Electrocaloric Cooling Efficiency of Perovskite Ferroelectric Thin Films

Shawn C. Fonseca
shawn.fonseca@gmail.com

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Electrocaloric Cooling Efficiency of Perovskite Ferroelectric Thin Films

Shawn Couceiro Fonseca

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Electrocaloric Cooling Efficiency of Perovskite Ferroelectric Thin Films

Presented by

Shawn Couceiro Fonseca, B.A.

Major Advisor

Dr. Pamir Alpay

Associate Advisor

Dr. George Rossetti

Associate Advisor

Dr. Rampi Ramprasad

University of Connecticut

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ABSTRACT

Ferroelectric thin films have been investigated recently for their electrocaloric properties. The electrocaloric effect is a coupling of electrical and thermal properties that results in a temperature change in response to an externally applied electric field. Through extensive material coefficient of performance (COP) calculations for Barium Titanate (BTO) and Lead Titanate (PTO), it is shown that electrocaloric materials provide comparable cooling efficiencies to thermoelectrics. The calculation is based on the Ericsson refrigeration cycle and results compare material COP values for various thermal and electric field boundary conditions. Direct application of this technology will be discussed, including on-chip cooling and different device geometries. However, there are some known challenges and opportunities regarding the ability to control directions of heat flow, which will also be reviewed.
1.0 INTRODUCTION

Electrocaloric materials are perovskite ferroelectrics that exhibit a phenomenon known as the electrocaloric effect (ECE). This effect is a coupling of electrical and thermal properties of such materials that display a change in temperature in response to an applied external electrical field. EC materials are of interest in many solid-state cooling applications, especially as thin film mediums. Early works with EC materials reported very low efficiencies, resulting in a lack of interest in the topic for several years. Following the discovery by A. Mischenko et. al. of an EC material exhibiting giant ECE up to 12 degrees, interest has once again resurfaced.

In this work, the ECE is investigated using BTO and PTO thin film mediums. A calculation is conducted to determine the coefficient of performance (COP) of these materials at different temperature boundary conditions and varying levels of applied electric field. The results are then compared to thermoelectrics, a common market solution used for solid-state cooling. The results show that the COPs for the EC materials under investigation are far superior to the thermoelectric competition.

1.1 PREVIOUS RESEARCH

Several papers were consulting in the execution of this investigation. The A. Mischenko et. al. paper already discussed was critical in sparking interest in the topic and established meaning in the investigation. Another paper by J. Zhang et. al. was crucial in determining the properties and potential of the BTO and PTO films used in the calculation for this thesis. This paper was also used to validate initial results of the COP calculation done. Finally, J. He et. al.
showcases the calculation method to determine the COP of a ferroelectric Ericsson refrigeration cycle. This work was followed for the process of calculating the COP for BTO and PTO.

In the Mischenko paper, Zirconium rich PZT thin films were investigated in terms of their EC capability. Previous studies had shown that bulk materials exhibited a small ECE, but in this work, Mischenko defends that PZT thin films indicate large ECE up to 12 degrees Celsius. In his work, characterization of the material was completed by calculating the change in entropy, polarization, and temperature across the ferroelectric-paraelectric transition at 222 degrees Celsius. The figure below shows the result of this work. The highest temperature change seen is 12 degrees at the transition temperature with a change in electric field of 480 kV/cm. (Mischenko, 2006)

![Figure 1: Electrocaloric temperature changes for Pb0.99Nb0.02(Zr0.455Sn0.455Ti0.09)O3 Using an Upper Electric Field of 776 kV/cm (Mischenko, 2006)](image)

The paper written by Zhang was used to validate initial calculations done in this investigation. In this work, Zhang has calculated several properties and parameters for BTO and PTO thin films including polarization, specific heat, entropy, and temperature change all as a function of temperature. The same material properties and input parameters used in Zhang’s
paper are used in this thesis calculation. The figures shown below are used to validate the calculation done in this thesis. The plots on the left are the results published in Zhang’s paper, whereas the plots on the right are the results of the calculation done in this thesis. As is seen, the two results correlate very well. (Zhang, 2009)

Figure 2: Left, polarization as a function of temperature and applied electric field as is found in the Zhang results. Right, validation of polarization calculations done in this thesis. (Zhang, 2009)

Figure 3: Left, entropy as a function of temperature and applied electric field as is found in the Zhang results. Right, validation of entropy calculations done in this thesis. (Zhang, 2009)
In the paper written by He, a detailed outline of how to calculate the coefficient of performance for a ferroelectric Ericsson refrigeration cycle is documented. The process laid out by He is followed throughout this thesis and all parameters are calculated in the same fashion. The figure below shows the generic electric field versus temperature plot used to describe the refrigeration cycle. The states a, b, c, and d are defined by respective thermal and electric field boundary conditions used to calculate the heat exchanged throughout the process designated here by $Q_c$, $Q_{bc}$, $Q_h$, and $Q_{da}$. The regenerator illustrated is assumed to be an ideal heat regenerator with no losses associated. The conclusion put forth by He is that the coefficient of performance of a ferroelectric Ericsson refrigeration cycle is always less than that of a Carnot refrigeration cycle for the same temperature range. (He, 2003)
1.2 APPLICATION

There are several applications for this technology, but the most intuitive application would be to cool computer chips and devices by employing a refrigeration cycle with an electrocaloric material as a thin film medium.

The way such a device would work would be to have the electrocaloric material in a centralized location in between a cold and hot temperature reservoir. The cold reservoir could be the ambient air, whereas the computer chip could be the hot reservoir. Then, an electric field must be applied across the electrocaloric material through the use of electrodes. In this example, the hot and cold reservoirs would work as the regenerators separately. The computer chip would continue to generate heat and the ambient air would continue to absorb heat from the electrocaloric thin film. A simple diagram below shows the basic outline for such geometry.
Upon defining this general geometry, there are some immediate concerns that must be addressed for this to be a viable solution. First, a thorough understanding of the transient must be established. Although these calculations are outside the scope of this thesis, the necessity is acknowledged. Essentially, it is important to know whether the time constant of heat transfer for the electrocaloric thin film is sufficient to actually draw heat from the hot reservoir. Are the heat transfer rate and thermal conductivity quick enough to actually absorb heat from a continually heat generating source and then release it to a colder atmosphere? There are concerns that this phenomenon will not occur quick enough.

Another concern is the ability to have control over the direction of heat flow throughout the cycle. In essence, it is necessary to separate the heating step from the cooling step of the electrocaloric thin film. The electrocaloric thermodynamically needs to focus on heating and drawing heat from the hot reservoir, and then sequentially focus on cooling and expelling heat to the cold reservoir. There are several solutions to this issue, but again, this is outside the scope of this thesis. Some solutions include thermal switches that act as thermal barriers to the hot and
cold reservoirs, as well as mechanically removing and establishing contact with the different reservoirs.

A final concern for this study is the overall mass of the thin film. In order to create a usable cooling device, the electrocaloric material must be able to provide enough heat transfer to cause a noticeable and usable temperature drop in the hot reservoir. Due to the nature of thin films, this is extremely difficult to be done with only “one” thin film. A solution to this is to increase the mass of the electrocaloric medium by stacking several thin films together either vertically or horizontally. Doing so will surely increase losses associated with the cycle, but ultimately will provide higher levels of cooling power.

