermal diffusivity is then calculated from the thickness of the sample and the temperature rise-time profile using the Parker equation

\[ d = 0.138 \frac{L^2}{t_{1/2}} \]  

(3.10)

where \( L \) is the thickness of the disk and \( t_{1/2} \) is the half-time of the maximum temperature rise of the other side of the sample. The Parker model assumes ideal conditions of adiabatic sample and instantaneous pulse heating, other models have been proposed over the years, which account for various losses in the measurement such as heat losses, finite pulse duration, non-uniform pulse heating and nonhomogeneous structures.

For all the SrTiO\(_3\) ceramics discussed in this work, we have used the Cowon + pulse correction model which is one of the most advanced methods. It should be noted that in order to maximize the amount of thermal energy transmitted from the front surface and to maximize the signal observed by the IR detector, the sample surfaces must be highly emissive. Usually this requires the application of a thin coating of graphite to the sample surfaces. Depending on the parallelism and flatness of the faces of the sample, an uncertainty of 2-5% in the measurement of thermal diffusivity, arising from the determination of dimension, exists. Netzsch LFA 457 thermal diffusivity measurement setup at the Complex and Advanced Materials Lab is shown in Figure 3.6 as well as the schematic of the flash method.

Measuring the constant-volume specific heat (\( C_V \)) required for the calculation of thermal conductivity would prove quite difficult in practice, since holding a materials volume constant as you vary the temperature is not very feasible for most materials. Therefore, \( C_V \) is approximated as \( C_P \). The high temperature \( C_P \) was measured using a Netzsch Pegasus 404C differential scanning
calorimetry (DSC). Due to the sensitivity of the method used for analysis three measurements must be conducted to determine the heat capacity including (1) a baseline measurement to subtract the background, (2) measurement of the specific heat of a standard material with a known $C_P$ (Sapphire used for the measurement of specific heat of SrTiO$_3$ samples in this work), and (3) measurement of the specific heat of the sample. [118] Samples must be flat and mirror-polished in order to make an ideal contact with the bottom of the measurement crucible (Pt/Rh pans with Al$_2$O$_3$ crucibles used in this work). More details on the exact structure of the DSC stage, a comparison of the DSC techniques to others, and exact instructions for measuring a sample can be found in various sources. [118]

Finally, the geometrical density of the samples was measured using the Archimedes method with ca. 1% uncertainty. Using the uncertainties of each of the measurements discussed above required to calculate thermal conductivity, a confidence level of 10% is achieved for the high temperature thermal conductivity results.
Figure 3.6: Photograph of the Netzsch LFA 457 Laser Flash System at Complex and Advanced Materials Lab at Clemson University. (Inset) the schematic side view of the Furnace/Sample setup.
Chapter 4

Synthesis and Processing of Bulk Polycrystalline SrTiO$_3$ Ceramics

A variety of synthesis routes, such as solid-state reaction, sol-gel, hydrothermal, molten-salt, and combustion synthesis have been employed to prepare polycrystalline SrTiO$_3$ depending on the nature of the property under study. This is in large due to the strongly process-dependent defect chemistry of SrTiO$_3$ which results in synthesis-dependent properties. In this chapter we review materials synthesis and densification techniques used to prepare powders and the corresponding bulk samples in this work as well as the in-depth investigation of the synthesis-property relationship and the optimization of the process parameters involved.

4.1 Powder Synthesis: Solid State Reaction

One of the oldest and still most widely used approaches to prepare polycrystalline solid materials, particularly oxides, is the direct reaction of the mixture of starting reactant powders at high temperatures (often 1000-1500°C). This method is known as solid-state reaction or the ceramic method. The basic idea here is to mix the stoichiometric amounts of the constituent oxides in powder form and then to heat the mixture to allow diffusion to achieve intimate mixing. Figure 4.1 shows a schematic diagram of the reaction between different particles in the solid-state mixture. For a given
temperature, the mass diffusion length, \( L_D \), can be estimated from

\[
L_D = \sqrt{4Dt}
\] (4.1)

where \( t \) is the reaction time and \( D \) the materials diffusivity given by

\[
D = D_0 \exp \left( -\frac{E_A}{RT} \right)
\] (4.2)

where \( D_0 \) is the materials diffusion coefficient, \( E_A \) the activation energy and \( R \) the gas constant. The coefficient of diffusion is an experimentally determined value that can range from \( 10^{-8} \) m\(^2\)s\(^{-1}\) for small molecules moving interstitially through a metal to \( 10^{-20} \) m\(^2\)s\(^{-1}\) for large molecules in organic materials. Oxides have a rather low melting point coefficient of diffusivity between \( 10^{-12}-10^{-14} \) m\(^2\)s\(^{-1}\) and a moderately high normalized activation energy between 22-25 \( E_A/(RT) \). Substituting these values into Equation 4.1 and 4.2 and assuming the mixture is held near the melting point for a week we observe that typical mass diffusion lengths could be as low as 5-25 nm. Decreasing the length of the diffusion path and increasing the number of points of contacts between the particles in the mixture can increase the reaction rate. This can be achieved by:

- Regrinding the mixture periodically (every 16-24 hours) to improve homogeneity,
- Improving contact between the particles by forcing the particles close together, e.g. via pressing the mixture into pellets,
- Increasing the temperature to increase the diffusion rate and consequently the reaction rate.

In practice, a combination of all three is used. This process of regrinding and heating is often referred to as "shake and bake" method which relies on the diffusion of elements at the molecular level to form a homogenous compound. The formation of the perovskite strontium titanate (SrTiO\(_3\)) by solid-state reaction of SrCO\(_3\) and TiO\(_2\) serves as a good example to explain the diffusion- or nucleation growth-controlled nature of the reaction.

Figure 4.1 schematically depicts the reaction of a SrCO\(_3\) grain with that of the TiO\(_2\) which are in intimate contact. SrO (formed by the decomposition of SrCO\(_3\)) has the rock-salt structure, while TiO\(_2\) has a hexagonal close-packed lattice. Following the reaction
the formation of SrTiO$_3$ takes place in at least three stages:

- After an appropriate heat treatment, first SrO reacts with the outer surface of TiO$_2$ grains to form the nuclei and eventually a surface layer of SrTiO$_3$. This nucleation is rather difficult because of the considerable difference in the structure of the reactants and product and the large amount of structural reorganization of the oxide lattice at the new TiO$_2$/SrTiO$_3$ reactant/product interface is required.

- Further reaction of SrO and the previously formed SrTiO$_3$ leads to the formation of the intermediate Sr-rich phase Sr$_2$TiO$_4$. The formation of this phase is necessary for the migration of the Sr$^{2+}$ ions.

- Sr$^{2+}$ ions from the Sr-rich intermediate phase Sr$_2$TiO$_4$ migrate into the remaining TiO$_2$ to form new SrTiO$_3$ layers. This step is controlled by the diffusion rates of the cations through the newly formed interfaces and especially the intermediate phase.
From the above discussion it is clear that reaction between two solids may not occur due to kinetic complications, even if thermodynamic considerations favor the product formation. However, the methods mentioned in the previous page can improve the rate of the reaction between the two components.

Niwa et al. [121] reported a high-temperature gravimetric study on the kinetics of formation of SrTiO$_3$. The results suggest the reaction time on the order of 1-2 days for calcination at ca. 1000°C to get a single phase compound. The reactivity of starting materials and the kinetics of the reaction of strontium carbonate with titanium dioxide have been also studied. The reaction of strontium carbonate with rutile obeyed the nuclei growth rate equation, with an activation energy of 409 kJ mol$^{-1}$. The kinetic of the reaction of strontium carbonate with anatase was described by a diffusion-controlled rate equation with a much lower activation energy of 279 kJ mol$^{-1}$. The difference between rutile and anatase in reacting with SrCO$_3$ has been related to the closer unit cell parameters of anatase and SrTiO$_3$. [122]

In this work, rare-earth (RE)-doped and undoped SrTiO$_3$ powders were prepared following the steps in the diagram shown in Figure 4.2. For a given doping composition, powders were prepared in 5 or 10g batches, depending on the number of samples needed from each batch. Stoichiometric amounts of SrCO$_3$ powder (99.9%; Aldrich), RE$_2$O$_3$ powder (99.9%; Alfa Aesar), and TiO$_2$ nanopowder (99.5%; Aldrich) were weighted following the reaction

$$ (1 - x)\text{SrCO}_3 + (x/2)\text{RE}_2\text{O}_3 + \text{TiO}_2 \rightarrow \text{Sr}_{1-x}\text{RE}_x\text{TiO}_3 + (1 - x)\text{CO}_2(g) \quad (4.4) $$

The starting powders were then mixed aggressively by mortar and pestle followed by 30 min mixing in the mixer. It is observed that for $x = 0$ the reaction is the same as the Reaction 4.3 above. The anatase TiO$_2$ nanopowder was deliberately chosen to increase the point of contact of starting materials in order to improve the reaction rate. The resulting mixture was then cold pressed into pellets, and calcined several times in air at 1400°C with intermediate grinding. The pellets were quenched in the furnace to room temperature after each calcination process. As it will be discussed in section 4 of this chapter, optimum synthesis parameters were determined by monitoring the X-ray diffraction pattern of the powders and electronic transport properties of the corresponding bulk ceramic.
Weigh soichiometric amounts of SrCO$_3$, TiO$_2$, and RE$_2$O$_3$

Grind and mix the powders

Calcination at 1400°C for 15 hours

Regrind and re-mix the powders

4.2 Powder Densification: Spark Plasma Sintering

Once the powder is prepared as discussed in the previous section, it is necessary to densify the powder into bulk samples in order to be able to measure the electronic and thermal transport properties. A variety of sintering techniques have been used in the literature to achieve bulk samples. However, hot press and spark plasma sintering are the most commonly used techniques for making high-density (typically > 90% of the theoretical density) bulk samples which are desired for thermoelectric studies and applications. In this work, bulk polycrystalline SrTiO$_3$ ceramics were prepared using spark plasma sintering.

