

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

**MACHINE LEARNING BASED PREDICTIVE MODELING AND
CORRELATION ANALYSIS OF THE ELECTROCALORIC
EFFECT IN FERROELECTRICS**

MUSTAFA AĐRI BAYIR

A THESIS OF DOCTORATE
DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

ADVISOR: PROF. DR. EBRU MENŐUR

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T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

FERROELEKTRİK MALZEMELERDE ELEKTROKALORİK
ETKİNİN MAKİNE ÖĞRENİMİ TABANLI ÖNGÖRÜSEL
MODELLEMESİ VE KORELASYON ANALİZİ

MUSTAFA ÇAĞRI BAYIR

DOKTORA TEZİ
MALZEME BİLİMİ VE MÜHENDİSLİĞİ
ANABİLİM DALI

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to Luna...

ABSTRACT

The electrocaloric effect is an important and exciting phenomenon for the development of solid-state cooling technologies. However, the effect brings complex relationships between processing parameters, material composition, and performance. This complexity emphasizes the importance of systematic optimization. This thesis fills that gap by using the data-driven materials science approach and machine learning to reveal the correlations, predict, and optimize the electrocaloric behavior. Comprehensive datasets have been created from the published studies in the literature and machine learning model trained to accurately predict the adiabatic temperature change. SHAP analysis showed the important features and trend that are dominant in the specific system. Bayesian optimization frameworks were used to search and find the best possible set of processing parameters that increases the electrocaloric response under different constraints. Virtual datasets have been generated, and predictive contour maps are created to find the high-performance areas. This thesis shows that the data-driven materials science and machine learning can reveal and recognize the hidden patterns and guide the researchers for achieving high-performance materials.

Keywords: Electrocaloric, Machine Learning, Optimization

ÖZET

Elektrokalorik etki, katı hal soğutma teknolojileri için oldukça umut verici ve önemli bir fiziksel olgudur. Bu olgu, üretim parametreleri, malzeme kompozisyonu, ölçüm değişkenleri ve performans arasındaki kompleks ilişkileri de beraberinde getirmektedir. Bu kompleks ilişkiler ise sistematik bir optimizasyon sürecinin önemi ortaya koymaktadır. Bu tez, malzeme bilimi doğasındaki korelasyonları ortaya çıkarmak, elektrokalorik davranışı ve performansı modellemek ve optimize etmek için veri odaklı malzeme bilimi yaklaşımını ve makine öğrenimini kullanarak bu boşluğu doldurmaktadır. Literatürde yayınlanmış çalışmalardan kapsamlı veri kümeleri oluşturulmuş ve adyabatik sıcaklık değişimini doğru bir şekilde tahmin etmek için makine öğrenimi modeli eğitilmiştir. SHAP analizi, belirli bir sistemde baskın olan önemli özellikleri ve eğilimi göstermiştir. Bayesian optimizasyonları, farklı kısıtlamalar altında elektrokalorik yanıtı artıran mümkün olan en iyi işleme parametreleri kümesini aramak ve bulmak için kullanılmıştır. Sanal veri kümeleri oluşturulmuş ve yüksek performanslı alanları bulmak için öngörüsül kontur haritaları oluşturulmuştur. Bu tez, veri odaklı malzeme bilimi ve makine öğreniminin gizli kalıpları ortaya çıkarıp tanıyabileceğini ve yüksek performanslı malzemeler elde etmek için araştırmacılara rehberlik edebileceğini göstermektedir.

Anahtar Kelimeler: Elektrokalorik, Makine Öğrenimi, Optimizasyon

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LIST OF SYMBOLS AND ABBREVIATIONS

AER	: Active electrocaloric regenerator
AFE	: Antiferroelectric
ANN	: Artificial neural network
BCZT	: Barium calcium zirconate titanate
BTO	: Barium titanate
T_B	: Burns temperature
$^{\circ}\text{C}$	: Celsius degree
R^2	: Coefficient of determination
COP	: Coefficient of performance
E_c	: Coercive electric field
CNN	: Convolutional neural network
T_C	: Curie temperature
$^{\circ}$	: Degree
T_d	: Depolarization temperature
ϵ	: Dielectric permittivity
DSC	: Differential scanning calorimetry
E	: Electric field
EC	: Electrocaloric
ECE	: Electrocaloric effect
ΔT_{EC}	: Electrocaloric temperature change
S	: Entropy
XGBoost	: Extreme gradient boosting
FeRAM	: Ferroelectric random accessible memory
T_f	: Freezing temperature
G	: Gibbs free energy
GWP	: Global warming potential
Q	: Heat
C	: Heat capacity
h	: Hour
HFC	: Hydrofluorocarbon
K	: Kelvin
kNN	: k-Nearest neighbour
PLZT	: Lead lanthanum zirconate titanate
PMN-PT	: Lead magnesium niobate – lead titanate
PST	: Lead scandium tantalate
PZT	: Lead zirconate titanate
ML	: Machine learning
Magpie	: Materials agnostic platform for informatics and exploration
MAE	: Mean absolute error
MSE	: Mean squared error
Q_M	: Mechanical quality factor
MV	: Megavolt
mm	: Millimeter
min	: Minute
MPB	: Morphotropic phase boundary
MLC	: Multilayer ceramic
MLCC	: Multilayer ceramic capacitor

%	: Percentage
ϵ_0	: Permittivity of vacuum
PNR	: Polar nano region
PVDF	: Polyvinylidene fluoride
RF	: Random forest
P_r	: Remanent polarization
P_s	: Spontaneous polarization
ST	: Strontium titanate
SVM	: Support vector machine
SVR	: Support vector regression
χ	: Susceptibility
T	: Temperature
V	: Volt



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1. INTRODUCTION

Advancements in the material science have brought a new way of designing materials by combining the physical understanding with data-driven methods. As the need for energy-efficient, compact and environmentally friendly technologies grows, functional materials are expected to perform reliably under controlled conditions. Electrocaloric ceramics offer a promising option for solid-state cooling technologies. However, even though the potential is clear, it is challenging to process the materials to actual performance due to the many interacting factors in materials science nature. This thesis is aiming to build a clear, data focused framework for understanding and improving electrocaloric materials.

1.1. Motivation and Scientific Background

The development of high-performance and functional materials is a key point of materials science, and it enables the technological advancements in the world from nano to macro scale. Among these materials, electrocaloric (EC) materials, solids that exhibit reversible adiabatic temperature change under an applied electric field, have drawn increasing attention because of their potential to serve as solid-state cooling systems. The electrocaloric effect (ECE) is particularly promising as a replacement or match to conventional vapor-compression refrigeration which is environmentally harmful due to its reliance on greenhouse gas refrigerants and moving mechanical components despite its universality. Electrocaloric materials promise compact, scalable, and efficient cooling solutions without any moving parts, making them ideal for applications from microelectronics to biomedical devices [1], [2].

Most of the research on electrocaloric materials to date has focused on ferroelectric ceramics, particularly perovskite-structured oxides such as $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT), BaTiO_3 (BTO), and relaxor ferroelectrics like $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT). These systems are well-known as they exhibit strong polarization changes near phase transition temperatures, which are essential for large electrocaloric responses. However, achieving high ΔT_{EC} values in real world conditions is challenging, as the response depends on a combination of different factors such as chemical composition,

processing route, microstructural features, and measurement itself. Therefore, the experimental landscape is quite wide, with data scattered across publications that vary in methodology, material form, and measurement type.

On the other hand, the increasing availability of material databases and the development of data-based methods in physical sciences have created new ways to handle such complexity. Machine learning (ML) has emerged as a powerful tool to uncover structure–property relationships, perform stand-in modeling, and even propose inverse design strategies. However, it is always problematic to gather comprehensive and reliable dataset that can be used in machine learning for materials science and this drawback have limited the use of it in areas with high complexity systems such as electrocaloric materials.

At this point, the mentioned challenges and the opportunities creates the main motivation of the thesis. The thesis aims to open a way and create a link between the experimental knowledge with the predictive modeling of the electrocaloric materials by using a data-focused framework including the statistics, machine learning, virtual experiments. The work aims to contribute to the material informatics literature by discussing the process-property relations and addressing the practical needs for sustainable solid-state cooling technologies.

1.2. Importance of Electrocaloric Materials in Cooling Technologies

In our daily life we constantly use refrigeration and climatizing technologies from preservation to maintain the performance of the electronic systems. The widest method that being used for the refrigeration activities are mostly based on conventional techniques which rely on harmful and volatile gases such as hydrofluorocarbons (HFCs) and resulting with high global warming potential (GWP). On the other hand, these systems mostly use mechanical compression components, moving parts which are problematic for the miniaturization of the systems and bringing high level noise, vibration and finally requires intensive maintenance activities. In today's world, it is really critical to find alternative solutions to these systems for cleaner, quieter, and scalable since the refrigeration is one of the main cause that boosts the global energy consumption [3], [4].

Solid-state cooling method stands as an important alternative and promising solution to this need, and it mostly refers to the electrocaloric effect. Electrocaloric materials simply possess a temperature change when they are subjected to an external electric field under adiabatic conditions. This physical phenomenon comes from the entropy variations linked to polarization transitions induced by external electric fields, particularly around the ferroelectric–paraelectric phase boundaries [4], [5]. Electrocaloric materials are more suited to microfabrication techniques than magnetocaloric or elastocaloric materials as they can be operated using small electronics and do not require rare-earth elements or high mechanical stresses [6].

There are various pros that makes electrocaloric materials especially promising as a solid-state refrigeration technique. One of them is the high speed of the electric field application. This advantage stands for great dynamic thermal control of the electrocaloric devices as they can respond quite fast. Also, as electrocaloric devices would not require any moving parts, it results with a silent system, longer lifetime and more importantly dependable. It is important to keep in mind that for devices such as implantable medicals, thermally sensitive electronic systems where the mechanical systems are impractical, these advantages take the electrocaloric cooling devices to front. On the other hand, modular and local electrocaloric cooling would allow the proper heat distribution on integrated circuits, microelectromechanical systems [1], [2], [5], [6].

Even though the material discovery and processing methods have advanced significantly, electrocaloric cooling devices have not become commercially feasible mostly because of the difficulties in simultaneously obtaining large ΔT_{EC} , low driving voltage, thermal stability, and manufacturability. Therefore, we definitely need some design strategies that can optimize the material chemistry, and the processing routes are strongly required.

At this point, the thesis defends that the improved optimization strategies and systems that includes the predictive modeling is essential. It is required to reach to a comprehensive understanding of the structure-processing-property triangle in electrocaloric materials for development of the solid-state cooling technologies and bringing them into real life as efficient, environmentally friendly and integrable solutions.

1.3. Challenges in Experimental Design and Process Optimization

Even though the electrocaloric materials show important potential for solid-state cooling, the process to implement this potential into device applications starting from the discovery of the material is really challenging. The experimental design and the process optimization phases requires intensive effort since during these steps many interdependent factors affect the resulting electrocaloric response. Some of these internal and external factors that influences the electrocaloric response are chemical composition, starting materials and their chemistry, purity and form, thermal processing conditions including the reliability to the equipments, sample geometry and morphology, texturing techniques if used, and measurement protocols again including the parameters reasoned from the equipment itself, each in nonlinear and generally coupled ways to the polarization behavior and finally to electrocaloric temperature change [7].

One of the primary problems is the lack of standardization in the reporting of the experimental studies in materials science but especially of advanced ceramics including the electrocaloric materials. It is possible to find a broad range of compositions, dopants, various calcination and sintering conditions, multiple geometries (such as pellet, multilayer, textured, thin film). Also, it is important to keep in mind the other variables coming from the measurement of the electrocaloric performance which includes varying external electric field strengths, temperature ranges, the stage of the taken measurement (during heating or cooling of the sample). All these wide range of variables are, most of the time, inconsistently reported in the articles [8]. This brings a challenge to replicate the results, evaluate the materials independently, or most important for this study, finding generalizable trends.

Additionally, the electrocaloric response is highly sensitive to microstructure, which in turn is dependent on thermal history, densification, and texture development. Minor variations in sintering temperature or dwell time can modify grain size distributions, generate internal stresses, or change phase coexistence, all of which influence polarization dynamics. The presence or absence of template particles in textured ceramics adds another layer of process-dependent complexity but limited research systematically changes these parameters or seeks to isolate their distinct effects, resulting in a considerable deficiency in mechanistic comprehension.

When we discuss about finding the best electrocaloric performance of a system, it is for sure not spotting a single point or single variable but in reality, finding favorable configurations in a high-dimensional input space. Traditional experimental methodology follows the combined exploration of the possible parameters, and this is highly time and cost intensive especially when we talk about advanced ceramics synthesis and testing.

Therefore, using the data-based approach which can use the existing experimental knowledge, constraints and other inputs can lead the studies in a way that researchers can directly investigate the specific process windows. Virtual experimentation and optimization systems can suggest new configurations that worth to synthesize and machine learning models trained on existing knowledge can offer a path to intricate interactions of the parameters. Finally, we reach to a more integrated, data driven design strategy instead of trial-and-error methodology.

1.4. Scope and Objectives of the Thesis

The main aim of the thesis is providing a potential solution to the problems in optimization of the electrocaloric performance by using a data focused methodology including the statistical analysis of the previous study results, virtual experimentation and machine learning modeling. The study accepts the complex and multi-parametric, nonlinear nature of material science as a basis and then adopts a comprehensive perspective on the structure-processing-property relationship based on the existing literature and improved by including the machine learning tools.

The primary focus is placed on perovskite-based electroceramics, particularly the lead-containing PMN-PT and the lead-free BCZT systems, which have both showed strong electrocaloric responses under optimized conditions in the literature. The materials under investigation are represented through curated datasets constructed from the literature, encompassing a wide range of compositional variations, thermal processing routes, measurement conditions, and reported ΔT_{EC} values. These datasets are refined, structured, and enlarged with derived features (such as $T-T_C$ and Magpie elemental descriptors), forming the basis for the modeling pipeline.

Two main goals of the thesis are, first to create predictive models able to estimate ΔT_{EC} from a given set of material and process parameters with great accuracy, and second

to use these models in process design suggesting new, optimal parameter sets for maximizing electrocaloric performance.

To achieve this, following sub-objectives are addressed in the thesis:

- Using consistent encoding schemes, extract, unify, and preprocess experimental EC data from the literature by including both numerical and categorical aspects.
- Finding dominant variables, nonlinear trends, and coupled effects by means of thorough correlation studies and statistical diagnostics.
- Training and assessing supervised machine learning models with interpretability and generalizing capacity that map from high-dimensional input spaces to ΔT_{EC} .
- Guaranteeing the model resilience by hyperparameter optimization and cross-valuation.
- Identifying the optimal combinations of composition and processing parameters under physical feasibility constraints by means of a limited optimization framework employing Bayesian search methods.
- Creating virtual datasets and use the trained models to build electrocaloric behavior predictive maps, seeing the high-performance regions without the intention of optimization but just searching the parameter space.

The thesis includes the bulk, textured and multilayer ceramics and excludes the thin films due to the basic differences in scaling laws, microstructure, and measurement techniques.

By the end of the research, it is aimed to provide not only a generalizable methodological template for materials informatics in functional ceramics but also a predictive tool for ΔT_{EC} estimate.

1.5. Structure of the Thesis

The thesis has a structure to build each section conceptually and methodologically upon the previous one and starting from the base theory and motivation to the deep discussions of statistical analysis and machine learning application. The structure aims to provide a comprehensive flow of the work with the knowledge of electrocaloric

materials and machine learning technique to process-property optimization while also aiming to clearly introduce machine learning as easily understandable.

The thesis starts by introducing the motivation and scientific background of the work while mentioning the issues in experimental design and process optimization. Solid-state cooling and the position of the electrocaloric materials in this topic is defined in the first section as well as the aims and the methodological scope of the thesis.

2nd Chapter provides a comprehensive literature review. This review starts with giving the fundamentals of ferroelectricity and also includes the domains, phase transitions, relaxor character. After that, the electrocaloric effect, its thermodynamic origins, measurement techniques and the performance indicators are defined in detail as this phenomenon is the core of the thesis. Afterwards, lead-based (PMN-PT, PZT, PST) and lead-free (BCZT) electrocaloric systems relevant to this study are defined and their characteristics and properties are introduced. The literature review continues with the machine learning applications in materials science and with the gaps in the literature that motivates the data-based study developed in this study.

3rd Chapter covers the data gathering, feature engineering, statistical analysis and pipeline of model development. The section includes how the algorithm selections, validation design, hyperparameter optimization and evaluations were done. Process parameter optimization framework is also covered in this section that integrating the models with constrained search algorithms and then generation of the virtual dataset for large-scale predictive mapping.

4th Chapter gives the results and deeply discuss them. The results and discussions are given in different subsections for each material system, and it covers the descriptive statistics, correlations, performance of the model, results of the optimization study and the virtual dataset predictions. Also, comparison of the different systems is included in this chapter to have an overview over the findings, generalizability, feature importance and optimization behavior.

5th Chapter concludes the entire thesis and defines key scientific and methodological contributions to the literature. All findings, advantages and disadvantages of the method, and suggestions for the future studies on this topic are summarized.

2. LITERATURE REVIEW

2.1. Ferroelectricity

This section covers the basis of ferroelectricity, its features and the mechanisms that are causing this phenomenon.

2.1.1. Fundamentals of Ferroelectricity

Ferroelectricity is an important phenomenon that can be observed in specific group of materials that are exhibiting the natural and permanent dipole moment which is defined as spontaneous polarization as a feature of their crystal structure [9], [10]. This natural polarization is reasoned from the center of symmetry within the crystal. If the charge centers of the positive and the negative ions don't positioned at the same point, this leads to a dipole and ferroelectricity can change this polarization state as reversible [11]. Therefore, we can mention minimum two equilibrium states in ferroelectric materials even in the absence of any external electric field and they are reversible [12].

The name “ferro” comes from the “ferromagnetism” which is the permanent magnetic moment in iron. As an analogy, this term is used for ferroelectrics as well. The discovery of the ferroelectricity goes back to 1921, and it was first seen in Rochelle salt which is potassium-sodium tartrate-tetrahydrate. The actual discovery of this specific material dates back to 1600s and then further studied for its pyroelectric property in 1800s. Even though the ferroelectricity was discovered with Rochelle salt, it was mostly investigated within barium titanate (BaTiO_3) in 1940s. The importance of this switch was due to polycrystalline studies. Barium titanate was also used widely in technological applications specifically for high-capacity capacitors. Later on, lead-based materials started being researched due to their superior properties. Lead zirconate titanate (PZT) and lead lanthanum zirconate titanate (PLZT) was the most studied lead-based ferroelectrics [9], [13–15].

Every ferroelectric material possesses a change in their crystal structure called phase transition, resulting with the change in their electrical behavior. These phase transitions make ferroelectric materials interesting for scientific investigations. The

ferroelectric behavior disappears when the temperature of the material exceeds a certain level called “Curie temperature”. The reason of this change lies in the induce of the dipoles to align natural with the energy brought to the system by heat. The change in the behavior might be either sharp or over time. This difference allows us to categorize ferroelectrics as normal ferroelectrics, and relaxor ferroelectrics by the sharpness and the nature of the transition [9–12].

Another important categorization of the ferroelectrics is based on the crystal structure type of the material as; tungsten-bronze, oxygen octahedral, pyrochlore, and layer structure. Oxygen octahedral structure is also widely known as ABO_3 perovskite structure and most studied structural system for ferroelectrics in the literature. This group includes extensively investigated ceramics such as lead zirconate titanate, lead lanthanum zirconate titanate, lead magnesium niobate [14].

The phenomenon subject to this thesis, electrocaloric effect, is fundamentally linked to field-induced change in polarization in ferroelectrics at especially Curie temperature, where the entropy change is maximized [2]. Therefore, it is important to mention and explain the polarization and phase transition dynamics which will be given in the next chapter.

2.1.2. Polarization, Domains, and Phase Transitions

Spontaneous polarization in dielectrics is caused by the displacement of the ions due to the lattice vibrations within the crystal system to lower the total energy. As a result of these vibrations crystal systems are being distorted and level of the distortion is mainly related with the energy level. These distortions change the central point of the positive and negative ions and results with a dipole moment within the crystal. This dipole moment is one of the two main points to define a material as ferroelectric. Second point is the reversibility of this dipole moment. In order to define the material as ferroelectric, the ability to switch the polarization under applied field is required. Therefore the material should have reversible polarization state [9], [11], [14], [16].

Polarization stage of the ferroelectrics is reoriented by the application of an external electric field to the system. The most characteristic property of the ferroelectric materials is the hysteresis behavior of the polarization when alternating electric field is applied to the material. The spontaneous polarization of the system switches to the

direction of the electric field when it is applied. In the absence of the electric field, total polarization within the material is expected to be zero. This is due to the cancellation of each dipole moment by a different dipole oriented in the other direction. Therefore, when the external electric field applied to the material, it reveals the spontaneous polarization. Schematic diagram of a typical ferroelectric material hysteresis is given in **Figure 2.1**. The electric field application starts from zero and the polarization increases linearly with the low electric field levels as it is not enough to cause the reorientation of the domains. As the field increases, polarization also increases nonlinearly and at high level electric fields polarization reaches to its maximum which is defined as saturation. At this region, most domains are aligned toward the field direction. When the field is decreased to zero back again, polarization decreases by following the BAO line and not as the same path it was polarized. An extrapolation line drawn to the polarization axis from the linear portion gives the spontaneous polarization (P_s) level of the system and the polarization value when the electric field is zero is defined as remanent polarization (P_r). Even in the absence of the electric field, this polarization exists within the material and in order to remove this polarization from the material, an electric field in the opposite direction has to be applied. This electric field is defined as coercive electric field (E_c) and if this is field kept increasing, polarization state occurs again in the opposite direction. This entire process of complete reorientation is called “polarization switching” and it is the key feature of the ferroelectrics. The area of the hysteresis loop is related to the energy dissipated at each cycle and this energy has direct relations with the dielectric losses and device energy efficiency which is aimed to be minimized for the practical applications [10], [12].

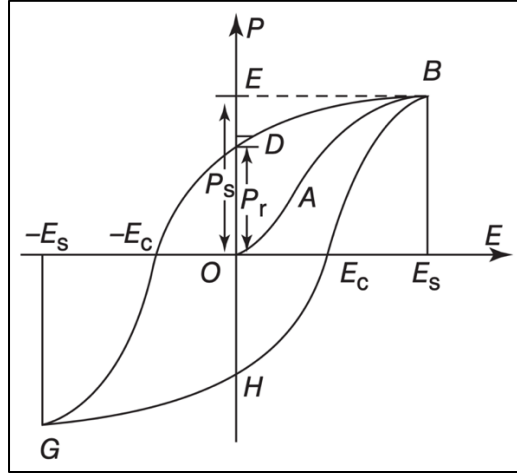


Figure 2.1: A typical ferroelectric hysteresis loop.

Below the Curie temperature, ferroelectric systems exhibit the abovementioned spontaneous polarization, and the dipole moments are either expected to be aligned randomly in case the material have never subjected to an external electric field or not aligned fully in one direction since this state increases the total energy in the system significantly. All material systems prefer lower energy states, and this preference causes to formation of regions which are having dipoles aligned in the same orientation, so called domains [10]. These homogenously polarized regions form the domains in a way that the total polarization vanishes due to cancellation of by each other. The domains form to reduce the electrostatic energy of depolarizing fields and the elastic energy from mechanical constraints during the paraelectric-ferroelectric phase transition which will be mentioned later.

Spontaneous polarization within the system creates surface charges which generates a depolarizing field in opposite direction to polarization. At this stage, material forms the domains with opposite polarization or receives external charge compensation to minimize this energy. Mechanical stresses during cooling also drives domain formation. Finally, the domain configuration balances both electrostatic and elastic energy contributions. Order of the domains are mainly found as the positive heads are held near negative tails and therefore the energy in the system is lowered. In polycrystalline materials, a relation between the domains and the grain size can be mentioned. If the grain size is small enough, the domains can be found per grain. However, for the coarse grain structures, it is possible to have more than one domain in one single grain [9], [10], [12]. The border between two domain is called as domain

wall and these walls are named 90° or 180° depending on the domains they are separating. Schematic illustration of 90° and 180° domain walls is given in **Figure 2.2**. If the wall separates two polarization state which is perpendicular to each other, this domain wall defined as 90° wall and if they are oppositely oriented, it is named as 180° wall [10], [12].

It is important to mention that in uniaxial ferroelectrics, the domains can have only two possible dipole orientations and therefore the domains will be always in opposite alignments which results with 180° walls. Multiaxial ferroelectrics on the other hand, can have more than two orientations. The materials can have 6 dipole directions in total, caused by the cubic structure axes. This condition can be also defined as three pair of antiparallel dipoles and antiparallel ones are separated with 180° walls while others with 90° walls [10]. The presence and mobility of domain walls also play a vital role in functional responses such as dielectric permittivity and piezoelectricity, as these walls can respond to external fields and contribute to the overall polarization change. Hysteresis loop of the ferroelectric materials is caused by the switching of these domains by an external electric field. This is possible either with the growth of the domains or formation of the new domains. Domain formation through nucleation and growth occurs at specific locations which are energetically favorable, leading a repeated switch at the same location. Therefore, nucleation of the domains is mostly inhomogeneous. Growth of the existing domains is mostly based on the applied electric field, its duration and the geometry of the sample. Factors such as defect density, internal stress, and electrode interface conditions also influence the ease of domain switching, thereby affecting hysteresis characteristics [9].

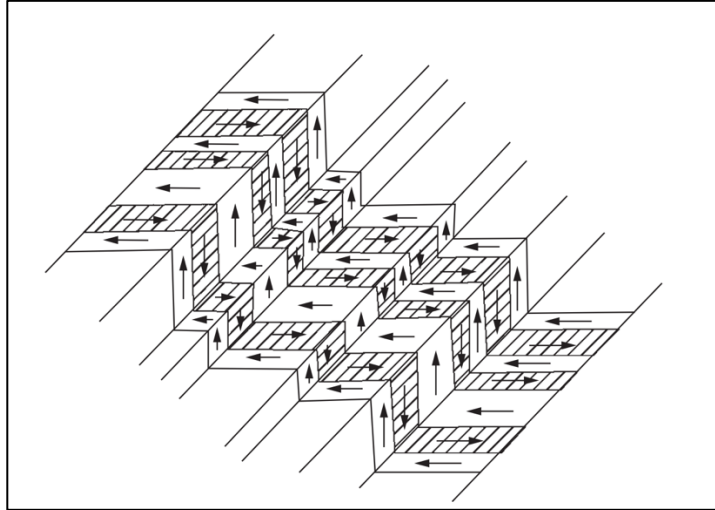


Figure 2.2: Schematic illustration of domains with 90- and 180-degree walls.

The dynamic behavior of domains and polarization is closely linked to the phase transitions of the ferroelectrics. Transitions are typically driven by temperature or external electric field and structural changes in the system influences the electrical character of the system. It is important cover these transitions to control and tailor the functional properties of ferroelectrics, particularly for applications involving temperature dependent phenomena such as electrocaloric effect.

Phase transition can be defined as a thermodynamical phenomenon takes place in a system that changes the phase or state from one to another. Phase transitions are affected from different parameters including intrinsic features of the system but also external parameters such as temperature and pressure. Ferroelectrics lost their spontaneous polarization character above Curie temperature since the polarity of the material disappears above it. These transitions bring entropy and volume change into the material. If spontaneous polarization decreases with a clear discontinuity, this type of transition named as first-order transition. When the change of the polarization is continuous, this refers to second-order transition. The important difference between first order and second-order transitions is the change of entropy and latent heat. Schematic illustration of first order and second-order phase transitions are given in **Figure 2.3**. The entropy changes at constant temperature in first-order transition, which is often Curie temperature, and there is no change in entropy and latent heat at the transition temperature in second-order transitions. During the first-order transition, temperature of the system remains constant despite the increasing heat. From a thermodynamic perspective, this behavior is captured by discontinuities in the first

derivative of free energy with respect to temperature or field. The hysteresis loop is also reflecting these the phase transitions. The loop gets slimmer above Curie temperature and turns into a straight line which is the characteristic of linear dielectrics [9–12]. This transformation marks the boundary between ferroelectric and paraelectric phases and represents a fundamental limit for many applications that rely on field-induced polarization change, such as electrocaloric refrigeration or non-volatile memory devices [11].

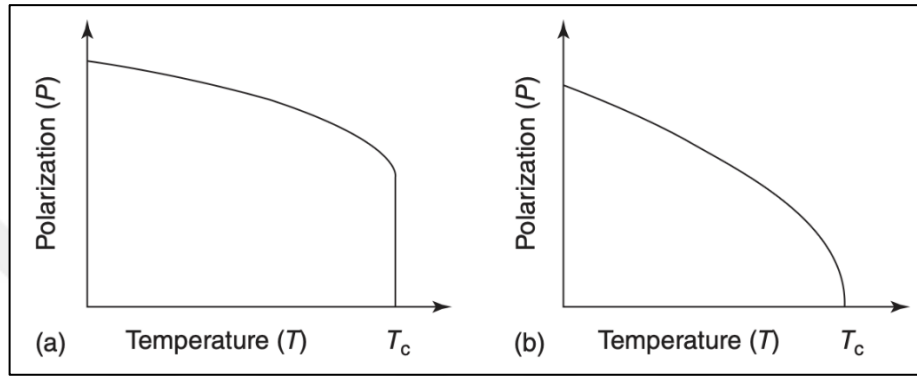


Figure 2.3: Schematic illustration of the (a) first-order transition and (b) second order transition.