Despite these concerns, researchers have found solutions to continue to demonstrate the applicability of electrocalorics as mediums in cooling devices. A patent was discovered that understands the technology and attempts to provide several geometrical solutions to how to organize the components of the cycle. The first solution, shown below, is very similar to the basic geometry described above, whereas the remaining 3 are variations to the geometry. In the following geometries, components labeled 10 are the thermal transfer devices, 20 are the electrocaloric devices, 30 are the power supplies, 22 are the electrodes, 24 are the electrocaloric materials, 40 are the thermal loads, 50 are the heat sinks, 60 are the heat exchangers, 26 are internal vias that define thermal flow passages, 28 are heat transfer mediums, and 70 are resonating circuitries (Lawless, 2005).
Figure 7: Potential electrocaloric cooling device geometry where the electrocaloric material is the medium in a capacitor that increases temperature with increasing applied voltage. Here, the heat exchanger is coupled with the thermal load and sink. (Lawless, 2005)

Figure 8: Another potential geometry where resonating circuitry couples a pair of electrocaloric devices. (Lawless, 2005)

Figure 9: An electrocaloric device geometry in which the electrocaloric devices are stacked horizontally with heat exchangers in between. (Lawless, 2005)
The figures seen above are potential geometries found in US patent number 6,877,325 written by William N. Lawless. In his patent, he describes these geometries with the intent of applying the technology to transfer thermal energy.

Another promising application is found in the work done by Y. Sungtaek Ju in the Department of Mechanical and Aerospace Engineering at the University of California, Los Angeles. In his research, Ju begins by creating an electrode assembly that is interdigitated, so that the electrocaloric material can then be inserted in between each set of electrodes. This is demonstrated in the figure below.

This assembly is then attached to MEMS devices on either end with the intent of mechanical movement. The MEMS then provide the movement of the assembly to make physical contact with the hot and cold thermal reservoirs respectively. At the moment that the
assembly is in contact with the cold reservoir, it is not in physical contact with the hot reservoir. The cycle is illustrated below.

![Diagram of the Ericsson refrigeration cycle]

Figure 12: Hot EC assembly (top left) moves to heat sink (top right) by MEMS. EC assembly releases heat, cools off, and moves to cold side (bottom left). (Ju, 2010)

Although there are many challenges in applying EC materials as cooling device mediums, there are several potential and viable solutions that can revolutionize this area of technology. EC materials would provide a far more efficient alternative to thermoelectrics if the devices described above can be fabricated.

1.3 Uniqueness of This Research

It is evident that a lot of research has been done in this field of study. The research presented in this thesis is different from the investigations found in the articles described above, as well as other work done. The study done in this thesis provides a calculation based investigation on the efficiency of using electrocaloric materials as the mediums used in an Ericsson refrigeration cycle. Specifically, the coefficient of performance for barium titanate
(BTO) and lead titanate (PTO) are calculated through numerical and iterative methods. In addition to this, the calculation is also done for PTO using dimensionless parameters. The results are then directly compared to thermoelectrics and represented favorably in terms of coefficient of performance. This work shows that electrocalorics are superior to thermoelectrics in cooling applications.

1.4 ELECTROCALORIC EFFECT

By definition, the electrocaloric effect is a thermoelectrical phenomenon that couples the electrical and thermal properties of dielectric materials when an electric field is applied under adiabatic conditions, resulting in a temperature change in the dielectric material (Akçay, 2007). Essentially, the application of the electric field causes a spontaneous change in the polarization of the dielectric material, causing an alignment of dipoles and resulting in a reduction of entropy of the system (Lu, 2010). The figure below helps to demonstrate this effect.

![Figure 13: Spontaneous polarization of dipoles in a dielectric material upon the application of an electric field (Lu, 2010).](image)

In adiabatic conditions, the entropy of the system must remain constant. For this to occur, heat is either accepted into the dielectric material or rejected to the atmosphere, depending on whether the electric field is increased or decreased. The change in temperature is then related
to this heat by the equation below, where C is the heat capacity of the dielectric material (Lu, 2010).

\[ Q = C\Delta T \]

In a refrigeration cycle application, the addition and removal of an electric field can be leveraged to make and break this spontaneous polarization, resulting in heat addition or removal.

1.5 Ericsson Cycle

The Ericsson Cycle is a thermodynamic refrigeration cycle. In traditional means, the cycle is typically used in engine type applications where air or some other medium is used to provide mechanical energy. When a ferroelectric material is used as the medium for an Ericsson Cycle, the cycle consists of two isothermal and two constant electric field processes. For this reason, the ferroelectric application of the Ericsson Cycle is more readily applicable than other thermodynamic cycles such as the Stirling Cycle because of its ability to be controlled by electric field instead of polarization (He, 2003).

To understand how the Ericsson Cycle works, it is most easily described in terms of its traditional thermodynamic application as an engine. The figure below shows the temperature versus entropy plot for the cycle. In this plot, it can be seen that there are two isothermal processes and two constant pressure processes. Process 1 to 2 is an isothermal compression at the lower temperature reservoir, where all heat is rejected to the surroundings. Process 2 to 3 is an isobaric heating process. Process 3 to 4 is an isothermal expansion process at the higher temperature reservoir, where all external heat is added. Finally, process 4 to 1 is an isobaric cooling process in which heat is rejected and used for heat input for process 2 to 3.
It can be seen that this traditional Ericsson cycle is very similar to the traditional Brayton Cycle. The difference between the two cycles is that the Brayton cycle uses adiabatic processes instead of using isothermal processes (Michael J. Moran, 2008). The figure below illustrates how a typical Ericsson engine would produce mechanical energy.

In this external combustion engine, air is the medium. Air would enter the non-return supply valve at the top right of the image and deposit into the supply cylinder. This air would then be compressed by the piston, which is moving in the upward direction. As this is done, the air passes through the exhaust valve at the top and into the tank. The high-pressure air would
then pass through the supply valve at the bottom left and into the regenerator where the air is preheated. Following the regenerator, the air is externally heated causing the air to expand. As the air expands, the piston is pushed upwards and the cycle begins again.

### 1.6 Ferroelectrics and the Ericsson Cycle

To apply the Ericsson cycle to ferroelectrics, first the medium must be changed from air to a ferroelectric material such as BTO or PTO. Then, instead of controlling the pressure of the medium, the electric field is controlled. This is typically done by applying a voltage across the medium. The figure below shows the temperature versus entropy plot for an Ericsson cycle utilizing a ferroelectric as the medium.

![Figure 16: Ericsson cycle utilizing a ferroelectric material as the medium (Ju, 2010)](image)

In the adiabatic process A to B, the ferroelectric experiences the electrocaloric effect where the electric field is increased, causing dipoles to align at the higher electric field. This spontaneous polarization results in an increase in temperature in the ferroelectric material. Process B to C is a constant electric field cooling process where the ferroelectric is releasing heat.
to the surroundings. Process C to D is another adiabatic process in which the ferroelectric experiences the electrocaloric effect. As the electric field is changed from maximum to minimum, the ferroelectric becomes spontaneously depolarized, thus causing a drop in the temperature of the ferroelectric. The final process of the cycle is a constant electric field process that heats the ferroelectric. This final process would be the step at which the ferroelectric would be absorbing heat from a heat source, like a computer chip. From here, the cycle begins again.

The ferroelectric application of the Ericsson Cycle is critical to this thesis because all calculations described throughout the remainder of this paper are based on the cycle just described.

1.7 THERMOELECTRICS

In the marketplace today, thermoelectrics are sold for the same applications as is envisioned for electrocalorics. Thermoelectrics are a different class of materials that utilize the Seebeck and Peltier effect. It is well-known, however, that thermoelectrics have a reputation of being extremely inefficient. In order for the efficiency of these materials to be relevant, the hot and cold temperature reservoirs need to be very close to each other in temperature, i.e. a small temperature delta.