Spark plasma sintering is a pressure-assisted rapid solidification method using pulsed DC current which enables the densification of the powder at lower temperatures and much shorter times.
(order of 1-10 min) which is favorable for suppressing the undesired grain growth. Also, as will be presented later, the high heating rates achievable via spark plasma sintering method bring about additional advantages over the other sintering techniques for the preparation of high-performance bulk SrTiO$_3$ ceramics. Figure 3 shows the schematic of the spark plasma sintering setup.

Figure 4.3: (Right) Schematic of Spark Plasma Sintering setup and (b) schematic of joule heating mechanism and coulomb discharge between powder particles upon applying pulsed current.

The initial spark plasma sintering conditions were chosen based on the reported process parameters in the literature. Table 4.1 lists the hot press or SPS parameters employed to prepare doped SrTiO3 powders reported in the literature by several groups.

<table>
<thead>
<tr>
<th>SPS or HP Condition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP @ 1400°C under 100 MPa (air)</td>
<td>[23]</td>
</tr>
<tr>
<td>HP @ 1200°C and 1400°C</td>
<td>[26]</td>
</tr>
<tr>
<td>HP 1 hour @ 1450°C under 36 MPa (Ar)</td>
<td>[25]</td>
</tr>
<tr>
<td>SPS 5 min @ 1200°C under 40 MPa (vac.)</td>
<td>[30]</td>
</tr>
<tr>
<td>SPS 30 min @ 1300°C under 34 MPa (vac.)</td>
<td>[123]</td>
</tr>
<tr>
<td>SPS 5 min @ 1300°C under 34 MPa (vac.)</td>
<td>[29]</td>
</tr>
</tbody>
</table>

Spark plasma sintering atmosphere, load, pulse ratio, heating rate, holding temperature, and holding time were chosen as dynamic vacuum, 60 MPa, 12:2, 50-100 A min$^{-1}$, 1400°C and 5 min, respectively. These conditions were optimized in order to benefit the electronic transport in bulk SrTiO$_3$ ceramics as will be discussed below.
4.3 Defect Chemistry

Vacancies and their complexes are dominant point defects in most perovskites, and their presence crucially affects electron mobility, electrical conductivity, and physical properties such as defect-induced ferroelectricity and blue and green emission in SrTiO₃ as well as defect-driven changes to the thermal conductivity. The defect structure of SrTiO₃ and its defect chemistry model have been extensively studied. In this section we briefly summarize the main concepts and findings of the defect chemistry of the donor-doped SrTiO₃, which is the focus of the current study. The reader is encouraged to consult the work of Eror and Balachandran, [124,125] Moos et al., [14,39].

Unlike pure and acceptor-doped SrTiO₃, donor-doped SrTiO₃ exhibits n-type electrical conductivity, with \( \sigma \) decreasing upon increasing oxygen partial pressure (\( P_{O_2} \)), regardless of the thermodynamic conditions under which the sample is synthesized and measured. From the experimental data, two main regions of partial pressure can be distinguished. In the first region (I and III in Figure 4.4a), the electrical conductivity decreases sharply for all compositions as the oxygen partial pressure increases. In the second region (II), the conductivity is almost independent of the oxygen partial pressure, and for higher concentration of dopants a plateau is formed (sometimes referred to as the plateau region). Figure 4.4b shows this behavior of electrical conductivity as a function of oxygen partial pressure.

![Figure 4.4: (a) Schematic log-log plot of electrical conductivity as a function of oxygen partial pressure for donor doped SrTiO₃ with slopes of \(-1/6\), \(0\), and \(-1/4\) in the low-, intermediate-, and high-\(P_{O_2}\) ranges, respectively, (b) Conductivity of donor-doped and undoped SrTiO₃ ceramics at 1300°C versus oxygen atmosphere pressure (symbols represent measurements and lines represent calculations). [14]](image)

An oxygen vacancy defect model has been proposed to account for the observed variations...
in the electrical conductivity. The basis of the model is the loss of neutral oxygen from the regular oxygen site (written as $O^\times_\text{O}$ according to Kröger-Vink formalism) in the lattice to the gas phase leaving behind a doubly-ionized vacancy ($V^{\bullet\bullet}_\text{O}$) while donating the two electrons to the conduction band. Kröger-Vink formalism is typically used to write and discuss defect reactions in materials. In this formalism, the subscript indicates the type of site the species occupies and the superscript indicates the excess effective charge associated with the species in that site. A positive unit of charge (equals in magnitude to the electron charge) is indicated by a dot ($\bullet$) superscript, a corresponding negative charge by a prime ($'$) superscript, and zero charge (a neutral situation) by a times ($\times$) superscript. Therefore, in this formalism we have

$$O^\times_\text{O} \rightleftharpoons V^{\bullet\bullet}_\text{O} + 2e + \frac{1}{2}O_2(g) \tag{4.5}$$

Denoting the concentration of defects by angular brackets ("[ ]") and assuming $[O^\times_\text{O}]$ as a constant, the mass-action law of Eq. (2) is given:

$$[V^{\bullet\bullet}_\text{O}]n^2P_{O_2} = K_{\text{Red}}(T) = K_{\text{Red}}^0 \exp\left(-\frac{\Delta H_{\text{Red}}}{kT}\right) \tag{4.6}$$

where $K_{\text{Red}}$ represents the formation constant of doubly-ionized oxygen vacancies (often called intrinsic donors) and $n$ is the concentrations of donated electrons. [14] Extrinsic donors, D, are trivalent ions occupying $\text{Sr}^{2+}$ sites ($D^{\bullet}_{\text{Sr}}$) or pentavalent ions occupying $\text{Ti}^{4+}$ sites ($D^{\bullet}_{\text{Ti}}$) whose concentrations are fixed by the initial composition. Due to their low ionization energies they remain fully ionized during the whole temperature range above room temperature. Upon doping the lattice, electroneutrality dictates a balance sum of positively and negatively charged mobile and immobile (frozen) defects and charge carriers (i.e. electron or holes). Taking into account the fact that strontium vacancies have been found to be predominant metal defects in SrTiO$_3$, the complete electroneutrality condition for the donor-doped SrTiO$_3$ is given by

$$n + 2[V^{\bullet\bullet}_{\text{Sr}}] = 2[V^{\bullet\bullet}_\text{O}] + [D^{\bullet}_{\text{Sr}}] \tag{4.7}$$

Depending on the thermodynamic conditions (e.g. oxygen partial pressure, temperature, etc.) and the originally weighted-in quantity of dopants, Equation 4.7 can be simplified considering only the majority defects. Ignoring the $P_{O_2}$-independent ionic contributions, the electrical
conductivity only varies with the carrier concentration and mobility following $\sigma = ne\mu$.

At very low $P_{O_2}$ values, oxygen vacancies are the dominant ionic defects ($[V_O^{\bullet\bullet}] \gg [D^\bullet]$) which are charge-balanced by the conduction electrons and all other defects can be ignored, thus

$$n \approx 2[V_O^{\bullet\bullet}] \quad (4.8)$$

Combining this with Equation 4.6 leads to a $P_{O_2}^{-1/6}$ dependence of electrical conductivity (region I in Figure 4.4a). At intermediate oxygen pressures, the concentration of oxygen vacancies becomes small, comparing to that of the extrinsic donors ($[V_O^{\bullet\bullet}] < [D^\bullet]$). Therefore, we have

$$n \approx [D^\bullet] \quad (4.9)$$

This results in an electrical conductivity that is dependent only on donor concentration and temperature-dependent electron mobility. This corresponds to the plateau region (region II) in Figure. At high $P_{O_2}$ values (up to 105 Pa = 1 bar $\approx$ 1 atm), intrinsic acceptors in the form of strontium vacancies compensate the donors, hence, we have

$$2[V_{Sr}''] \approx [D^\bullet] \quad (4.10)$$

leading to a $P_{O_2}^{-1/4}$ dependence of $\sigma$ (region III in Figure 4.4a). It is observed in Figure 4.4 that increasing the temperature increases the electrical conductivity for all $P_{O_2}$ values through the exponential term in eq. (3). Figure 4.4b shows the log $\sigma$-log $P_{O_2}$ plots of undoped and La-doped SrTiO$_3$ (Sr$_{1-x}$La$_x$TiO$_3$) reported by Moos et al. [14] It is observed that an increase in the donor concentration (La in this case) results in an increase in the electrical conductivity which is the most significant in the plateau region (region II) than the increase in region III. It is also observed that the plateau region extends to a lower oxygen partial pressure and region I practically disappears in the oxygen partial pressure range under study (see $x = 0.1$).