2.1.3. Relaxor Ferroelectrics and Polar Nanoregions

Relaxor ferroelectrics are an important part of the ferroelectrics with characteristic behavior under external electric field. Lead magnesium niobate (PMN) was the one of the first material that was studied for its relaxor characteristic. Relaxor ferroelectrics are promising with their high strain levels, high dielectric constant values and with their main difference from normal ferroelectrics, the broad and diffuse phase transition behavior below Curie temperature. This characteristic allows them to possess high dielectric properties over a wide range of temperature. Unlike the conventional ferroelectrics, where the transition is sharp and well-defined, relaxors display frequency-dependent dielectric peaks that can extend across a temperature range of hundreds of degrees. On the other hand, it is not quite possible to mention about Curie temperature in relaxor ferroelectrics since there is no clear transition temperature from ferroelectric to paraelectric phase. Therefore, the temperature of the maximal dielectric constant is a critical property for these materials [9], [17–19].

Main reason of the diffuse behavior of relaxors are attributed to the heterogeneity in the system. Typically, relaxor ferroelectrics are defined with perovskite structure given in **Figure 2.4**, where they have one lower valance and one higher valance cation. When these two types of cations are not homogenously dispersed over the material in unit cell level and positional order, these results with non-stoichiometric regions, their different ferroelectric behaviors at different temperatures broaden the dielectric peak and slower decrease in spontaneous polarization. This randomness can be described in terms of chemical disorder in the A-site or B-site of the ABO_3 structure, where different ions such as A' and A'' or B' and B'' are distributed randomly, creating what is referred to as complex perovskites [9], [12], [17], [19].

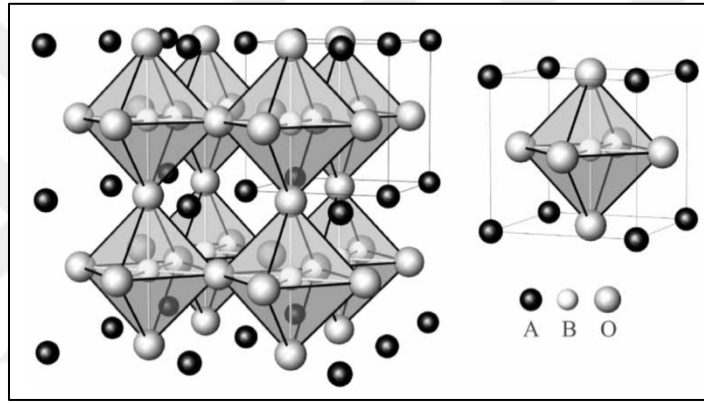


Figure 2.4: The ideal cubic perovskite structure with metal cations at A and B sites, and oxygen atoms.

Also, relaxors doesn't behave according to Curie-Weiss law above the temperature of maximum dielectric constant. Instead, they follow a modified form, such as $\epsilon \approx 1/(T - T_{\max})^2$ which qualitatively describes the broad dielectric anomaly observed in systems like PMN. A critical feature of the relaxor ferroelectrics is the frequency dependence. This frequency dependence is not limited to the dielectric constant alone but is also reflected in other properties such as specific heat, elastic constants, and Raman scattering, further highlighting the fundamentally disordered nature of relaxors [9], [17–20].

The complex dielectric and structural behavior observed in relaxor ferroelectrics has been attributed to the existence of polar nanoregions (PNRs), nanoscale regions with locally aligned dipoles in a macroscopically non-polar matrix. Schematic representation of PNRs is given in **Figure 2.5**. These PNRs nucleate at temperatures

above the dielectric maximum and play a critical role in defining the relaxor characteristics by disrupting long-range ferroelectric order while maintaining local polarization. PNRs are considered a defining feature of relaxors due to their high sensitivity to external stimuli and their distinctive temperature dependent dynamics. As temperature drops below the Burns temperature (T_B), these polar regions begin to emerge within the cubic matrix. Initially, they are highly dynamic and ergodic, capable of reorienting under thermal fluctuations or electric fields. Upon further cooling, their motion slows down, and below a critical freezing temperature (T_f), they become nonergodic. Despite the cubic symmetry at the macroscopic level, electric field poling can still induce long-range ferroelectric domains, especially below the depolarization temperature (T_d), highlighting the underlying polar nature of the material [17], [21], [22].

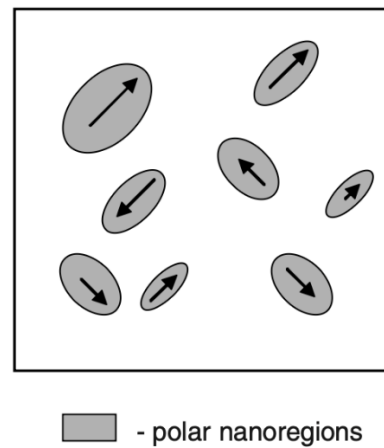


Figure 2.5: Schematic representation of PNRs in relaxors.

The origin of PNRs has been approached through different theoretical perspectives. One widely discussed model suggests that compositional disorder leads to spatial fluctuations in the local Curie temperature, allowing certain regions to undergo local ferroelectric transitions before the rest of the material, resulting in the formation of stable nanoscale polar clusters. Another model, based on random field theory, proposes that quenched random fields, arising from this same disorder, suppress long-range ferroelectric order and instead stabilize nanoscale domains. Both approaches point to the importance of disorder in preventing a conventional phase transition. The evolution of these PNRs with temperature, from dynamic to frozen states, directly influences the

frequency dispersion, phase stability, and electromechanical response of the material [21], [22].

The temperature range between T_B and T_d marks the area where PNRs are most active, giving rise to the broad and frequency-dependent dielectric peaks that are characteristic of relaxors. Below T_d , as the system enters a frozen state, the relaxor behavior transitions into glass-like dynamics. However, external fields can still reveal hidden. This interactions between local disorder, nanoscale polarization, and macroscopic-field response are what ultimately governs the unique functional properties of relaxor ferroelectrics [21], [22].

2.2. Electrocaloric Effect

The electrocaloric effect (ECE) can be briefly described as a physical phenomenon found in a specific group of materials where it results in isothermal entropy or adiabatic temperature change in the material in case of an externally applied electric field [4], [23]. This phenomenon was first discovered by Kobeko and Kurchatov in 1930 as part of the studies to extend the research on the magnetocaloric effect to an electrical base. Under adiabatic conditions, driven by fluctuations in the external electric field, explanations of the electrocaloric effect on a macroscopic scale center on the entropy exchange between two energy or entropy reservoirs, the dipolar and thermal entropy subsystems. An applied electric field raises the order level in the crystal structure and lowers it when the electric field is removed. This entropy change results in an adiabatic temperature change [4], [23–25]. This whole process is reversible; in case of cyclic application and removal of the electric field, heat transfer to or from the material itself, a cooling cycle is obtained. A schematic representation of the electrocaloric cycle and the vapor-compression cycle is given in **Figure 2.6** [5].

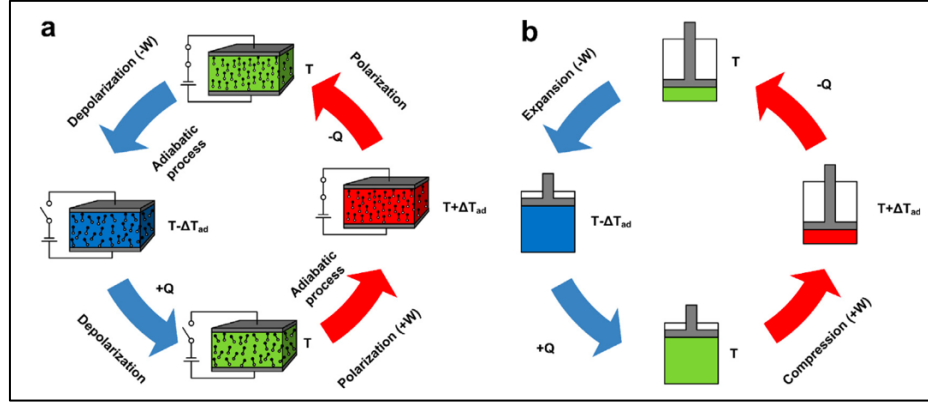


Figure 2.6: Comparison between the two different cooling cycles (a) electrocaloric, (b) vapor-compression.

2.2.1. Thermodynamic Origin and Entropy

Although the complete mechanism underlying the electrocaloric (EC) effect is not yet fully understood, its fundamental thermodynamic origin has been explained in literature using two main theoretical frameworks: the Maxwell approach and the Landau phenomenological approach [3], [5], [23], [25], [26].

When electric work is applied to a dielectric material, it results in a displacement of the bound charges in the crystal structure and polarizes the system.

$$D = \epsilon_0 E + P \quad (2.1)$$

$$D = \epsilon_0 + \epsilon_0 \chi E = \epsilon_0 E (1 + \chi) = \epsilon_0 \epsilon_r E = \epsilon E \quad (2.2)$$

The equations given above explain displacement in a crystal structure. E represents the electric field, D is the electric displacement, ϵ_0 is the permittivity of vacuum, while ϵ_r is relative permittivity and ϵ dielectric permittivity. χ represents the electric susceptibility of the system. As the equation shows, in linear materials, polarization acts linearly to the electric. On nonlinear materials like ferroelectrics, piezoelectrics, and relaxors, however, polarization shows a hysteretic behavior from field-induced phase transitions and domain reorientation. From a thermodynamic perspective, for a reversible process, the change in specific internal energy of an electrocaloric material

is related to both the entropy change with respect to temperature and the polarization change with respect to the electric field [2], [3], [5].

The Maxwell thermodynamic approach derives from the Gibbs free energy density of the system, the source of the electrocaloric effect:

$$dG = -SdT - x_i dX_i - P_i dE_i \quad (2.3)$$

From this equation, standard thermodynamic relations give:

$$\left(\frac{\partial S}{\partial E}\right)_T = \left(\frac{\partial P}{\partial T}\right)_E \quad (2.4)$$

This Maxwell relation enables the indirect determination of the adiabatic temperature change as:

$$\Delta T_{ad} = - \int_{E_1}^{E_2} \frac{T}{c_E} \left(\frac{\partial P}{\partial T}\right)_E dE \quad (2.5)$$

Here, C_E is the heat capacity at a constant electric field. The integrand features the pyroelectric coefficient, which governs the entropy change as a function of field and temperature. This formulation assumes continuous $P(E, T)$ and $C_E(T)$ functions. However, near second-order phase transitions, singularities in C_E or P can introduce significant inaccuracies in this indirect method.

As evident from Equation (5), the adiabatic temperature change depends on both the temperature and the temperature derivative of polarization under a constant electric field. The largest electrocaloric response is typically observed near the Curie temperature, where the entropy change is most significant due to enhanced polarization fluctuations. Therefore, maximizing the polarization and its temperature sensitivity is key to enhancing the electrocaloric effect [2], [3], [5]. A schematic representation of the entropy change during the cooling cycle is given in **Figure 2.7**. The line from $S(E_1, T_1)$ to $S(E_2, T_1)$ is the isothermal process while the line from $S(E_1, T_1)$ to $S(E_2, T_2)$ represents the adiabatic process [23].

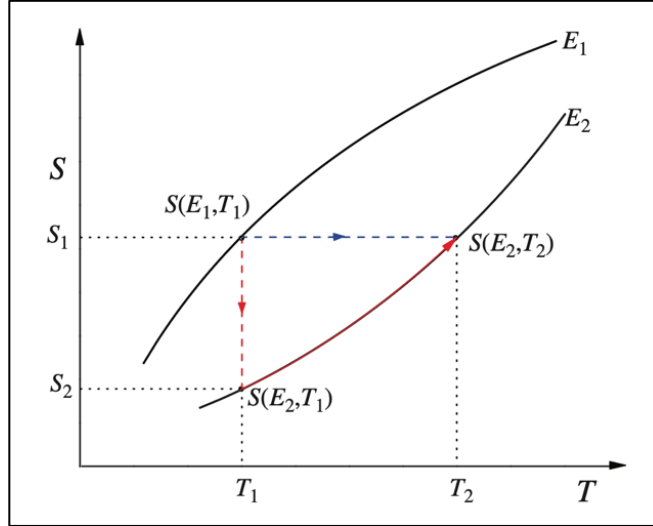


Figure 2.7: The entropy changes during the electrocaloric cycle.

An alternative and more detailed description of the electrocaloric effect, particularly in ferroelectrics, is given by the Landau theory of phase transitions. In this approach, the total entropy is separated into lattice and dipolar components:

$$S(E, T) = S_{latt}(T) + S_{dip}(E, T) \quad (2.6)$$

Under adiabatic conditions, the total entropy is conserved, and the lattice contribution is derived from the heat capacity:

$$S_{latt} = \int_{T_1}^{T_2} \frac{C_{latt}(T)}{T} dT \approx C_{latt}(T_1) \log\left(\frac{T_2}{T_1}\right) \quad (2.7)$$

The dipolar entropy is derived from the Landau free energy expansion and defined as:

$$S_{dip} = -\left(\frac{\partial F}{\partial T}\right)_E = S_0 + S_1(P) \quad (2.8)$$

As the last step, the final temperature under adiabatic switching of the electric field is:

$$T_2 = T_1 \exp\left(\frac{S_{dip}(E_1, T_1) - S_{dip}(E_2, T_2)}{C_{latt}(T_1)}\right) \quad (2.9)$$

This approach is particularly powerful near phase transitions, where polarization fluctuations dominate the entropy landscape. However, solving this equation often requires numerical iteration due to its self-consistent nature and the nonlinearity of $P(E, T)$.

2.2.2. Direct and Indirect Measurement Methods

In order to measure the electrocaloric temperature change, there is no commercial equipment or standard measurement system. Therefore, the measurement systems being used for the experimental investigations are mostly custom made. Even though it can be measured by the released heat, the electrocaloric effect is mostly defined as the temperature change. As the electrocaloric effect is a field-dependent phenomenon, these values are sensible when combined with the information about the external electric field. There are some important data needed for interconversion between these forms such as converting heat release (Q) into temperature change (ΔT) requires knowing the mass and specific heat capacity of the sample, whereas estimating electrocaloric coefficients requires parameters like electrode area, sample capacitance, and the applied voltage [2].

Direct measurement technique basically captures the electrocaloric effect in its most basic form by measuring the actual temperature change or the heat exchanged in the material when an external electric field is applied or removed. It is important to note that true adiabatic and reversible conditions are not fully possible under real world practical applications. Therefore, it is required to include the measurement error that are reasoned from the heat leakage, Joule heating, latent heat and also imperfect thermal contact with the sensor or other parts [27]. Differential scanning calorimetry (DSC) given in **Figure 2.8** and adiabatic calorimetry are the most used and well-known methods to characterize the electrocaloric effect. These two methods can be really precise, especially adiabatic calorimeters up to 10^{-4} K, when they are properly designed to reduce the heat losses that ensures the sample thermal mass balances the surrounding. However, as mentioned, true adiabatic conditions are simply can't be achieved. This is mainly due to the Joule heating and latent heat contributions specifically near the phase transitions. On the other hand, it is still advantageous to observe thermal deviations which are exothermic or endothermic peaks through modified DSC equipments which are enabling the indirect detection of the heat exchange reasoned from the electrocaloric effect. The conditions are still not adiabatic as these equipments are not designed for this. However, they are able to provide the data with high sensitivity if the switching of the electric field is quick enough and the equipment is in calibration [2], [27].

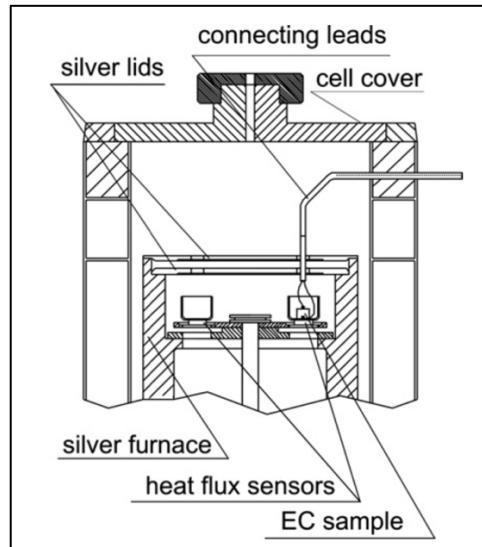


Figure 2.8: Schematic representation of differential scanning calorimeter tailored for the electrocaloric effect.

There are other direct methods in use as well. Some of them are thermocouples, infrared thermography, scanning thermal microscopy and specially microcalorimeters. As expected, thermocouples record the temperature change on a bulk sample directly. They are not easily usable for thin films because of the low spatial resolution and easily being affected from ambient thermal noise. Infrared cameras and micro sensors stand as local thermal probing solutions, but they require intricate experimental setups and corrections of the noise reasoned from substrate induced clamping and elastocaloric coupling. Also, small thermal mass and high thermal interactions with the substrate brings additional difficulties to the direct measurement of the thin films. All these systems might be effective but the application of direct measurements in electrocaloric experiments is still lesser than direct methods because of the availability, technical difficulties such as strict thermal isolation and some other restrictions. According to a study given in **Figure 2.9**, only 13.1% of the electrocaloric research publications used direct measurements [27].

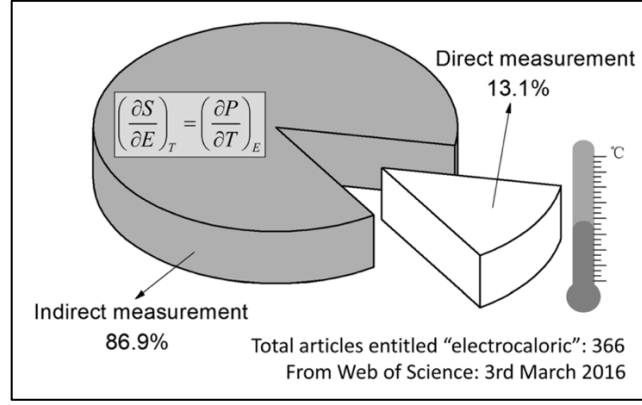


Figure 2.9: Statistical distribution of direct and indirect measurements according to Web of Science.

Indirect measurement techniques are much more popular to measure the electrocaloric effect due to their compatibility with generic ferroelectric characterization methodologies. In general, indirect methods are also much simpler than the direct methods. Indirect measurement simply depends on Maxwell relation to achieve the electrocaloric temperature change from the temperature dependency of polarization.

$$\left(\frac{\partial S}{\partial E}\right)_T = \left(\frac{\partial P}{\partial T}\right)_E \quad (2.10)$$

In this method, isothermal polarization (P) versus temperature (T) data is measured and then temperature change is being computed by integrating P-T relation while assuming the adiabatic conditions. The P-T curves are typically obtained by polarization measurement at various temperatures. Indirect measurement brings practical consideration to take into account. Generally, upper branches of the polarization loops are accepted to suppress domain switching. This is mainly due to the potential occurrence of the field-induced switching or incomplete polarization saturation which can underestimate the electrocaloric response. It is also important to consider the electrical dependence of the specific heat in indirect measurements. A constant heat capacity is assumed during integration in many studies, which can result in imprecise predictions, particularly in the vicinity of phase transitions where C_E may vary greatly. Another point is the hysteresis losses. These losses may bring asymmetries to the measurements between heating and cooling, specifically at the higher external fields. One method to lower these kinds of uncertainties is using

Gaussian models or high-order polynomials. Lastly, the temperature increments have to be sufficiently enough to capture a continuous trend of polarization [27].

2.2.3. Performance Indicators in Electrocaloric Materials

In order to define and evaluate the performance of an electrocaloric material and system, there are different parameters needs to combinedly evaluated. These parameters include thermodynamic, electrical, and thermal ones. It is important to consider the operational dependability, efficiency, and potential for device applications of the electrocaloric material besides just considering the magnitude of its response [4].

The most important and the main figure of merit for the electrocaloric materials is the adiabatic temperature change which is the reversible temperature change reasoned from the application and removal of the external electric field under adiabatic conditions. It is well known in the literature that, with greater electrocaloric response, higher potential for practical applications such as heat pumping comes front. It should be noted that due to the nature of the electrocaloric phenomenon, this temperature change is directly linked to the entropy change and then to dipole order state transitions. Therefore, electrocaloric temperature change is intrinsically temperature and electric field dependent with higher peaks near transition point [4].

Isothermal entropy change (ΔS) is another direct indicator of the amount of the heat exchanged per unit mass or volume in electrocaloric material. This performance indicator can be acquired through direct calorimetric measurements but also it can be calculated through the polarization-temperature data by using the Maxwell relations [4].

The electrocaloric coefficient ($\Delta T/\Delta E$, in K.mm/kV) is another indicator mostly used for the comparison of different electrocaloric material measured under different electric field levels. This indicator is a useful one to describe the efficiency of the transformation of electrical energy to thermal energy. During the experiments, it is well known that higher electric field applications bring the risk of dielectric breakdown as well as excessive Joule heating. Therefore, most of the studies aim for high coefficient values under moderate electric field levels [4].

The operational temperature range of an electrocaloric material is just as important as peak performance values. Generally, broad peaks bring more suitability for device applications where the thermal fluctuations occur. Materials with high performance in a broad range allows continuous operations which is desired. Reversibility and cycling stability must also be taken into account from an engineering standpoint. Over many cycles of applying an electric field, the electrocaloric effect should continue to be stable and reversible because aging, domain fatigue and space charge accumulation limits the usage of the device and decreases the performance [4].

It is also important to note that, apart from material level performance indicators, there are also system- and device-level performance indicator to be taken into account. These metrics might be cooling power density, coefficient of performance (COP), and energy conversion efficiency. These system level performance indicators are directly linked to the intrinsic electrocaloric characteristic of the material itself [4].

2.2.4. Application Areas and Device Potential

As the world strongly needs a cooling technology which is compact, environmentally friendly and also solid-state, the electrocaloric effect have drawn more interest as a potential replacement to traditional vapor-compression refrigeration systems which is the main energy consumption reason in household electricity as it can be seen from **Figure 2.10**. The great advantage of performing the refrigeration by electric field induced entropy change, without any harmful gases or moving mechanical parts put electrocaloric materials in front. Recent advancements in device architectures and material synthesis have opened the way for useful applications in fields like energy harvesting, heat pumping, and microelectronic circuit cooling [3], [28–30].

Mischenko et al., who reported a giant electrocaloric effect of 12 K in 350 nm thick PZT thin films under a field of 48 MV/m, corresponding to 0.48 K/V, established the term "giant electrocaloric effect" and sparked the modern resurgence of EC research for thin films and multilayer systems [5, 26]. Even though the data acquired through indirect means, the results bring an important light to the intense research on thin film electrocaloric materials. As their dielectric strength is exceptional which frequently above 100 MV/m, thin films are able to resist much higher electric fields which makes them enable for the induction of higher temperature changes ($\Delta T > 10$ K). For instance,

one of the highest values recorded for oxide ceramics was a ΔT of 31 K in a PMN-PT thin film at 75 MV/m, as reported by Saranya et al. [5], [31].

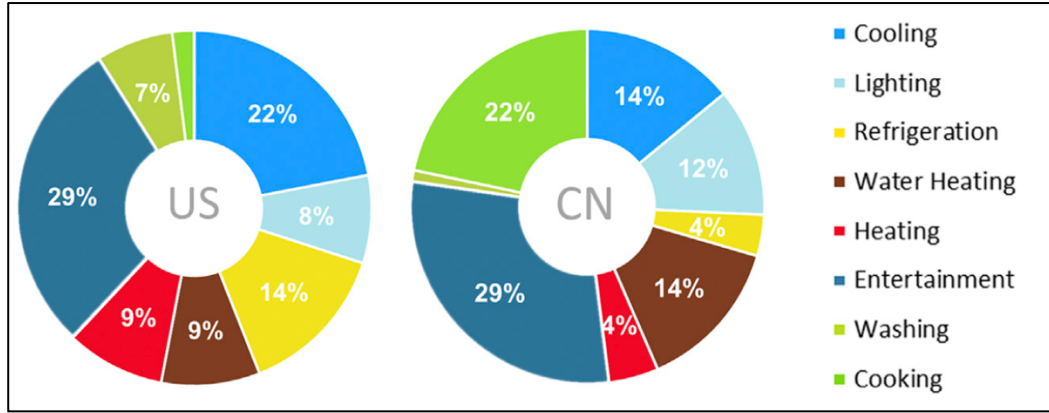


Figure 2.10: Household electricity consumption in the USA and China.

Multilayer ceramic capacitors (MLCs) have been proposed as a solution to the problem of low thermal mass in thin films. Hirose et al. manufactured a 49-layer multilayer capacitor with 90PMN-10PT composition and reported a reversible ΔT of 1.2 K at 10.3 V/ μm close to 100 °C. These results are quite in terms of the scalability of electrocaloric effect by using the multilayer integration, which makes the material suitable and usable for embedded electrodes to improve heat flow and cooling capacity. However, it is important to keep in mind that as the number of the layers and the total area of the electrode increase, breakdown strength of the MLC also tends to decrease. Therefore, for the electrocaloric devices requiring large area, there are important blocks such as internal stress, interfacial defects, or edge field concentrations [32].

As the electrocaloric effect not only exist in ceramics, polymer electrocaloric materials are also promising for device applications. These materials have important advantages such as high dielectric strength and mechanical flexibility. Polyvinylidene fluoride (PVDF)-based copolymers and terpolymers (such as P(VDF-TrFE) and P(VDF-TrFE-CFE)) are important candidates for the device applications of electrocaloric materials. Neese et al. reported an important level of entropy change as 56 J/kg.K and temperature change of 21 K under 300 MV/m electric field in P(VDF-TrFE) systems. These values are quite higher than the typical values achieved in ceramic thin films [5], [33]. These high values of the entropy attributed to the ferroelectric-paraelectric

phase transition and also the resistance of the polymer material to high electric fields. On the other hand, it is important to consider the low electrocaloric efficiency ($\Delta T/\Delta E$) of the polymer materials. Another drawback is the cycling stability as well as the poor thermal conductivity of these materials. These obstacles slow down their practical applications.

Active electrocaloric regenerators and electrocaloric devices with thermal diodes are the two main categories of electrocaloric systems under development at the device level. Passive heat switches are used to direct heat during field cycling in electrocaloric devices with thermal diodes. These systems enable high-frequency, discontinuous operation and resemble magnetic refrigeration devices. However, because of reliability issues and limited thermal rectification, thermal diode development continues to be a block. In Active Electrocaloric Regenerators (AERs), the electrocaloric material serves as both the regenerator and the refrigerant at the same time. In simulations and early prototypes, AERs have shown notable temperature spans and enable continuous operation with two EC stacks operating out of phase [5]. These systems are appropriate for incorporation into small solid-state heat pumps and micro-refrigerators and can implement Brayton, Ericsson, or Carnot-like thermodynamic cycles.

Additionally, electrocaloric materials show great promise for on-chip micro-cooling of electronics, where miniaturization is essential. Another important use for these materials is solid-state refrigeration for portable systems, where gas-free and vibration-free operation are crucial. They are also promising for energy harvesting systems with the piezoelectricity, heat pumping, and thermal management in defense and aerospace applications. Even though there are still solid obstacles such as breakdown strength, hysteresis losses that blocks the practical applications of the electrocaloric materials, the development of their performance is quick especially in multilayer systems. These systems are competitive alternatives to both magnetocaloric and vapor-compression techniques due to their important advantages, compatibility with current microelectronic manufacturing techniques and low environmental impact (ODP/GWP=0) [29], [30].

2.3. Electrocaloric Materials and Systems

There are numerous electrocaloric materials exists however only some of them are suitable for high performance applications. In order to consider the usage of an electrocaloric material in a device or application, there are several factors that makes them attractive. Electrocaloric materials are expected to have strong response levels, high electrical breakdown strength, low electrical conductivity to reduce Joule heating and lastly high thermal conductivity for the quicker heat exchange. These materials structurally can be divided to three major categories as polymers, ceramics, and monocrystals. Besides the structure, it is also possible to divide them by their form factors as bulk, thin-film, and multilayer capacitor. Each of these forms brings important advantages including easier integration, thermal response, field strength, depending on the target application. Ferroelectric materials have shown important level of electrocaloric performance amongst other materials, especially in thin-film and multilayer forms. More specifically, lead-based and lead-free ceramic based electrocaloric materials are the most attractive materials in terms of cooling performance [29], [30].

2.3.1. Lead-Based Electroceramics: PMN-PT, PZT, PST

Lead zirconate titanate (PZT), chemically represented as $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ($0 \leq x \leq 1$), constitutes a solid solution of two perovskite-type ferroelectric oxides: lead zirconate (PbZrO_3) and lead titanate (PbTiO_3). It is one of the most studied and widely used materials among functional ceramics because it has great electromechanical, dielectric, pyroelectric, and ferroelectric properties. Electrocaloric properties of PZT makes the material very useful for solid-state cooling applications but also its other electrical properties make them widely used as sensors, actuators, ultrasonic transducers, capacitors and memory devices (FeRAM) [34–36].