The fundamental phenomenon that drives thermoelectricity is the Seebeck effect. Basically, this effect describes the observation that when two different materials are placed juxtapose to each other at different temperatures, there is a noticeable voltage difference that results. The relationship between the difference in temperature and the difference in voltage is driven by a material property known as the Seebeck coefficient (Subramanian, 2006).
A similar and analogous effect that also drives thermoelectricity is the Peltier effect. Essentially, when the same two materials are placed alongside each other and allowed to have electrical current pass through them, heat can either be absorbed or rejected depending on the direction of the current. The Peltier coefficient is also used to describe thermoelectricity and is directly proportional to the Seebeck coefficient (Subramanian, 2006).

In the marketplace, there are many manufacturers of thermoelectric materials and thermoelectric devices used for cooling and refrigeration purposes. One of these device manufacturers is Marlow Industries, Inc. The data obtained from the product listing on the company website was used for a comparison between thermoelectrics and electrocalorics. Most of the thermoelectric devices manufactured by Marlow Industries, Inc. are based on a bismuth telluride alloy. Further references to the thermoelectrics manufactured by Marlow Industries, Inc. will be referred to as Bi$_2$Te$_3$ (Marlow Industries, Inc., 2012).
2.0 Theory

In this section, an in depth look at the calculations done throughout this research will be provided. First, a brief overview of the process of the calculation will be described. Next, required input parameters and material properties will be listed. Finally, a step-by-step outline of the calculation for the COP of electrocalorics will be provided.

It is to be noted that the calculation steps outlined here are an incorporation of the theoretical discussion provided by J. Z. He to BTO and PTO as acknowledged in the work done by J. Zhang. In He’s article, an Ericsson refrigeration cycle is outlined using electrocalorics as the medium for the cycle. Continuing through the article, an outline for calculating the coefficient of performance for this electrocaloric Ericsson refrigeration cycle is provided. This process was followed meticulously throughout the calculations outlined in this research (He, 2003) (Zhang, 2009).

2.1 Process

It is sometimes easiest to describe the goal of a calculation and work backwards until a starting point is determined. Such is the case here. The purpose of the calculation described later in this thesis is to calculate the coefficient of performance for BTO and PTO. Calculating the COP for BTO will be done by using parameters with dimensions, while the PTO calculation will be done using dimensionless parameters. The two methods are same, but have some slight variations to between them in order to accommodate the differences between the parameters available. To begin to highlight the calculation process, the coefficient of performance will be described.
2.1.1 COEFFICIENT OF PERFORMANCE

The coefficient of performance (COP) is an evaluation of the performance of a refrigeration cycle. For a refrigeration cycle, it is not enough just to mention the efficiency of the cycle, because the operating conditions can be very influential as well. The COP combines the efficiency of the cycle with the operating conditions in one simple quantity, which can be and often is a number larger than 1. The COP is often defined as the ratio of cooling to the energy consumed as seen in the equation below.

\[
COP = \frac{\text{Heat Energy Out}}{\text{Energy In}} = \frac{Q_c}{W}
\]

In the expression above, the work done by the system is considered the Energy In, and the heat energy out, \(Q_c\), is the same \(Q_c\) as described earlier in the introduction section of this thesis.

2.1.2 HEAT EXCHANGE

As shown in the equation for the COP above, there are two quantities that now need to be defined, \(W\) and \(Q_c\). The heat energy out term is one of four heat exchange processes that occur throughout the cycle. The field-temperature schematic diagram is reproduced below for ease of reference.
The four heat exchange processes are $Q_c$, $Q_h$, $Q_{bc}$, and $Q_{da}$. Two of these terms, $Q_c$ and $Q_h$, are the heat exchange during the two isothermal processes of the cycle, while the other two terms are the heat exchange during the two constant electric field processes. In this case, $T_c$ is the low temperature reservoir, $T_h$ is the high temperature reservoir, $E_1$ is the high electric field potential, and $E_2$ is the low electric field potential.

The two isothermal heat exchange processes are governed by the following equation, where $G$ is the free energy and $s$ is the entropy.

$$Q = T * S(T, E) = -T \frac{\delta G}{\delta s}$$

The temperature in this equation is represented by $T$ and is dictated by which temperature reservoir the heat exchange is being calculated. So if $Q_c$ is desired, then $T_c$ would replace $T$ in this equation. The free energy and the entropy are terms that will need to be calculated iteratively as a function of temperature and electric field and will be discussed later.

The two constant electric field heat exchange processes are governed by the following equation, where $C_E$ is the heat capacity.
\[ Q = \int_{T_c}^{T_h} C_E dT = C_E (T_h - T_c) = -T \left( \frac{\delta^2 G}{\delta T^2} \right)_E (T_h - T_c) \]

Again, the free energy will need to be calculated iteratively to provide an accurate calculation for the heat capacity. This will be discussed later as well.

2.1.3 Work

The other term in the COP equation that needs to still be defined is the work term, \( W \). Work in this cycle is the energy applied to the system, i.e. the electrical energy applied. The work of a closed cycle is generally equivalent to the area within the thermodynamic cycle seen in the field-temperature schematic diagram. So in this case, work can be defined by the following equation.

\[ W = (Q_h - Q_c) + (Q_{bc} - Q_{da}) \]

At this point, all terms for calculating the coefficient of performance of the refrigeration cycle are accounted for and the equation for the COP can be rewritten as is seen below. The free energy, entropy, and heat capacity are all terms assumed to have been already calculated at this point. Those calculations will be described later on in this thesis.

\[ COP = \frac{Q_c}{(Q_h - Q_c) + (Q_{bc} - Q_{da})} \]

There is still another consideration to take place before the COP calculation is complete. The following section describes the importance of the entropy curves at the two electric fields and how this affects the \( Q_c \) quantity.
2.1.4 Regenerative Characteristics

When considering the regenerator in the refrigeration cycle, there are two scenarios that can arise: either the heat transferred into the regenerator is greater than the heat transferred out, or the heat transferred into the regenerator is less than the heat transferred out. Basically, this means that either $Q_{bc}$ is greater than or less than $Q_{da}$. When $Q_{bc}$ is greater, redundant heat in the regenerator can only be released to the cold reservoir in a timely manner. When $Q_{bc}$ is less than $Q_{da}$, there is inadequate heat in the regenerator and it can only be compensated from the hot reservoir in a timely manner (He, 2003).

To understand this more clearly, the entropy curves must be considered. Within these curves, three temperatures will be considered: $T_c$, $T_h$, and $T_m$. $T_m$ is the temperature at which the entropy difference between the two constant electric field curves is at a maximum. Often, this temperature is very similar to the Curie temperature of the material, but does not necessarily mean that the two temperatures should be equal. $T_m$ is dependent on the ferroelectric properties of the materials being used as well as the magnitudes of the two constant electric fields at hand (He, 2003).