Akhtar et al. studied the energetics of defect formation and the charge compensation mechanisms for different type of dopants theoretically. [126] In case of a trivalent dopant $M^{3+}$ (e.g. La$^{3+}$) substituted at the Sr$^{2+}$ sites, the effective positive charge needs to be compensated as it was mentioned before. This can be done in three ways: (i) by the conduction electrons the concentration of which will be equal to the concentration of the extra positive charge (called electronic compensa-
tion), or (ii) by the formation of metal vacancies (i.e. $V_{Sr}''$ and/or $V_{Ti}'''$) (called ionic compensation), or (iii) by substitution in both Sr$^{2+}$ and Ti$^{4+}$ sites (called self-compensation). They calculated the solution enthalpies for the corresponding reactions:

(i) Substitution of M$^{3+}$ at Sr$^{2+}$ site with electronic compensation,

$$\frac{1}{2}M_2O_3 + Sr_{Sr}^x \longrightarrow M_{Sr}^* + \frac{1}{2}O_2(g) + e + SrO$$ (4.11)

(ii) Substitution of M$^{3+}$ at Sr$^{2+}$ site with strontium vacancy compensation,

$$\frac{1}{2}M_2O_3 + Sr_{Sr}^x \longrightarrow M_{Sr}^* + \frac{1}{2}V_{Sr}'' + \frac{2}{3}SrO$$ (4.12)

or titanium vacancy compensation,

$$\frac{1}{2}M_2O_3 + Sr_{Sr}^x + Ti_{Ti}^x \longrightarrow M_{Sr}^* + \frac{1}{4}V_{Ti}''' + \frac{1}{4}SrTiO_3 + \frac{3}{4}SrO$$ (4.13)

(iii) Self-compensation,

$$\frac{1}{2}M_2O_3 + Sr_{Sr}^x + Ti_{Ti}^x \longrightarrow M_{Sr}^* + M_{Ti}^r + SrTiO_3$$ (4.14)

It was found that depending on the dopant ion, for substitution at the Sr$^{2+}$ sites, electronic compensation or self-compensation are both possible. On moving along the lanthanide series, charge compensation mode changes from strontium vacancy compensation to self-compensation. Therefore, although in all cases donor-type behavior is expected, the effectiveness of later lanthanides (heavy lanthanides) as donor dopants should be reduced by self-compensation. According to Akhter et al. calculations, for La and Pr dopants, which will be discussed in this work, electronic compensation is the main charge compensation mechanism. [126]

### 4.4 Optimization of the Process Parameters

Solid-state reaction parameters as well as spark plasma sintering condition were optimized by monitoring the X-ray diffraction pattern, optical and electron micrographs, and electronic transport properties. From the rare-earth elements, lanthanum (La) was chosen as the benchmark dopant for
the optimization of parameters since it is the most studied dopant for n-type SrTiO\(_3\) which makes it a good reference to compare our results to the ones reported in the literature. Table 4.2 lists the optimum La concentration for both single- and polycrystalline samples reported in the literature. We have chosen 5mol% La:STO (i.e. Sr\(_{0.95}\)La\(_{0.05}\)TiO\(_3\)) as it has been reported as doping concentration resulting in a single phase compound.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optimum Doping (mol%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Crystal</td>
<td>0.015 &lt; x &lt; 0.05</td>
<td>[22]</td>
</tr>
<tr>
<td>Ceramic</td>
<td>x = 0.1</td>
<td>[22]</td>
</tr>
<tr>
<td>Single Crystal</td>
<td>x = 0.05</td>
<td>[19]</td>
</tr>
<tr>
<td>Single Crystal</td>
<td>x = 0.05</td>
<td>[22]</td>
</tr>
<tr>
<td>Ceramic</td>
<td>x = 0.08</td>
<td>[29]</td>
</tr>
<tr>
<td>Ceramic</td>
<td>x = 0.08</td>
<td>[123]</td>
</tr>
<tr>
<td>Ceramic</td>
<td>x = 0.12</td>
<td>[33]</td>
</tr>
</tbody>
</table>

It is worth noting that La-doped SrTiO\(_3\) was chosen over the undoped SrTiO\(_3\) for the optimization due to (1) more complex reactions and number of parameters involved in the preparation of La:STO which would make it a better control experiments as the future investigations require heavy doping of SrTiO\(_3\), and (2) higher carrier concentration and electrical conductivity is required than that of undoped SrTiO\(_3\) in order to be able to accurately monitor the effect of process parameters by measuring the transport properties. Here we present the results of our investigations on the optimization of both the solid-state reaction parameters as well as the spark plasma sintering condition.

### 4.5 Effect of the Number of Calcination Steps

The initial solid-state reaction parameters, especially calcination temperature, were chosen based on the reported process parameters in the literature. Table 4.3 lists the solid-state reaction recipes in order to prepare doped SrTiO\(_3\) powders reported by several groups. It is observed that calcination temperatures between 1300-1500\(^\circ\)C have been mainly used. Also, it is reported that the reactions were performed under Ar, 5%H\(_2\) in Ar (known as the forming gas), vacuum, and in air. Of course since we are dealing with an oxide system, the atmosphere and atmospheric pressure can significantly affect the defect chemistry and the kinetics of the reaction.
Table 4.3: Reported Solid State Reaction Condition for SrTiO$_3$

<table>
<thead>
<tr>
<th>Process Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 hours @ 1400°C (Ar)</td>
<td>[22]</td>
</tr>
<tr>
<td>several times @ 1400°C (air and Ar)</td>
<td>[23]</td>
</tr>
<tr>
<td>6h @ 1300°C (air) + 4 hours @ 1400°C (5%H/Ar)</td>
<td>[25]</td>
</tr>
<tr>
<td>6h @ 1300°C (air) + 4 hours @ 1460°C (5%H/Ar)</td>
<td>[16]</td>
</tr>
<tr>
<td>4 hours @ 1400°C (Ar)</td>
<td>[127]</td>
</tr>
<tr>
<td>15 hours @ 1400°C (vac.) + 15 hours @ 1400°C (vac.)</td>
<td>[128]</td>
</tr>
<tr>
<td>6 hours @ 1350°C (air) + 4 hours @ 1460°C (5%H/Ar)</td>
<td>[129]</td>
</tr>
<tr>
<td>12 hours @ 1300°C + 24 hours @ 1520°C (9%H/N)</td>
<td>[31]</td>
</tr>
<tr>
<td>6 hours @ 1000°C (5%H/Ar)</td>
<td>[33]</td>
</tr>
</tbody>
</table>

Based on these reports and the operation limitation of our tube furnace (T$_{max}$ = 1500 °C), $T_{\text{calc}}$ = 1400°C was chosen as the temperature for the calcination during which the decarbonation of SrCO$_3$ (decomp. temperature = 1494°C) to SrO (T$_m$ = 2530°C) occurs. Since we are not concerned with the grain growth at this point, a calcination time of 15 hours (with a heating rate of ca. 460° hour$^{-1}$) was chosen to allow the reaction sufficient time. As it was mentioned, the pellets were quenched in the furnace to room temperature after each calcination process, reground, mixed for 30 min, pelletized and re-calcined in the furnace. In order to systematically investigate the effect of the calcinations steps, we have prepared 5 batches of 5 mol% La:STO powders calcined in 1 to 5 steps. The final powders are labelled SL5TO-1C, SL5TO-2C, SL5TO-3C, SL5TO-4C, and SL5TO-5C, respectively. Figure 4.5a shows the x-ray diffraction pattern of these powders as a function of calcination time. Figure 4.5 shows the indexed lattice parameter (using DICVOL built-in program in PDXL software package) for the SrTiO$_3$ phase as a function of calcination time. Additional reflections for LaTiO$_3$, La$_2$O$_3$ and TiO$_2$ are observed in the patterns for 1 and 2 calcinations. However, no change in the diffraction pattern is observed after 3 calcinations. Similar behavior is observed in the estimated lattice parameters.

Powders were then densified under same spark plasma sintering condition reported earlier. It is observed that the density of the samples monotonically decrease until it reaches a plateau of 5.18 g cm$^{-3}$ for the sample with 3 calcinations and more. Figure 4.6a and b shows the temperature-dependence of the electrical conductivity and Seebeck coefficient of these samples.