PZT crystallizes in the ABO_3 perovskite lattice. In this structure, Pb^{2+} is on the A-site and Zr^{4+} and Ti^{4+} cations are on the B-site. PZT shows a centrosymmetric cubic paraelectric phase when the temperature is high enough. When the temperature drops below its Curie temperature (T_C), which depends on the composition and also to other factors, the structure changes into a ferroelectric phase. This phase can be either tetragonal or rhombohedral, depending on the Zr/Ti ratio in the composition according

to phase diagram given in **Figure 2.11**. Compositions with higher Ti tend to have a tetragonal ferroelectric structure, while compositions with higher Zr tend to have a rhombohedral or even antiferroelectric phase. The area where these both phase types coexist is named as morphotropic phase boundary (MPB) and typically located around $x \approx 0.48$. MPB is an important point in ferroelectric materials because the crystals possess the highest electromechanical coupling performance in this area. This is simply due to having more energetically equivalent polarization directions as six for tetragonal and eight for rhombohedral phases. This makes it easier for polarization to rotate when external electric field is applied to the material. This is the main reason of the PZT materials having composition around MPB are the best at changing electrical energy into mechanical or thermal energy and back again [34], [37–39].

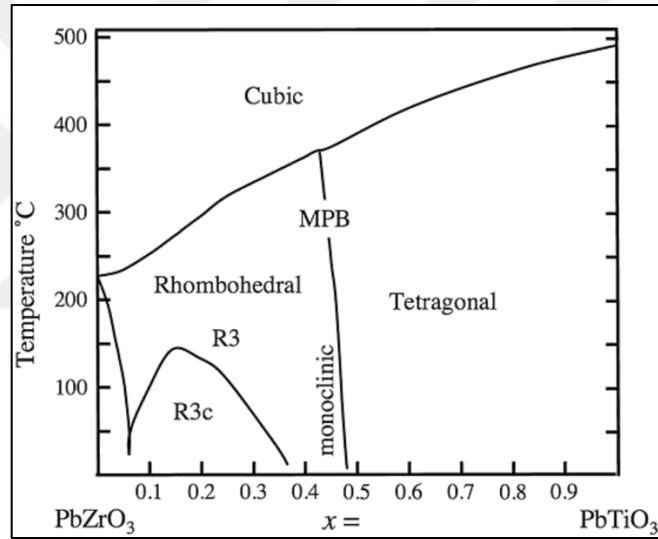


Figure 2.11: Phase diagram of Lead Zirconate Titanate.

Functional behavior of the PZT materials can be tuned significantly by dopant engineering as well as compositional changes. In general, PZT materials are defined in two main categories as soft and hard PZTs. Soft PZT refers to a material system doped with donor ions such as La^{3+} (A-site) or Nb^{5+} (B-site) resulting with higher domain wall mobility, dielectric permittivity, and piezoelectric constants. This is especially important for the cases where the materials will be used in low voltage electrocaloric applications as well as actuation and sensing. On the other hand, hard PZT refers to a material system doped with acceptor ions such as Fe^{3+} or Mn^{3+} resulting with higher mechanical quality factors (Q_M), lower dielectric loss and also better

thermal stability. These materials are better suited for high-power and high-frequency applications. These differences between the soft and hard PZT systems arises directly from the dopants influencing the defect chemistry and resulting with behavior changes in aging, conductivity, fatigue as well as domain wall dynamics [38], [40–43].

PZT system have an important property named as field-induced phase transition and this property is quite important particularly in Zr-rich compositions where antiferroelectric (AFE) ordering predominates. Pure PbZrO_3 is a classical AFE with Curie temperature around 230°C which can be driven to ferroelectric state when high level electric fields are applied. This transition results in distinctive double hysteresis loops and enhances the electrocaloric effect as they bring significant entropy changes to the system. It is possible to use this phenomenon to bring peak electrocaloric effect response close to room temperature in properly doped and engineered compositions [34], [43–47].

PZT materials are usually synthesized using conventional solid-state reactions and in the form of polycrystalline ceramics. Its characteristics are strongly affected from important process related parameters such as grain size, porosity, and processing conditions [47]. On the other hand, polycrystalline materials require to be macroscopically polarized by poling since they are made up of randomly oriented grains. This is done by applying a strong external electric field at specific temperatures. Poling is a crucial step to activate the ferroelectric and piezoelectric functionality of the material. It is important to keep in mind that the stabilization of the domains, defect migration, and internal stress relaxation cause ceramic to age over time [40], [47], [48].

Thin film and multilayer forms of PZT is also an important research area to fulfill the requirements of miniaturized systems. Since the thickness of these systems are typically less than $1\text{ }\mu\text{m}$, they enable application of high electric fields even with low voltages which results with enhanced electrocaloric effect. MLCs are especially promising for the solid-state cooling applications of electrocaloric materials as they balance the volumetric electrocaloric effect and device robustness. These MLCs are mostly manufactured by stacking of thick films typically around $\sim 10\text{--}50\text{ }\mu\text{m}$ and electrodes between these films [49]. Further, relaxor-like behavior has been demonstrated by PZT-based materials like PLZT (lanthanum-doped PZT), where the presence of polar nanoregions (PNRs) further enhances the entropy change under electric field, thereby improving EC performance. Relaxor character of the system is

tunable through grains size, processing method, and doping levels [44], [45]. When we compare PZT with other polymer based electrocaloric material, it has relatively high Curie temperatures. This might be an advantage for the applications requiring stability at high temperatures. Also, its dielectric strength and low conductivity makes them suitable for high electric field application without dielectric breakdown which is crucial for having greater electrocaloric response levels. Lastly, PZT possess important thermal conductivity over polymers that facilitating quick heat exchange, which is critical for high frequency electrocaloric cycles.

PZT is one of the most significant electroceramics in both established electromechanical applications and new solid-state cooling systems due to its compositional, structural, and form factor versatility. It is positioned as a key component for the development of lead-based, compact, and efficient electrocaloric devices in the future due to its capacity to achieve notable electrocaloric cooling values, field-induced AFE-FE switching, and fine-tune its ferroelectric-paraelectric transitions, particularly in thin films and MLCs.

PMN-PT, also known as $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$, is a complex perovskite solid solution system that has become the leading candidate for electrocaloric cooling applications. PMN-PT offers a special combination of high dielectric permittivity, large electric field-induced polarization changes, and tunable phase transitions by fusing the relaxor ferroelectric nature of PMN with the classical ferroelectric behavior of PbTiO_3 (PT). PMN-PT's crystal structure is based on the ABO_3 perovskite framework, with Pb^{2+} occupying the A-site and a complex configuration of Mg^{2+} , Nb^{5+} , and Ti^{4+} ions sharing the B-site. The coexistence and easy rotation of polarization vectors between rhombohedral and tetragonal phases make the morphotropic phase boundary (MPB) region which is typically found between 31 and 37 mol% PbTiO_3 , particularly interesting. By providing an energetically favorable route for electric field-induced polarization rotation, the emergence of monoclinic intermediate phases within this compositional window maximizes the EC response [50], [51].

PMN-PT possesses diffuse phase transition and also frequency dependent dielectric peaks. These characteristics are typical relaxor ferroelectric behavior that we observe in PMN-PT, in contrast to PZT. A key factor in electrocaloric performance is the existence of polar nanoregions (PNRs), which are caused by random fields and local chemical inhomogeneity as a result of B-site disorder. Under an external electric field,

these PNRs allow for a slow and reversible evolution of polarization, which leads to significant entropy change and enhanced electrocaloric temperature shifts. Composition of PMN-PT can be adjusted for highest electrocaloric coefficients typically around the depolarization temperature (T_d) and slightly above the temperature of dielectric maximum (T_m) [51–54].

Studies have shown that doping PMN-PT with La enhancing the relaxor character and causing the long-range ferroelectric order. Substitutions of La^{3+} causing electrocaloric effect to close to room temperature at low level electric fields due to modulation of the domain structure. This also lowers the Curie temperature and expands the operating temperature window [55], [56]. These systems also possess improved electro-optic properties and larger quadratic coefficients.

Pure phase PMN-PT ceramics are still difficult to achieve from a processing perspective because of the propensity to form undesired pyrochlore phases. The columbite precursor method has been the most successful synthesis technique in encouraging the formation of the perovskite phase. This method aims to minimize the impurity phases. Also, it ensures the repeatable electrical behavior by firstly forming MgNbO_6 and then having the reaction with PbO and TiO_2 to produce the aimed solid solution [31], [57].

PMN-PT materials in every form have shown promising electrocaloric performances in the vicinity of the MPB with both direct and indirect measurements. There are certain simulation techniques such as Landau-Devonshire phenomenological theory, shell model molecular dynamics to clarify the atomic level mechanism behind their electrocaloric responses. These studies showing that the field-induced phase transitions, random fields, and local structural heterogeneity are really important and effective to optimize the electrocaloric performance.

All the mentioned tunability, makes PMN-PT a particularly effective and highly adjustable relaxor ferroelectric. It is one of the leading candidates for the development of next generation cooling techniques with its electrocaloric properties boosted from the intricate interaction of polar nanoregions, chemical disorder, and structural phase behavior.

PST, a member of the Pb-based ABO_3 perovskite family, is a promising candidate for pyroelectric infrared detectors and electrocaloric applications due to its rich interplay

between chemical ordering, microstructural heterogeneity, and functional properties. The general formula for PST is $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$. In this system Sc^{3+} and Ta^{5+} cations are distributed throughout the B-site locations of the perovskite structure, and Pb^{2+} ions occupy the A-site. Arrangement of these B-site cations might be disordered or show different levels of disordering depending on the synthesis conditions and thermal treatment. Its dielectric, ferroelectric, and electrocaloric behavior are all strongly influenced by this B-site ordering. When the B-site occupancy is disordered, PST exhibits a diffuse ferroelectric–paraelectric transition and a broad, frequency-dispersive dielectric permittivity peak, indicating a strong relaxor character. On the other hand, PST tends to exhibit more classical ferroelectric behavior with a sharper transition and less dielectric dispersion as the degree of ordering increases. Thermal annealing modifies the chemical order parameter, allowing for a systematic tuning of the transition from relaxor to ferroelectric behavior. The electrocaloric activity of PST is caused by polar nanoregions (PNRs) embedded in a non-polar matrix, which dominate the dielectric response in the disordered state, and they are also sensitive to the external electric fields [20], [58], [59].

Due to its high permittivity, pyroelectric coefficients, and electrostrictive strain, PST is used in infrared detectors and thermal imaging sensors. Even though it has important advantages, its low Curie temperature, which typically ranges from -10°C to 25°C depending on the B-site order, restricts the wider applications. At this point creating solid solutions of PST is a possible solution. PST-PT systems have been studied to improve the sintering process behavior and to raise the Curie temperature. PST-PT system have shown a MPB at about 40–45 mol% PT with higher dielectric and piezoelectric properties [60].

Processing of PST is typically done using the two-step sintering method which involves ScTaO_4 precursor in order to reduce the pyrochlore secondary phase that is reducing the performance. Also, traditional mixed oxide sintering in one step is used for industrial applications to ease the scalability even though it can result in lower phase purity [60], [61]. Like other relaxors, PST exhibits aging phenomena as a result of internal field redistribution over time, domain wall pinning by defects, and gradual equilibration of internal structures. Its complex and adjustable functional behavior is influenced by internal stresses, polar nano- and microstructures, and chemical heterogeneity. PST is an important system among relaxor ferroelectrics with its

pyroelectric and dielectric characteristics which makes it useful for advanced energy, sensing, and thermal management applications.

2.3.2. Lead-Free Electroceramics: BCZT

Lead-free electroceramic materials alternatives are also in demand due to the toxicity of the lead. At this point, a solid solution of barium titanate (BaTiO_3) named barium calcium zirconate titanate (BCZT) stands as the most promising material due to its high performance with significant electrocaloric potential. BCZT has ABO_3 perovskite structure just like the other materials mentioned earlier. In this system Ti^{4+} and Zr^{4+} partially occupy the B-site and Ba^{2+} and Ca^{2+} cations partially occupy the A-site. Compositional tunability of the material and also the lattice distortions caused by dual site substitution, electrical properties of BCZT can be really high and tunable. The functionality of BCZT is mainly reasoned from its MPB which is usually concentrated around compositions like $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$. At MPB, tetragonal and rhombohedral phases coexist and makes the material able to polarize in total 14 possible orientations, six for tetragonal phase and eight for rhombohedral. Having this amount of possible domain states makes the material simply to rotate and reorient the polarization when an external electric field is applied. This also directly increases the entropy change and therefore resulting with greater adiabatic temperature change [62–64].

Ca and Zr content in BCZT systems strongly affects the ferroelectric behavior of the material as either displaying relaxor-type or classical behavior. As mentioned in earlier sections, PNRs are a natural feature of relaxor ferroelectrics. The formation of these regions is promoted by the increased chemical heterogeneity and ionic mismatch at higher Ca concentrations ($x > 0.5$ in $\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$). BCZT is suitable for applications needing thermal regulation under a range of circumstances because these PNRs broaden the temperature range over which strong electrocaloric responses can be obtained and aid in diffuse phase transitions. For practical cooling devices, relaxor-like BCZT compositions provide a wider and smoother operating window than classical ferroelectrics with abrupt transitions [62], [65].

Electrocaloric responsivity values ($\Delta T/\Delta E$) in BCZT systems have been reported to range from 0.25 to 0.38 K.mm/kV, particularly in the vicinity of the cubic-to-

tetragonal phase transition. Therefore, they are comparable to many of their lead-based alternatives as being more sustainable alternative in solid-state refrigeration. Furthermore, BCZT has low dielectric losses ($\tan\delta < 0.02$), large spontaneous polarization ($2P_r > 30 \mu\text{C}/\text{cm}^2$ in optimal compositions), and weak thermal and field hysteresis, all of which are favorable for reversible, energy-efficient electrocaloric cycles [64], [66].

The final electrocaloric behavior of BCZT ceramics is largely determined by the fabrication process. While traditional solid-state methods provide solutions to industrial scalability, it has been shown that sol-gel and hydrothermal synthesis routes might offer really high chemical homogeneity and finer control over grain size, and this can result with improved ferroelectric and electrocaloric responses. Additional sintering parameters that impact BCZT's density, phase purity, and domain structure are temperature and holding time. Ceramics sintered at approximately 1500°C , for example, have shown recoverable energy densities exceeding $0.5 \text{ J}/\text{cm}^3$ and optimized ferroelectric properties ($2E_s \approx 3\text{--}4 \text{ kV}/\text{cm}$), indicating their potential in energy storage and cooling applications [62], [63], [67]. Also, the coexistence of both positive and negative electrocaloric effects in BCZT compositions has been investigated in recent studies. This behavior which varies with field and temperature history, reflects the rich domain dynamics and field-induced phase transition mechanisms in BCZT systems [68]. The development of adaptive or programmable thermal devices based on BCZT may be made feasible by this feature.

In conclusion, BCZT ceramics are a type of eco-friendly, high-performance ferroelectrics that can be employed in electrocaloric cooling systems. Their compositional flexibility, large polarization changes, low hysteresis losses, and capacity to support both classical and relaxor-like behavior make them exceptionally promising for next-generation solid-state refrigeration and energy management systems [69].

2.4. Process-Structure-Property Relationships in Electroceramics

2.4.1. Effect of Heat Treatment and Atmosphere

Thermal processing parameters strongly affects the phase composition, microstructure, and the functional properties of the material. These parameters mainly include calcination, sintering, and sometimes annealing temperature, duration and the atmospheric environment that this treatment performed. All of the dielectric, ferroelectric, piezoelectric, and electrocaloric behavior are directly impacted by the design of these processes and parameters. The impacted properties are not limited with the electrical characteristics but also includes the important structural characteristics such as grain size, porosity, phase purity, defect configuration, and domain wall dynamics. Therefore, heat treatment and the processing environment is carefully adjusted to engineer domain configurations, suppress secondary phases like pyrochlore, and improve the overall electromechanical response. The studies reported in the literature and given below clearly shows the impact of these thermal and atmospheric control, and how careful adjustment of processing parameters in different ferroelectric material systems such as PST-PT, PSTT, BCZT, and PMN-PT results.

Mo et al. showed a close connection between the thermal history, microstructural development of the material, and electrofunctional performance. The study covered a systematic investigation of the annealing time effect on functional properties of $0.85\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3\text{--}0.15\text{PbTiO}_3$ ceramics. Bulk samples were synthesized by conventional solid-state reaction and afterwards annealed at 1100°C for 10 to 50 hours. Clear improvements in electrical properties such as dielectric constant, polarization, electrocaloric effect, and energy storage density were found. The electrocaloric performance of the material was measured up to 1.63 K at 40 kV/cm. These improvements are clearly indicating that the influence of annealing time on structural evolution of domain dynamics and defect redistribution. Controlled annealing optimizes polarization mechanisms by modulating grain-boundary behavior, domain wall mobility, and defect configurations, as evidenced by a non-linear, peak-shaped dependency of these properties on annealing time. Especially when the sample annealed 30 hours, it has shown maximized energy storage capacity. Also, the ferroelectric and electrocaloric performance was observed when the annealing time is

set to 40 hours. The study clearly highlights the importance of annealing as a crucial process to fine tune the structure and for property enhancements in PST-PT relaxor ferroelectrics [58].

In another study on PST-PT, Zhu et al. used one-step sintering method to study the synthesis and the phase development characteristics. PST-PT was calcined between 900 and 1100 °C and then sintered between 1100 and 1300 °C with extra PbO to compensate the volatilization. This method made it possible to create highly crystalline ceramics with clean grain boundaries and well-stacked grains, as seen in SEM images, and perovskite phase purity of up to 100%, as verified by XRD. Crucially, the study presents a new perovskite forming impact factor (F) that was found to correlate favorably with the ease of phase formation across compositions. This factor is simply the product of two values which are the tolerance factor and the ionic bonding fraction. The study promoted the dense microstructure and high perovskite purity to achieve higher dielectric and ferroelectric properties by optimized sintering. The observed change in the Curie temperature difference from 6°C to 12°C across compositions is a reflection of the compositional tuning made possible by processing conditions. This highlights the critical role that customized thermochemical parameters play in achieving functional ferroelectric behavior in PSTT ceramics [60].

Buatip et al. systematically studied the effects of sintering temperature and duration on the phase evolution, microstructure, and electrical properties of BCZT ceramics with the composition $\text{Ba}_{0.85}\text{Ca}_{0.75}\text{Zr}_{0.10}\text{Ti}_{0.90}\text{O}_3$, produced through the conventional solid-state reaction method. The research demonstrated that densification and grain development were significantly influenced by the implemented sintering temperatures (1250°C, 1300°C, and 1350°C for 2 and 4 hours). The study shows that the formation of a pseudo-cubic perovskite structure occurred under all conditions. However, the most favorable results were observed for ceramics sintered at 1300°C for 4 hours. The material showed a high densification (about 98% of the theoretical value), a better grain structure (average size $2.19 \pm 0.87 \mu\text{m}$), and better dielectric ($\epsilon_r=2840$), ferroelectric ($P_r=5.84 \mu\text{C}/\text{cm}^2$), and piezoelectric ($d_{33}=167 \text{ pC}/\text{N}$) properties under these conditions. These findings emphasize the significance of optimized sintering in facilitating domain reorientation and alignment, thereby improving the electromechanical performance of lead-free BCZT ceramics. The study underscores

the critical significance of processing parameters in modulating structure–property relationships for advanced ferroelectric applications [70].

Zhang et al. synthesized 75PMN-25PT by using three different sintering methods which are uniaxial hot-pressing, oxygen atmosphere pressing, and two-step sintering. The study showed the importance of the processing routes for the microstructure and the electro-optic characteristic of the relaxor ferroelectrics. Due to the effective suppression of the pyrochlore phase and removal of porosity, the two-stage sintering method which combines pressure and a controlled oxygen atmosphere, produced the highest densification and optical transparency (approximately 70% at 900 nm). The dielectric and ferroelectric measurements, which showed relaxor behavior in all samples with slight variations in diffusivity coefficients and P–E loop shapes, provide additional evidence of the structure–property linkage. To tune transparency and electrical functionality in PMN-PT-based electroceramics, careful control over sintering conditions is crucial, as only the samples processed using the two-stage method demonstrated optimal phase purity and microstructural uniformity [55].

2.4.2. Effect of Doping, Grain Size, and Texture

Fine tuning of the processing parameters are quite important to enhance the functional characteristic of ferroelectrics and it is being more studied literature every day. During the processing of the electroceramics, from dopant addition to the sintering profiles and control of microstructure, phase stability, defect structures, domain behavior and a lot of other characteristics are deeply influenced. In this section, examples from literature to the chemical doping, texturing, and synthesis route optimization studies are given for PMN-PT, PZT, and BCZT system to show the complex process-structure-property relations.

Sun et al. examined the effects of Sm doping on 88PMN-12PT ceramics that were synthesized with columbite precursor route and sintered under controlled conditions to prevent the formation of pyrochlore phases and preserve a pure perovskite structure. Two steps in the processing route are considered crucial for tailoring the defect chemistry and domain architecture of the ceramics. First, dual-step calcination (1050 °C and 850 °C) and then final sintering at 1200 °C under oxygen atmosphere. The structural addition of Sm led to the formation of polar nanoregions (PNRs) and the

controlled introduction of oxygen vacancies, as shown by piezoresponse force microscopy (PFM) and X-ray photoelectron spectroscopy (XPS). The results demonstrated that the functional properties were significantly influenced by microstructural features, which allowed for a broader operating temperature range (30–180 °C) and important adiabatic temperature change ($\Delta T = 2.07$ °C at 50 kV/cm) due to enhanced entropy change mechanisms. The results show that domain engineering and defect management can enhance the electrocaloric performance of relaxor ferroelectrics, as a promising path for next-generation solid-state cooling applications [71].

In a comparative study on 92PMN-8PT, Li^+ , Mn^{2+} , Sr^{2+} , and Ta^{5+} dopants were studied to optimize electrocaloric behavior and dielectric characteristics. The samples were processed through controlled solid-state route and resulted with dense ceramics having low level porosity (~3%). Calcination was done at 800°C and sintering at 1200°C in a Pb-enriched atmosphere. Measurements have shown classic relaxor characteristics such as diffuse permittivity peaks and slim P-E loops and the phase purity was also examined by structural analysis. Li doped composition showed enhanced entropy change and lowest hysteresis losses, indicating higher refrigerant capacity and energy efficiency, even though all doped samples showed reduced electrocaloric temperature change. The study showed the complex process-structure-property relations and how dopants affect the phase transition temperatures and relaxor dynamics as well as thermal responses for electrocaloric applications [72].

Chen et al. studied 0.5 mol.% La doped 088PMN-12PT relaxor ceramics synthesized with columbite precursor method to prevent secondary phase development and enhance densification. Two-step sintering method was performed at 1210°C under uniaxial pressure following high-temperature treatment at 1230°C in an oxygen atmosphere. Analyses showed a dense and pure phase perovskite matrix with only traces of pyrochlore. Direct measurements of electrocaloric resulted with dual peak of ΔT_{EC} due to La^{3+} doping which changed the domain configuration and defect structure. This response showed better thermal tunability over a broader operating window (40–70 °C) with a peak ΔT_{EC} of 0.44 K at 4 kV/mm. The broad temperature range and robust electrocaloric response above the dielectric maximum underscore the efficacy of process-induced structural tailoring, particularly in the regulation of polar nanoregions and lattice disorder. The field-driven dynamics of PNRs are directly

linked to the emergence of dual peaks in ΔT_{EC} -T profiles, underscoring the essential interplay between functional response optimization and defect engineering for electrocaloric applications [55].

Intentional defect engineering through doping can dramatically alter the structure–property relationship in electroceramics, as Gözüaık et al.'s study on La-doped $PbZr_{0.70}Ti_{0.30}O_3$ ceramics demonstrates. The authors noticed a gradual slanting of ferroelectric hysteresis loops and a decrease in the Curie temperature upon adding La^{3+} to the perovskite lattice's A-site. This suggests a shift from traditional ferroelectric behavior to relaxor-like behavior. Landau–Ginzburg-based thermodynamic simulations that included elasticity and electrostatics supported this structural evolution, which was ascribed to the formation of defect–dipole complexes. Dense ceramics appropriate for EC evaluation were guaranteed by the processing method, which involved conventional mixed oxide sintered at 1320 °C. Indirect measurements for the composition doped with 8 mol-% La showed an important level of ΔT_{EC} of 1.15 °C at 45 kV/cm. This value highlights that ideal amount of doing can result wider broader temperature window for electrocaloric performance by promoting the diffused phase transitions without completely stabilizing single phase. The study have shown that electrocaloric behavior can be tailored by controlled doping that creates intended defects and it is possible to balance the increased entropy change and decrease breakdown risks [44].

Berksoy-Yavuz et al. compared randomly oriented and highly <001>pc-textured samples made by using tape casting with $BaTiO_3$ single crystal templates in order to study the impact of crystallographic texturing on the electrocaloric properties of 90PMN-10PT ceramics. By addition of 5 vol.% template, the processing method using template-assisted grain orientation achieved a >95% degree of texturing which is clearly indicating the structural control through processing. Despite this structural modification, dielectric and ferroelectric measurements showed that texturing caused a loss in polarization hysteresis and a slanting without changing the transition temperature, indicating that template-induced constraints might impede ferroelectric switching. The observed decrease in electrocaloric effect was further corroborated by thermodynamic modeling using Landau theory, which demonstrated that the textured samples had a lower ΔT_{EC} than their randomly oriented counterparts. This study is showing that complex process-structure-property interaction as texturing to align

grains enhances some characteristics, such as piezoelectric coefficients, but it may also restrict entropy-driven polarization dynamics, which are essential for reaching high electrocaloric response. Depending on the aimed function, the orientation and constraint effects introduced during processing need to be carefully adjusted [50].

Li et al. synthesized $\text{PbZr}_{0.55}\text{Ti}_{0.45}\text{O}_3$ ceramics with varying grain sizes (3.57 μm to 10.85 μm) by using the conventional solid-state reaction method. The study aimed to investigate the grain size dependency of dielectric, ferroelectric, and piezoelectric properties. The processing steps controlled the sintering conditions to make samples with different average grain sizes and revealed the link between thermal treatment and changes in the microstructure. Piezoresponse force microscopy shows that larger grains made more non-180° domain walls and made them move more easily. This structural change made the material softer and gave it much better electromechanical properties, such as higher d_{33} , remnant polarization, and negative strain. Also, the mechanical quality factor Q_m also increased, even though the mobility of the domain walls increased. This suggests that the larger grains may have a bulk effect that makes the material harder. These results show that microstructural design, especially grain size, is very important for changing the functional performance of PZT ceramics. This information could help make piezoelectric materials better for high-performance uses [42].

In another study on BCZT ceramics showed the importance of particles size in structure-property relations. The ceramics were synthesized by two different methods which are solid-state and sol-gel. Sol-gel method resulted with finer and more consistent particle size distributions. This consistency even increased with further combination with planetary ball milling. It is mentioned that this improvement results with the promotion of the development of polar nanoregions and diffuseness in the phase transition as a reflection of densification and microstructural homogeneity during the sinter process. The study reported dual ΔT_{EC} peak with a maximum of 2.5 K at 80 kV/cm. This value shows the importance of the mentioned characteristics on electrocaloric response. Smaller particle size also helped to improve the domain alignment and polarization switching which emphasized the importance of post-processing and precursor chemistry [62].

2.5. Machine Learning in Materials Science

There are three main methods in materials science for the research. These are computer-based simulations, theoretical modeling, and experimental studies. All of them have strong advantages for specific cases but also drawbacks. It is well known that performing experimental studies are time and cost intensive. Also, complex system is most of the needs to be simplified for theoretical models. On the other hand, simulations might be limited with specific systems or require important computational power. These approaches are not able to meet the requirements of new material research by their own as the material science becomes more data-rich through all abovementioned techniques.

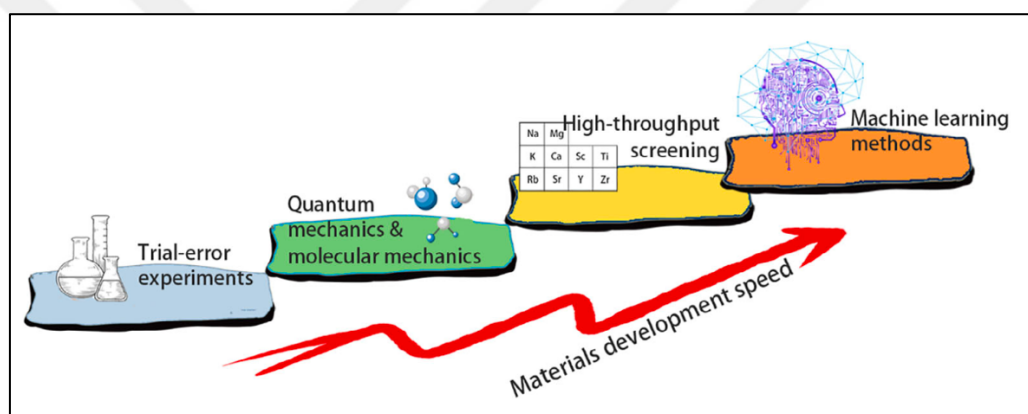


Figure 2.12: Development in the methods that accelerates the new material discovery.