The first plot to consider is the scenario where $T_m$ falls below the cold temperature reservoir of the cycle. The respective entropy versus temperature plot is shown below.
Figure 18: Entropy vs. temperature plot for $T_m < T_c < T_h$ (He, 2003)

In this case, the heat transferred into the regenerator, $Q_{bc}$, is greater than the heat transferred out of the regenerator, $Q_{da}$. The best way to visualize this is to look at the length of the curves between states a, b, c and d. $Q_c$ would be the heat exchange at the low temperature reservoir, $T_c$. Notice that if the low temperature reservoir were to line up with $T_m$, the length of the line between c and d would be longer. Basically, because $T_m$ falls below the low temperature reservoir, the cycle is operating at a less-than-optimal entropy difference, resulting in a reduction in refrigeration heat, $Q_c$. Therefore, when calculating COP, a slight difference needs to be applied. For this case, the equation for COP is as follows and incorporates the reduction in $Q_c$ (He, 2003).

$$COP = \frac{Q'_c}{W} = \frac{Q_c - \Delta Q}{W} = \frac{Q_c - (Q_{bc} - Q_{da})}{W}$$

The next case to consider is the opposite, where $T_m$ falls above the high temperature reservoir of the cycle. The respective entropy versus temperature plot is shown below.
In this case, the heat transferred into the regenerator, $Q_{bc}$, is less than the heat transferred out of the regenerator, $Q_{da}$. Again, the cycle is not operating at an optimal entropy difference and inadequate heat in the regenerator needs to be compensated from the hot reservoir. In this case, however, $Q_c$ remains unaffected, so the equation for COP remains the same as the original (He, 2003):

$$COP = \frac{Q_c}{W}$$

The final scenario to consider is the situation when $T_m$ is in between the low and high reservoir temperatures. The respective entropy versus temperature plot is shown below.
Within this scenario, there are three separate cases, depending on the exact temperature that the entropy difference is at a maximum. The difference in the heat exchange \((Q_{bc} - Q_{da})\) can either be greater than 0, less than 0, or equal to 0. In any of these three cases, when the temperature of the electrocaloric material is less than \(T_m\), the heat transferred into the regenerator is less than the heat transferred out of the regenerator, meaning that the inadequate heat in the regenerator can only be compensated from the hot reservoir in a timely manner. When the working temperature of the electrocaloric material is higher than \(T_m\), this means that the heat transferred into the regenerator is greater than the heat transferred out of the regenerator, meaning that the redundant heat in the regenerator can only be released to the cold temperature reservoir in a timely manner (He, 2003).

This once again affects the COP calculation because \(Q_c\) is affected. The calculation for COP can be rewritten for this case as is shown below.

\[
COP = \frac{Q'_c}{W} = \frac{Q_c - \Delta Q'}{W} = \frac{Q_c - (Q_{bc'} - Q_{da'})}{W}
\]
Essentially, this rewritten equation shifts the points c and d to c’ and d’ for calculation purposes, to accommodate the losses to $Q_c$. As stated, this can be positive, negative, or equal to 0 (He, 2003).

2.2 **Input Parameters and Output Parameters**

To begin the calculation, there are several parameters that must be determined and decided. The figure below provides a quick overview of the parameters required in the calculation. Below the input parameters is a list of parameters that will be output from the calculation.

![Input Parameters:](image)

1. Assume thin film
2. Strain: $U_m = 0$
3. Applied electrical field - low boundary: 0 – 120 kV/cm
4. Applied electrical field – high boundary: 150 kV/cm
5. Low temperature boundary:
   a. BTO: 10 K
   b. PTO: 529 K
6. High temperature boundary:
   a. BTO: 760 K
   b. PTO: 978 K

![Output Parameters:](image)

1. Polarization as a function of temperature
2. Heat capacity as a function of temperature
3. Coefficient of performance
4. Carnot coefficient of performance

**Figure 21:** Input and output parameters for COP calculation

There are a couple of points to reiterate from this chart. The first is bullet number 2 in the input parameters. In this calculation, it is assumed that there is no in plane strain restricting the thin film. Next, the way the calculation is done, the upper boundary of the electric field is
always maintained at 150 kV/cm whereas the lower boundary is a variable that can range from 0 to 120 kV/cm. In terms of the output parameters, all of these results can be output to an excel table and then plotted as needed.

2.3 MATERIAL PROPERTIES

In terms of material properties, there are several quantities that are required for both BTO and PTO. The table below summarizes the material properties used in these calculations. For reference, the Landau polynomial is provided as well.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Description</th>
<th>BTO</th>
<th>PTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$</td>
<td>Curie Temperature</td>
<td>383 K (109.85°C)</td>
<td>752 K (478.85°C)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>6.02x10$^3$ kg/m$^3$</td>
<td>7.90x10$^2$ kg/m$^3$</td>
</tr>
<tr>
<td>$M$</td>
<td>Molecular Weight</td>
<td>0.23 kg/mol</td>
<td>0.30 kg/mol</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>1$^{st}$ Order Dielectric Stiffness</td>
<td>3.3(T-383)x10$^3$ (J*m)/C$^2$</td>
<td>3.8(T-752)x10$^3$ (J*m)/C$^2$</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>2$^{nd}$ Order Dielectric Stiffness</td>
<td>3.6(T-448)x10$^6$ (J*m$^3$)/C$^4$</td>
<td>-7.3x10$^7$ (J*m$^3$)/C$^4$</td>
</tr>
<tr>
<td>$\alpha_{111}$</td>
<td>3$^{rd}$ Order Dielectric Stiffness</td>
<td>6.6x10$^9$ (J*m$^3$)/C$^6$</td>
<td>2.6x10$^9$ (J*m$^3$)/C$^6$</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>Electrostrictive Coefficient</td>
<td>-0.043 m$^2$/C</td>
<td>-0.026 m$^2$/C</td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>Elastic Stiffness</td>
<td>1.76x10$^{11}$ N/m</td>
<td>1.75x10$^{11}$ N/m</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>Elastic Stiffness</td>
<td>8.46x10$^{10}$ N/m</td>
<td>7.94x10$^{10}$ N/m</td>
</tr>
</tbody>
</table>

Figure 22: Table of material properties for BTO and PTO (Zhang, 2009)
2.4 Calculation

The entire calculation was done utilizing Matlab and writing extensive code to provide one code for a solution to the calculation. First, all of the appropriate parameters and properties are defined. Within the code, there are 4 major “for” loops that are used to iterate the calculation. The first and outermost loop is to iterate the electric field. This loop iterates the lower electric field until it reaches the constant higher electric field.

The second loop, which is contained within the electric field loop, is to iterate the lower temperature boundary.

The next loop, now within the lower temperature boundary, is the upper temperature boundary. Essentially, the code starts at a very low upper temperature boundary and has the lower temperature boundary increment until it reaches the upper temperature boundary. Once this occurs, the upper temperature boundary is then incremented higher. There are several reasons to increment the temperatures in such a way. This way provides a thorough sweep of a full temperature range from well below to well above the Curie temperature of the material. The other reason is that this method provides a way to run the calculation at several different deltaT values ($T_h - T_c$).

The last loop is yet again nested within the previous loop. This final loop is used to run through the entropy calculations at the temperature boundaries during the iteration. Following this last loop, the maximum entropy difference will be calculated and $T_m$ will be known for that set of $T_c$, $T_h$, and $E_2$ ($E_1$ is always 150 kV/cm).

Following the completion of the maximum entropy difference loop, the calculation for the COP can continue. Throughout the calculation, the polarization, entropy, specific heat
capacity, and COP will be calculated for each set of boundary conditions. After the calculation is completed, an Excel file will be output with a table of all the data points.

2.4.1 Calculating Maximum dS

To calculate the maximum entropy change, dS, the entropy for the high electric field and the entropy for the low electric field must be calculated at each set of temperature boundaries. Ultimately, the largest difference between these two entropies will be used to hold the temperature for $T_m$ for that set of boundary conditions.