Similar electronic transport behavior was observed for La-doped SrTiO$_3$ powders prepared after 3 or more calcination steps at 1400°C. Figure 4.6a shows an increase in the electrical conductivity as a function of calcination steps up to 3 calcinations. Similar behavior is observed in
Figure 4.5: (a) X-ray diffraction pattern of 5mol% La-doped SrTiO$_3$ powders as a function of number of calcination steps from 1 calcination (SL5TO-1C) to 5 calcinations (SL5TO-5C). (b) Indexed lattice parameter of the corresponding powder as a function of the number of calcination steps. Line is just a guide to the eye.

Figure 4.6: Temperature-dependence of electrical conductivity (a) and thermopower (b) as a function of the number of calcination steps.

the temperature-dependence of Seebeck coefficient in Figure 4.6b. Similar values of electrical conductivity and Seebeck coefficient for SL5TO-3C and SL5TO-4C suggest that the reactions involved were completed after the 3rd calcination and further calcination of the powder does not change the nature of the compound. Therefore, solid-state reaction with 3 calcination steps was chosen as the optimum number of calcination steps for powder synthesis.
4.6 Effect of Spark Plasma Sintering Heating Rate

In the spark plasma sintering technique, the heating rate is controlled by the amount of input current through the sample. Typically, 50-100 A min$^{-1}$ is used for ramping the temperature to the desired holding temperature. Since there were not enough reports in the literature on the effect of solidification heating rate (either SPS or HP) on the electronic properties of SrTiO$_3$ ceramics or other electronic oxides, we performed a systematic study on 5mol% La:STO powder. Two samples were SPSed from the same batch of SL5TO powder, under exact similar SPS condition but with different heating rates of 100 °C min$^{-1}$ and 400 °C min$^{-1}$, respectively (corresponding to 50 A min$^{-1}$ and 200 A min$^{-1}$). Figure 4.7a-c compares the temperature dependence of electrical conductivity, Seebeck coefficient and thermoelectric power factor.

![Figure 4.7a](image1)
![Figure 4.7b](image2)
![Figure 4.7c](image3)

Figure 4.7: Temperature-dependence of (a) electrical conductivity, (b) thermopower, and (c) the power factor for two samples SPSed under 100°C min$^{-1}$ and 400°C min$^{-1}$ heating rates.

Significant improvement in the thermoelectric power factor (50%) was achieved by tuning...
the SPS heating rate. This enhancement originates from a much improved electrical conductivity. Very similar values of Seebeck coefficient throughout the whole temperature range ($\alpha_{100} \approx \alpha_{400}$) suggest similar values of carrier concentration ($n_{100} \approx n_{400}$). Therefore, the observed enhancement in the electrical conductivity is mainly attributed to the increased carrier mobility ($\sigma = ne\mu$) in the sample SPSed with higher heating rate. This enhancement might arise from better compaction of the samples or diffusion of the dopants from the grain boundaries to within the grains due to the higher heating rate. Migration of dopants in both SrTiO$_3$ and BaTiO$_3$ has been reported in the literature. Further increase in the heating rate up to 500 $^\circ$C min$^{-1}$ results in similar power factor values. However, partial melting occurring close to the edges of the sample and formation of cracks of the sample is observed in these samples. Therefore, SPS heating rates of ca. 400 $^\circ$C min$^{-1}$ (200-250 A min$^{-1}$) was adopted as the optimum heating rate for powder solidification.

### 4.7 Batch-to-Batch Variations

Variations in the electronic transport properties of the samples SPSed from different batches of powders were also investigated. Two samples were SPSed from 2 different batches (batch P5 and P6, respectively) of 5 mol% La:STO prepared following the same solid-state reaction recipe and solidified into bulk ceramics using similar SPS parameters. Figure 4.8a and b compare the electrical conductivity and thermopower behavior of these two samples as a function of temperature.

![Figure 4.8: Temperature-dependence of electrical conductivity and Seebeck coefficient](image)

It is observed that results are reproducible between different batched within 10-15% for $\sigma$. 

53
and < 10% for α. A slightly higher electrical conductivity for the sample prepared from batch P5 is likely due to the slightly higher SPS heating rate (150 °C min\(^{-1}\) vs. 100 °C min\(^{-1}\)).

### 4.8 Effect of SPS Sintering Temperature

Effect of the spark plasma sintering (holding) temperature on the electronic transport properties of 5mol% La:STO bulk ceramics was investigated beyond what was reported in the literature (T > 1400°C). Figure 4.9a and b show the temperature-dependence of two samples prepared from the same batch of powder and SPSed under the same condition but with different holding temperature of 1400°C and 1500°C, respectively.

A significant improvement in the electrical conductivity is observed upon 100°C increase in the SPS holding temperature. A corresponding decrease in the Seebeck coefficient for the whole temperature range under study suggest an increase in the carrier concentration which might be either due to an increase in the oxygen vacancy content of the sample or an increase in the incorporation of the La\(^{3+}\) dopants in Sr\(^{2+}\) sites. This led to a 15% improvement in the thermoelectric power factor above 200°C. Therefore, an SPS holding temperature of 1500°C was adopted as the optimum temperature for future samples. Further increase in the SPS temperature leads to mechanically unstable samples.

![Graphs showing temperature-dependence of electrical conductivity and Seebeck coefficient](image)

Figure 4.9: Temperature-dependence of electrical conductivity (a) and Seebeck coefficient (b) showing the effect of SPS holding temperature.
Chapter 5

Thermoelectric Properties of Bulk Polycrystalline Pr-doped SrTiO$_3$ Ceramics

In this chapter, we present the results of our investigations on the thermoelectric properties of bulk polycrystalline SrTiO$_3$ ceramics doped with praseodymium, Pr, prepared using a novel synthesis strategy. As it will be shown later, significant enhancement in the properties, particularly electronic transport, is observed in these samples. Both electronic and thermal transport properties will be presented and the investigations in order to understand the origins of the improved properties will be discussed in detail. The contents of this chapter were mainly composed of the three papers recently published by Dehkordi et al. [20,21,130] The reader is encouraged to consult these references for detailed discussions which are out of the scope of present dissertation.

5.1 Literature Review

As it was mentioned in the previous chapters, tunable electrical conductivity along with a large carrier effective mass and degenerate conduction band, which leads to a large Seebeck coefficient at high carrier concentrations, promise a large thermoelectric power factor. However, a low carrier mobility ($\mu \sim 6$ cm$^2$ V$^{-1}$ s$^{-1}$ at 300 K for single crystals) [19] and a large total thermal conductivity
\( \kappa \sim 12 \text{ W m}^{-1} \text{ K}^{-1} \) at 300 K for single crystals) [19] detrimentally affect the thermoelectric performance which is evaluated by a dimensionless figure of merit, ZT. Maximum ZT values of 0.27 and 0.17 at 800°C were reported for La-doped and Nb-doped single crystals, respectively, [19] which need to be further enhanced in order for STO-based oxides to be able to compete with the other high temperature candidates, such as SiGe alloys.

Figure 5.1: Temperature-dependence of ZT of the doped SrTiO\(_3\) ceramics in the literature reporting improvement over the values for single crystals. Samples include polycrystalline bulk Pr-doped, [15] La- and Dy- double doped, [16] Nb-doped, [17] and Nb-doped with potassium titanate nanowires composite [18] as well as Nb doped epitaxial film. [17, 19] Pr-doped sample was reported after our initial reports and is shown to highlight the importance of synthesis strategy used in the current work. [20]

The majority of the experimental investigations in order to improve the thermoelectric performance of STO beyond that of the single crystal have focused on the reduction of \( \kappa \) mainly through lattice distortion and mass fluctuation scattering mechanisms. These attempts include: (i) Single- [22,23,26,28,29,33,123,129] or double-doping [16,31,32] of the Sr\(^{2+}\) and/or Ti\(^{4+}\) sites, which comprise the main efforts with respect to this direction. The maximum ZT values of 0.36 at 800°C for co-doped La\(_{0.08}\)Dy\(_{0.12}\)Sr\(_{0.8}\)TiO\(_3\) and 0.35 at 730°C for SrTi\(_{0.8}\)Nb\(_{0.2}\)O\(_3\) are the highest previously reported so far for bulk polycrystalline STO ceramics, [16,17] (ii) Synthesis of natural superlattice Ruddlesden–Popper structures is another attempt to reduce thermal conductivity. [25] However, it is observed that the detrimental effect of the insulating SrO layers on carrier mobility reduces electrical conductivity, hence it impairs the thermoelectric power factor (herein defined as \( PF = \alpha^2 \sigma T \)) more significantly than it reduces thermal conductivity. [131] (iii) Composite engineering is
also another strategy which was employed to reduce the thermal conductivity by addition of a nanosized second phase. Inclusion of YSZ nanoparticles and potassium titanate nanowires in Nb-doped STO matrix resulted in maximum ZT values of 0.21 and 0.34 at 630°C, respectively. [18,127] It is worth mentioning that due to the very small phonon mean free path in SrTiO$_3$ ($l_{ph} \sim 2$ nm at 300K for single crystal) [132], nanostructuring is not a viable option for the improvement of the TE performance of bulk STO ceramics primarily through the reduction of the lattice thermal conductivity.