At this point machine learning stands as the most important tool to learn the patterns within the data as opposed to depending only on human intuition or physical theories. This includes predicting a material's characteristics from its structure and composition. Machine learning is tool that can help to researchers for utilizing the existing knowledge and exploring the hidden patters, highlighting performance boosting combinations rather than trial-and-error methodology. Usage of machine learning is expanding really quick. There are studies where the machine learning is used to categorize materials, investigate structure-property relationships, reinforced learning to experiments, and of course creating predictive models and optimization routes for various properties. While transfer learning and data fusion techniques aid in the utilization of both experimental and simulated datasets, deep learning is being applied to problems such as crystal structure prediction and microscopy image analysis. Even

though it is really powerful, machine learning itself also brings new difficulties such as gathering meaningful dataset, selection of correct features and descriptors. But in the end, it offers a new way to accelerate and improve materials science studies [73], [74].

2.5.1. Machine Learning Pipelines in Materials Science

A structured, multi-step pipeline is used in materials science to apply machine learning. This pipeline basically converts data about materials into useful information for process optimization, materials design, and property prediction. Data collection, preprocessing, feature engineering, descriptor selection, model building and training, assessment, and application or prediction are typically the main parts of this sequence. Even though each of these steps can be changed for the specific tasks they are the key points for successful machine learning workflow.

The first step in the process is always the data gathering, which frequently combines data from experimental measurements, outputs from simulations and also selected databases. These databases might provide the information on variables like elemental composition, crystallographic structure, electronic configuration, mechanical properties, and thermodynamic parameters. Relevant data portions are chosen based on the target application. The collected data is most of the time not ready for modeling as it must be cleaned and formatted through a step called preprocessing. This step takes places for eliminating outliers, standardizing units and formats, and detecting and managing missing values. Handling of the missing values can be either by removal, statistical imputation, or model-based estimation. Normalization is another preprocessing step where the values are scaled between 0 and 1 or standardization where the data scaled to zero mean and unit variance. These methods guarantees that no single feature's magnitude dominates the learning process. Also, the data with categorical information needs to be numerically encoded, for example, using ordinal or one-hot encoding.

One of the most important parts of machine learning for materials science is feature engineering and descriptor selection. Descriptors are the meaningful numerical representations of physical, chemical, or structural properties, generally created from the raw input data. Descriptors can be automatically extracted using data-driven

methods or can be derived from knowledge, such as atomic radii, electronegativity, or mixing enthalpy. Combination of compositional and thermodynamic descriptors is important especially when modeling complex materials as studies like He et al. have shown [75]. By matching learned relationships with established physical mechanisms, effective descriptor engineering not only increases interpretability but also improves the performance of the model. Descriptor selection is important to remove the features that are irrelevant from the dataset. When this selection is done in a meaningful way, it increases the generalizability and computational efficiency of the model. The ideal feature set is frequently context-specific and needs to be confirmed for every new material class or trait under study.

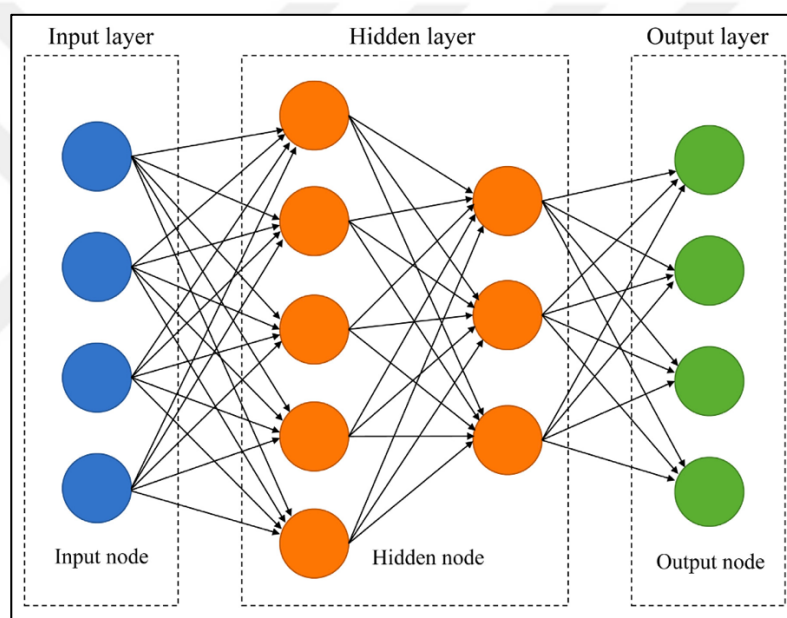


Figure 2.13: A typical artificial neural network (ANN) neural network with input, hidden, and output layers where each circle represents the neurons and arrows represents the connections.

Construction of the model and its training comes after when the dataset is ready. Generally, the algorithm is selected based on the type of task. Models like Linear Regression, Support Vector Regression (SVR), Random Forest Regressors, or Artificial Neural Networks (ANNs) are frequently used for regression problems. Support Vector Machines (SVM), Decision Trees, Random Forests, and k-Nearest Neighbors (kNN) are more used for classification problems and deep learning

architectures, like Transformer models, Convolutional Neural Networks (CNNs) for are use more in complex scenarios.

In order to achieve the best results hyperparameter tuning is essential in machine learning regardless of the algorithm selected. Hyperparameters tunes how the model learns and works. There are many types of hyperparameters depending on the model, such as the regularization parameter in SVMs, the maximum depth in decision trees. These parameters are better to be set before the training and are not learned from data. To determine the optimal set of hyperparameters based on cross-validated performance, methods such as grid search, random search, and Bayesian optimization are mostly used.

Model evaluation shows that the trained model can use its knowledge on new data. These evaluations are basically done by using techniques such as cross-validation, hold-out validation, or bootstrap methods. The evaluation metrics are determined by the task. Common metrics for regression include R^2 score, mean absolute error, and mean square error. Important thing about the evaluation is that it includes detecting and avoiding overfitting. These two behaviors specifically occurs either when a model learns training data but performs bad on new data, or when a model is too simplistic to identify patterns in the data. Regularization techniques, feature selection, and model complexity control can all help manage these issues.

2.5.2. Machine Learning Algorithms

The algorithms used in the machine learning can recognize and reveal the patterns within a given dataset and extend these patterns to unknown regions of the data. This recognition process differs depending on the algorithm and some of the algorithms performs better in specific types of problems. In this section, different machine learning algorithms used in this thesis are introduced.

2.5.2.1. Decision Tree

Decision Tree is a supervised learning algorithm, and one of the most used and basic prediction models used in machine learning regression tasks. The main method of the algorithm is splitting the data based on their properties and modeling the decision-making process as a tree structure. This structure consists of internal and leaf nodes

variable. This methodology also eliminates the less important features during the regularization process [74], [78], [79].

The algorithm specifically shows advantage on linear relations and to reducing the complexity of the model without loss in prediction power. However, the model mostly selects a single variable from the features that is showing the highest correlation and tends to discard the others. This results with a sharp decision on feature selection, which can be both an advantage and disadvantage depending on the task [74], [78], [79].

2.5.2.3. Extreme Gradient Boosting (XGBoost)

XGBoost is a really powerful algorithm with a wide range of usage area based on gradient boosting. The method is an ensemble learning algorithm which gives the output based on a series of decision trees. The algorithm iteratively creates decision trees and each of the trees learns the patterns from the previous trees and minimizes the loss and residual errors while maximizing the prediction accuracy. Therefore, the model achieves high prediction accuracy without tendency to overfitting. A simple scheme of XGBoost algorithm is given in **Figure 2.15** [78–80].

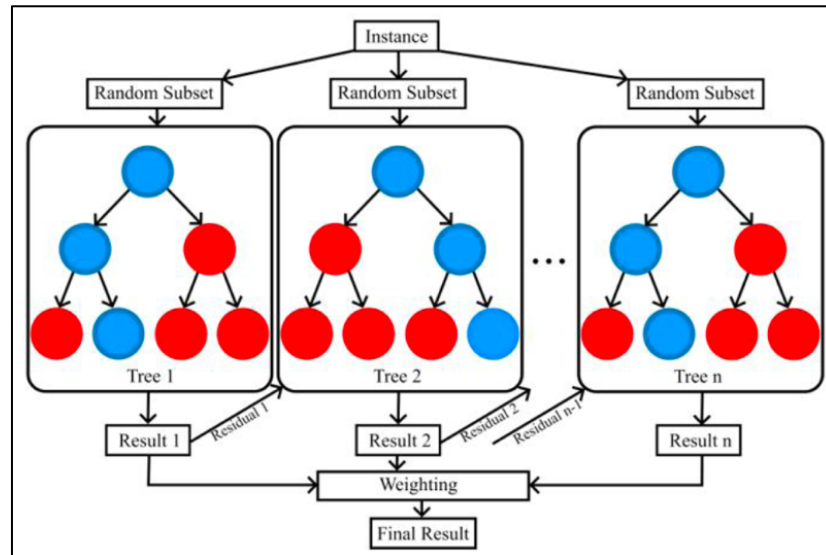


Figure 2.15: XGBoost algorithm structure.

The algorithm has an important advantage due to its scalability and flexibility which means that both of the machine learning tasks, classification and regression, are

handled in a robust way by the model. As an additional power of the model related with the materials science dataset, its capability to handle the missing data. Finally, it uses two regularization mechanism to control the complexity of the model and enhance the generalization [78–80].

As a results of these advantages, XGBoost is capable to work effectively in large datasets where the relations are strongly complex and non-linear. It is able to catch the interactions between each feature and their importance on a given task. This makes the model especially useful for industrial applications [78–80].

2.5.3. Machine Learning Applications in Materials Science

Machine learning brought an important ability to materials science in terms of modeling, predicting, and designing materials with certain properties. This advancement has been reflected into ferroelectric materials as well. In this section, different examples from the literature that used machine learning applications covered.

One of the most important examples of applying machine learning to functional ceramics is the work of Su et al. They developed a comprehensive framework made possible by machine learning to predict the adiabatic temperature change in lead-free BaTiO₃-based electrocaloric ceramics. They created a dataset from the published electrocaloric measurements representing different compositions in the Ba_{1-x}A_xTi_{1-y}B_yO₃ system, where B is Zr, Hf, and Sn and A is Ca, Sr, and Cd. Two regression-based machine learning models were developed to handle both direct and indirect electrocaloric measurements. The compositions were encoded using physically meaningful descriptors such as electronegativity, tolerance factors, ionic radii, and Mendeleev numbers for both A- and B-site cations. Different descriptor vectors were also introduced for compositions containing dopants in order to preserve the chemical sensitivity of the system [81].

Yuan et al. performed a study to predict the expected structural phase of the material as a function temperature and composition. They constructed a model to solve this classification model and then design space was made possible by this two-step machine learning approach, which involved regression for ΔT_{EC} and classification for phase. One important finding confirmed that the importance of the phase stability in electrocaloric applications. The maximum electrocaloric performance tends to occur

close to phase transition boundaries like tetragonal-to-cubic or rhombohedral-to-cubic. In order to make their models publicly available and encourage researchers to create more materials, the team also published an open-source web application [82].

In another study, Sapkal et al. used the machine learning based modelling to (K,Na)NbO₃-based ferroelectric ceramics to identify the functional property predictors such as dielectric permittivity and piezoelectric constants. Their key focus was on materials science-based descriptor engineering where they included the ionic radii, atomic volume, polarizability, structural tolerance factor as well as the stoichiometric contribution of the elements. They also enriched this feature space more with derived features by mathematically combining other features. The study used built-in functions from the Random Forest and XGBoost algorithms to track the feature importance and model interpretability. Root mean square error (RMSE) was used to evaluate the models, and grid search with cross-validation was used to optimize the hyperparameters. The study mentions the importance of domain informed feature selection in machine learning modeling. Also, tolerance factor, electronegativity, and atomic size, were found to be as important predictors, highlighting their fundamental role in the design of perovskite structured materials [83].

Askanazi et al. used three machine learning techniques which are k-Nearest Neighbors, Random Forest (RF), and Support Vector Regression (SVR) to study the prediction of Curie temperatures for Bi-based PbTiO₃ solid solutions. They found that SVR provided an important trade-off between performance and overfitting, particularly for small datasets, while RF offered the best accuracy with relatively less sensitivity to hyperparameters in a systematic comparison of model performance across different training data compositions. The study showed the importance of descriptor selection for prediction accuracy. Ionic radius, displacement tendencies, B-cation valence states, and Bi content found to be the most related features for ferroelectricity. Both homovalent and heterovalent data were necessary to fully capture the behavior of Bi-PTO systems, revealing the complex interplay between composition and T_C in these oxides [84].

Many studies focus on oxide ceramics, but Kushwaha et al. used the machine learning for the comparison of five different regression models to forecast super capacitive performance of carbon-based materials. Their work is quite important because it highlights the model selection process in relation to dataset complexity, computational

cost, and overfitting. The study has shown that XGBoost and Random Forest performing better than artificial neural networks in managing small-to-medium datasets, providing a better balance between accuracy and interpretability. This comparison study clearly showed that how crucial it is to match the complexity of machine learning models with the availability of data and the context of applications [85].

2.5.4. Challenges and Limitations

Machine learning can significantly affect the material science in a positive way but still its performance and acceptance among the researchers are problematic due to several drawbacks such as data accessibility, model generalizability, interpretability, and domain knowledge integration that blocks the real applications.

The major problems are having and accessing to high quality and labeled dataset as well as their heterogeneity. Machine learning requires large amount data in a cleaned, labeled and annotated format. But in materials science, the experimental data is mostly scarce, noisy especially for complex systems. Mobarak et al. mentioned that most of the low generalization and prediction accuracy are mostly reasoned from sparse sampling of the input space, low quality of the data and quite importantly absence of negative results. As material science works with high-dimensional descriptors, small datasets bring overfitting and makes reproducibility more difficult [73].

Machine learning models often ignore the physical and chemical constraints inherent in materials systems, despite their exceptional ability to recognize patterns. The inability of standard algorithms to integrate domain knowledge limits their scientific validity. Data-driven models may violate established thermodynamic laws or ignore crystallographic symmetries [74].

Another critical disadvantage of several machine learning algorithms is their black box nature. The machine learning models generally don't offer much insight into the logics behind the predictions. This nature hinders the scientific discovery because it makes it hard for researchers to validate the findings based on really well-established theories. Xu et al. mentions that explainable AI tools need to be developed in the context of materials modeling to foster trust and usability in scientific settings [86].

Training the models on biased or incomplete datasets is also a critical issue. These models as expected fail at generalizing and predicting. Studies highlight the importance of the algorithmic bias which can unintentionally mirror or magnify the sampling bias in training data, producing predictions that are unreliable in uncharted chemical spaces [73], [86].



3. EXPERIMENTAL STUDY

3.1. Overview of Research Flow

The purpose of the study is using the adiabatic temperature change in ferroelectrics to reveal the hidden patterns between the compositional variables, material processing parameters, and electrocaloric performance. The study has different stages to achieve this aim. Some of these stages are the feature engineering, statistical inference, machine learning based predictive modeling, data extraction from the literature, and also the process optimization procedures. The study was designed to investigate the potential of machine learning methodology in materials science and gathering insights into the process-property relations as well as process optimizations, by discussing the electrocaloric effect in different material systems in detail. Overview of the full workflow is given in **Figure 3.1**.

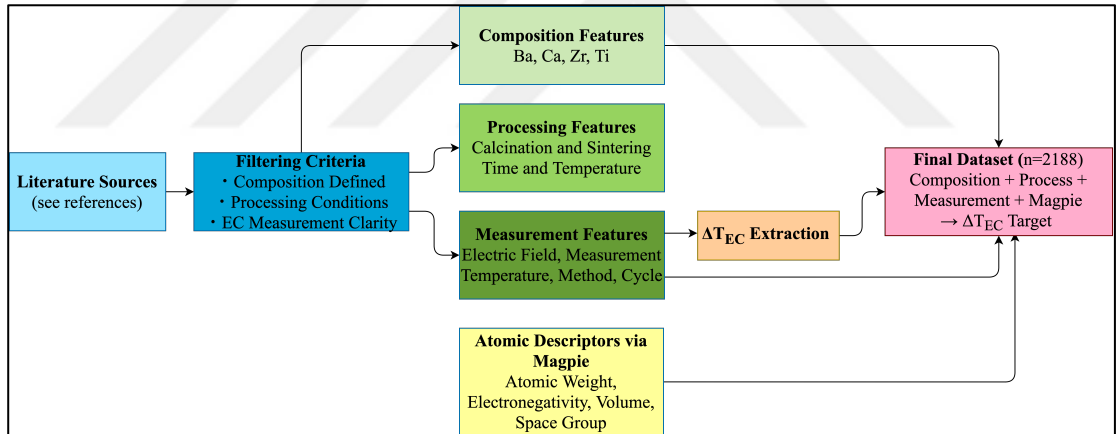


Figure 3.1: Research flow of the thesis.

As the first step, the publications reporting the experimental measurements of electrocaloric materials, were gathered to create a dataset. In addition to the electrocaloric performance specific compositional parameters, processing conditions (such as sample type, calcination and sintering time and temperature), and measurement parameters (such as applied electric field, measurement temperature, and cycle) were also collected. In order to have a reliable model, only data with comprehensive and traceable experimental data were included. As a result, a diverse dataset covering several material systems was created.

Second step was to handle the missing values, encoding the categorical variables such as measurement type and also other preprocessing points. Also, the offset between the measurement and Curie temperatures were included by computation.

Third step was for correlation analyses between the input variables and the electrocaloric response. This step was designed to choose the right feature sets and modeling approaches by exposing underlying dependencies, and nonlinear trends.

As the fourth step a number of supervised regression algorithms, such as gradient boosting, decision trees were assessed. The models were validated using cross-validation after being trained using stratified data splits. Bayesian optimization was used for hyperparameter optimization and mean squared error, mean absolute error, and R^2 score were the metrics used to evaluate the model. The feature importance was measured using model-specific approaches.

In the fifth step, optimizations to maximize the electrocaloric response was carried out. Bayesian optimization was used for this task and searched for the best process parameter sets while considering the constraints that are defined. The aim of this step is simply to direct the researchers to promising conditions and parameters sets before trial-and-error loops.

In the sixth and last step, a synthetic dataset was created by sampling the data within physically possible bounds for each parameter defined in the dataset. The aim was to increase the design space and check randomly selected but wide parameters. After its creation, the dataset was predicted by the trained model to highlight areas with possibly better electrocaloric behavior. The purpose of these predictive mappings is to generate hypotheses for subsequent experimental validation.

3.2. Dataset Generation

The dataset from the experimental studies on electrocaloric materials stands as the basis of this study. The derived dataset includes the key parameters from composition to processing, and measurement conditions of electrocaloric performance. The important aspect of the dataset is its nature as being completely experimental in contrast to computational datasets or synthetic data. Next sections describe the main steps of the dataset generation.

3.2.1. Data Gathering Strategy

The main goal while gathering the data for a comprehensive dataset was curation of it in a rich format that includes process-structure-property relations and also broad in chemical scope. Therefore, a deep look in experimental publications was required to manually extract the data that presents the measurements of adiabatic temperature change.

Therefore, the first starting point was reviewing the academic databases to collect data. At this stage, the peer-reviewed experimental studies and the studies performed within our research group was considered. One of the key points was including the studies that specifically reports the temperature change in a meaningful manner to guarantee the modeling integrity. Following parameters were the least required set to be included in the dataset: precisely described chemical formula to ensure stoichiometric constraints, parameters specific to the synthesis process which are calcination and sintering details, electrocaloric measurement conditions, and Curie temperature of the material.

These values were taken directly from the articles as well as the figures and tables within. WebPlotDigitizer was used to digitize the temperature change values from the electrocaloric measurements. The aim was not only including the highest value of ΔT_{EC} but also capturing the trend over the measurement cycle in the dataset. While adding the data into the dataset, references was also included to enable traceability. Because of their distinct scaling laws and processing behaviors, thin film studies were not included in the dataset.

3.2.2. Features and Parameters

A physically meaningful representation of the material-processing-property relationship was ensured by the feature space used in this study. This was created to reflect both experimentally reported variables and domain-informed derived descriptors. Every feature that was included was chosen based on its proven or potentially known impact on electrocaloric behavior. In order to increase the amount of information that the algorithm could uncover between input and outputs, the entire set of input parameters was also recorded. Chemical descriptors, processing

parameters, and measurement conditions are the three primary categories into which these chosen parameters can be divided.

The crystal chemistry and phase stability of the perovskite systems are determined by the molar fractions of each component element. The ratio of Ba/Ca in BCZT influences ferroelectric polarization and lattice distortion, and the Zr/Ti ratio adjusts tetragonal-rhombohedral phase transitions that are known to increase ΔT_{EC} close to morphotropic boundaries. These factors are therefore crucial for both physical interpretability and performance prediction and were included. The molar fractions were used to define the composition for PMN-PT, with the constraint of sum of them 1. The relaxor-to-ferroelectric transition behavior, which has a significant impact on electrocaloric performance was tried to be captured in this representation. Similarly, with the restrictions that Ba and Ca as well as Zr and Ti equal one, elemental compositions for BCZT were explicitly recorded as individual. Numerous studies independently alter these elemental ratios to optimize functional response and tune structural phase transitions, necessitating this level of resolution.

As the dataset also included the textured samples, template materials and their fraction were also included to the dataset. Strontium Titanate (ST) and Barium Titanate (BT) were the two types of template materials that were added to the dataset as columns and their amount was added to the dataset. For the samples without texturing, these values were set to 0. Therefore, it was aimed to capture the performance enhancements in electrocaloric behavior reasoned from the anisotropy and not only reasoned from compositional or processing parameters.

On the other hand, a set of composition-derived descriptors were included into the dataset. These descriptors were from the Magpie (Materials-Agnostic Platform for Informatics and Exploration). The aim was to include more details about the chemistry of the materials in the dataset by bringing additional descriptors beyond raw elemental fractions. In order to achieve this descriptors, matminer library was used which is initially created by Ward et al. ^[87]. Atomic size, electronegativity, valence structure, and crystal tendencies are some of the knowledge that can be encoded as numerical features and define the chemical identity of the material more in depth. Magpie directly converts a given composition into fractions and collects the elemental properties. These properties then given with their mean, maximum, range, or standard deviation values. In this study, six of the Magpie descriptors given in **Table 3.1** were used. The

selection of these descriptors was based on their potential effect on electrocaloric behavior. Also, some other descriptors were naturally excluded due to their low variance.

Table 3.1: Selected Magpie descriptors for the datasets.

Descriptor Name	Physical Meaning	Reason to Include
Mean Atomic Weight	Weighted average mass of constituent atoms	Proxy for density and mass transport behavior
Mean Electronegativity	Average electron-attracting ability of constituent atoms	Correlates with bond ionicity and phase stability
Mean NdUnfilled	Average number of unfilled d-orbitals	Related to transition metal reactivity and electronic structure
Mean NUnfilled	Average total number of unfilled valence orbitals	Approximate indicator of bonding capacity
Mean GSvolume_pa	Mean ground-state volume per atom ($\text{\AA}^3$)	Linked to lattice parameters and polarizability
Mean SpaceGroupNumber	Weighted average of space group numbers of constituent elements	Rough structural classification proxy

As the important features of ferroelectric ceramics such as microstructure, density, phase purity, and domain configuration are directly affected by the processing conditions, one categorical sample classification and four thermal process parameters were included into the dataset.

Calcination stands as an important step in electroceramic processing since the first solid-state reaction, crystallization, occurs in the precursor powder. The first step of the phase formations and homogeneity is dependent and determined during the calcination. It is known that the secondary phases which are reasoned from the incomplete or low temperature calcination might affect the electrocaloric behavior strongly. On the other hand, longer or high temperature calcination also may result with the volatilization of elements and also can cause premature grain growth. Calcination temperature and time directly influences the diffusion amount and also the phase transitions therefore it is crucial to optimize it.

Another important thermal process for electroceramic processing is for sure sintering as the main densification step of the material. Sintering results with the final domain configuration and grain structure of the ceramics while significantly influencing the structural characteristics such as porosity, grain size, and internal stresses. It is really important to optimize the sintering parameter as it affects the ΔT_{EC} by decreasing dielectric losses and increasing domain wall mobility. Other factors that are influenced by the sintering parameters are grain coarsening, defect diffusion, and domain wall pinning effects. It is known that grain growth or A-site volatilization can result from excessive sintering time, which can impair functional performance.

Therefore, these two important thermal processing parameters were precisely included into the dataset. All temperature readings were standardized to degrees Celsius, and time was expressed in hours. These variables were left in their unprocessed state for model training without normalization because the tree-based models utilized in this study are invariant to monotonic scaling.

A categorical variable was needed to define the form of the sample configuration since each of the sample type have characteristic impact on microstructural, electrical and anisotropic properties. The sample forms included into the dataset were pellet, random oriented tape-casted (denoted as random), textured tape-casted (denoted as textured), and multilayer. As well known, pellets are the conventional forms of the ceramics which are untextured and typically uniaxially or isostatically pressed. Random-oriented tape-casted samples are the samples manufactured by stacking of thick films into pellets and textured tape-casted samples are same but having templates to boost anisotropic electrocaloric behavior, and lastly multilayers are made by stacking of thin films having electrodes between each layer and they really interesting in terms of breakdown strength and electrocaloric response.

As a result of these categorical variables, it was aimed that the model captures the differences in electrocaloric material which is caused by the geometry or orientation which are not explainable by thermal parameters alone. These variables were one-hot encoded which means that they were represented as either 0 or 1 in the dataset.

It is known that ΔT_{EC} have strong dependence on the measurement variables. Therefore, the electrocaloric response is always strongly affected by the variance in the external electric field level, the proximity to the phase transition temperatures, and

also the temperature scan direction as either cooling or heating. Because of these important effects, it is required to include them as numerical and categorical features into the dataset.

Electric field strength influences the domain alignment, and the entropy change of the system naturally and directly during the electrocaloric measurements. In accordance with the Maxwell relations, stronger electric fields increase the ΔT_{EC} as they result with higher polarization change. It is important to note that, stronger electric field also may cause to Joule heating or even to dielectric breakdown. The relationship indicates that electric field should be modeled as a continuous feature in the dataset. While adding these values into the dataset, all of them were converted to kV/cm unit to ensure the consistency.

Another critical measurement variable is the temperature at which ΔT_{EC} was measured, typically named measurement temperature. This value gives important information and insight about the electrocaloric behavior of the material as it is also related with the Curie temperature. Electrocaloric effect usually peaks close to this temperature. The Curie temperature refers to the ferroelectric-paraelectric phase transition point where the material loses its spontaneous polarization. Its value is generally composition dependent and acts as a target or tuning variable. The Curie temperature was directly taken from the published study if it is reported. Otherwise, it was extracted from the generic phase diagrams. At this point, an important derived feature was included into the dataset, proximity of the measurement temperature to the Curie temperature. This feature is simply defined as temperature offset as it is the difference between these two temperatures. It was aimed to give to model another layer of information which can be useful for predictive resolutions.

The ΔT_{EC} values are also affected by two other measurement dependent variable, measurement method and the cycle that was measurement taken. Electrocaloric measurements can be taken during the heating or cooling of the sample, and this direction is known to affect the observed ΔT_{EC} because of the hysteretic effect which have reflections on transition points. Measurement method is also known to affect the ΔT_{EC} response and may cause potential biases and systematic variations. Therefore, these two categorical variables were included in the dataset with one-hot encoding method.

3.2.3. Data Cleaning, Transformation and Encoding

Before going into the statistical analysis or implementation of machine learning based analysis, an important step was performed. This step was the cleaning of the data, transformation and required encodings. It is important to perform this step precisely for the heterogeneity and the partial reporting in the materials literature. All of the parameters included in the dataset was check in terms of unit consistency, handling of missing values, categorical encoding, and feature normalization. The aim was having a physical integrity of the data while making it statistically sound and also understandable by the model precisely.

All of the variables were changed to a consistent unit to avoid biases. As temperature unit °C, as electric field kV/cm, as duration hours, as compositional fractions molar ratios were used. Also, the numerical data was included into the dataset at its highest resolution.

Even though there were not so many blank cells due to the lack of complete reporting, a practical imputation approach was used:

- If a processing feature has missing information within the dataset, global mean of that feature was filled out to that cell. This approach was only used for processing features such as calcination or sintering temperature or time. Advantage of this approach is preventing the bias through arbitrary or system specific estimations.
- In case of any missing information of key measurement variables or essential structural or compositional information, that study was completely left out.
- The entries with imputation derivation were marked for better traceability and the usability of the dataset.

In terms of Curie temperature values, all BCZT samples had available Curie temperature values and therefore it was possible to directly calculate the temperature offset. However, for PMN-PT compositions, not all of the studies were reported this value. Therefore, generic phase diagram of PMN-PT was used to extract the Curie temperature of that specific composition. To prevent systematic bias, these estimates were used with caution and, when feasible, cross-validated.