To begin, the Landau polynomial is expressed as a function of temperature, T, electric field, E, and polarization, P. In the expression shown below, $G_0$ is the free energy density of the paraelectric phase.

$$G_{film} = G_0 + \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6 - EP + G_{el}$$

The elastic free energy term can be defined by the following expression where the in-plane polarization-free misfit strain, $u_m$, is zero, and $Q_{12}$ is the self-strain due to polarization.

$$G_{el} = \tilde{C}(u_m - Q_{12} P^2)^2$$

The effective elastic modulus is given as follows.

$$\tilde{C} = C_{11} + C_{12} - \frac{2C_{12}^2}{C_{11}}$$

Next, the equilibrium polarization can be determined by taking the derivative of the Landau polynomial with respect to polarization, setting the expression equal to zero, and solving for the polarization.
\[ P_o = \text{solve} \left( \frac{dG}{dP}, P \right) \]

For ease of calculation, the free energy density equation can now be rewritten as is shown below.

\[ G_{film}(P_o) = G_o + \alpha_1^{-} P^2 + \alpha_1^{+} P^4 + \alpha_{111}^{-} P^6 - E P + u_m^2 C^\sim \]

Notice that in this expression there are two new coefficients defined.

\[ \tilde{\alpha}_1 = \alpha_1 - 2u_m Q_{12} \tilde{C} \]
\[ \tilde{\alpha}_{11} = \alpha_{11} + Q_{12}^2 \tilde{C} \]

All quantities at this point are known and the free energy density can be calculated. It is important that the free energy density be calculated for both the low electric field potential and the high electric field potential. These calculations need also to be calculated at the next temperature increment as well to provide a change in free energy and a change in temperature.

The entropy can be calculated for the high and low electric field potentials by using the following equation.

\[ S = - \left( \frac{dG}{dT} \right) = - \frac{G_{film}^{T+1} - G_{film}}{\Delta T} \]
\[ dS = S_{E_2} - S_{E_1} \]

Logic is then incorporated into each temperature iteration of this maximum entropy difference loop to ensure that the maximum entropy difference is determined. Once it is determined, the code will hold the maximum entropy difference as well as the respective temperature for future calculations.
As previously described, this calculation is important because it will determine which scenario of the regenerative characteristics will be applied.

2.4.2 Calculating Qbc and Qda

The only difference between calculating $Q_{bc}$ and $Q_{da}$ is the electric field potential. The process is exactly the same and will only be described here once. However, it is to be noted that the $Q_{bc}$ calculation uses the elevated electric field potential, $E_1$ (150 kV/cm), while $Q_{da}$ uses the lower electric field potential at whatever iteration the code is currently at.

For the boundary conditions applied during the iteration at hand, the equilibrium polarization, $P_0$, the free energy density, $G_{film}$, and the entropy, $S$, are calculated in the exact same manner as previously described above. The following steps utilize these quantities to calculate the heat capacity.

As previously described, the equations that define $Q_{bc}$ and $Q_{da}$ contain the heat capacity. Therefore, it is a necessary step in this calculation. The heat capacity has two separate parts to it that are calculated separately and added together: the excess heat capacity, and the heat capacity that is a function of the temperature. The equation for the excess heat capacity is shown below.

$$CE_{xs} = \frac{-1 \cdot T \left( G_{film}^{T+1} - (2G_{film}) + G_{film}^{T-1} \right)}{\text{delta}T^2}$$

In this expression, notice that the free energy density is utilized from three different temperature iterations: the current temperature iteration, the previous temperature iteration, and the next temperature iteration. The temperature, $T$, and the change in temperature are also used.
in this expression. The heat capacity as a function of temperature is a little bit more complex and is shown below.

\[ CE_T = 8.314 \times CF_{BTO} \times (9 \times 5) \times \left( \frac{T}{TD} \right)^3 \times Z \]

\[ Z = trapz(X, Y) = trapz \left( 0.001: \frac{TD}{0.001T}: \frac{TD}{T} \cdot \frac{e^{X^4}}{(e^X - 1)^2} \right) \]

Here, the 8.314 is a factor used to ensure that units match, while CF\text{BTO} is a coefficient that relates the density to the molar mass and is equal to 25815.6369 kg/m^3K. The factor TD is a simple shift of the Curie temperature by 100 degrees, T_c + 100. The second part of this portion of the heat capacity calculation utilizes the trapezoidal method of integral calculation. The integrand is the function seen at the right of the parentheses with the exponentials and the X terms. This function is integrated from 0.001 to \( \frac{TD}{T} \) with an incrementing factor of the term seen in between these two boundaries. Once the integral is calculated, Z can be inserted into the CE_T equation. Now, both of these heat capacities can be added together.

\[ CE_{TOT} = CE_{XS} + CE_T \]

Finally, to calculate Q_{bc} or Q_{da}, the following expression is used. It is important that the value calculated during each iteration is added to the previous iteration, so that once the “For” loops are complete, a total sum for the loop is realized. This can be done by using the following expression.

\[ Q = Q + \frac{(CE^{T-1}_{TOT} + CE_{TOT}) \times deltaT^2}{2} \]
2.4.3 Calculating S at Each State

The calculation for $Q_{bc}$ and $Q_{da}$ are now complete and the next step is to calculate $Q_c$ and $Q_h$ as well as the remaining COP calculations. However, an important part of that calculation is coming up with all the state entropy values. The entropy needs to be calculated for each boundary condition: $S_a$ is at $E_2$ and $T_h$, $S_b$ is at $E_1$ and $T_h$, $S_c$ is at $E_1$ and $T_c$, and $S_d$ is at $E_2$ and $T_c$.

To do this, the same process is again repeated as was done at the beginning of the $Q_{bc}$ and $Q_{da}$ calculation and the maximum $dS$ calculation. The equilibrium polarization, $P_0$, the free energy density, $G_{film}$, and the entropy, $S$, are calculated in the exact same manner as previously described above.

It is critical that the calculation for these parameters be repeated for each entropy calculation, because each entropy uses different boundary conditions.

At this point, all required parameters have been calculated and the final calculations for COP can proceed.

2.4.4 Calculating COP

The remaining calculations should be relatively straight-forward and readily attainable. The first step is to calculate $Q_c$ and $Q_h$. The equations below show how to calculate these quantities.

\[ Q_h = T_h \times (S_a - S_b) \]

\[ Q_c = T_c \times (S_d - S_c) \]
As was described in the regenerative characteristics section, there are different scenarios which affect which $Q_c$ that will be used in the COP calculation. At this point in the Matlab code, logic is applied to sort through the data compiled and calculations made to determine which $Q_c$ to use. A brief overview of the logic is provided here.

When $T_m<T_c<T_h$,

$$Q_c = Q_c' = Q_c + \Delta Q = Q_c - (Q_{bc} - Q_{da})$$

When $T_c<T_h<T_m$,

$$Q_c = Q_c$$

Finally, when $T_c<T_m<T_h$,

$$Q_c = Q_c'' = Q_c - \Delta Q' = Q_c - (Q_{bc'} - Q_{da'})$$

It is noticed that in this final scenario there are different versions of $Q_{bc}$ and $Q_{da}$ to be calculated. Essentially, this is taken care of towards the beginning of the Matlab program when the maximum entropy difference is calculated. At that point in the program, it is known which of these $Q_c$ scenarios will be required. Therefore, the appropriate boundary conditions can be applied to the $Q_{bc}$ and $Q_{da}$ calculations described earlier.

The final calculation to be made before utilizing the equation for the COP is to calculate the work.

$$W = Q_h - Q_c + Q_{bc} - Q_{da}$$

Of note, it is understood that the work equation shown above does not incorporate the work done during the dielectric displacement that occurs in the perovskite crystal structure. The
work associated with this atomic displacement is not incorporated in this thesis. The calculation would consist of the area under curve for the polarization versus electric field plot, essentially the integral.