![Figure 5.2: Temperature-dependence of maximum power factor (defined here as $PF = \sigma\alpha^2T$ values reported in the literature for polycrystalline SrTiO$_3$-based oxides. An upper limit of 1 Wm$^{-1}$K$^{-1}$ is observed for the reported values. Reference numbers from [1] to [17] in the Figure from [21] refers to the following references in similar order in this dissertation: [15–18,22–34]

Figure 5.1 shows the temperature-dependence of the thermoelectric figure of merit for the samples reported in the literature possessing relatively high values of ZT. It is observed that similar values and temperature-dependence have been reported for these samples through the reduction of lattice thermal conductivity.

However, no enhancement strategy has been reported to substantially increase the thermoelectric power factor in these oxides. The reported maximum $PF$ values in bulk single- and poly-crystalline STO have been confined to an upper limit of $PF \leq 1.0$ W m$^{-1}$ K$^{-1}$. Figure 5.2 shows the maximum power factor values at their respective temperatures reported in the literature for polycrystalline doped SrTiO$_3$ samples.
5.2 Motivation

The following conclusions were made from in-depth literature review: (i) As it was mentioned in the previous chapter, La was found to be the most studied Sr\(^{2+}\) site dopant for thermoelectric applications, (ii) Ti\(^{4+}\) site doping has not been investigated much and there is definitely room for further optimization and improvement, (iii) As it can be inferred from Figure 5.1, the majority of the attempts to improve the thermoelectric properties through the reduction of lattice thermal conductivity via mass fluctuation and strain field scattering mechanisms have achieved similar results. Therefore, there is a need to propose alternative enhancement mechanisms in order to be able to further improve the properties in SrTiO\(_3\)-based ceramics, and (iv) optimization of the electronic transport has not been investigated much as a function of synthesis parameters in order to improve thermoelectric properties. We found the optimization of the electronic transport as a good starting point strategy.

As it was discussed in chapter 4, the synthesis and processing of the doped SrTiO\(_3\) powders as well as bulk ceramics were optimized in the current work using La as the benchmark dopant. Significant improvement in the electronic properties was achieved over the values reported in the literature for similar doping concentration of 1 at\%. However, due to the formation of the unwanted insulating lanthanum oxide secondary phase for samples with La content above 1 at\% prepared following our synthesis recipe, further improvement of the properties was not possible. Figure 5.3 shows the periodic table of elements showing the other dopants which have been investigated as donors for thermoelectric applications in the literature (for Sr\(^{2+}\) site) when we started the current investigations.

Praseodymium was chosen as one of the candidates for our investigations motivated by intriguing structural properties recently observed in lightly Pr-doped SrTiO\(_3\), which have been investigated for ferroelectric applications. Ranjan et al. reported a doping-independent lattice parameter which has been partially attributed to multivalent nature of Pr (existence of both Pr\(^{3+}\) and Pr\(^{4+}\)). [133] This would be ideal for the purpose of the current work since the distortion of the lattice, which detrimentally affects the carrier mobility, can be eliminated in theory upon doping with Pr. As it will be discussed later, no such anomalous behavior of lattice parameter was observed in the Pr-doped SrTiO\(_3\) samples prepared in the current work. However, it was observed that Pr doping can bring about an additional enhancement in the thermoelectric performance of doped
5.3 Large Thermoelectric Power Factor in Pr-doped SrTiO$_3$−$\delta$ Ceramics

5.3.1 Synthesis

Pr-doped strontium titanate powders Sr$_{1-x}$Pr$_x$TiO$_3$ (with 0 < $x$ < 0.15) were prepared using the solid-state reaction process presented in Chapter 4. Stoichiometric amounts of SrCO$_3$ powder (99.9%; Aldrich), Pr$_2$O$_3$ sintered lumps (99.9%; Alfa Aesar) and TiO$_2$ nanopowder (99.5%; Aldrich) were mixed, cold pressed into pellets and then calcined in air at 1400$^\circ$C with intermediate grinding. The pellets were quenched in the furnace to room temperature after each calcination process. The calcined pellets were subsequently pulverized into powders using a mortar and pestle. The resulting powders were then wrapped in graphite foil and loaded into graphite dies. Powders were solidified into disks (≈12.7mm diameter and 3mm thick) using spark plasma sintering (SPS).
technique (Dr. Sinter Lab, SPS-515S) under vacuum at 1500°C for 5min. Samples were SPSed at 300°C min\(^{-1}\) heating rates (except the sample discussed in Figure 5.7, which was SPSed at 100°C min\(^{-1}\)). All samples were sintered under the same current pulse pattern on/off ratio. All samples were polished down for 0.25-0.5 mm from each side to ensure the complete removal of the graphite foil. Densities of all the samples were determined using the Archimedes method and they were all higher than 95% of their theoretical values.

### 5.3.2 Synthesis-Microstructure-Property Relationship

X-ray diffraction profiles of the \(\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_3\) powders for \(x = 0, 0.05, 0.075, 0.1,\) and 0.125 are shown in Figure 5.4a. All the diffraction peaks of the un-doped powder (i.e. \(x = 0\)) can be indexed to the \(\text{SrTiO}_3\) cubic perovskite structure with the space group \(\text{Pm}\overline{3}\text{m}\) and no other phases were observed. However, with increasing the nominal Pr content of the powders above \(x > 0.05\), small diffraction peaks corresponding to the \(\text{Pr}_5\text{O}_9\) phase (monoclinic, space group \(\text{P2}_1/c\)) were identified. [136] The intensity of these peaks increases with increasing Pr concentration as shown in Figure 5.4b. To the best of our knowledge, there are no reports on the solid solubility of \(\text{Pr}_2\text{O}_3\) in \(\text{SrTiO}_3\) (SrO-TiO\(_2\)) system.

As it was mentioned in the previous chapter, bulk ceramics were solidified from the as-prepared powders using the spark plasma sintering (SPS) technique. We found that the SPS heating rate can play a crucial role with respect to the modification of the electronic transport in these ceramics. To the best of our knowledge, no such analogous observations have been reported for oxide ceramic materials. Figure 5.4c shows the X-ray diffraction profiles of the as-prepared powder with \(x = 0.075\) before SPS and the one of the ceramic solidified with optimized SPS condition, corresponding to the sample shown with triangle markers in Figure 5.7a. A shift to higher angles is observed for all the STO peaks implying a further shrinkage of the lattice in the ceramic samples. This might suggest a further incorporation of Pr ions into STO lattice and/or creation of oxygen vacancies during SPS. Figure 5.4d exhibits the complete disappearance of the main Pr oxide peaks observed in the powder after SPS using an experimentally optimized heating rate.

It is known that the solid state reaction kinetics in these oxides is sensitive to reaction atmosphere and temperature as well as the choice and size of raw materials. We have taken advantage of the highly reducing atmosphere and high heating rate of the SPS technique to control the kinetics of the reaction of the residual Pr oxide in the as-prepared powder with the surrounding partially
Figure 5.4: (a) X-ray diffraction (XRD) profiles of $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_3-\delta$ powders before SPS as a function of nominal Pr content. (b) Close-up view of the dashed rectangle in (a), showing an increase in the Praseodymium oxides content of the powders with increasing doping concentration. (c) Comparison of XRD profiles of $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_3-\delta$ with $x = 0.075$ before SPS and after high-heating-rate SPS. Photographed images of cold-pressed powder after solid-state reaction and the corresponding SPSed ceramics are shown. The change in color is due to change in the oxidation state of Ti$^{4+}$ to Ti$^{3+}$. (d) Close-up view of the dashed rectangle in (c), showing the disappearance of the Praseodymium oxide peaks after high-heating-rate SPS. [21]
Figure 5.5: High resolution X-ray photoelectron spectroscopy (XPS) spectrum of Pr 3d core levels shown along with the deconvoluted components. Notice the absence of the characteristic peak of PrO$_2$ at $\sim$ 967 eV. [35] The binding energies of Pr 3d$_{5/2}$ and Pr 3d$_{3/2}$ core levels, the doublet energy separation, the shape of spectrum are characteristics of Pr$_2$O$_3$. [36, 37] The Pr 3d$_{5/2}$ and Pr 3d$_{3/2}$ core levels exhibit a shoulder $\sim$ 4.3 eV on the lower binding energy side corresponding to shake-off satellites. [20] The extra structure situated at the higher-energy of Pr 3d$_{3/2}$ core level is caused by the multiplet coupling effect. [21, 37]

doped SrTiO$_3$ grains (Figure 5.6b, inset). X-ray photoelectron spectroscopy (XPS) results confirmed that Pr$^{3+}$ is the dominant oxidation state of Pr in the ceramic materials made with the optimum SPS heating rate and the PrO$_2$ (Pr$^{3+}$) signature peak is absent in the Pr spectrum, as it is shown in Figure 5.5. However, the effect of the multivalent nature of Pr, which differentiates Pr from other reported Sr$^{2+}$ site dopants, on the kinetics of phase formation needs further investigations. Recently, we investigated the effect of the Pr doping source, Pr$_2$O$_3$ (Pr$^{3+}$) comparing to Pr$_6$O$_{11}$ (predominantly Pr$^{4+}$), on the synthesis and electronic transport properties for a given concentration of Pr ($x = 0.075$). It was found that the properties are independent of the type of the doping source used in the samples prepared following the recipe of the current work.