The categorical features that were mentioned earlier were encoded as binary variables, 0 or 1.

3.3. Correlation Analysis

A deep correlation analysis was done before going into the model development with the aim of understanding the statistical dependencies between the parameters and their relationship with the target property. In this stage, redundancies, linear and non-linear relations, overall structure of the dataset was reviewed from a multivariant statistical point of view.

In order to have meaningful correlation analysis, the first step was calculation of the pairwise Pearson correlation coefficients. This was done between the continuous features with the temperature change. These features include measurement conditions, processing temperatures and durations, compositional ratios, and Magpie descriptors. For better visualization of the interactions, a heatmap was plotted and colored by the correlation strength and correlation values was also included.

Another informative plot type which was generated was bivariate scatter plots. In these plots each continuous feature was plotted against the temperature change. Also, the magnitude of the temperature change was encoded with color mapping. This enables to understand and spot the thresholds, saturations, and other non-linear behaviors.

An important metric which gives insight about the correlations is the mutual information scores. This is an additional and non-parametric measure of dependencies. These scores were calculated by using the scikit-learn mutual information function and the significance of this method arises from the concept of the metric. This approach does not assume linearity or monotonicity when estimating the reduction in uncertainty of one variable given another. In order to have a comparative overview of the values and their relevancies, resulting scores were plotted with a color-mapped bar.

Different heatmaps based on pivot tables were also plotted for checking the categorical variable influences on temperature change. The average ΔT_{EC} and the number of samples that contributed to that value were displayed in each cell of the heatmap. This information was important to cover because of the validity of any relation.

All of these analyses were conducted to get insights on dataset structure, and they were not a part of either model training, or prediction and validations. However, these steps enlightened and emphasized important correlations within the datasets and their importance on electrocaloric behavior.

3.4. Statistical Approach

Another step before the model development was having a look into the statistical features of the dataset to gain more insights as this information can be useful while decision making points like transformation, imputation, or validation.

Firstly, a simple approach was followed and the data types included in the dataset, their quantity, count of missing values and other metrics were extracted. This was also supportive for the preprocessing steps related to the model training and gave information on feature consistency and completeness. Quantitative features of each variable were also extracted and checked. These features include the mean, standard deviation, minimum and maximum, and interquartile ranges (25th, 50th, and 75th percentiles) of the values. This step gave an information about the heterogeneity among the features, possible outliers, and also about the necessity of any normalization or transformation. Even though no actual scaling was done at this point, features with wide value ranges or skewed percentiles were noted for possible transformation or regularization.

Categorical features such as the sample form, measurement type, measurement cycle was assessed for class balance and distribution consistency. As these variables are categorical, their consistent presence in training and test splits are really important and affective on model performance. Therefore, bar plots were generated for better visualization of relative frequency distributions. These checks gave insight on category imbalances that can skew the model evaluation or training itself.

3.5. Machine Learning Model Development

After the completion of the prior important steps and acquiring the important information, next step was setting up a machine learning model framework to reach to the aim of the study which is predicting the electrocaloric temperature change from material composition, processing details, and measurement conditions. The model

itself was aimed to be precise, generalizable in a way that can capture the complex relations and interactions while keeping the consistency with model decisions. Each model for the material system was developed by using the supervised regression methods and then trained with the dataset.

3.5.1. Algorithm Selection

Modeling the electrocaloric temperature change as function of variety of parameters is a clear regression problem. The parameters have highly non-uniform density throughout the dataset, possessing complex non-linear but also linear dependencies, different data types as continuous and categorical. At this point, three different regression model was chosen to represent different types of algorithms which allows comparisons. These were Lasso regressor, Decision Tree regressor and XGBoost. These algorithms were aimed to address the other one's issues, giving reliable and understandable results as well as accurate modeling. Another reason on the selection of these algorithms was their ability to generalize without overfitting and their compatibility with our data structure.

Lasso regressor is a linear baseline and performing best when a group of features are dominant, underlying relationship is almost linear. As we know the complex nature of electrocaloric effect, Lasso was included the algorithm selection as a benchmark to understand how much of the variety of ΔT_{EC} can be explained by a linear relationship. Therefore, it was useful for establishing a lower-bound reference, but its limitations in modeling curvature and feature interactions were expected.

Decision Tree regressor was included into the selected algorithm due to its ability on capturing non-linear relationships. Decision trees fit constant outputs within each of the axis-aligned regions that they create from the feature space. Therefore, the model becomes possible to understand local dependencies as well as the thresholds. On the other hand, they give clear interpretability with visualized rules and metrics. Another strong aspect of them is their categorical feature handling capacity when the features are encoded. The major drawback of this algorithm is its tendency to overfit the predictions. It is important to perform pruning or ensemble stabilization of the model to reduce this behavior.

In order to avoid from the disadvantages or limitations of the abovementioned algorithms, ensemble tree models were also assessed and considered for better interpretability and adaptability. XGBoost is a well know algorithm with its robustness, high accuracy, and regularization capabilities including its effectiveness on complex datasets. Basically, this gradient boosting is similar to the decision trees but it is able to model the extreme complexities and non-linearities which we required to model ΔT_{EC} . Another important advantage of XGBoost is its ability to give critical metric values such as feature importance based on gain and SHAP. The use of XGBoost as a principal candidate was motivated by preliminary correlation analyses that revealed strong non-linear and coupled effects.

The algorithms were first evaluated with their default settings and as the outcome of its robustness and consistent performance, XGBoost was selected as the main model for this study. On the other hand, all of the algorithms were kept for comparisons.

3.5.2. Data Splitting and Validation

The splitting of the data into two groups as training and test is a critical step before the implementation of the model. Here, a methodical approach was followed to achieve an objective evaluation. The dataset was split into two as 80% of the data to be used for the training of the model while 20% was saved for the performance evaluations. The split was done in a random way, and this randomness was fixed to reproduce the results over different runs.

The training portion of the dataset was cross validated to reduce the overfitting risk and also to validate the model generalization. The partition of the dataset was done according to the shuffle split which is creating the randomness. This allowed the more flexibility and also the equal opportunity of the appearance in both the training and validation folds during different iterations. All of the models were trained on the same portion of the data and validated against the same portion of test set. In order evaluate the stability of the model, assessments were carried out several times and the metrics that were produced were averaged. The set for testing was completely separated and used to estimate out-of-sample prediction performance was only available after model development and selection were finished.

In order to check the split balance, categorical distributions were visualized for training and test subsets. Also, numerical evaluations such as mean values of the parameters within the subsets were checked. The main aim during the splitting was ensuring that all models are trained and tested in representative but also repeatable settings while avoiding from data leakage.

3.5.3. Hyperparameter Optimization

Hyperparameter optimization was a step applied to all machine learning algorithms. This is an essential step for achieving the best possible predictive performance as well as the generalization ability. The optimizations were focused to handle overfitting, balancing the model variance and complexity, and finally adapting an algorithm specific behavior fitting to the dataset structure. Each task was created as a supervised regression problem and Optuna framework was used. During the optimizations, by using the Optuna, each trial aimed to minimize the errors by allowing an adaptive and effective search. The search space was created to represent to ranges derived from the literature and reflected to the dataset and also all trials were repeatable by fixing the random seed. Optuna trials were mostly done until 750 iterations for each model.

XGBoost received the most detailed tuning due to its high baseline performance and flexibility. The search space for XGBoost is given in **Table 3.2**. These ranges enabled the model to adjust its regularization and learning dynamics which will be discussed in later chapters.

Table 3.2: Hyperparameter optimization search space for XGBoost algorithm.

Hyperparameter	Range
n_estimators	100-1000
max_depth	3-15
learning_rate	0.005-0.3 (log-uniform)
subsample	0.6-1.0
colsample_bytree	0.5-10
gamma	0-10
reg_alpha and reg_lambda	0-10
min_child_weight	1-20

Decision Tree Regressor, while less expressive than the gradient-boosted models, was also subjected to hyperparameter search to obtain a well-calibrated baseline. The optimization focused on the ranges given in **Table 3.3**. The maximum depth of the trees was limited to 5 as a solution to overfitting.

Table 3.3: Hyperparameter optimization search space for Decision Tree algorithm.

Hyperparameter	Range
max_depth	3-5
min_samples_split	2-10
min_samples_leaf	1-10
max_features	auto, sqrt, fraction (0.3-1.0)

Based on the lowest mean validation error across cross-validation folds, the final set of hyperparameters was chosen for each model.

3.5.4. Evaluation Metrics

The performance of each algorithm requires to be evaluated against several objective criteria. These are named as evaluation metrics and gives insights on model's predictive accuracy. The information that can be acquired from these metrics are typically the model variance, bias, and accuracy during the cross validations and tests. In this study three evaluation metrics were used and they are mean squared error, mean absolute error and coefficient of determination.

The Mean Squared Error (MSE) is a generic metric giving information on model performance. Especially high error predictions are strongly highlighted by this metric as it is the average of squared differences of the prediction and the actual value. Therefore, this metric is highly sensitive to significant deviations as strongly penalizing outliers.

$$MSE = \frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (3.1)$$

Another important metric that was used is the Mean Absolute Error (MAE). This metric provides a scale aware and interpretable measure of the average error. As expected, MAE is less sensitive to outliers as it provides a direct value of the deviation

in the same unit. It was used as being useful for assessing whether the model's predictions were practically accurate within the domain of electrocaloric applications.

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - \hat{y}_i| \quad (3.2)$$

The Coefficient of Determination (R^2 Score) is an important measure of the model performance compared to mean predictor. R^2 simply shows the proportion of the variance in the target. This value becomes really informative during the cross validation of the models as their capability changes depending on the complexity. It should be kept in mind that this metric might be misleading on small or skewed datasets and does not penalize overfitting directly.

$$R^2 = 1 - \frac{\sum_i (y_i - \hat{y}_i)^2}{\sum_i (y_i - \bar{y})^2} \quad (3.3)$$

During model development, these three metrics were computed for each validation fold in cross-validation, and their averages were used to guide model comparison and selection. The testing set was used to assess final performance following model tuning and selection. Model accuracies were reported in the Results section using test set metrics.

3.6. Process Parameter Optimization Framework

As mentioned earlier, the main objective in this study was to train the machine learning model as a virtual experimentation area to find and suggest the best processing and measuring conditions that can increase the ΔT_{EC} while predicting its value precisely. In order to realize this and explore the design space for practical constraints, probabilistic optimizations with Optuna were used and then predicted by the model itself.

3.6.1. Objective Function

The aim of the entire optimizations was to maximize the ΔT_{EC} and the inputs for these tasks were chemical composition, process parameters, categorical sample form, and measurement conditions. The prediction each optimization iteration was done by the

already trained and optimized XGBoost model and returned the predicted ΔT_{EC} value to the optimizer. On the other hand, the optimizer used these predictions as the main goal score to be maximized.

The optimization study was created to investigate all possible combinations which are inside the interpolation range but not already present in the experimental dataset. By this, identification of novel material-processing-measurement configurations was aimed which may be investigated experimentally in subsequent studies.

During optimization, different cases were created to maximize the ΔT_{EC} under various conditions. These conditions were specifically selected to represent the typical operational conditions of an electrocaloric system, such as under 40 kV/cm electric field and exposed to 24 °C.

3.6.2. Constraints Definitions

Optimization studies require a set of logical and physical constraints to have a guided process which results with chemically and physically meaningful. These constraints were directly implemented into the optimizer as rules instead of filtering out the unmeaningful iterations later on. Of course, these limitations have resulted with a narrower but feasible search space.

All of the material systems were subjected to basic stoichiometric constraints to have proper molar ratios. Also, the parameter sets that are referring to templated grain growth was controlled. Since barium titanate (BT) and strontium titanate (ST) are mutually exclusive template agents, it was mandated that only one of the two could be used in a particular configuration. Additionally, only if the sample was specifically labeled as textured could the amounts of ST or BT be non-zero. These values were defined as zero in case of the parameter set refers to not textured sample. By implementing these constraints templated grain growth methodology was reflected into the optimizations.

Another important constraint was the selected sample type. Only one of the sample type had to be selected and this was maintained by a rule that fixes the sum of their encodings to 1. Therefore, a sample with more than one structural form was not possible to be selected, guaranteeing the logical consistency of the model.

Similar restriction was applied to the measurement condition as well. The thermodynamic reversibility of polarization response was reflected by restricting the two binary indicators that represented measurement direction so that only one could be active in a particular trial. The difference between indirect estimations based on Maxwell relations and calorimetric measurements was also captured by defining the two measurement method indicators as mutually exclusive.

All other continuous process parameters such as electric field, calcination and sintering parameters were limited to be sampled between their range in the dataset. This was selected because these values are being studied for a long time and have lot of examples in the literature. It was aimed to limit the inaccurate prediction in extrapolated areas without training data or also resulting with extreme values.

Finally, any optimization output that brakes any of the constraints was directly penalized and eliminated from the iteration so it was visible how much unfeasible iterations was done in the trials.

3.7. Virtual Dataset and Predictive Mapping

Another study that was done for creating a map of performance was virtual dataset generation and predictive mapping. In contrast to the guided optimizations that was described in earlier section, in this part, physically significant input scenarios were randomly generated and predicted. By using a virtual dataset, methodological mapping of electrocaloric performance over a wide range of parameters was done and high-performance regions were aimed to be find.

3.7.1. Virtual Dataset Generation

Virtual dataset was generated to cover uneven and sparse experimental conditions. In this part of the study, a dataset with 100.000 synthetic data points was generated by randomized sampling strategy which is limited with the borders of the existing dataset. This was done to bring much more combinations of the reported data in a single dataset. All values were sampled from the dataset for each synthetic entry.

Main constraints to ensure the compositional values, sample form and others were taken into accounts just as the study for optimization. The sample form was used to

conditionally regulate variables related to the template, specifically the ST-ratio and BT-ratio. Either ST or BT was chosen at random and given a value between 0 and 5 mol% if the sample was deemed textured, while the other was set to zero. Both template values were set to zero if the sample was not textured.

Also, just as the optimization study, if any data is generated with breaking the constraints, it was directly eliminated and excluded. Therefore, the final virtual dataset was completely physically valid and also statistical diverse.

3.7.2. Model Application and Predictive Mapping

After generating the virtual dataset, trained XGBoost regressor was used to predict each data lines and turning the ΔT_{EC} value. The entire dataset was subjected to a batch application of the fully automated prediction process. Following the predictions, results were visualized for mapping.

Most important visualization was the two-dimensional contour plot where the predicted ΔT_{EC} values were reflected to a grid with electric field and measurement temperature axes. Also, the interaction of electric field, measurement temperature, and the predicted ΔT_{EC} value was plotted in a three-dimensional scatter form to see the high-performance areas.

These predictive mappings were generated as they make it possible to perform sensitivity analysis, which determines which variables or combinations have the biggest effects on electrocaloric response and also, they show the saturation regimes and performance plateaus. It is also possible mention that they are design focused visual tools especially for the materials have not been investigated intensively.

4. RESULTS AND DISCUSSION

This section gives the findings from the trained models and performed optimizations and discusses the physical significance of these results. The results are given in different sections for each material systems for better readability and followed by a cross-system analysis.

4.1. PMN-PT System

4.1.1. Dataset Summary and Descriptive Statistics

The statistical characteristics of the dataset which consists of 2863 different experimental entries extracted directly from the literature and given in **Table 4.1**, reflects the highly non-linear and multivariant response character of PMN-PT.

Mean value of the PMN content in the dataset was found as 86% and its mode and median were centered at 90%. This distribution also has a small fraction extending to the low PMN, high PT content levels. Therefore, it is possible to mention about the bias of the dataset to PMN-rich compositions. This behavior is expected and implies that most of the research focuses on the relaxor end of the compositional spectrum as relaxors have strong entropy driven electrocaloric responses near room temperature. When we check the values for the PT content, it reaches to maximum 40% with a sharp cutoff corresponding to the upper limits of the relaxor character. This correspondence might be explained with the tetragonal phase with classical ferroelectric area at over 35% PT content [88]. According to the statistics most of the studies are concentrated between 80-90% PMN ratio which also related with the possibility of the field-induced structural transitions.

A small portion of the studies included in the dataset have SrTiO_3 (ST) or BaTiO_3 (BT) addition for the templated grain growth. This shows that there are limited number of textured samples exist in the dataset and results with them being underrepresent, and not enough for a stand-alone model interpretation. On the other hand, their existence in the dataset of course brings new patterns that might be effective in the process.

Table 4.1: Descriptive Statistics of PMN-PT Dataset

Parameter	mean	std	min	25%	50%	75%	max
PMN-ratio	86.24	8.16	60.0	90.0	90.0	90.0	100
PT-ratio	13.82	8.11	0	10.0	10.0	10.0	40.0
ST-ratio	0.38	1.33	0	0	0	0	5.0
BT-ratio	1.70	2.37	0	0	0	0	5.0
Pellet	0.32	0.46	0	0	0	1	1
Random	0.08	0.27	0	0	0	0	1
Textured	0.41	0.49	0	0	0	1	1
Multilayer	0.17	0.37	0	0	0	0	1
mean Atom Wei.	64.43	0.35	63.27	64.60	64.60	64.60	65.09
mean EN	2.83	0.00	2.83	2.83	2.83	2.83	2.83
mean Volume	14.95	0.05	2.93	3	3	3	3.20
mean SpaceGroup	95.02	0.37	93.80	95.20	95.20	95.20	95.69
Upon Cooling	0.75	0.43	0	1	1	1	1
Upon Heating	0.24	0.43	0	0	0	0	1
Indirect Method	0.77	0.41	0	1	1	1	1
Direct Method	0.22	0.41	0	0	0	0	1
Calcination Temp	851.69	76.31	750	850	850	850	1200
Calcination Time	4.07	1.82	2	4	4	4	12
Sinter Temp	1211.05	63.10	975	1200	1250	1250	1280
Sinter Time	5.22	2.99	1	2	6	6	16
Electric Field	29.58	26.40	0.5	10	25	40	192
Meas.Temp	62.68	37.10	0	34.65	60	85	225
T _C	54.11	45.20	-23	32.6	32.6	32.6	197
T _C -T	8.57	50.80	-170	-17.8	12.40	42.46	149.6
ΔT_{EC}	0.45	0.43	0	0.15	0.33	0.58	2.74

Calcination temperature values have an average 851 °C while sintering temperatures are centered at 1211 °C, and these parameters have relatively narrow range in terms of variance. Narrow standard deviation and mode value of these parameters indicates the process consistency across the different studies. Calcination and sintering durations also cluster around 4 to 6 hours as highlighting the optimized kinetics for these thermal processes. Even though this consistency is meaningful, it affects the generalizability of the model to new processing variables even though it enhances the learning behavior of the model by lowering the process noise.

The variations in the electric field ranges from 0.5 kV/cm to a maximum of 192 kV/cm. This diversity is an important statistical feature. Also, the distribution of the field levels exhibits a long tail of high-level values which are mostly related with multilayer samples having higher dielectric breakdown thresholds. Besides having the physical direct relations, the electric field data characteristic also highlights its dependence as

major factor influencing the performance variation. It also brings significant non-linearity to model behavior especially for the compositions having sensitivity to the polarization rotation and domain reorientation.

The measurement temperature with a mean value of 63 °C and interquartile ranges from 35 °C to 85 °C indicates that most of the temperatures were done between room temperature to intermediate temperature levels. This can be interpreted as another reflection the relaxor behavior in the system as the entropy transitions are dispersed over a wide range of temperature window. The measurements for PMN-PT samples are done from 0 °C to 225 °C with a high standard deviation of 37 °C. These statistics suggest that the variance in the ΔT_{EC} can't be simply explained only with the measurement temperature, but it is also affected by the compositional characteristic, electric field, and with the conjunction of different physical patterns.

The proximity of the measurement temperature to the Curie temperature stands as a valuable information. PMN-PT system shows its non-uniform relaxor character with a mean Curie temperature around 54 °C and with standard deviation of approximately 45 °C. It should be also noted that there is significant amount of T_C values under room temperature which as an indication of PNR contribution into the paraelectric region. Measurements spans both under and above T_C values enough to capture the trends. This wide window is already seen by the $T-T_C$ values ranging from -170 °C to 149 °C and it can help on capturing both relaxor entropy spread and also ferroelectric transition spikes that affects the ΔT_{EC} .

The most important metric, the ΔT_{EC} shows a mean value of 0.46 °C with a long tail end at 2.74 °C as a clear indication of positively skewed distribution. This behavior also emphasizes how hard it is to attain high-field alignment as well as the inherent limitation of entropy. Even though ΔT_{EC} values above 2 °C exists, they are quite uncommon and similar to the patterns observed in BCZT system, which will be covered in the next sections. On the other hand, the dataset offers rich variance in ΔT_{EC} values with 1803 different values among 2863 entries. This variety of course results with an improvement in model performance while potentially introducing sparsity in extreme performance regions.

The Magpie derived material specific descriptors show an indirect but useful statistical behavior. They exhibit high discriminative potential, but their variance is significantly

low especially for system like PMN-PT which is relatively homogenous in the dataset. As an example, even though the mean electronegativity across the dataset ranges from 2.8308 to 2.8336, PT-ratio is naturally correlated with this slight shift that is affecting the polarization strength and the order/disorder level at the B-site. Therefore, we can say that these descriptors are not expected to be direct performance drivers but more like supporting the global modifiers.

Finally, in order to get insight on diversity of the features in the dataset, the unique value count was extracted. Many of the continuous features such as electric field, measurement temperature, Curie offset, and temperature change exhibits really high distinct values. On the other hand, model capacity is probably limited due to the highly discretized parameters with low variance such as calcination and sintering times. This case naturally brings and imbalance to the model [89].

4.1.2. Correlation Analysis

The electrocaloric behavior of the system shows the complex and multilayered interactions within the dataset and also as phenomenological. These interactions between the compositional variations, structural characteristics, and the boundary conditions are clearly reflected in the correlation analysis. It shows that the performance is defined by the simultaneous coordination of different interdependent factors. This highlights the reality of there is no single variable controlling the temperature change. The diffuse phase transition behavior of the PMN-PT system is controlled by the nanoscale PNRs which are resulting with non-linearity as well as compositional sensitivity. Some of these correlations are examined in detail in this section.

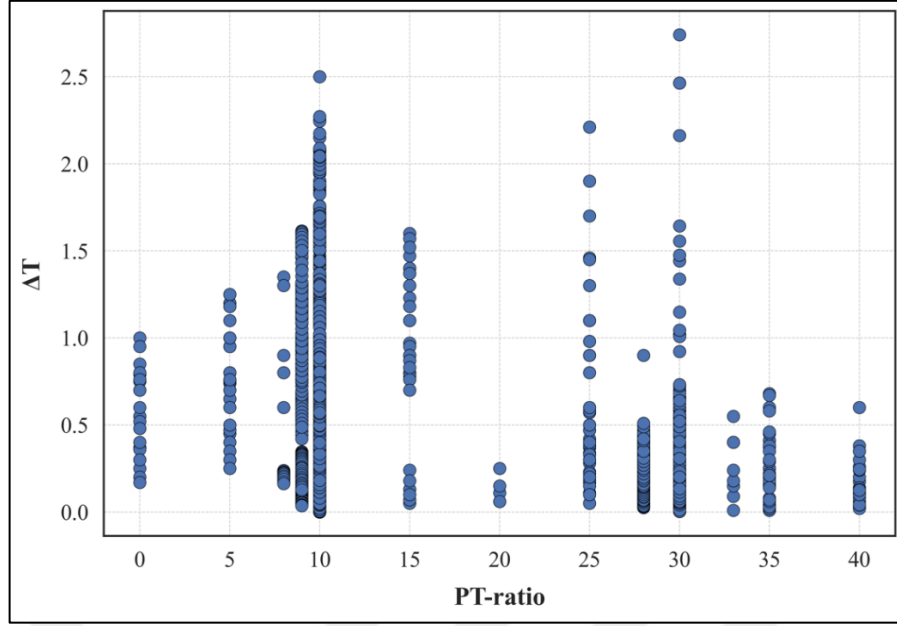


Figure 4.1: Correlations between the temperature change (ΔT_{EC}) and PT-ratio.

Important and clear relationship between the PT ratio and ΔT_{EC} given in **Figure 4.1** is one of the most obvious trends that emerged from the correlation analysis. The peak performance of the system is observed around 30 mol-% instead of the higher PT concentrations as if the system was only dependent on polarization-drive. This window is also related with the MPB of the system where the ferroelectric long-range order begins to appear while the relaxor character still persists. It is expected that the PNRs are active in this regime and their field driven reconfiguration influences the total entropy change. When the PT concentration is greater than 30 mol-%, specifically around 40 mol-%, there is a clear decrease in ΔT_{EC} most probably due to the over-stabilization of long-range ferroelectric domains [54]. These domains might possess larger remnant polarizations but also the limited amount of configurational entropy change may cause this decrease in the temperature change. Therefore, the coexistence and opposition between two structures causes these unique behaviors in relaxor systems.

A deeper understanding comes out when the Curie temperature offset ($T-T_C$) and temperature change (ΔT_{EC}) interaction given in **Figure 4.2** is taken into account. The offset from T_C strongly affects the ΔT_{EC} values and according to the correlations it reaches to its maxima above T_C usually between 10 °C and 60 °C. Dipolar fluctuations exist in the narrow range which can be defined as a quasi-critical regime with maximized entropy change. Even though the PNRs are mobile enough to reorient

themselves under electric field, they are not fully disordered to completely eliminate long-range interactions. It should be also noted that the peak values not always coincide with the T_C , but it occurs relatively within the positive offset region. This behavior might be attributed to the availability of the entropy change mechanisms in phase transition region.

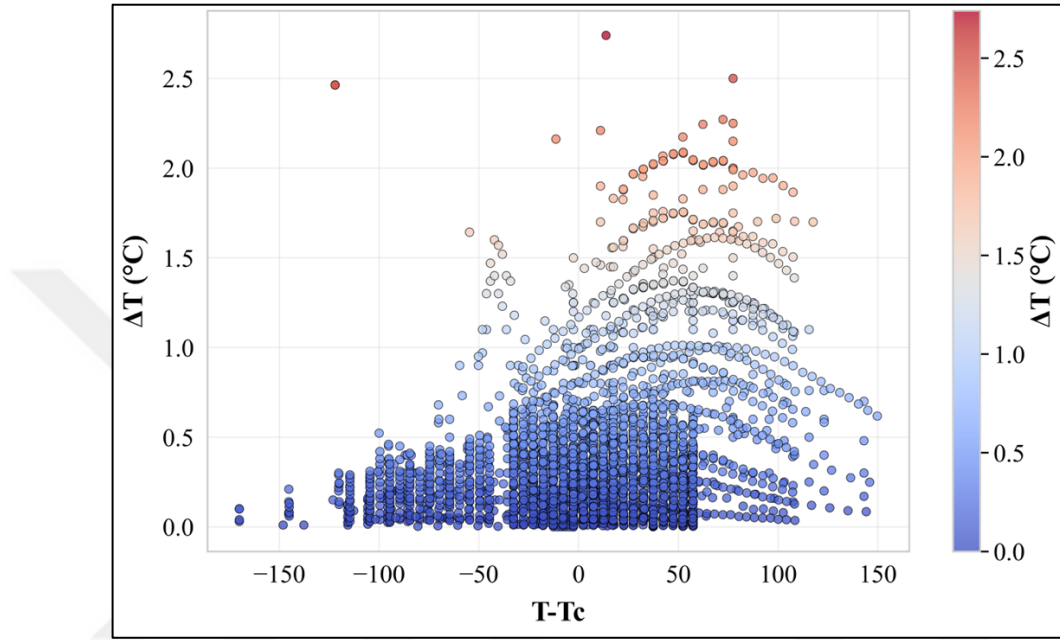


Figure 4.2: Correlations between the temperature change (ΔT_{EC}) and $T-T_C$.

The correlation of the electric field with the ΔT_{EC} is quite interesting, and not possible to capture easily. The link between these two characteristics doesn't possess a simple flat increase but reveals non-linear connections referring to electric field threshold value to trigger the ΔT_{EC} . From **Figure 4.3**, it can be seen that not many of the compositions show a clear thermal response under 10 kV/cm electric field level. This behavior persists no matter the PT concentration or proximity to T_C . After the electric field is reached to this activation threshold, ΔT_{EC} starts to rise with the increasing field strength. This increase also reaches to its limits as the saturation takes places. It should be kept in mind that dielectric breakdown, Joule heating, and irreversible domain switching is well-known results of the high-level electric fields especially in bulk and weakly textured samples [90], [91]. Therefore, it highlights the importance of device form factor as well as the processing quality to achieve high field strengths to induce the entropy change while not resulting with the negative effects.