Now the COP can be calculated.

\[ COP = \frac{Q_c}{W} \]

One final step is to calculate the Carnot COP. This is essentially the ideal COP for the boundary conditions applied. This is a good way to ensure that the calculation has been done appropriately because the calculated COP should not be larger than the Carnot COP. The Carnot COP can be calculated using the following equation.

\[ COP_{carnot} = \frac{T_c}{T_h - T_c} \]

2.4.5 Calculation Variations for Dimensionless PTO

In order to begin the dimensionless calculation for PTO, it needs to be understood that there will be several new material parameters required. The table below lists the new material parameters that will need to be used in the dimensionless version of the calculation that were not used in the calculation done for BTO with dimensions.
In addition to new material parameters, it is much easier to discuss the dimensionless version of this calculation using a different Landau polynomial. The equation below represents the free energy equation used as the crux of this dimensional calculation.

\[
\frac{dG}{dp} = a_2(\tau - \tau_c)p + a_4p^3 + a_4(n_1^4 + n_2^4 + n_3^4)p^3 + a_6p^5 + a_6(n_1^6 + n_2^6 + n_3^6)p^5 - e
\]

In this expression, all of the analogous variables that are lower case, like \( p \) for polarization, \( e \) for electric field, and \( \tau \) for temperature, are all the dimensionless versions of polarization, \( P \), electric field \( E \), and temperature \( T \), used in the BTO calculation earlier. The Curie temperature in this case is \( \tau_c \) and is equal to 1.

Immediately, it is noticed that this free energy equation is slightly different than the one used in the calculation done with dimensions; there are different coefficients used in this equation. These coefficients are theoretically determined and are summarized in the table below.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Description</th>
<th>PTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_c )</td>
<td>Curie Temperature</td>
<td>752 K (478.85°C)</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density</td>
<td>7.90x10^2 kg/m³</td>
</tr>
<tr>
<td>( M )</td>
<td>Molecular Weight</td>
<td>0.30 kg/mol</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>Unit Cell Volume</td>
<td>6.4x10^-9 m³</td>
</tr>
<tr>
<td>( P_0 )</td>
<td>Zero-temperature Saturation Polarization</td>
<td>0.83 C/m²</td>
</tr>
<tr>
<td>( k_0 )</td>
<td>Boltzmann Constant</td>
<td>1.38x10^-12 m²kg/s²K</td>
</tr>
</tbody>
</table>
Figure 24: Table of coefficients for the free energy equation used in the dimensionless PTO calculation

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Description</th>
<th>PTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_2$</td>
<td>Reduced Dielectric Stiffness of Paraelectric Phase</td>
<td>2.45</td>
</tr>
<tr>
<td>$a_4$</td>
<td>Quartic Coefficient of Composition and/or Temperature</td>
<td>1.92</td>
</tr>
<tr>
<td>$a_{12}$</td>
<td>Quartic Coefficient of Composition and/or Temperature</td>
<td>-2.55</td>
</tr>
<tr>
<td>$a_6$</td>
<td>Sextic Coefficient Independent of Composition and/or Temperature</td>
<td>2.7</td>
</tr>
<tr>
<td>$a_{61}$</td>
<td>Sextic Coefficient Independent of Composition and/or Temperature</td>
<td>0.3</td>
</tr>
<tr>
<td>$a_{611}$</td>
<td>Sextic Coefficient Independent of Composition and/or Temperature</td>
<td>-0.9</td>
</tr>
<tr>
<td>$n_1$</td>
<td>Polarization Vector, Direction 1</td>
<td>1</td>
</tr>
<tr>
<td>$n_2$</td>
<td>Polarization Vector, Direction 2</td>
<td>0</td>
</tr>
<tr>
<td>$n_3$</td>
<td>Polarization Vector, Direction 3</td>
<td>0</td>
</tr>
</tbody>
</table>

As stated, there are two new variables in this version of the calculation: dimensionless temperature, $\tau$, and dimensionless electric field potential, $e$. These variables will be iterated in the Matlab code instead of $T$ and $E$ as previously used in the BTO code.

All of these dimensionless parameters can easily be converted to known parameters with units by using simple conversion factors.

First, to convert dimensionless temperature to temperature in Kelvin, the following equation is used.

$$T(K) = \tau \times T_c$$

The next equation is used to convert dimensionless electric field potential to electric field potential in V/m.

$$E \left( \frac{V}{m} \right) = e \times E_0$$

In this previous expression, $E_0$ is a conversion factor where
\[ E_0 = \frac{u}{P_0} \]

Where

\[ u = C E_0 \times T_c \]

Where

\[ C E_0 = \frac{k_b}{\Omega} \]

It is seen then, that these variables are easily transferable to parameters with units.

The majority of the calculation remains the exactly the same as the BTO calculation with the exception of a different free energy equation, new variables, different coefficients, and the lack of units. However, the process remains exactly the same. For this reason, the calculation will not be run through step-by-step in this section. Rather, only the minor changes to the calculation will be highlighted.

For the \( P_0 \) calculation, the new free energy equation is shown below. It is again noted that this calculation needs to be repeated for both the lower and higher boundary condition for the electric field potential.

\[
\frac{dG}{dP} = a_2(\tau - \tau_c)p + a_4p^3 + a_4(n_1^4 + n_2^4 + n_3^4)p^3 + a_6p^5 + a_6(n_1^6 + n_2^6 + n_3^6)p^5 - e
\]

Applying the values for the coefficients, this equation becomes,

\[
\frac{dG}{dP} = 2.45(\tau - 1)p + 1.92p^3 + 1.92p^3 + 2.7p^5 + 2.7p^5 - e
\]
Once $P_0$ is calculated, the value can then be inserted into the new free energy equation. This is shown in the equation below.

$$G = \frac{1}{2} a_2 (\tau - \tau_C) P_0^2 + \frac{1}{4} a_4 P_0^4 + \frac{1}{4} a_4 (n_1^4 + n_2^4 + n_3^4) P_0^4 + \frac{1}{6} a_6 P_0^6 + \frac{1}{6} a_6 (n_1^6 + n_2^6 + n_3^6) P_0^6$$

$$- e P_0$$

The same coefficients can be applied to this equation as well. Following this calculation, all of the equations and calculations for entropy remain exactly the same as was done for BTO.

The major change in the PTO calculation comes in the calculation for the heat capacity. As in the BTO equation, the heat capacity calculation will need to be done for the current temperature step, the previous temperature step, and the next temperature step, for each temperature iteration. The boundary condition is shown below.

$$X = 0.001 \cdot \frac{\tau_D}{\tau} \cdot \frac{\tau_D}{1000}$$

In this expression, $\tau_D$ is determined by the following calculation.

$$\tau_D = \frac{TD}{T_C} = \frac{T_C + 100}{T_C}$$

Next, the integration function is determined and set.

$$Y = \frac{e^{X^2}}{(e^X - 1)^2}$$

In Matlab, this integration is calculated using the “trapz” function as shown below.

$$Z = \text{trapz}(X, Y)$$

Now the heat capacity as a function of temperature can be calculated.
Then, the heat capacity as a function of temperature is inserted into the equation for the excess heat capacity, as shown in the following equation.

\[ CE_T = 8.314 \times (9x5) \times \left( \frac{\tau}{\tau_D} \right)^3 \times Z \]

The remainder of the calculations done on route to calculate the coefficient of performance for PTO is exactly the same as the calculations done for BTO. To review how to calculate the coefficient of performance, please refer to the previous sections of this thesis.
3.0 Results

In this section, the results of the aforementioned calculations are presented. First, the results for the BTO calculation are presented using quantities with dimensions. Then, the results for the PTO calculation are shown with dimensionless quantities. Finally, the results for both of the electrocaloric materials are compared to a common thermoelectric material, bismuth telluride alloy, manufactured by Marlow Industries.