The effect of SPS heating rate on the modification of electronic transport, particularly the temperature dependence of electrical conductivity is shown in Figure 5.6a for two ceramics prepared from the same Sr$_{1-x}$Pr$_x$TiO$_3$ powder with $x = 0.075$. It is observed that the two samples possess similar temperature-independent carrier concentrations ($n \sim 1.10 \pm 0.2 \times 10^{21}$ cm$^{-3}$) and Seebeck coefficient (thermopower) values (Figure 5.6a, inset). However, a significant improvement in the electrical conductivity (60% improvement at room temperature) was achieved through enhancing the carrier mobility. It should be noted that both samples possess the same density. Such an increase
Figure 5.6: (a) Temperature-dependence of electrical conductivity and Seebeck coefficient (inset) for $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_3-\delta$ ceramic with $x = 0.075$ prepared using low (100°C min$^{-1}$) and high (300°C min$^{-1}$) SPS heating rates. Schematic on the right shows the presence of Praseodymium oxide ($\text{PrO}_y$) particles in the partially formed Pr-rich grain boundaries upon applying low heating rate (corresponding to 50 A min$^{-1}$ current rate). Schematic on the left indicates the complete dissolution of the praseodymium oxide particles in the Pr-rich grain boundaries under high heating rate (corresponding to 250 A min$^{-1}$). (b) Backscattered electron (BSE) micrograph of the ceramic made under a SPS low heating. Typical Pr spectrum of EDS line scan across a $\text{PrO}_y$ particle is shown. Inset shows the BSE micrograph of corresponding powder showing Pr5O9 particles sitting by the grain boundaries of Pr-doped SrTiO$_3$ grains. (c) Backscattered electron micrograph of the ceramic made under a high SPS heating rate. Typical Pr spectrum of EDS line scan across two grains, grain 1 and grain 2 is shown. Inset depicts the BSE micrograph of the Sr$_{0.95}$La$_{0.05}$TiO$_3$ ceramic prepared following the same recipe showing no such grain boundaries. [21]

in the electron mobility and electrical conductivity thus lead to a significant enhancement (30%) in the thermoelectric power factor over the whole temperature range that has been achieved primarily through tuning the SPS heating rate.

The proposed microstructure formation is depicted schematically in Figure 5.6a for both
samples. As it is shown in the backscattered electron (BSE) micrographs in Figure 5.6b and c, the Pr$_5$O$_9$ particles present by the grain boundaries in the as-prepared powder (Figure 5.6b, inset) form Pr-rich grain boundaries during SPS in both samples. However, the Pr$_5$O$_9$ species, in the form of PrO$_y$ (1.5 < y < 1.8) phases, are occasionally observed in the grain boundaries for the samples made by typical SPS heating rates of ~ 100°C min$^{-1}$ (corresponding to 50 A min$^{-1}$ current rate), as shown in Figure 5.6b and the schematic on the left. The EDS line scan performed across the bright praseodymium oxide region shows the typical sharp increase in the Pr counts. We found that by increasing the SPS heating rate (up to 300°C min$^{-1}$) enough energy can be provided for the Pr$_5$O$_9$ particles in the as-prepared powder to fully and locally dope the grain boundary region, as shown in Figure 5.6c. Such in-situ Pr-doped SrTiO$_3$ samples, in essence, can be thought of as two-component core-shell like composites with both core and shell features being a Pr-doped SrTiO$_3$, with the grain boundary phase having higher concentrations of Pr dopants. As we will see, these Pr-rich grain boundaries (shells) play a decisive role in improving the carrier mobility and hence the thermoelectric power factor. It is quite obvious in the inset of Figure 6 (c) that such boundaries were not observed for the samples doped with other dopants (e.g. La) following the same recipe. Much thicker average Pr-rich grain boundaries (~ 1µm) in Figure 5.6c, versus that of the sample made with lower heating rate (~ 200 nm), suggest a more localized distribution of dopants in the vicinity of the grain boundaries in this sample. Diffusion of the dopants from the grain boundaries to within the grains in the sample made with the lower SPS heating rate is believed to be the reason behind the reduction in the average grain boundary thickness. We believe this was facilitated by much lower heating rate and thus consequently longer SPS process time at elevated temperatures.

5.3.3 Electronic Transport Properties

Temperature dependence of electronic transport properties of Sr$_{1-x}$Pr$_x$TiO$_{3-δ}$ ceramics as a function of x is plotted in Figure 5.7a-c. These samples were all prepared with high SPS heating rate (~ 300°C min$^{-1}$). Figure 5.7a shows electrical conductivity (σ) as a function of temperature for these samples. All samples exhibit a degenerate semiconducting behavior, i.e. a decreasing electrical conductivity with increasing temperature.

It is also observed that the electrical conductivity increases with increasing Pr content. However, this increase is more significant for temperatures close to the room temperature, T < 200°C (473K). The dominant charge carrier scattering mechanism in STO at this temperature
region is a combination of polar optical phonon scattering, originating from the ionic nature of the STO lattice (Debye temperature, $\Theta_D \sim 390-413$K for un-doped STO), [137,138] and scattering from the deformation potential of acoustic phonons. [19] It is possible that the presence of the Pr-rich boundaries have alleviated the polar optical phonon scattering of carriers at these temperatures.

In fact, our experimental results show a more relaxed temperature-dependence for Hall mobility ($T^{-1.5}$), close to room temperature, than reported in the literature ($T^{-M}$, $2.0 < M < 3.2$). [19,38,39,139–141] In the view of the composite picture, theoretical efforts were made to explain the effective electrical conductivity of the composite from that of its constituents, namely the grain and the Pr-rich grain boundary phase. However, effective medium theories such as Bergman-Fel [142] fail to explain the effective properties. This might suggest the presence of a charge transfer mechanism.
or a contribution from phase interface which were not accounted for in the Bergman-Fel model. The reader is encouraged to examine the supporting information of reference [21] for the detailed calculations and discussions. Temperature dependence of Seebeck coefficient ($\alpha$) is depicted in Figure 5.7b. Diffusive-like thermopower is apparent for all the samples over the entire temperature range of this investigation (25°C to 500°C). No sign of any minority carrier contributions and bipolar effects are observed, in agreement with what would be expected due to the large band gap of this material. Low temperature (30-300K) measurements of the transport properties using a custom-designed four probe measurement system show excellent agreement with our high temperature measurements. The diffusive-like nature of the thermopower is extended to these low temperatures.

Thermoelectric power factor ($PF$) of these samples as a function of temperature and Pr content is plotted in Figure 5.7c. The power factor is increasing with an increase in Pr concentration. Sr$_{1-x}$Pr$_x$TiO$_{3-\delta}$ ceramic with $x = 0.125$ shows, to the best of our knowledge, the highest ever reported power factor of $\sim 1.3$ W m$^{-1}$ K$^{-1}$ at 500°C for a doped SrTiO$_3$ material system (see Figure S1 of the Supporting Information). It should be noted that the PF exhibits values above 1 W m$^{-1}$ K$^{-1}$ over a wide temperature range ($T > 200^\circ$C) for samples with $x > 0.075$. All the samples are reproducible and the transport measurements are repeatable with very good accuracy up to 500°C, the upper limit of our investigation, under a Helium atmosphere. A maximum power factor value as high as PF $\sim 2$ W m$^{-1}$ K$^{-1}$ can be predicted at 1000°C by fitting the experimental transport properties, if the measurement is to be performed under a highly reducing atmosphere (see Figure S9 of the Supporting Information).