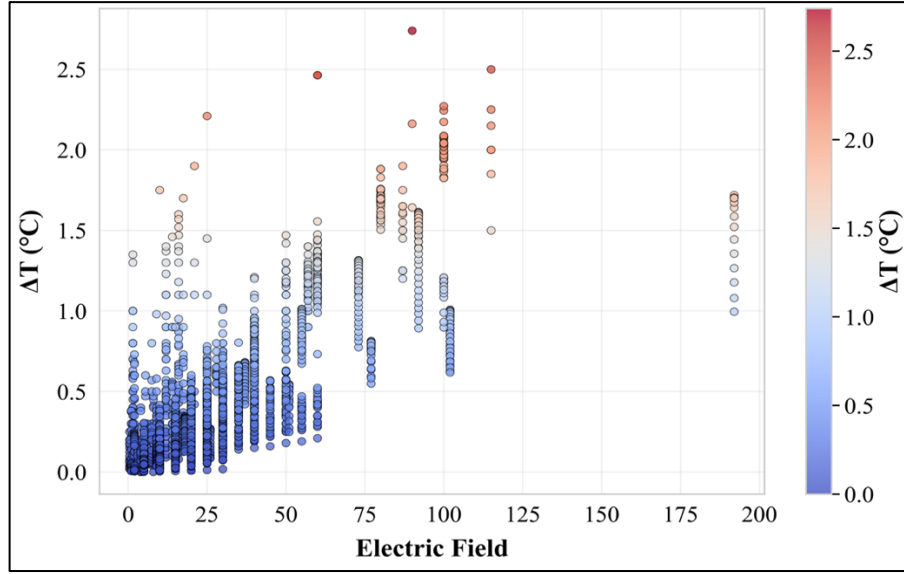


Figure 4.3: Correlations between the temperature change (ΔT_{EC}) and Electric Field.

Pellet samples resulted with much more variety in ΔT_{EC} value switch can be attributed to having a broader range of microstructural characteristics such as grain boundary effects, porosity, domain pinning, all of are critical especially in bulk ceramics. Another point to consider is the presence of the pellet samples in the dataset. As the majority of the samples included in the dataset are pellets, their variance is also expected to be wider. On the other hand, pellets can show particularly high ΔT_{EC} values if they are processed under ideal conditions. Multilayer samples provide a higher median ΔT_{EC} compared to the pellets. This is because of they limit the electric field within thin layers resulting with the advantages of thin film geometries which facilitates effective thermal exchange and field-polarization coupling. Textured samples, on the other hand, enabling the effective entropy to change thanks to their partially aligned domains event at low-level electric field applications [92–94].

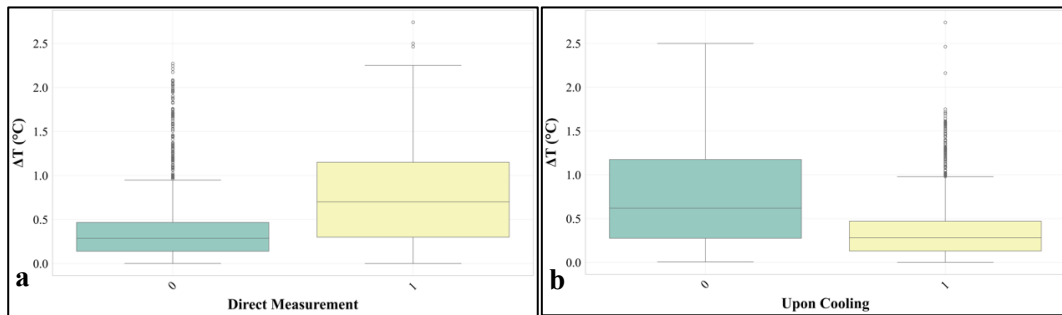


Figure 4.4: Correlation boxplots of the temperature change (ΔT_{EC}) depending on (a) measurement type; (b) measurement direction.

The correlation of ΔT_{EC} with the measurement method and cycle was evaluated by using boxplots. **Figure 4.4(a)** shows the measurements performed by indirect (0) and direct (1) methods and it can be seen that the direct measurements exhibit higher ΔT_{EC} values. This difference might be attributed to the nature of the method as it captures the actual adiabatic temperature change, while the indirect measurements use Maxwell relations. This behavior aligns with the findings of Mischenko et al., stating that the necessity of the direct measurements for more precise and accurate evaluation of the electrocaloric effect [26], [27], [95], [96]. In **Figure 4.4(b)**, this correlation can be seen for the direction of the measurement. The measurement performed during the heating (0) tends to yield higher ΔT_{EC} values compared to measurement taken during the cooling. This is an important indication of the discrepancies between two measurement direction due to the natural effect of thermal hysteresis and domain realignment lags. The results are suggesting that the ΔT_{EC} values are expected to be read higher during the heating cycles, possibly because of incomplete domain back switching or other transient thermal effects [97].

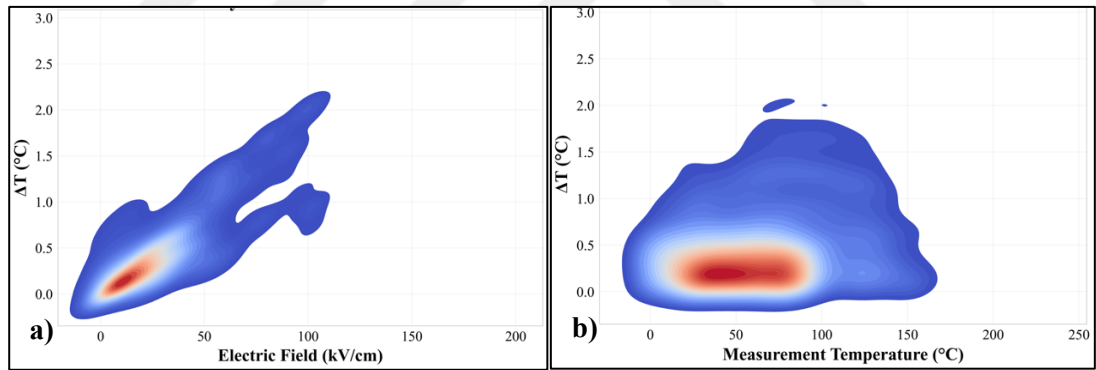


Figure 4.5: Contour plots of the temperature change (ΔT_{EC}) depending on (a) electric field and (b) measurement temperature.

Contour plots given in **Figure 4.5** were used as a representation of ΔT_{EC} in the electric field versus temperature multidimensional performance landscape. The curved, non-separable regions of high ΔT_{EC} usually found close to moderate-to-high fields (30-60 kV/cm) and high temperatures (~ 60 -90 °C). The response surface appeared to be non-flat, with a ridge-like shape and flattening around high temperatures and also decreasing sharply around the low-level electric fields. The maps also show plateaus of low ΔT_{EC} values at lower electric fields which is another indication the minimum

required driving force for any considerable electrocaloric effect to take place [98], [99].

Despite the low frequency of data for the effects of template particles, they provide useful information regarding to their presence. In PMN-rich systems, ST appears to be as a lattice softener where it enhances the electrocaloric and the dielectric response especially at low level electric fields. On the other hand, BT templates result with more variance. BT might influence the system in a way of stabilizing effect on ferroelectric domains which can result with limited entropy flexibility. The variety of performance metrics for the samples textured with BT indicates that it requires precise processing and compositional control. According to the results, ST might be a safer and dependable addition to the systems for texturing.

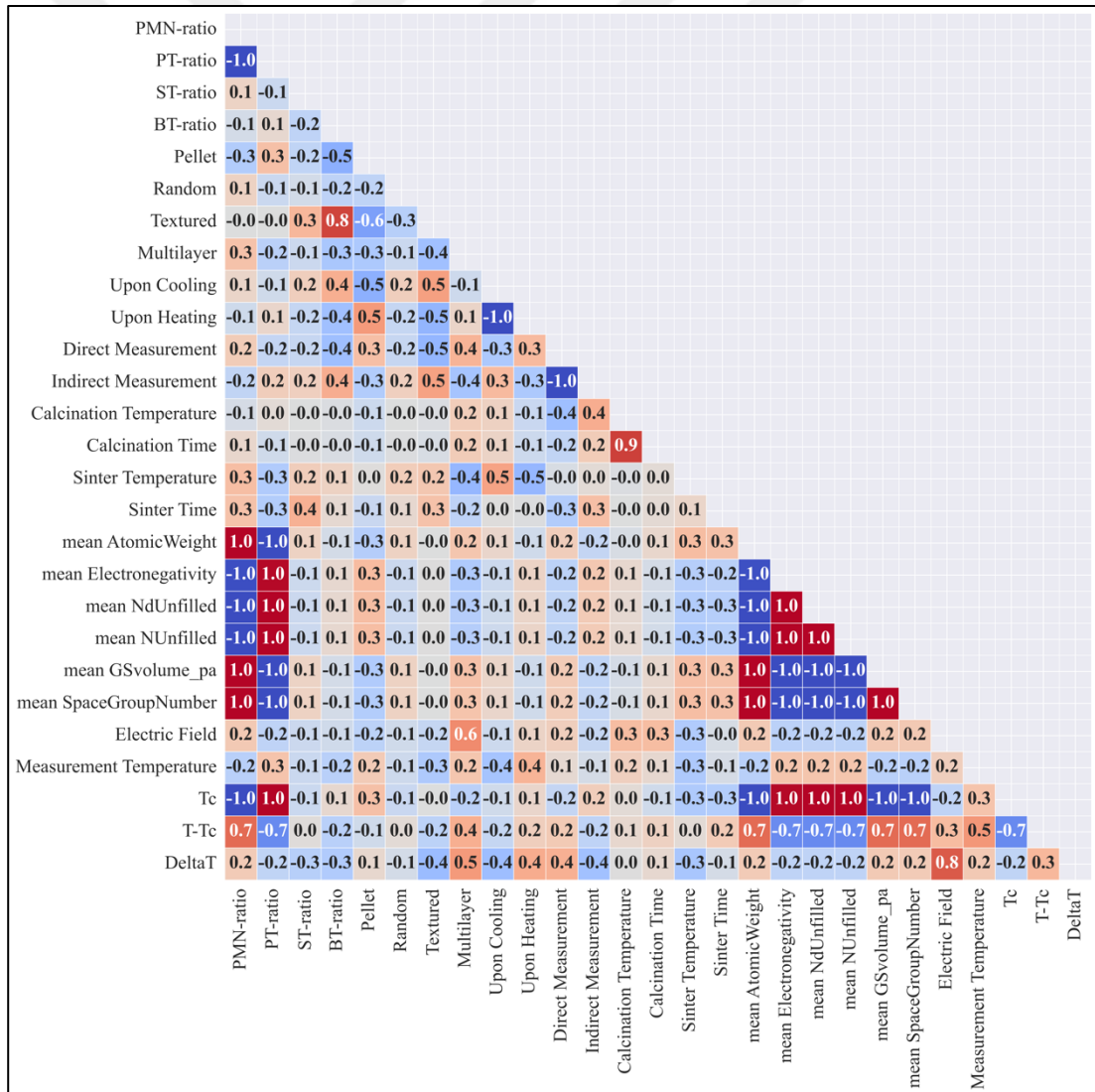


Figure 4.6: Pearson correlation matrix of PMN-PT system.

Lastly, the Pearson correlation matrix is given in **Figure 4.6**, and it provides a clear overview of the correlations of different parameters that are relating to the electrocaloric performance of the material. The inverse relation of PMN and PT concentration can be seen directly from the matrix. ΔT_{EC} is showing a moderate positive correlation with the Direct Measurement, Upon Heating and high correlation Electric Field, which indicates that these measurement conditions tend to increase the observed electrocaloric response. In contrast, Upon Cooling and Indirect Measurements have negative correlations with the ΔT_{EC} which is aligning with the known limitations in the literature mentioned earlier. Interestingly, the sinter temperature shows a negative correlation with the electrocaloric response. This might be mainly highlighting the effects of excessive sintering temperatures through microstructural coarsening or reduced domain mobility which are limiting the electrocaloric response. The strong interdependence between the Magpie derived descriptors is result of their simultaneous change in a narrow window. It should be noted that correlation coefficients only reflect the linear pair associations and not capturing in detail, high order non-linear interactions. Therefore, these values can't be interpreted as single values but instead they are a part of multivariant analysis framework covering the complex interdependencies.

4.1.3. Machine Learning Performance

Machine learning algorithm performed with an exceptional accuracy and reliability for the PMN-PT system. An R^2 value of 0.96, MSE of 0.005, and MAE of 0.03 °C shows that the XGBoost algorithm have reached to a high-level of performance. It is important to evaluate these metrics in the light of the dataset and the regression problem itself. The resulting performance clearly demonstrates the generalizability success of the algorithm under a variety of input parameters and also verifies and validates the correct training of the model. The parity plot given in **Figure 4.7** shows the predicted and actual ΔT_{EC} values. It can be clearly seen that the predictions are closely aligned with the actual values almost over the entire spectrum of testing from low to high electrocaloric responses. This is an important indicator of the model's balancing capability across different performance regions even though the dataset affects the model to overfit at peak performance zones.

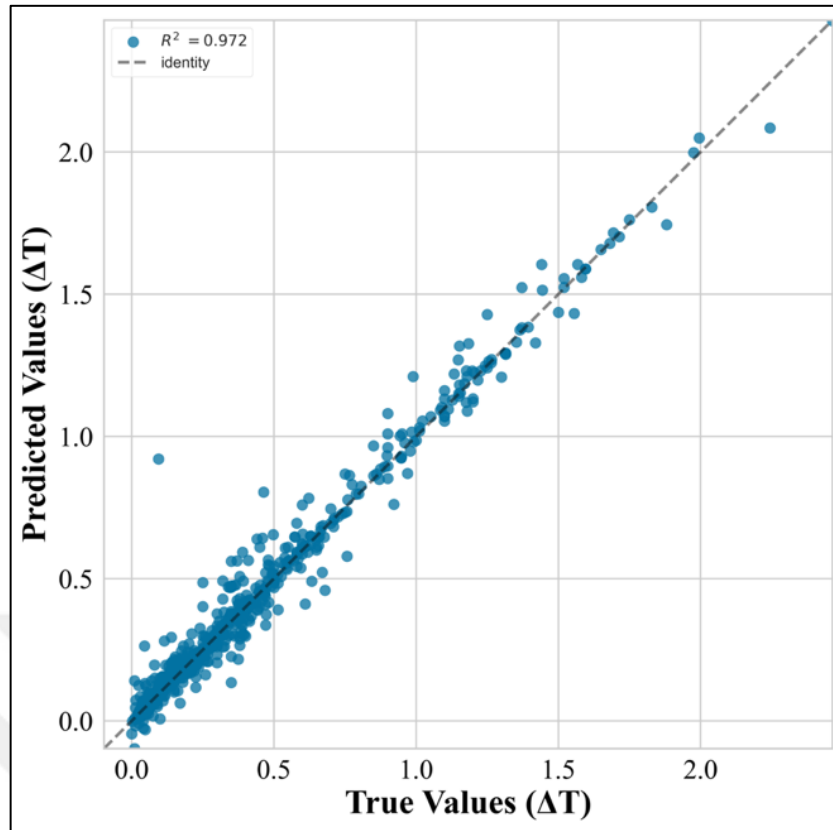


Figure 4.7: Prediction error plot of the XGBoost algorithm tested against the test subset.

Another important result obtained from testing of the model is symmetrical distribution of the errors. This is quite important in terms of detection of skewness, and heteroscedasticity. The prediction residuals given in **Figure 4.8**, show a symmetrical, unbiased distribution around zero. This outcome emphasizes that the model doesn't consistently predict lesser or higher than the actual values in different feature spaces. On the other hand, the composition with the extreme processing parameters and rare profiles where the experimental uncertainty is high, results with larger residual values. The low variance between the training and validation errors suggests that there is an acceptable compromise between bias and the variance even though cross validation doesn't appear in folds. This behavior is really important when the is planned to be used for both prospective design but also retrospective analysis.

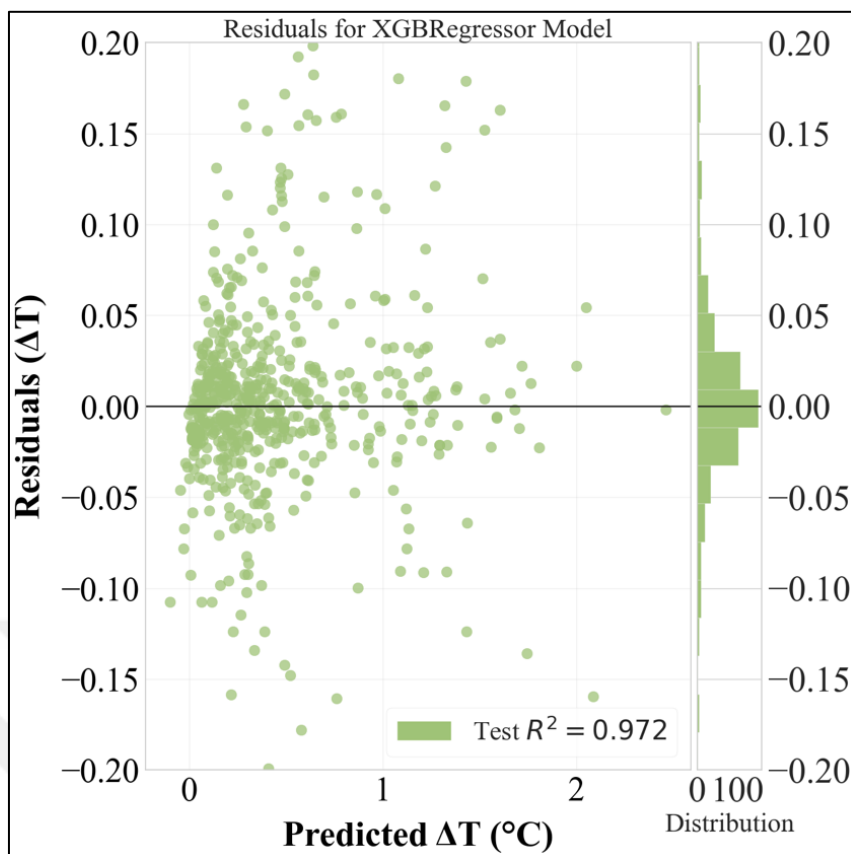


Figure 4.8: Residual values plot of the XGBoost algorithm tested against the test subset.

SHAP analysis of the feature importances given in **Figure 4.9**, showed the Electric Field as by far the most important parameter that is affecting the ΔT_{EC} . As discussed earlier, this aligns with the theoretical predictions. The electrocaloric effects is known to be primarily dependent on the reorientation capacity of the dipolar entities. This reorientation takes places by the external stimuli which and driven by field-induced entropy change [98].

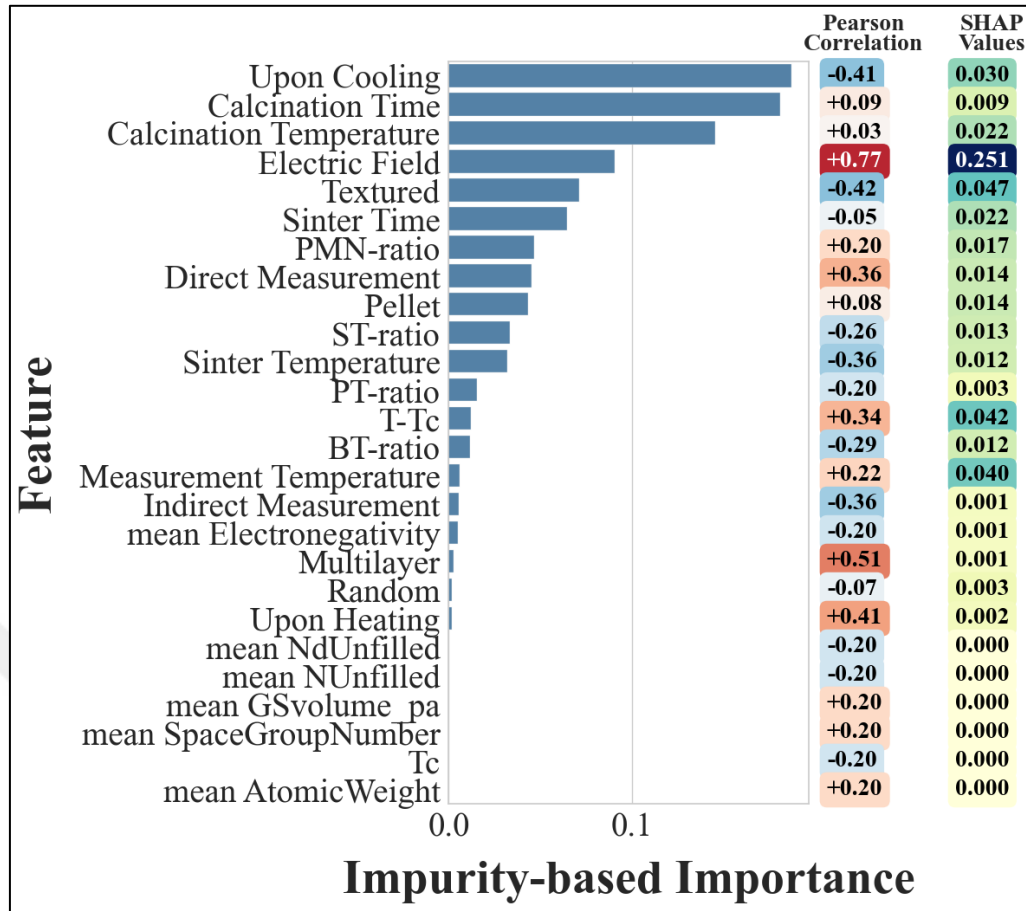


Figure 4.9: Pearson correlation and SHAP dependency values for the features in the PMN-PT dataset.

The SHAP dependence plot for the Electric Field given in **Figure 4.10** shows the clear relationship as the field effects are minimal below 10 kV/cm and then SHAP values increase sharply between 20 to 50 kV/cm. Later on, the values start to accumulate around same SHAP values particularly around 80 to 100 kV/cm, indicating polarization saturation. This captured behavior is in line with the PNR response's known saturation as well as the beginning of dielectric losses or leakage in thin films and multilayers. This threshold behavior is clearly captured and internalized by the model according to the plot.

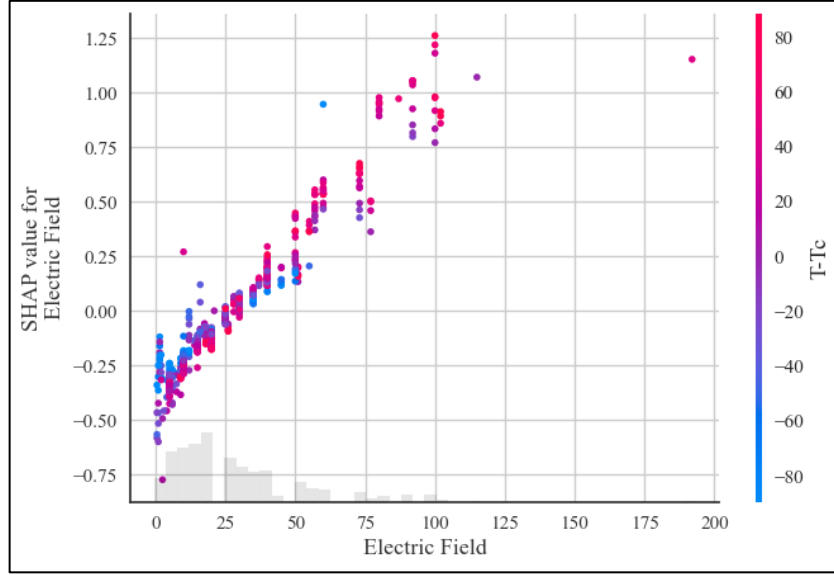


Figure 4.10: SHAP dependency plot for Electric Field in PMN-PT dataset.

The Curie temperature offset stands as the second important variable, and it shows a curve-shaped SHAP response given in **Figure 4.11** in accordance with the thermodynamic theory. As the ΔT_{EC} is maximized closer to the materials transition temperature, which is also the region where the configurational entropy is high [100–102]. It should be mentioned that the model still favors operation within 30 °C vicinity of T_C despite the disorder-induced broadening of the transition in relaxors. This point refers to the underlying entropy landscape is still sharply peaked around the transformation region.

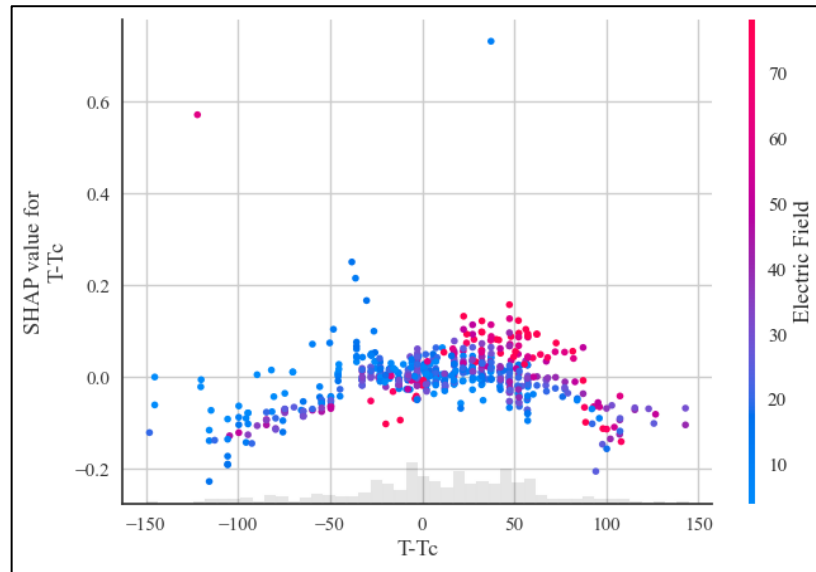


Figure 4.11: SHAP dependency plot for Curie temperature offset in PMN-PT dataset.

The PT concentration in the PMN-PT system as being the tetragonal character, has two main functions. PT sets the location of the MPB where the monoclinic, rhombohedral, and tetragonal phases coexist to result with improved electromechanical properties [103], [104]. The SHAP distribution which demonstrates that ΔT_{EC} is maximized in 10-20 mol-% PT range, reflects the importance of polar fluctuations without long-range order. This is consistent with earlier research indicating that high ΔT_{EC} in relaxors is more likely to be related to the simplicity of field-induced reconfiguration than to spontaneous polarization.

The form of the sample also has an important impact on SHAP values. Multilayer samples with their thin and active layers improving the electric field handling and also quick thermal response, produces positive SHAP contributions. This indicated that this sample form influences the ΔT_{EC} in a positive way particularly when they are measured directly. Textured ceramics have also positive contributions to the ΔT_{EC} . Even though these variables are categorical, and the binary encoding brings a coarse nature, model is able differentiate these structure-dependent effects.

The multivariant nature of the relaxor ferroelectric materials is possible to be seen in the SHAP interaction plots. Electric field and PT concentration ratio relationship shows that the high level of ΔT_{EC} values is only possible when the electric field is above 30 kV/cm and PT concentration is between 10-20 mol-%. When the conditions are set to the outside of this area, the significant ΔT_{EC} values are harder to reach. This might be related with the lack of polarization flexibility in PT-rich and -deficit phases. If the material is being operated slightly above the Curie temperature, multilayer samples possess an important increase in the ΔT_{EC} which is suggesting a thermal resonance effect that could be reasoned from interfacial strains, clamping between the layers, or improved heat flow between the layers [31], [105–107]. These insights can be assessed as design strategies and device operational temperature, composition selections might be specifically selected.

Interestingly, even though ST and BT ratios are globally minor features in terms of average SHAP importance, they exhibit hot spots in the SHAP interaction maps with mostly localized regions of compositional space where their presence increases the ΔT_{EC} . This might be an indication of promising phenomena, such as field-induced phase instability or local polar heterogeneity enhancement. The ability of the model to

detect such deep behavior demonstrates its power in identifying design subspaces that might otherwise be unseen.

Despite the strong statistical performance, residual error analysis shows more variability in areas with low data density. This is to be expected as ensemble tree models typically perform well when interpolating but poorly when extrapolating outside the convex hull of training data. It should be noted that these errors not consistently deviate from defined physical bounds, or cluster in a physically not consistent manner. This suggests that the model is still physically acceptable even in the presence of partial a lack of knowledge. On the other hand, the future iterations of the model might include linear prediction intervals, or Bayesian tree regressors to provide confidence bounds This might be helpful in relaxor systems, where the high levels of experimental variability and measurement inconsistency make it ideal for modeling to distinguish between predictive error and data noise.