3.1 BTO Results

Once the BTO calculation was complete, data was compiled for a range of temperatures of the cold reservoir from 10 to 700 Kelvin and a range of lower electric field potential from 0 to 120 kV/cm.

The plot below shows the coefficient of performance versus the temperature of the cold reservoir for several different values of delta T. To determine the hot reservoir temperature, simply take the temperature of the cold temperature reservoir on the x-axis and add the respective delta T value. Also in this plot, the lower electric field potential is compared from its lower bound, 0 kV/cm, to its upper bound, 120 kV/cm. There are several takeaways from this plot. The COP for BTO tends to increase as the temperature of the cold reservoir increases. Also, the COP increases as the delta T decreases, shown by the data represented by the black boxes. Finally, as the lower electric field potential is increased, the COP again increases. In all of these cases, the higher electric field potential is 150 kV/cm.
Figure 25: COP for BTO versus temperature of the cold reservoir for various delta T values.

The following plot is very similar to the plot just described. The purpose of the plot below is to show the effect of the change in the lower electric field potential. The red circles are the data points that correspond to when the lower electric field potential is 120 kV/cm. Generally speaking, the COP is greater at all temperatures at this electric field potential. One noticeable difference between the two data sets in the plot below is the significant drop in the COP of the $E_2 = 120$ kV/cm data set right around the Curie temperature of BTO. This temperature represents the phase change in BTO and it is at this point that the polarization becomes zero. As you increase the lower electric field potential to a value larger than 0, there will still be some polarization in the BTO, as was described earlier in this thesis. Therefore, this large drop in the COP is minimized as the lower electric field potential is increased.
The plots below show a direct comparison of different delta T values. Immediately it is noticed that as attention moves from the plot on the left to the plot on the right, the COP begins to drop rather quickly. This undoubtedly shows that as the delta T, temperature difference between the hot and cold reservoirs, increases, the COP of BTO decreases.

Next, it is common for manufactures of thermoelectric materials to present specification data on their materials by creating plots in which the y-axis shows the COP of the material and the x-axis shows the temperature difference between the hot and cold reservoirs. The following plots below show this data. However, it is important to understand that there are several...
combinations at which a certain delta T value can occur. For example, a delta T of 10 degrees can occur when the cold reservoir is 50 K, but also when the cold reservoir is at 550 K. In order to present this data effectively, the maximum values were taken. But, the maximum calculated COP for BTO for a specific delta T boundary condition didn’t always necessarily coincide with the maximum Carnot COP for the same specific delta T boundary condition. As such, two different plots were created. The plot on the left is of the data set when the calculated COP is at a maximum, and the plot on the right is of the data set when the Carnot COP is at a maximum. Both of the plots below are for when the lower electric field potential is 0 kV/cm. The calculated COP in both cases tends to have a good correlation with the Carnot COP values, but is always below the Carnot value. In the COP max plot, the calculated COP and the Carnot values are very similar to each other around the Curie temperature of BTO.

![Figure 28: COP for BTO versus delta T for a lower electric field potential of 0 kV/cm when COP is maximum (left) and when Carnot is maximum (right)](image)

The last plots, shown below, are exactly the same as the plots above, except that the lower electric field potential is 120 kV/cm. There are very slight differences between the plots at 0 kV/cm and the plots at 120 kV/cm. Yet, the COP values for the plot below are in fact slightly
higher than when the lower electric field potential is 0 kV/cm. On average, the increase in the maximum COP is about 0.2 when the lower electric field potential is increased to 120 kV/cm.

![COP Graph](image)

**Figure 29: COP for BTO versus delta T for a lower electric field potential of 120 kV/cm when COP is maximum (left) and when Carnot is maximum (right)**

### 3.2 PTO Results

The results for the calculations done for PTO were done using dimensionless quantities. Although all the calculations use dimensionless quantities, the COP values presented in the plots below are relevant and can be compared to the BTO data presented above, as well as the thermoelectric data that is presented in the next section.

All of the plots shown in this section are exactly the same as the plots for BTO and generally speak to the same conclusions. For the most part, all of the following plots show that as the delta tau increases, the COP decreases. Also, the plots demonstrate that as the lower electric field potential is increased, the COP values also increase slightly.
One point of caution is that most of these plots do not show data beyond the phase transition, i.e. beyond a cold reservoir dimensionless temperature of 1. The data beyond this point becomes extremely unstable due to the phase transition from a ferroelectric phase to a paraelectric phase. Therefore, any data beyond this point should not be considered.

The plot below shows the COP of the PTO calculation versus the dimensionless temperature of the cold reservoir at various delta tau values. The immediate observation from this data set is that when the delta tau is at a minimum, 0.01, the COP is at a maximum. Once the delta tau is increased, the COP values drop significantly. A general trend of these data points is that the COP value tends to decrease as the tau value approaches the phase transition tau value. In all of the following plots, the higher electric field potential value is 0.08.

![Figure 30: COP for PTO versus dimensionless temperature of cold reservoir at various delta tau values for a dimensionless electric field potential value of 0](image)

The following plot takes the same data points as the previous plot, but changes the lower electric field potential to a higher dimensionless value of 0.06. The same conclusion can be drawn from this plot, in that it shows that when the delta tau is at a minimum, the COP is at a
maximum. Also, the COP values for this elevated electric field potential are indeed larger than the COP values for the dimensionless electric field potential of 0. A general trend of these data points is that the COP value tends to increase as the tau value approaches the phase transition tau value.

The plot below shows the difference in data trends between the previous two plots. This plot only utilizes the data for when delta tau is at a minimum value of 0.01. It can be seen more clearly that as the lower electric field potential is increased to 0.06, the COP value is larger. Also, at this elevated electric field potential, the COP values seem to increase asymptotically as the $\tau_c$ value is approached. Rather, at a lower electric field potential of 0, the COP values seem to drop suddenly to 0 as the $\tau_c$ value is approached.
The next figure is a comparison plot of the COP for PTO as the delta tau is increased. Just as was seen with the data from the BTO calculations, as the delta tau values are increased, the COP values decrease significantly. This is demonstrated by observing the COP values for the plots from left to right. In the left plot, the largest calculated COP value for PTO is roughly 65, whereas on the rightmost plot where the delta tau is at a maximum, the maximum COP value is closer to 5. The plots also include the data points beyond the $\tau_c$ value. These data points demonstrate the instability of the COP in the paraelectric phase, as was described above.

Figure 33: COP for PTO versus dimensionless temperature of cold reservoir comparing several delta tau values and several dimensionless lower electric field potential values
The final two plots correspond to the last two plots in the BTO section. Here, the COP is plotted against delta tau. The plot below shows the data for when the lower electric field potential is 0. The plot on the left is of the data set when the calculated COP is at a maximum, and the plot on the right is of the data set when the Carnot COP is at a maximum. The data again correlates with the Carnot COP very well, demonstrating that the PTO material is an efficient alternative to thermoelectric materials.

![Figure 34: COP for PTO versus delta tau for a lower electric field potential of 0 when COP is maximum (left) and when Carnot is maximum (right)]](image)

The last plot shown below is the case where the lower electric field potential is increased to 0.06. The data set at this elevated electric field potential shows a very slight increase in the COP when considering the optimal boundary conditions. In either case, the calculated COP is compares favorably to the ideal case represented by the Carnot COP curves.
3.3 **Electrocalorics vs. Thermoelectrics**

Once all the data was compiled and presented for the BTO and PTO calculations, it was important to compare the results to the current market solutions. Marlow Industries is a manufacturer of thermoelectric devices comprised of a bismuth telluride alloy. The data obtained from their website was used to compare the COP data for BTO and PTO.