In order to investigate the origins of the excellent electronic transport properties in Pr-doped SrTiO$_{3-\delta}$ ceramics, Hall measurements were performed on these samples. Figure 5.8a shows the carrier concentration as a function of nominal Pr content. All samples were synthesized under the same solid-state reaction and spark plasma sintering (SPS) conditions. A linear increase in carrier concentration is observed with increasing Pr concentration in the samples. It is also apparent that no unusual behavior, such as self-compensation or a change in Pr incorporation as a function of doping concentration, is observed. Excellent agreement between Hall carrier concentration and as predicted by simple electron counting is observed suggesting the incorporation of the majority of Pr dopants in Sr sites. The measured Hall carrier concentration for un-doped STO (red marker) suggests the creation of a large density of oxygen vacancies during SPS process. Figure 5.8b visualizes the dependence of effective mass ($m^*$) on carrier concentration ($n$) and Pr doping. Seebeck coeffi-
Figure 5.8: Electronic transport data for ceramics prepared under high SPS heating rates: (a) Hall and calculated carrier concentration as a function of nominal Pr content. Red marker represents un-doped oxygen deficient SrTiO₃ sample and the blue ones show Pr-doped ceramics. Solid and dashed lines are just guides to the eye. (b) The "Pisarenko plot" at room temperature. Solid curve is based on single parabolic band model, described by Equation 5.1, with $m^* = 3.83 m_e$ (300K). (c) Room temperature mobility of Pr-doped (blue squares) SrTiO₃ ceramics as a function of carrier density. Reported mobility values in the literature were also shown for comparison (square markers represent poly-crystalline samples and diamonds the single crystalline). (Reference numbers in Figure from [21] correspond to the references on this dissertation as follows: 27, [38] 29, [19] 56, [39] 63, [17] 64, [40] 65, [41] 66, [42] 67, [43] 68, [44] 69, [45] 70, [46]) The dashed line indicates the average of the reported values. All samples exhibit improved mobility values versus comparative reported values for single crystals. To the best of our knowledge, there has been no report on the carrier mobility of Pr-doped SrTiO₃ single crystals. [21]
described by [143,144]

\[ \alpha = \left( \frac{8\pi^2 k_B^2}{3e^2 h^2} \right) m^* T \left( \frac{\pi}{3n} \right)^{2/3} (1 + r) \]  

(5.1)

where \( k_B \) is the Boltzmann constant, \( e \) is the electronic charge, \( h \) is the Planck constant, \( m^* \) is the effective mass, \( n \) is the carrier concentration and \( r \) is the scattering parameter. The scattering parameter, \( r \), determines the energy-dependence of the relaxation time in the power law form, \( \tau(E) = \tau_0 E^{r-1/2} \). Deviations from this baseline curve described by Equation 5.1 are easily observed if \( m^* \) changes. It is found that the experimental transport data are well-described by a single parabolic band model (solid curve) for \( r = 0.5 \) [19, 66] (for ionic lattices) and \( m^* = 3.8m_e \) at 300K. It is also apparent that a slight increase in the effective mass occurs upon doping of the SrTiO\(_3\)–\( \delta \) lattice with Pr (for pure SrTiO\(_3\)–\( \delta \) ceramic, an effective mass of \( m^* = 3.0m_e \) is estimated from Equation 5.1 at 300K with \( r = 0.5 \)). By comparing the \( \alpha \) (V K\(^{-1}\)) vs. \( n \) (cm\(^{-3}\)) values of Pr-doped ceramics to our other STO samples doped with different dopants (e.g. La or Tb) as well as other reports in the literature, similar effective mass behavior was observed for ceramics doped with different dopants. It can be concluded that the improvement in the mobility of these ceramics is not rooted in any band structure modification mechanisms through Pr doping. Figure 5.8c shows the room temperature mobility values calculated from Hall carrier concentration and electrical conductivity (\( \sigma = ne\mu \), where \( \sigma \) is electrical conductivity, \( n \) is Hall carrier concentration, \( e \) is the elementary charge, and \( \mu \) is the electron mobility) for Pr-doped SrTiO\(_3\)–\( \delta \) ceramics. Reported mobility values in the literature are also shown for comparison.

An enhancement in the mobility of all poly-crystalline samples prepared following our synthesis strategy is observed versus the reported values for single crystals with similar carrier concentrations. This behavior is observed over the whole temperature range from 20K to room temperature. However, it is known that the carrier mobility of a material is typically always higher in a single crystal versus its polycrystalline counterpart due to carrier scattering by the defects and the grain boundaries in polycrystalline samples. This counter-intuitive observation suggests the presence of a "process-dependent mobility-enhancing mechanism". As a result of such a seemingly small increase in mobility, the thermoelectric power factor was enhanced from the previously reported maximum values of approximately 1 W m\(^{-1}\) K\(^{-1}\) at \( \sim 800^\circ\)C to 1.3 W m\(^{-1}\) K\(^{-1}\) at 500°C.

In conclusion, results on polycrystalline Pr-doped SrTiO\(_3\)–\( \delta \) as prepared using a new syn-
thesis strategy via spark plasma sintering (SPS) technique were presented. It is found that the SPS heating rate can play a crucial role in the modification of the electronic transport properties in these ceramics through the formation of a Pr-rich grain boundary phase. The nature of these grain boundaries and their role in improving mobility of the samples are not yet fully understood. However, it can be concluded from the transport data that there needs to exist a "carrier mobility-enhancing mechanism" in order to be able to explain the improved carrier mobility of polycrystalline samples prepared in this work versus the reported values for their single crystal counterparts. To the best of our knowledge, there has been no report of such a significant (∼ a factor of 2) enhancement of the mobility of SrTiO$_3$ oxides at or above room temperature. Bulk polycrystalline Sr$_{1-x}$Pr$_x$TiO$_3$ samples with $x = 0.125$ show the highest ever reported values of the power factor of ∼ 1.3 W m$^{-1}$ K$^{-1}$ at 500°C among n-type doped SrTiO$_3$ ceramics as well as single crystalline STO.

5.3.4 Optimized Pr Concentration

In order to determine the optimum Pr concentration in order to maximize the thermoelectric power factor, Sr$_{1-x}$Pr$_x$TiO$_3$ powders were prepared using a similar synthesis process beyond the Pr content reported previously (up to $x = 0.175$). Figure 5.9a shows the temperature dependence of electrical conductivity as a function of nominal doping concentration. All the samples exhibit a degenerate semiconducting behavior. It is observed that $\sigma$ monotonically increases with increasing Pr content up to $x = 0.15$ (shown with red arrow). Samples with $x = 0.15$ possess the largest electrical conductivity leading to the maximum power factor of 1.32 W m$^{-1}$ K$^{-1}$ at 500°C, the largest ever reported for either single- or poly-crystalline SrTiO$_3$ ceramics. However, a further increase in the Pr content up to $x = 0.175$, results in a marked decrease in the electrical conductivity (shown with gray arrow), most likely originating from a reduction in carrier mobility, $\mu$.

Figure 5.9b shows the Seebeck coefficient as a function of temperature. Diffusive-like thermopower (in agreement with the degenerate semiconducting behavior) is observed for all the samples and no sign of minority carrier contribution and bipolar effects are observed. The absolute $\alpha$ monotonically reduces with increasing the Pr content due to an increase in the carrier concentration, $n$, which is reported in Table 5.1. However, the increase in the carrier concentration and the corresponding reduction in the absolute thermopower is less pronounced for $x > 0.125$ which suggests the partial incorporation of the Pr dopants in the lattice. Appearance of small peaks of praseodymium oxide in the X-ray diffraction pattern for these samples confirms this suggestion. Room temperature
Figure 5.9: Temperature dependence in Celsius of (a) electrical conductivity and (b) Seebeck coefficient for Sr\textsubscript{1-x}Pr\textsubscript{x}TiO\textsubscript{3} polycrystalline ceramics as a function of Pr content. [20]

Properties are reported in Table 5.1.

5.4 Significant enhancement in thermoelectric properties of polycrystalline Pr-doped SrTiO\textsubscript{3−δ} ceramics

In this section we present the results of our further investigations to determine the thermal transport in order to evaluate the overall thermoelectric performance. As it will be shown, simultaneous enhancement in the thermoelectric power factor and reduction in thermal conductivity in these samples resulted in more than 30% improvement in the dimensionless thermoelectric figure of
Table 5.1: Room temperature measured and calculated materials properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrical Conductivity (S cm$^{-1}$)</th>
<th>Seebeck coefficient ($\mu$V K$^{-1}$)</th>
<th>Carrier concentration (cm$^{-3}$)</th>
<th>Mobility (cm$^{2}$V$^{-1}$s$^{-1}$)</th>
<th>Density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.075</td>
<td>2740</td>
<td>$-92$</td>
<td>$1.4 \times 10^{21}$</td>
<td>12.2</td>
<td>5.21</td>
</tr>
<tr>
<td>x = 0.10</td>
<td>3535</td>
<td>$-76$</td>
<td>$1.8 \times 10^{21}$</td>
<td>12.2</td>
<td>5.24</td>
</tr>
<tr>
<td>x = 0.125</td>
<td>4135</td>
<td>$-75$</td>
<td>$1.9 \times 10^{21}$</td>
<td>13.6</td>
<td>5.27</td>
</tr>
<tr>
<td>x = 0.15</td>
<td>4365</td>
<td>$-67$</td>
<td>$2.3 \times 10^{21}$</td>
<td>11.8</td>
<td>5.31</td>
</tr>
<tr>
<td>x = 0.175</td>
<td>2170</td>
<td>$-62$</td>
<td>-</td>
<td>-</td>
<td>5.33</td>
</tr>
</tbody>
</table>

merit (ZT) for the whole temperature range over all previously reported maximum values.