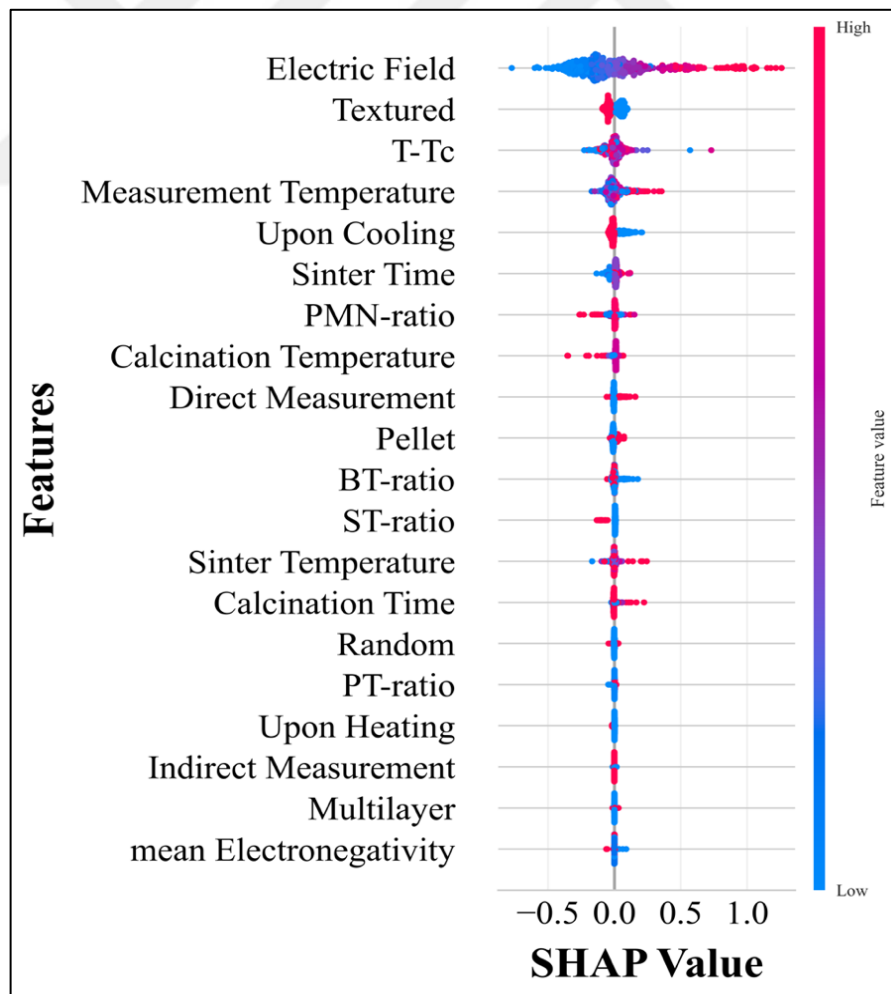


Figure 4.12: SHAP value ranges of the features within the PMN-PT dataset.

This capacity of the model to close the gap between scientific knowledge and statistical prediction may be its most significant feature. The XGBoost model is promising for reconstructing physical principles such as field-dependent entropy change, phase transition proximity, microstructural enhancement, and measurement bias. In datasets derived from literature, where compositional variety, inconsistent measurement standards, and data heterogeneity frequently block systematic conclusions, this interpretability is really crucial.

The machine learning model created for the PMN-PT electrocaloric system exhibits both strong physical alignment with both known and emerging phenomena in addition to high predictive performance. The model combines various signals into a logical, physically meaningful structure, from the dominance of Electric Field and T-T_c to the subtle contributions of PT ratio, multilayer architecture, and measurement bias.

4.1.4. Optimization Results

The performance landscape in the design of electrocaloric materials is not only nonlinear but also extremely multifaceted, influenced by complex interactions between measurement limitations, processing conditions, and composition. Bayesian optimization was used to provide a solution to this problem by global optimization task across large design spaces while preserving sample efficiency.

Firstly, the optimizations were performed with unrestricted exploration space to achieve the maximum electrocaloric response. The entire parameter space was available to tune the composition, processing variables, measurement temperature, and electric field strength. Even though this search is unrelated to immediate experimental practicality, it was performed for highlighting the theoretical maximum of electrocaloric performance. Iterations have resulted with a 71PMN-29PT pellet sample that was calcined at 758 °C for 12 hours, sintered at 1280 °C for 6 hours, and measured with direct measurement during the cooling cycle at 161.3kV/cm and 21.5 °C. The optimizer came to a configuration that produced a maximum predicted ΔT_{EC} of 3.70°C.

Table 4.2: Optimization history of the PMN-PT electrocaloric system.

Trials	PMN	PT	Sample Type	T_{calc}	t_{calc}	T_{sint}	t_{sint}	E	T	Method	Cycle	ΔT_{EC}
500	50.82	49.18	Pellet	797	3	1280	14	131.54	20.98	Direct	Cooling	3.45
1000	53.07	46.93	Pellet	785	4	1280	9	138.32	21.05	Direct	Cooling	3.55
2000	58.93	41.07	Pellet	799	5	1280	7	130.99	21.59	Direct	Cooling	3.58
4000	71.43	28.57	Pellet	758	12	1280	6	161.31	21.52	Direct	Cooling	3.70
500	80.15	19.75	Multilayer	832	12	1218	16	128.65	24	Indirect	Heating	2.35
1000	82.68	17.32	Multilayer	808	2	1177	16	174.76	24	Direct	Heating	2.43
2000	82.68	17.32	Multilayer	808	2	1177	16	174.76	24	Direct	Heating	2.43
4000	84.60	15.40	Multilayer	825	3	1214	11	164.78	24	Direct	Heating	2.47
500	84.88	15.12	Multilayer	827	3	1181	6	40	24	Direct	Heating	1.16
1000	84.23	15.77	Pellet	769	2	1280	3	40	24	Direct	Heating	1.29
2000	84.85	15.14	Pellet	801	3	1280	2	40	24	Direct	Heating	1.38
4000	81.06	18.94	Pellet	810	3	1280	7	40	24	Direct	Heating	1.40

This result supports a number of fundamental observations. First, the composition is close to the classical MPB, the region where the field-induced entropy change is enhanced by energetically favorable polarization rotation and domain switching. Second, the processing conditions indicate a careful balancing between phase purity which is maintained by a moderated calcination temperature, and densification that made possible by long sintering. Third, the high electric field highlights the discrepancy between theoretical maxima and real-world application, as it is significantly higher than the safe operating range of bulk ceramics. The 3.70 °C prediction is an appealing value, but it also highlights a drawback of unconstrained optimization as the possibility of suggesting parameter regimes that are impractical or unfeasible, particularly because of the risks of dielectric breakdown, Joule heating, and structural fatigue. Lastly, it is meaningful to mention that the optimizer has reached to this value in a trial study having 4000 iterations. This also highlights the importance of the increased number of trials during the optimization studies.

A second optimization phase was introduced with the measurement temperature set at 24 °C in order to get closer to scenarios that are relevant to the application. This modification takes into account the fact that the majority of electrocaloric devices, like solid-state coolers and microthermal regulators, are designed to function in ambient or nearly room temperature conditions [30], [108], [109]. After 4000 trials, the optimal

configuration under this constraint was found and transferred to an 85PMN-15PT multilayer sample. It was defined to be calcined at 825 °C for three hours and sintered at 1214 °C for 11 hours, resulting in a predicted ΔT_{EC} of 2.47°C at an applied field of 164.8kV/cm. This change gives rise to several important trends. The composition first shifts deeper into the MPB region. There, the coexistence of tetragonal and rhombohedral phases allows for significant reversible polarization changes. Second, the form of the sample changes from pellet to multilayer, highlighting geometry effect on extreme electric fields. Multilayers are known as better platforms for high-intensity caloric effects because they improve thermal pathways, less local field stress, and allow for quick field modulation. Third, a microstructural refinement path that strikes a balance between phase stability and grain growth is suggested by the longer sintering time and lower sintering temperature. It's interesting and should be noted that while the field strength (164.8 kV/cm) stays high, it becomes somewhat more realistic in multilayer formats where careful layer control and encapsulation which can maintain dielectric integrity. However, in order to reduce the risks of dielectric breakdown and fatigue caused by hysteresis, such values still require careful material and device design.

The third optimization phase set the electric field at 40 kV/cm and the measurement temperature at 24 °C, which are values commonly found in the literature and safely below dielectric strength thresholds, in order to replicate realistic experimental conditions and referring to usual commercial device limitations. The optimization framework found a configuration with an 81PMN-19PT pellet sample that supposed to be sintered for seven hours at 1280 °C and calcined for 3 hours at 810 °C under these more tough restrictions. The expected ΔT_{EC} stayed at a reasonable 1.40 °C despite these restrictions. This result simply can be defined as an important finding. First of all, it shows that even at moderate electric field application, PMN-PT ceramics have latent potential. Secondly, it shows the compositional resilience of formulations that are adjacent to MPB despite a slight increase in the PT ratio (from 15 to 19%), the performance is still strong and promising, suggesting some margin in composition tuning for applications with limited field. Third, the higher sintering temperature of the processing route implies that full densification and defect mitigation are required to guarantee effective thermal exchange and field propagation. The interesting part of this output is a returning to the pellet form. Even though the multilayers perform best

in high-field regimes this architecture-field coupling seems to be internalized by the optimizer, which exhibits both statistical optimization and embedded physical sensitivity.

ΔT_{EC} vs. temperature mapping given in **Figure 4.13** was created by using the ideal 40 kV/cm, 24 °C composition in order to further validate the configurations that were found and broaden their applicability. There are important takeaways from the plot to consider. ΔT_{EC} stays low over the entire temperature range if electric field level is below 15 kV/cm, which is again highlighting the necessity of a minimum driving field to produce an entropy change. ΔT_{EC} value have peaks between 20 and 40 °C, where it increases. This is consistent with the thermodynamic explanations of the electrocaloric effect as the electric field increased, the temperature change is also increasing after the threshold. There is a spike around 70–80 °C which could be a sign of data sparsity in that area of the dataset or underlying relaxor-to-ferroelectric transitions. These peaks are interesting, but they need careful interpretation and experimental validation.

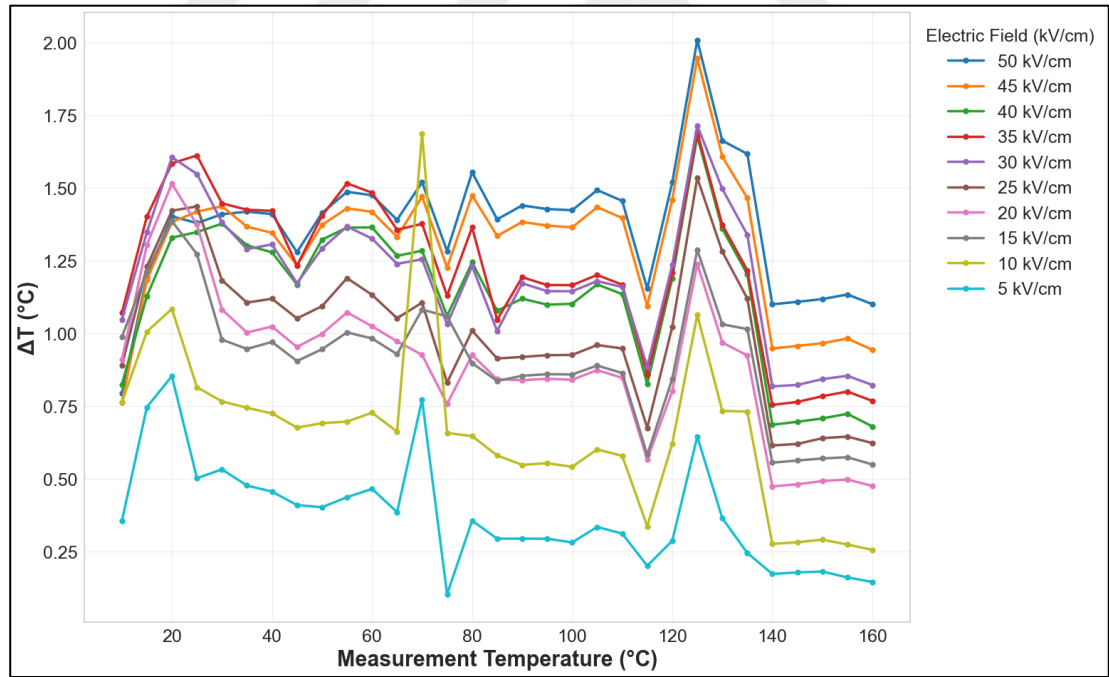


Figure 4.13: Predictive ΔT_{EC} versus T plot for the optimized processing parameters for PMN-PT.

This temperature-field landscape offers researchers and device engineers a useful design map, indicating that PMN-PT-based practical electrocaloric devices may function best in near-room temperature conditions when driven by moderate fields. A

consistent theme emerges throughout all optimization stages as careful alignment of phase boundary composition, microstructural refinement, and realistic field constraints, rather than forced parameter tuning, are the means by which maximum electrocaloric performance in PMN-PT is reached.

The centrality of MPB compositions (70–85% PMN), where polarization dynamics are enhanced by symmetry frustration, is reinforced by compositional trends. Processing trends place a strong importance on unusual balance between high-temperature sintering to encourage densification and low-temperature calcination to prevent volatilization and incomplete reaction. Due to their superior electrical and thermal characteristics, multilayer form samples are dominant in high-field regimes, whereas pellets are preferred in constrained situations because of their simplicity and integrity. Measurement setup is also important as direct methods consistently produce higher ΔT_{EC} values, especially when heated, which is probably due to entropy gain and less field lag.

The success of the optimization study in this setting supports the application of it into the materials science. In addition to finding near-optimal configurations with a significantly lower number of evaluations than grid search, it also shows that the structure–performance relationships that would otherwise be hidden by noisy or nonlinear data. The iterative design loop in the development of real materials, from simulation to prototyping, is copied in the layered constraint approach, which progresses from unconstrained discovery to fully constrained practicality. Even though the optimizer worked well in this study, of course there are still issues and important improvement windows. The uncertainty and variability present in experimental systems are ignored by our model which assumes deterministic mappings between inputs and ΔT_{EC} . To measure prediction reliability, future iterations should incorporate uncertainty-aware models such as Bayesian neural networks or Gaussian Process regression with confidence bounds.

Additionally, this study examines maximizing ΔT_{EC} as a single objective. Other considerations that need to be optimized in practice should include fatigue resistance, dielectric loss, response time, and fabrication cost. The path to truly optimized materials may be opened by the identification of trade-off surfaces between ΔT_{EC} and secondary objectives using multi-objective frameworks.

Finally, the physical fidelity of the model would be improved by enlarging the feature space to incorporate microstructural or dynamic descriptors, such as domain wall density, grain boundary area, or polarization fatigue behavior. Combining the optimizer with simulations based on physics such as phase-field models can also further improve the data-driven exploration.

4.1.5. Virtual Dataset Prediction and Predictive Mapping

The relaxor ferroelectric nature of PMN-PT naturally controls its electrocaloric behavior throughout the mapped parameter space. PMN-PT systems, especially those with PMN content above 65–70%, exhibit diffuse phase transitions characterized by the presence of PNRs in a non-polar matrix, in contrast to classical ferroelectrics, which have sharp phase transitions and clearly defined Curie points. Due to their heterogeneity and dynamic nature, these PNRs produce a wide range of local Curie temperatures and polarization switching activation energies. Macroscopically, this microscopic heterogeneity appears as a smoothed electrocaloric response over a broad temperature window and a broad, frequency-dependent dielectric peak [110], [111].

This is mirrored in the virtual dataset predictions, which show a slow rise in ΔT_{EC} with temperature rather than a sharp peak close to any one T_C . Rather, for PMN ratios between 80 and 90%, a long plateau of high ΔT_{EC} values exists, suggesting that the system maintains a high entropy-change capability over a wide thermodynamic space.

This behavior is aligned with the Vogel-Fulcher-type freezing observed in relaxors, where enhanced entropy fluctuations close to the freezing temperature (T_f) and non-ergodic glass-like states at low temperatures are caused by the dynamic slowing down of dipolar reorientation [112], [113]. This behavior directly supports a more extensive and long-lasting electrocaloric effect. Interestingly, the virtual dataset's high ΔT_{EC} values cluster around field-temperature conditions where PNRs are most responsive ($T_f < T < T_B$), supporting previous research by Bokov et al. that links the dipolar configurational entropy gradient to the electrocaloric effect strength [21].

The decrease in ΔT_{EC} at really high PMN ratios (>90%) may be explained as a change into an excessively disordered relaxor state, in which the material becomes closer to a dipolar glass phase and loses long-range polar coherence. Even in the presence of strong electric fields, the entropy change is suppressed in such systems due to blocking

and random fields that delay field-induced alignment. The observed decrease in polarization and pyroelectric coefficient in highly disordered PMN-rich compositions is consistent with this interpretation.

The segmented contour plots and 3D scatter given in **Figure 4.14** and **Figure 4.15** highlight how closely composition, measurement temperature, and electric field are related. The electrocaloric effect results from the nonlinear coupling of all three variables rather than being a simple linear function of one. A 70% PMN sample, for instance, might produce a moderate ΔT_{EC} at 100°C and 100 kV/cm, but it would perform noticeably worse at 75°C. On the other hand, the dataset's highest ΔT_{EC} might be obtained by applying the same field to an 85% PMN sample at 125°C [114].

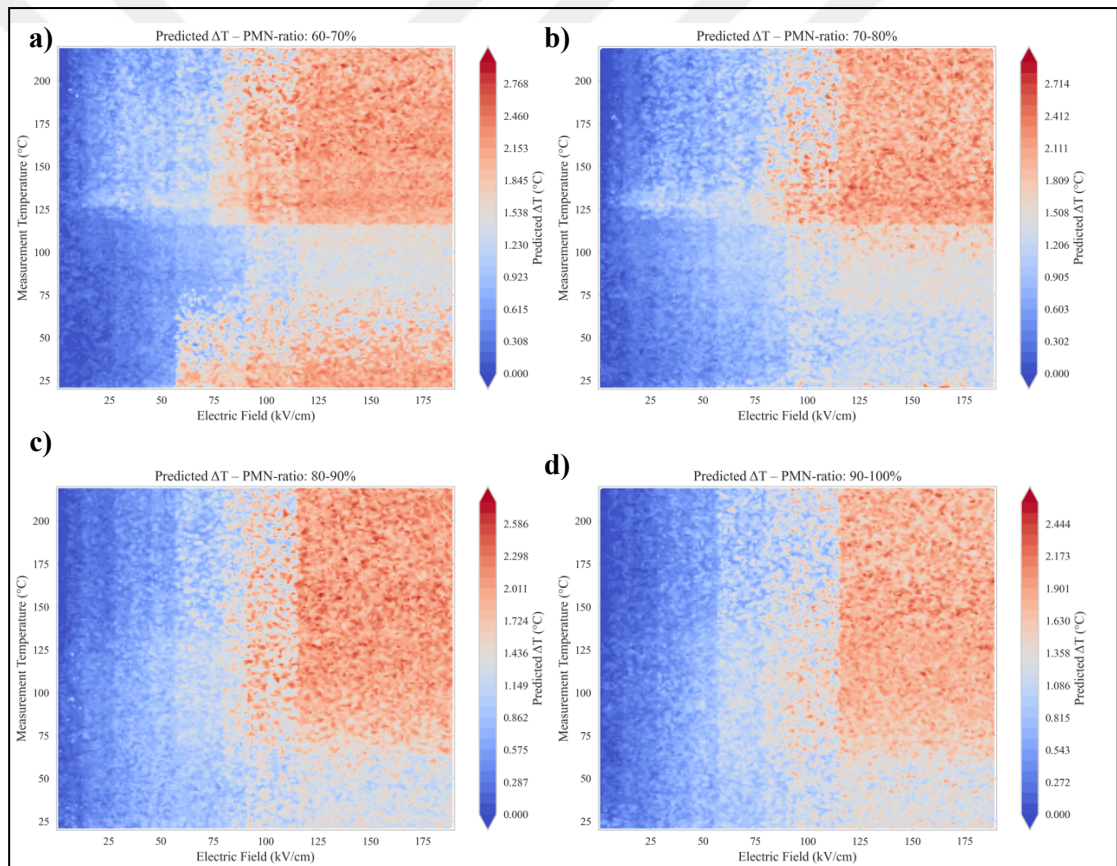


Figure 4.14: Segmented contour plots of different PMN-ratio regions for measurement temperature and electric field, PMN-ratios (a) 60-70%, (b) 70-80%, (c) 80-90%, (d) 90-100%.

This interdependence, which is also reflected in previous Bayesian optimization framework, suggests the importance of multi-objective optimization strategies rather than single objective. This means that, from the standpoint of materials engineering,

specific processing and composition strategies are needed to localize the ΔT_{EC} peak within the desired temperature–field regime when designing a PMN-PT-based device for a particular operating environment such as high-power electronics, automotive cooling, or wearable sensors.

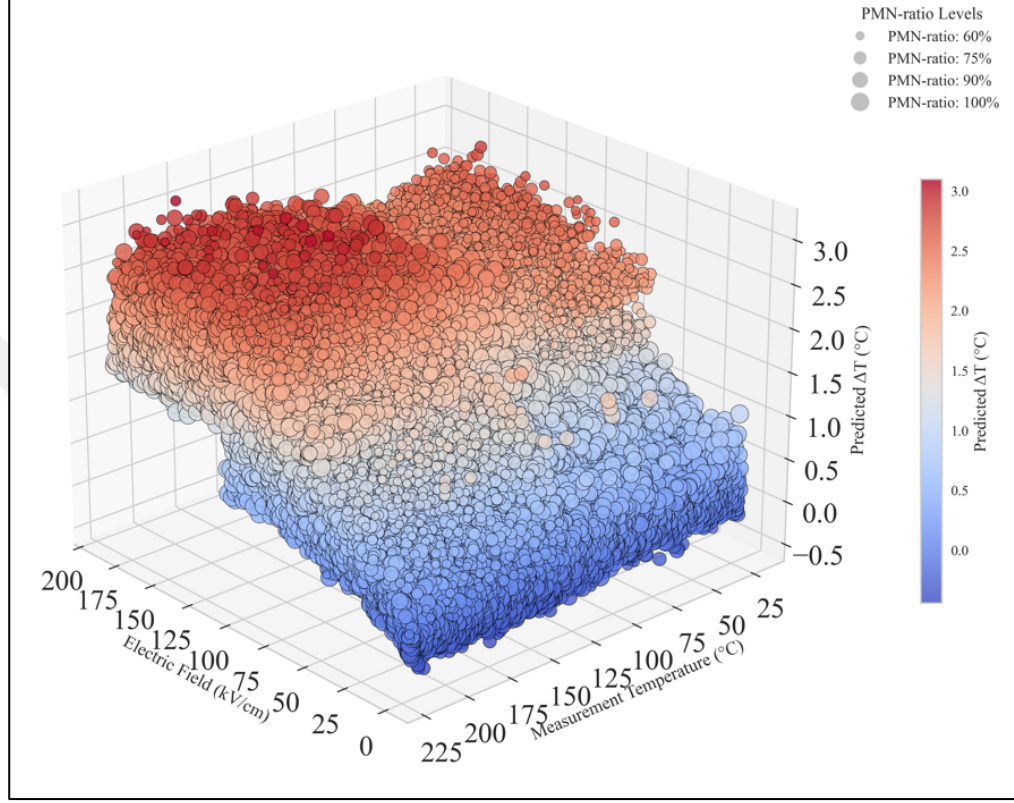


Figure 4.15: 3D visualization of predicted ΔT_{EC} with PMN-ratio, measurement temperature and electric field levels.

As mentioned earlier, single objective optimizations may ignore mechanical compatibility, fatigue resistance, dielectric breakdown strength, and thermal conductivity. However, our mapping approach lays the base for future co-design strategies that use multi-target surrogate modeling to optimize ΔT_{EC} alongside these secondary but practically important properties.

Depending on the processing route and poling conditions, the ΔT_{EC} values for PMN-PT reported in the literature typically fall between 0.5 and 2.8°C under 50 to 150 kV/cm and near-room to moderate temperatures [26]. In addition to accurately capturing the shift in performance trends across PMN ratios and operating conditions, the virtual dataset, which was trained and validated using experimental ΔT_{EC} data

across this space, replicates these magnitudes. The ability to interpolate and extrapolate ΔT_{EC} values in regions that are underrepresented in experimental datasets because of fabrication limitations or measurement constraints (such as above 150°C or >200 kV/cm) is one of the advantages of the current predictive approach. The model generates hypotheses for upcoming synthesis or measurement campaigns and offers useful design insights by capturing the learned response surface across this high-dimensional input space.

Predictive uncertainty is still a crucial factor for this. The contour maps show mean estimates of ΔT_{EC} , but they don't show model variance or confidence bounds. In order to maximize experimental efficiency and knowledge gain, future iterations of this analysis should incorporate ensemble methods or Bayesian regression techniques to quantify uncertainty and direct experimental prioritization toward high- ΔT_{EC} regions with high predictive uncertainty.

Lastly, the mapping results directly affect how PMN-PT is actually used in solid-state cooling devices. PMN-PT is very promising for applications like on-chip thermal regulation, microscale heat pumps, and smart textiles because of its predicted maximum ΔT_{EC} of $\sim 2.8^\circ\text{C}$ under realistic electric fields (≤ 150 kV/cm) and near-ambient temperatures. However, achieving these potential calls for device-level integration strategies in addition to material optimization. For example, compositional gradients or domain-engineered layers in multilayer ceramic capacitors (MLCCs) made of PMN-PT may increase the effective field across thin active regions without compromising breakdown safety. Furthermore, rapid heat transfer mechanisms and thermal insulation need to be co-optimized because the electrocaloric cycle depends on adiabatic conditions. By determining field-temperature-composition regimes that optimize ΔT_{EC} within safe operating limits, the knowledge gained from our mapping can help guide these device architectures. In addition to passive cooling, the PMN-PT system has the potential to be used in active thermal modulation, such as reconfigurable optics and infrared camouflage, where quick and reversible temperature changes on thin-film surfaces are useful. The mapped performance landscape can be used to investigate thin-film deposition techniques and doping strategies (with La or Gd) for such applications.

4.2. BCZT System

4.2.1. Dataset Summary and Descriptive Statistics

With 2188 lines of data, the dataset compiled for the BCZT system is a large and comprehensive electrocaloric literature data to date. The investigations and improvements on the electrocaloric response of lead-free perovskite systems are reflected in this dataset and a deeper examination of its statistical structure identifies underlying biases and patterns that have important results for the creation of machine learning models as well as the analysis of trends in electrocaloric performance. The statistical feature of the dataset is given in **Table 4.3**.

Table 4.3: Descriptive statistics of BCZT dataset.

Parameter	mean	std	min	25%	50%	75%	max
Ba-ratio	0.86	0.05	0.70	0.85	0.85	0.87	0.95
Ca-ratio	0.14	0.05	0.05	0.13	0.15	0.15	0.30
Zr-ratio	0.10	0.04	0.00	0.10	0.10	0.10	0.20
Ti-ratio	0.90	0.04	0.80	0.90	0.90	0.90	1.00
mean Atom Wei.	44.82	0.85	42.54	44.59	44.59	45.13	46.53
mean EN	2.55	0.00	2.55	2.55	2.55	2.55	2.55
mean Volume	20.93	0.23	20.23	20.87	20.87	21.00	21.39
mean SpaceGroup	91.69	0.04	91.56	91.68	91.68	91.70	91.76
Upon Cooling	0.05	0.22	0.00	0.00	0.00	0.00	1.00
Upon Heating	0.95	0.22	0.00	1.00	1.00	1.00	1.00
Indirect Method	0.84	0.37	0.00	1.00	1.00	1.00	1.00
Direct Method	0.16	0.37	0.00	0.00	0.00	0.00	1.00
Calcination Temp	1197.98	102.61	1000	1150	1225	1250	1350
Calcination Time	8.16	3.89	3.00	4.00	10.00	12.00	12.00
Sinter Temp	1389.38	54.64	1250	1350	1400	1420	1520
Sinter Time	4.55	2.38	2.00	2.00	4.00	7.00	10.00
Electric Field	14.04	11.46	0.50	6.00	12.00	16.00	60.00
Meas.Temp	87.35	32.91	0.00	63.93	88.43	110.56	188.79
T _C	94.00	13.49	49.50	88.85	93.00	96.85	125.85
T _C -T	6.65	32.63	-101.9	-14.1	8.00	31.81	95.85
ΔT_{EC}	0.25	0.32	0.00	0.07	0.15	0.31	2.26

The compositional variance in the dataset shows that the studies are mostly focused on Ba-rich and Ti-rich compositions with mean molar ratios as 86% and 90%, respectively. This composition simply refers to the enhanced polarization and well-known stability near the MPB of BCZT system. Therefore, most of the studies have been performed in this area resulting with a skew. Another result of this favored

composition is having limited amount of chemical diversity in the dataset with only 6-7 different compositional ratio. There are two important consequences of this compositional redundancy. It leads to a limited variability and therefore reduced generalization performance especially in the unknown regions and also increasing the risk of errors reasoned from extrapolation.

On the other hand, sintering and calcination variables have wide and again clustered distributions. Calcination temperature is ranging between 1150 °C to 1250 °C with a mean at 1198 °C. The average sintering temperature in the dataset is 1390 °C. However, the dataset itself is relatively under-sampled for the extreme values which can affect the ΔT_{EC} predictions because of the unclear effects. The durations of calcination and sintering are discretized with 5-6 unique values. This can lead to artificial flat zones on the learned model surface that highlights the limitation of the dataset. The most critical factors that are influencing the ΔT_{EC} response are electric field and measurement temperature have high resolution in the dataset with 45 different value and 975 different temperature point. This gives an important advantage to the model to learn localized behavior which is essential for interpolative machine learning. This is critical especially near Curie temperature where the entropy driven effects are dominant.