In the plot below, the black curves represent the COP data for the bismuth telluride alloy from Marlow Industries, the red curves represent the ideal Carnot case, and the blue curves are the calculated BTO curves. It can be seen that the Carnot curves establish the upper boundary for COP. Very close to the Carnot curves are the blue BTO curves, residing well above the black curves for the thermoelectric data. In all cases, as the delta T decreases, the COP increases. It is at very small delta T values that the thermoelectric devices can become competitive to BTO. However, once the delta T is elevated beyond 50 K, the thermoelectrics become extremely uncompetitive, with respect to COP.
This next plot is a filtered case from the plot above. The same data is represented, but no Carnot curves are shown, both BTO curves are shown, and only one bismuth telluride curve is shown. The intent of this plot is to portray the data more cleanly with less clutter. Regardless of the value of the lower electric field potential, BTO proves to be much more efficient with much higher COP values at all delta T values.
As was shown with the BTO data above, the PTO data is compared to the same thermoelectric data in the plots below. It is to be noticed that in these PTO plots, the lower electric field potential is presented with units. The dimensionless quantities were converted using the conversion factors shown previously.

This plot again shows the thermoelectric data in black, the PTO data in blue, and the Carnot data in red. The first takeaway is that the bismuth telluride seems to be a little bit more competitive against PTO than BTO, however the PTO is still far superior in terms of COP. Again, as the delta T decreases and approaches zero, the bismuth telluride and the PTO show similar COP values. Yet, once the delta T is increased, the PTO is far superior. At any case, the PTO data is much closer to the ideal case represented by the Carnot curves at all delta T values.
Figure 38: Change in temperature versus COP for PTO and Bismuth Telluride Alloy used by Marlow Industries

The next and final plot shows a filtered version of the previous plot, as was done with the BTO data above. This plot shows one data set for the bismuth telluride, both sets of data for the PTO, and no sets of data for Carnot. For the applicable delta T range of the bismuth telluride, roughly 40 K to 70 K, the PTO is more efficient for both levels of the lower electric field potential.
Figure 39: COP versus change in temperature for PTO and Bismuth Telluride Alloy used by Marlow Industries (Marlow Industries, Inc., 2012)
4.0 Conclusions

In this work, the polarization, entropy, and heat capacity for BTO and PTO were calculated as a function of temperature. These quantities were then used to calculate several quantities that define the heat exchange throughout the cycle. These heat exchange quantities were then used to calculate an overall efficiency for the refrigeration cycle, the coefficient of performance.

The Ericsson cycle was used to define the refrigeration cycle discussed throughout this thesis. The Ericsson cycle is a readily applied regenerative refrigeration cycle due to its definition using temperature and electric field as its state variables. Applications of this refrigeration cycle utilizing an electrocaloric material as the medium were discussed.

Following all the calculations and all the results shown in this thesis, the purpose of the investigation was attained. Recall that the purpose of this research was to show that electrocaloric materials like Barium Titanate and Lead Titanate are indeed more efficient than thermoelectric materials like Bismuth Telluride with regard to acting as the medium in a refrigeration cycle. In fact, in each and every plot shown in this thesis that compared electrocaloric materials to thermoelectric materials, the electrocaloric curves were shifted up and to the right from the thermoelectric curves. This indicates that the electrocaloric materials exhibited a higher coefficient of performance at each and every delta T point. Therefore, it can be concluded that electrocaloric materials are more efficient than thermoelectrics for use as a medium in a refrigeration cycle.

As with almost all results, questions can and should be asked regarding specific nuances in the data. In this case, the aspect of the results that jumps out the most is the instability of the
data for the PTO material when the temperature is beyond the Curie temperature. What is more interesting is that this phenomenon is not seen in the BTO data. This is due to the fact that PTO has a much stronger and higher order phase transformation than BTO. The major difference in the material is below the Curie temperature, PTO is in its ferroelectric phase and when the material is above the Curie temperature, PTO is in its paraelectric phase. Essentially, this means that PTO can have a spontaneous polarization below the Curie temperature regardless of the applied electric field, but above the Curie temperature PTO has a polarization that quickly approaches zero as the applied electric field approaches zero.

Upon closer look at the data, it can be seen that the instability occurs once the temperature of the hot reservoir crosses above the Curie temperature. Basically, as soon as the paraelectric phase is incorporated into the COP calculation for the cycle, the data becomes rather erratic. The instability cannot be fully explained and would require further investigation, but there are some possible explanations. The first is the simple nature of using assumptions and formulas that attempt to define a trend. There comes a point in most calculations at which these assumptions and formulas are pushed to their limit. Next, it is known that the spontaneous polarization that occurs in the paraelectric phase is not as strong as in the ferroelectric phase. This directly explains the drop in the COP once the paraelectric phase is incorporated into the calculation. Finally, it is also known that at a certain temperature above the Curie temperature spontaneous polarization cannot exist. This phenomenon can be explained using the respective free energy curves at different temperatures. It is very possible that the hot reservoir temperature may be approaching this temperature. As such, the polarization would rapidly vanish, resulting in an avalanching COP.
On a different note, with respect to the BTO data, it is curious to notice that there is a significant drop in the COP value around the Curie temperature when the lower electric field potential is 0 kV/cm. Once the lower electric field potential is increased, this rapid “jump” is no longer observed. This is due entirely to the electrocaloric effect. Just as the polarization versus temperature plots show, when the electric field is 0 kV/cm, the polarization drops immediately to 0 at the Curie temperature. However, once the electric field is increased, there is a spontaneous polarization and the polarization no longer drops to zero. This phenomenon is carried through all the calculations and is translated right into the COP value.

4.1 Next Steps

Although the research presented in this thesis provides a great breakthrough in the potential of electrocalorics, there is always reason to continue with the investigation. Some logical next steps would be to translate this calculation and Matlab code into several material systems. The dimensionless version of the code allows for this to happen rather fluently. Also, the calculation and code can be modified to account for different boundary conditions that could incorporate bulk materials and magnetic properties, for example. Finally, a long term goal would be to create a device that utilizes an electrocaloric medium to refrigerate a substrate.

Along these lines, defining an application or a device has proven to be a rather tricky task to date. Although there have been many theoretical ideas, as described earlier in this thesis, working devices have yet to be developed. There are several questions that first need to be answered prior to being capable of developing such a device.
What is the time constant of such an electrocaloric material? It is important that the medium is capable of not only absorbing heat from the hot reservoir, but also capable of releasing heat to the cold reservoir all in a timely fashion. Can such a thin film be able to conduct and convect at appropriate rates?

Another hurdle to climb would be how to solve the issue of directing the direction of heat flow. One solution provided by Ju is to mechanically create a physical contact between the electrocaloric and the hot reservoir, and then separately create a physical contact between the electrocaloric and the cold reservoir. This solution would allow for the electrocaloric to conduct heat from the hot reservoir and cool off using the electrocaloric effect. Another method to direct this heat flow would be to utilize thermal switches. By incorporating logic, one thermal switch would be opened to allow for heat transfer between the hot reservoir and the electrocaloric, while the other thermal switch would close off any heat transfer between the cold reservoir and the electrocaloric. At the appropriate time when the electrocaloric material is hot enough, the thermal switches would close and open respectively, and the heat transfer would continue along the cycle.

It is evident that there are still some challenges to overcome before developing an electrocaloric refrigeration device, but this provides a lot of opportunity. This thesis has proven the promise of electrocalorics and has provided a reason to pursue investigations utilizing electrocalorics as mediums for a refrigeration cycle. It is exciting to think about the possibilities to come in the near future stemming from this work.
5.0 WORKS CITED