### 5.4.1 Thermal Transport Properties

Figure 5.10a shows the high-temperature thermal conductivity as a function of temperature and Pr content. It is observed that $\kappa$ decreases over the whole temperature range with increasing the Pr content for $x \leq 0.15$. Considering the increase in $\sigma$ with Pr content, this reduction suggests the suppression of lattice thermal conductivity with an increase in Pr concentration as well. The lattice thermal conductivity was determined from the Wiedemann-Franz relationship, $\kappa_L = \kappa - \sigma LT$, where $\sigma LT$ is the electronic thermal conductivity and $L$ the Lorenz number for a degenerate semiconductor ($L = 2 \times 10^{-8}$ W$\Omega$ K$^{-2}$). [145] It was found that not only the magnitude of $\kappa_L$ above room temperature reduces with an increase in the Pr content, but the temperature dependence of $\kappa_L$ relaxes, from $T^{-0.72}$ for $x = 0.05$ to almost temperature-independent for $x = 0.15$. Weaker temperature dependence than $1/T$ (i.e. $T^{-1}$), which is expected for a crystalline material at high temperature, is expected for samples with atomic disorder or other point defects. Further increase in the Pr content of the sample up to $x = 0.175$ leads to an increase in $\kappa$ as well as $\kappa_L$.

In order to further highlight the reduction in $\kappa$ and the effectiveness of the synthesis strategy employed in this work, the minimum lattice thermal conductivity, $\kappa_{min}$, for SrTiO$_3$ is calculated using Cahill’s formula for disordered crystals. [134,146] The calculated $\kappa_{min}$ is approximately 1.5 W m$^{-1}$ K$^{-1}$ at room temperature for pristine SrTiO$_3$. Figure 5.10b shows the room temperature lattice thermal conductivity as a function of carrier concentration for samples investigated in this work as well as reported in the literature for other single- and poly-crystalline samples. This figure provides a measure of the impact of different dopants on the distortion of the lattice and its corresponding effect on $\kappa_L$. 

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Figure 5.10: (a) Temperature dependence in Celsius of total thermal conductivity as a function of Pr content and (b) room temperature lattice thermal conductivity as a function of the carrier concentration for doped single- (single) and polycrystalline (poly) samples. The lines are guides to the eye. [20]

The reported $n$ might possibly include contributions from oxygen vacancies as well which can influence $\kappa_L$. However, considering the fact that the measured $n$ are almost always lower than (within 10%) the nominal values, these contributions can be assumed negligible and thus the trends considered valid. A linear decrease in $\kappa_L$ is observed for La-doped SrTiO$_3$ single crystals with increasing La content. This reduction originates from the differences in mass ($M_{\text{Sr}} = 87.62$ g mol$^{-1}$ and $M_{\text{La}} = 138.90$ g mol$^{-1}$) and ionic radii ($R_{\text{Sr}^{2+}} = 1.26$ Å, and $R_{\text{La}^{3+}} = 1.16$ Å) [147] of La and Sr which give rise to the mass fluctuation and strain field effect phonon scattering mechanisms. Similar behavior is expected for Pr-doped samples due to the close vicinity of La and Pr in the periodic table and their similar mass ($M_{\text{Pr}} = 140.90$ g mol$^{-1}$) and ionic radius ($R_{\text{Pr}^{3+}} = 1.12$ Å) [147]. However,
a steep decrease in $\kappa_L$ was observed with an increase in Pr content of the samples presented in this work. Due to the relatively large average grain size (2–4µm) in our samples, three orders of magnitude larger than the phonon mean free path, polycrystalline nature of the ceramics and phonon scattering from the interfaces are not anticipated to play a significant role in the expected trend. In fact, similar values of $\kappa_L$ achieved for La-doped SrTiO$_3$ polycrystalline ceramic and its single crystal counterpart attests to this assumption. [148] The significant reduction in $\kappa_L$ for the non-uniformly Pr-doped SrTiO$_3$ ceramics suggests the possibility of another phonon scattering mechanism beyond that of mass fluctuation and strain field effect observed in single crystals. X-ray diffraction analysis of the samples supported by electron backscattered diffraction (EBSD) suggests the cubic (Pm$\bar{3}$m) to pseudo-cubic (P4/mmm) transition in the Pr-rich boundary region, which is more visible for the samples with $x > 0.125$. This kind of structural transition has been reported in uniformly Pr-doped SrTiO$_3$ ceramics with $x > 0.05$ which is ascribed to the tilting of the TiO$_6$ octahedra. [149, 150] This suggests that aside from the respective mass fluctuation and strain field scatterings within the grain and the grain boundary regions, phonons experience an extra stain field-type scattering as they travel from the core domain (grain) to the shell region (Pr-rich grain boundary), comparing to the uniformly doped sample. It is also observed that $\kappa_L$ for sample with $x = 0.15$ is approaching the calculated minimum at room temperature. The knowledge of the phonon dispersion curves and their modification with cubic to tetragonal transition is required to be able to conclusively discuss the phonon scattering mechanisms in these ceramics.

### 5.4.2 Enhanced Thermoelectric Figure-of-Merit

Figure 5.11 shows the temperature dependence of the figure of merit, ZT. Reported maximum ZT values in the literature for single- and polycrystalline SrTiO$_3$ are also shown for comparison. [15–19] Pr-doped SrTiO$_3$ polycrystalline samples prepared using the strategy employed in this work shows much higher ZT values over the whole temperature range under study. Maximum ZT values above 0.6 can be predicted at 1000°C by fitting the experimental electronic and thermal transport data, if the measurements are to be performed under a highly reducing atmosphere. Of course, these projections need to be validated experimentally. However, it is worth mentioning that such high ZT values are achieved with high electrical conductivity which makes these ceramics desirable candidates for device fabrication due to minimal electrical contact problems.
Figure 5.11: Temperature dependence of thermoelectric figure of merit, ZT. The lines are guides to the eye. [20]
Chapter 6

Concluding Remarks and Future Prospect

As it was highlighted in the beginning of this monograph, the primary goal of this dissertation was to experimentally re-investigate the thermoelectric properties of bulk polycrystalline SrTiO$_3$-based thermoelectrics in order to realize the potential of the material system as a high-temperature candidate and to new develop possible new improvement mechanisms to further enhance the thermoelectric performance of the material.

To this end, a solid state reaction was chosen as it is a very well-studied synthesis method for oxide powders in general and SrTiO$_3$ compounds in specific. Spark plasma sintering was employed for powder densification as high-density specimens are desired for thermoelectric applications. As it was presented and discussed in detail, the synthesis parameters were systematically studied for powders and bulk ceramics doped with La as our benchmark dopant. It was observed that a significant improvement in the electronic properties can be achieved by tuning these parameters. The experimentally optimized parameters were then used to synthesis and study SrTiO$_3$ samples doped with Pr, which was not investigated before for thermoelectric applications, to the best of our knowledge. It was found that by fine-tuning the densification heating rate the electronic transport can be significantly enhanced over all previously reported values for doped SrTiO$_3$. A large thermoelectric power factor was achieved as a result. The first report on the thermoelectric properties of Pr-doped SrTiO$_3$ bulk ceramics was presented at the MRS Fall Meeting 2012. Further investigations showed
that this enhancement originates from a much improved carrier mobility in these samples (~ a factor of 2) over the values for either poly- or single-crystalline samples reported in the literature. It was conclusively found that non-uniform distribution of Pr dopants in the grain and the grain boundary regions underlie the observed intriguing electronic properties. It is worth highlighting that the thermoelectric power factor was improved by > 70% at 500°C over the previously reported values.

Later investigations show that these non-uniformly Pr-doped SrTiO_3 ceramics exhibit desirable thermal transport properties as well. Simultaneous enhancement in the thermoelectric power factor and reduction in thermal conductivity in these samples resulted in more than 30% improvement in the dimensionless thermoelectric figure of merit (ZT) for the whole temperature range over all previously reported maximum values. Maximum ZT value of 0.35 was obtained at 500°C. Maximum ZT values above 0.6 can be predicted at 1000°C by fitting the experimental electronic and thermal transport data, if the measurements are to be performed under a highly reducing atmosphere. It is worth mentioning that the superlattice thin films prepared from the Pr-doped SrTiO_3 targets prepared using the findings of the current work also show intriguing properties.

We believe that several investigations can be performed to further improve the thermoelectric properties of SrTiO_3-based thermoelectric. Recently, we reported a significant reduction in the lattice thermal conductivity (> 40% at 300K) via nonstoichiometry tuning. [151] The possibility
of the incorporation of such effects into the Pr-doped samples would be of interest. Furthermore, since the Pr-doped samples prepared in this work possess large thermoelectric power factor over a broad temperature range, double doping with another heavy Sr$^{2+}$ dopant (such as Tb) or a Ti$^{4+}$ site dopant (such as Nb) is expected to further improve the overall thermoelectric properties by reducing lattice thermal conductivity.
Bibliography