Adding the Curie temperature offset is important as it allows the model to capture the proximity to the phase transition behavior which is linked to the electrocaloric effect. The distribution of $T_C - T$ is quite wide from -101.9 °C to 95.9 °C which indicates that both paraelectric and ferroelectric phases exists in the dataset and this variation increases the ability of the model on learn non-linear thermodynamic transitions.

Magpie-derived elemental descriptors are included in the dataset as they capture important compositional trends on atomic level. They are potentially useful for overcoming the coarse-grained nature of stoichiometric variables. Therefore, they can regularize the model behavior. On the other hand, as mentioned above, BCZT compositions have a low diversity in the dataset, and this also reflects to the Magpie elemental descriptors. Therefore, they are useful but not the primary drivers of the model predictions.

The dataset has a dense sampling in performance-optimized regions and limited examples from the edges of the dataset. Even though this limits the model usage for

inverse design tasks, it is still ideal for local optimizations. Some features offer rich variety and information while some of them are quite narrow. It is important to capture rare high-performance cases which is highlighted by the statistical variety of ΔT_{EC} with mean 0.255 °C and maximum as 2.26 °C. This shows that model requires to balance learning trends with focusing to the outliers.

These insights demonstrate that, despite the size and structure of the dataset, its true strength is localized learning rather than supporting the choice of tree-based ensemble models which can easily capture such behavior.

4.2.2. Correlation Analysis

The correlations within the dataset of BCZT ceramics are really critical as they are basically crystallographic and thermodynamic mappings that are showing the non-linear interactions. The discussion of these patterns is important for model development as well as understanding the electrocaloric behavior in the system.

Starting with the Curie temperature offset and transition trends, the fine structure in this correlation shows second-order transitions and diffuse phase effects in BCZT, even though the T_C -T vs. ΔT_{EC} peak given in **Figure 4.16** corresponds to the known expectation of maximal entropy change close to the ferroelectric–paraelectric boundary. In particular, the presence of important ΔT_{EC} above T_C shows that polar nanoregions might be partially preserved in the paraelectric phase. This behavior is well-known in BCZT that is Zr-rich or Ca-doped, where local chemical heterogeneity promotes relaxor-like characteristics. This is important since spontaneous polarization in a classical displacive ferroelectric decreases to zero above T_C , but short-range polar ordering can stay in disordered systems. Above T_C , this results in field-induced polarization and a limited electrocaloric response. The result is that the temperature window over which ΔT_{EC} is effective is determined by the phase transition character either diffuse or sharp. This is particularly important when considering application scenarios where wider operating ranges are beneficial, like near-room-temperature cooling devices. Therefore, even if it is derived indirectly, modeling efforts have to include not only T_C but also potentially descriptor features that encode transition space or diffuseness, such as dielectric dispersion parameters or Curie–Weiss deviation metrics.

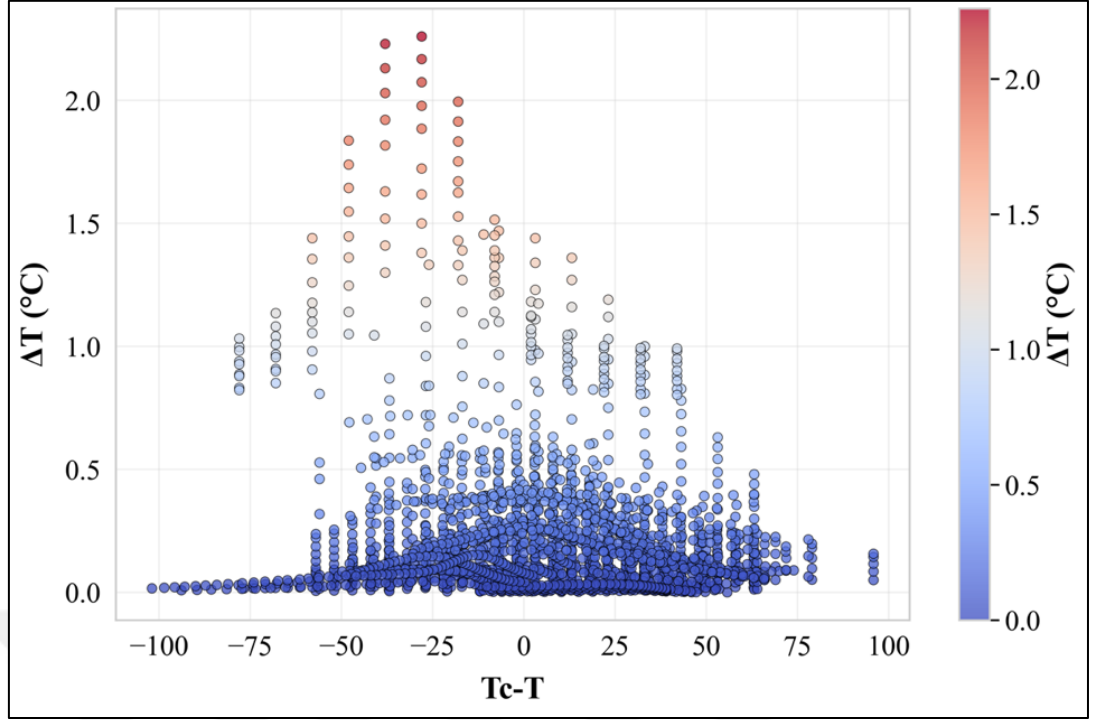


Figure 4.16: Correlations between the temperature change (ΔT_{EC}) and $T-T_C$ in BCZT dataset.

According to Landau-Ginzburg-Devonshire theory, the monotonous but saturating relationship between electric field and ΔT_{EC} which is given in **Figure 4.17** is a clear indicator of nonlinear polarization behavior under high field [115–118]. Particularly, the saturation seen in many data points above $\sim 40\text{--}50$ kV/cm indicates that polarization rotation reaches a thermodynamic limit and then entropy change can't increase anymore, either because of the completion of domain alignment or the start of dielectric breakdown. Interestingly, polarization rotation mechanisms are more common than polarization extension in BCZT systems close to the MPB [119], [120]. Therefore, low-energy barriers between domain states enable materials with low-symmetry coexisting phases (such as rhombohedral-tetragonal combinations) to exhibit large electrocaloric improvements even at moderate fields. The high ΔT_{EC} values around Ba 0.85-mol and Ti 0.90-mol are aligned with this behavior. The effect is clear from the perspective of materials design which is the optimal electrocaloric material is a material that is unstable but still polarizable near a phase boundary. At this point, symmetry linked descriptors such as polarization rotation path length, octahedral tilt angle, and tolerance factor might be essential additions in subsequent research.

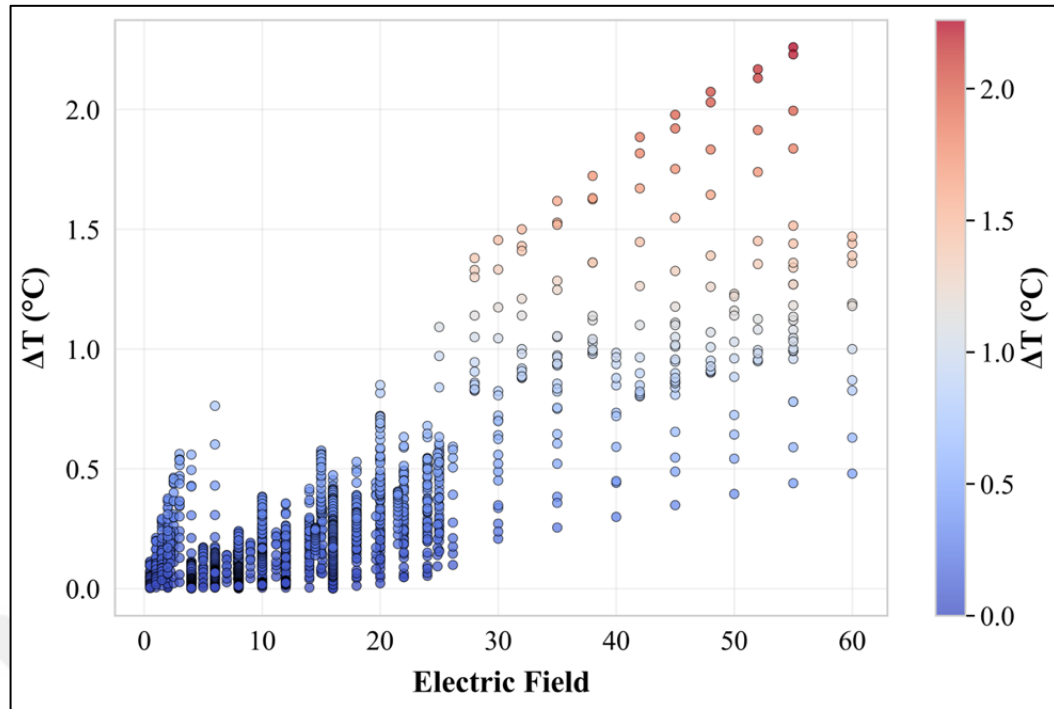


Figure 4.17: Correlations between the temperature change (ΔT_{EC}) and Electric Field in BCZT dataset.

Sintering temperature and time strongly impact the electrocaloric response and directly influences the domain wall density, grain boundary pinning, and internal stress distribution in addition to demonstrating processing quality. Insufficient temperatures during sintering frequently result in porous microstructures with pinched domains and disjointed grains, which inhibit the dielectric and electrocaloric response. However, over-sintering can cause grain coarsening, which lowers the density of the domain wall and raises the energy needed to perform dipole reorientation. Additionally, A-site or B-site cation volatilization, specifically Ba loss, can result from extended sintering durations. This can change the stoichiometry and even completely eliminate ferroelectricity [121], [122]. Therefore, compositional drift resulting from process-induced volatility, an underappreciated factor in many electrocaloric datasets, may be the cause of the observed drop in ΔT_{EC} beyond specific sintering conditions.

More significantly, the ideal sintering window which is approximately 1350–1420 °C for 4–8 hours probably correspond to a microstructural state in which domain walls are plentiful and mobile, allowing for entropy change without compromising mechanical integrity. Grain size distribution and relative density should be included as

variables in future work, either experimentally or through image analysis pipelines from SEMs found in the literature.

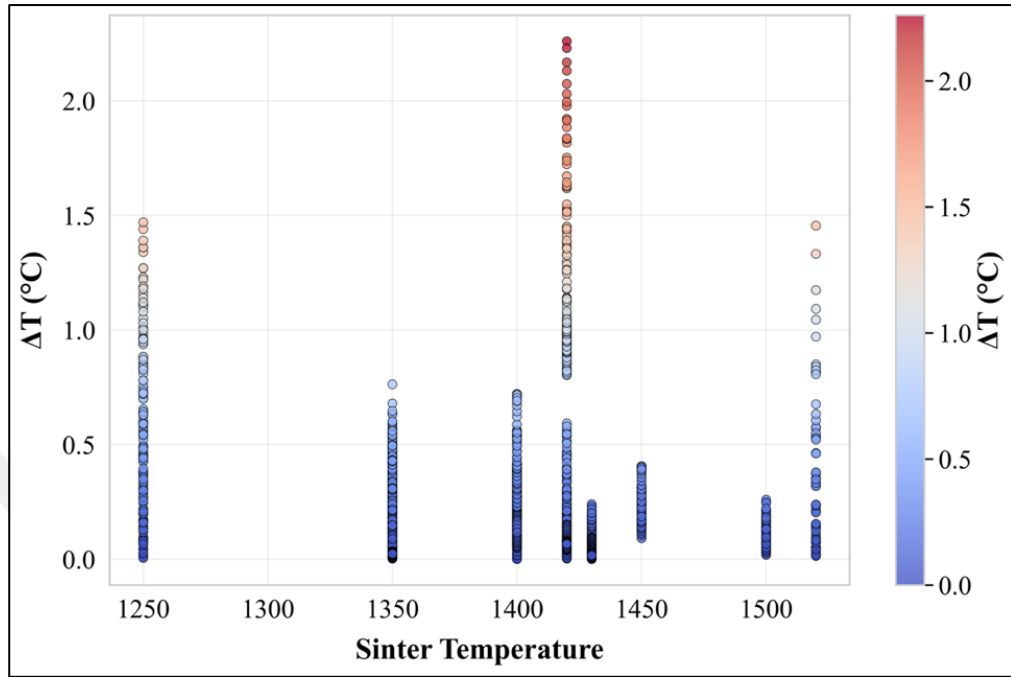


Figure 4.18: Correlations between the temperature change (ΔT_{EC}) and Sinter Temperature in BCZT dataset.

ΔT_{EC} and the compositional ratios also have correlation, and their physical significance cannot be ignored. Their contribution is actually synergistic and nonlinear. For example, adding Zr increases the dielectric constant and suppresses the coercive field, while increasing Ca disturbs the long-range polar order. These both result with an increase in lattice distortion, which, up to a certain point, improves polarizability up to a certain level and then the switchability is suppressed by local disorder. The low MI scores can be attributed to this inconsistent behavior. Furthermore, although statistically insignificant, descriptors such as mean electronegativity and atomic volume represent latent variables in the phase stability and polarization free energy, such as average bond polarizability and unit cell softness.

Finally, the difference between indirect and direct methods is a critical issue in electrocaloric research and it affects the measured values as given in **Figure 4.19**. Indirect methods rely on polarization versus temperature derivatives, which are sensitive to experimental noise, thermal lag, and field cycling rate. In contrast, direct measurements provide actual temperature change but suffer from thermal losses. The

direction of the measurement is also effective on the measured values. Generally, the measurement taken during the cooling often underestimates ΔT_{EC} and heating/cooling mode reflects thermal hysteresis and delayed domain realignment, both of which are rooted in energy dissipation rather than entropy gain. Therefore, a truly predictive and generalizable model must treat measurement modality as a core structural uncertainty component in the data.

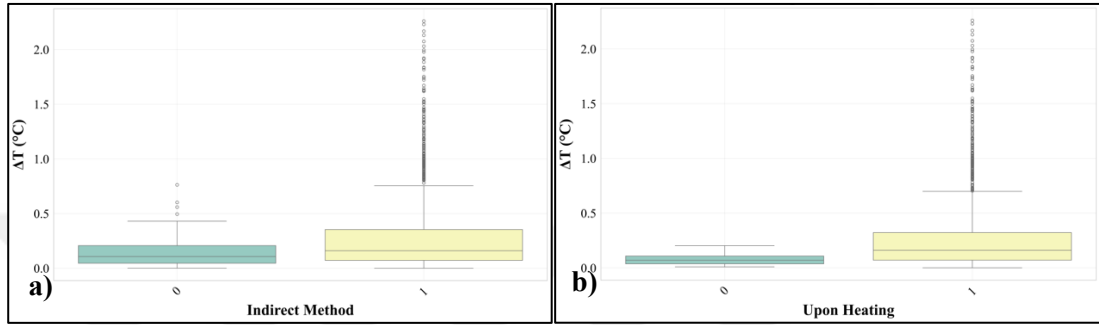


Figure 4.19: Correlation boxplots of the temperature change (ΔT_{EC}) depending on (a) measurement type; (b) measurement direction.

The relationship between the calcination time and ΔT_{EC} shows an interesting correlation character. It can be seen that the highest values but also the spread of ΔT_{EC} values are achieved with the 4-hour calcination. Other shorter and longer durations of calcination show relatively narrow distributions as well as lower ΔT_{EC} values. This asymmetric character might refer to a dual function of the calcination. It can either result with the volatilization of A-site cations Ba and Ca, which also changes the stoichiometry, or increased defect concentration [123]. According to the **Figure 4.20**, phase purity and chemical homogeneity seems to be balanced at 4-hour also preparing the microstructure for the final development during sintering. It is also important to keep in mind that the sample count for each duration also effects the interpretation of these plots.

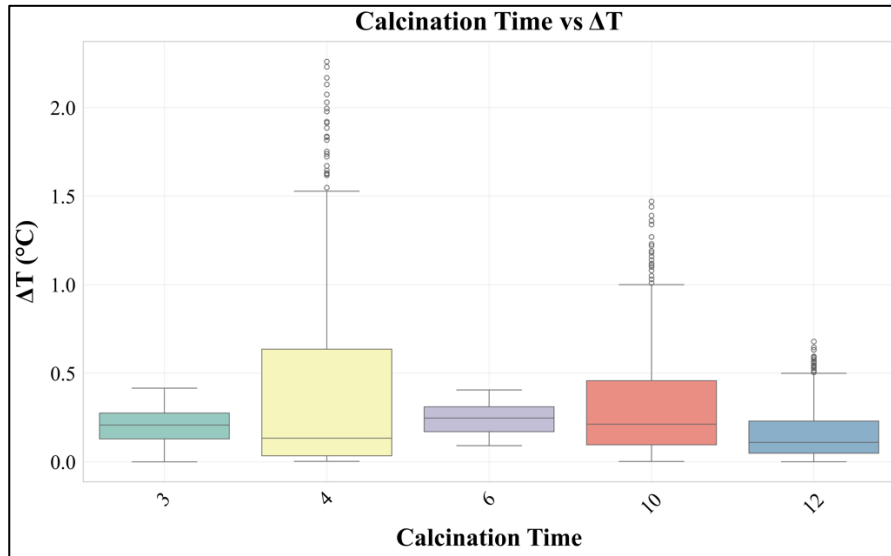


Figure 4.20: Correlation boxplot of the temperature change (ΔT_{EC}) depending on Calcination time.

The electrocaloric temperature change and sintering temperature relation is an important one to address in terms of correlations. As it can be seen from the **Figure 4.21**, it is not possible to mention a strong correlation. The regions in the plot are mainly corresponding to the low ΔT_{EC} values below 0.5 °C. On the other hand, there are clear local density concentrations around 1340-1360 °C and 1400-1440 °C. As the higher ΔT_{EC} values are quite scattered and doesn't accumulate in a specific temperature it is possible to say that there is no clear narrow temperature window for optimal electrocaloric response of the BCZT material specifically for this dataset.

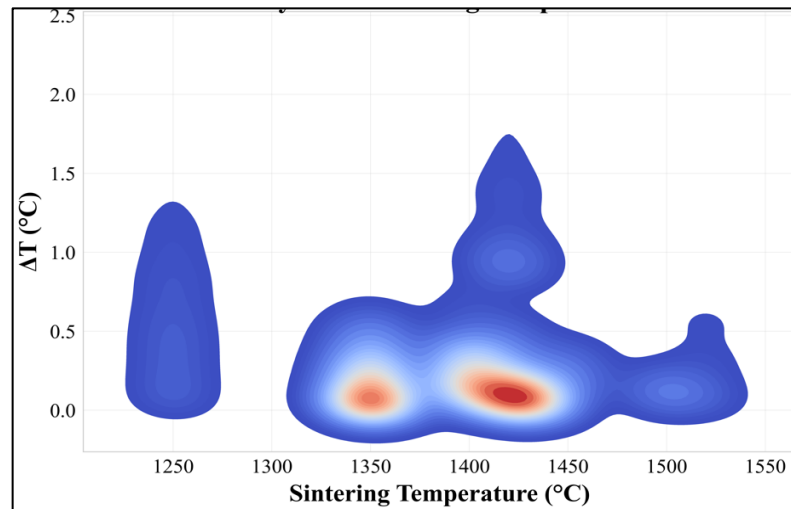


Figure 4.21: Density plot of the temperature change (ΔT_{EC}) depending on Sintering Temperature.

4.2.3. Machine Learning Performance

The algorithm performed with impressive accuracy and evaluation metrics were found to be really appealing with R^2 value of 0.99, MSE of 0.0005, and MAE of 0.013 °C. Just the PMN-PT system, XGBoost model have successfully captured the relationships within the dataset. The close alignment between the predictions and the actual values confirmed the model's high performance. These metrics shows that the model was capable in generalizing and captured the great majority of the variance in the data. The parity plot given in **Figure 4.22** shows the predicted and the actual values of ΔT_{EC} . Predictions are done with high accuracy throughout the test subset according to the figure. This refers to an important advantage, capability of the model to predict the conditions over a wide spectrum.

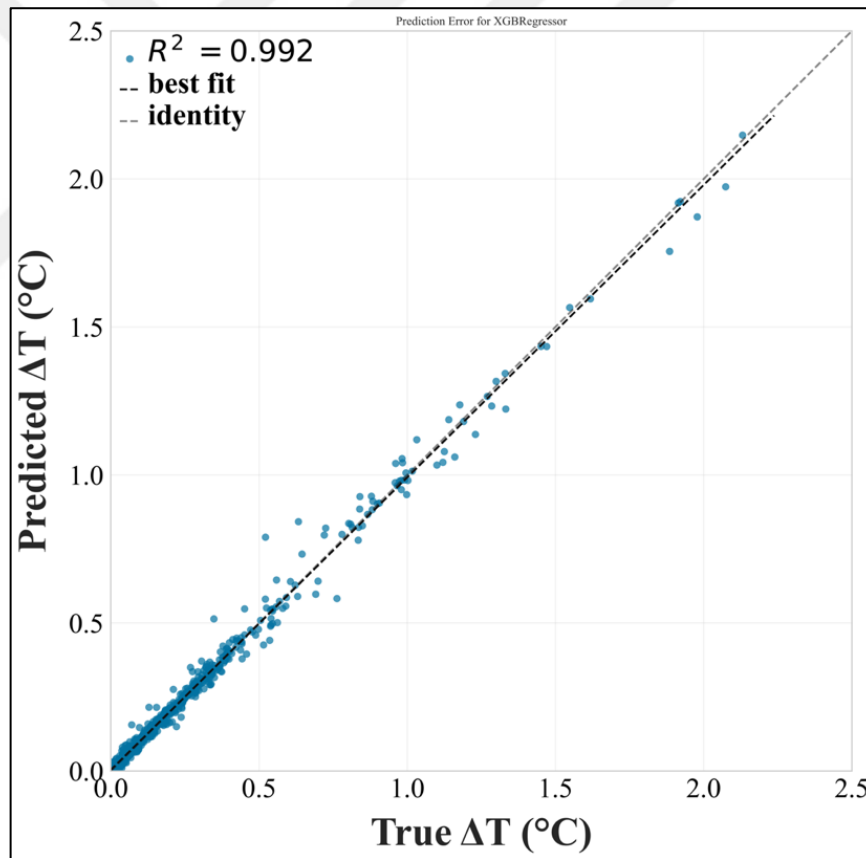


Figure 4.22: Prediction error plot of the XGBoost algorithm tested against the test subset in BCZT system.

The prediction residual of the model is given in **Figure 4.23** and demonstrates exceptionally successful performance of the model without any specific bias or low

performance region. This is an indication of the model's reliability in a wide range of processing parameter combinations. As expected, the scatter of the residuals increases with the increasing ΔT_{EC} values.

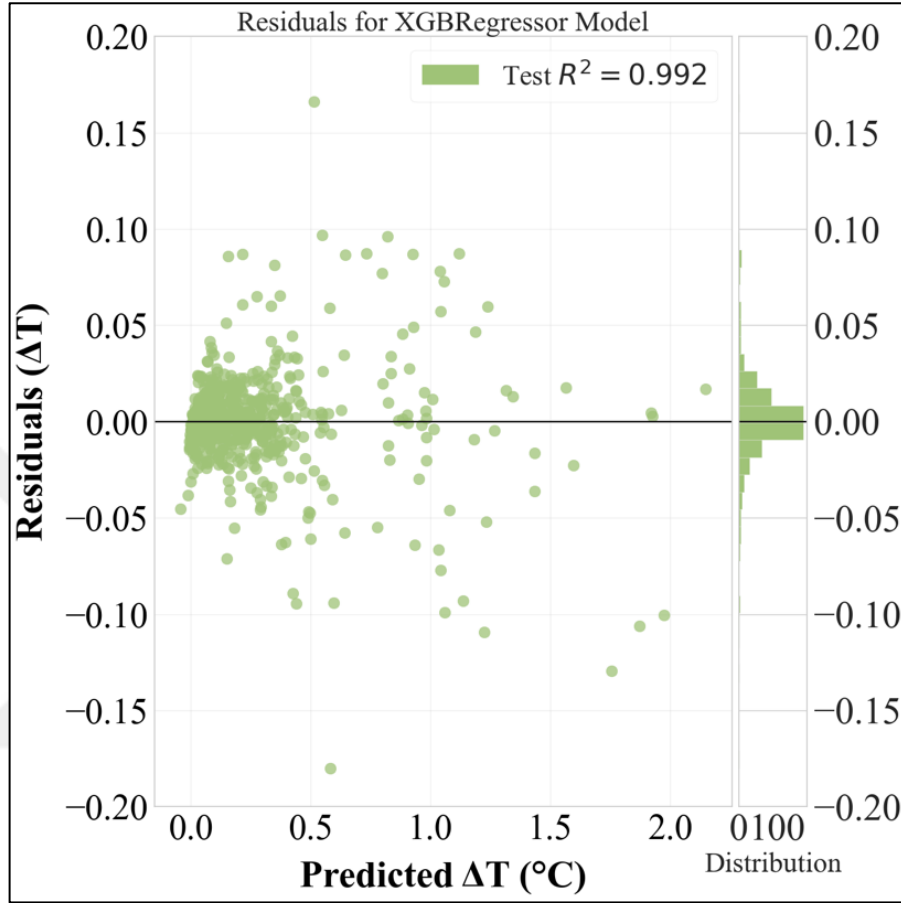


Figure 4.23: Residual values plot of the XGBoost algorithm tested against the test subset in BCZT system.

As statistical performance of the model isn't the only point and the fundamental query is another important aspect to understand if the model realistically captures the fundamental physics of electrocaloric behavior, or if it ignores the scientific causality and only interpolate patterns in a high-dimensional feature space. In order to address this, SHAP analysis was examined for the interpretability of the model, which offers a feature-wise breakdown of every prediction, providing information on the marginal contribution and context-specific impact of every input variable.

The SHAP analysis indicates that electric field strength is the most important predictor of ΔT_{EC} , which is once more entirely consistent with theoretical models of electrocaloric behavior. Since the electrocaloric effect is proportional to the product of

the electric field and the temperature derivative of polarization, stronger electric fields result in larger entropy changes in systems where polarization is thermally sensitive. The SHAP value distribution of the electric field shows a strongly positive contribution to ΔT_{EC} at intermediate and high field values as it can be seen from **Figure 32**. The SHAP scatter plots exhibit the expected saturation effect above 50 kV/cm as an outcome and it aligns with experimental reports of dielectric losses and polarization saturation at high field levels.

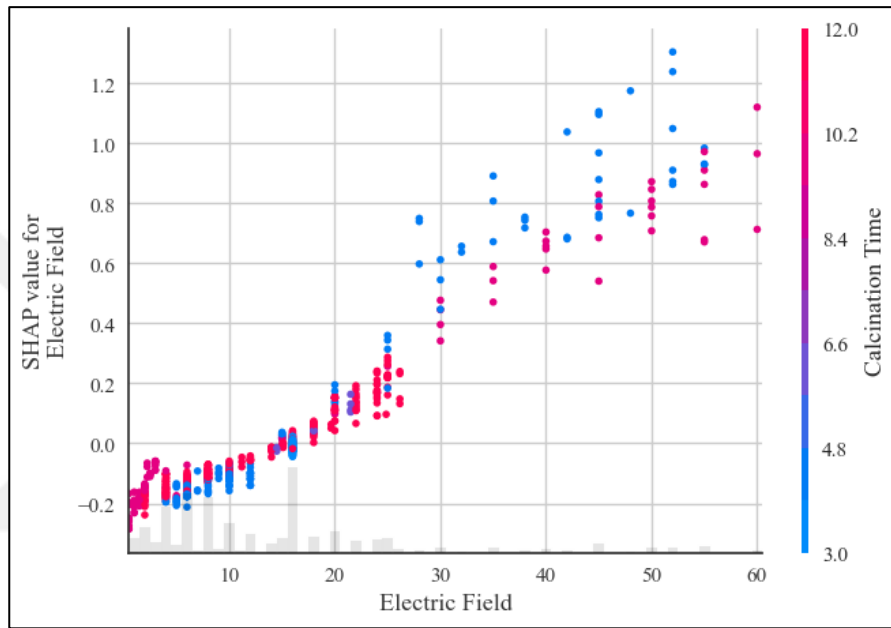


Figure 4.24: SHAP dependency plot for Electric Field in BCZT dataset.

The contribution of Curie temperature further supports the model's conformance to physical principles. The bell-shaped distribution of SHAP values given in **Figure 4.24**, which peaks when T_C falls between 90 and 110 °C, is consistent with the electrocaloric effect being maximized near the ferroelectric-paraelectric transition temperature. This peak occurs because the system is close to criticality, or at the phase transition, where the entropy change related to the reconfiguration of dipoles is greatest. Particularly, the model has implicitly learned to reward configurations where the measurement temperature matches T_C even though it was not explicitly trained on $(T_C - T)$ as a feature. This illustrates how the XGBoost model has successfully reconstructed a fundamental thermodynamic idea, entropy maximization at the transition point, from disaggregated features using interaction modeling and nonlinear partitioning. This

type of emergent interpretability shows that the model is a tool that encodes and reflects meaningful material behavior rather than just a statistical fit to the data.

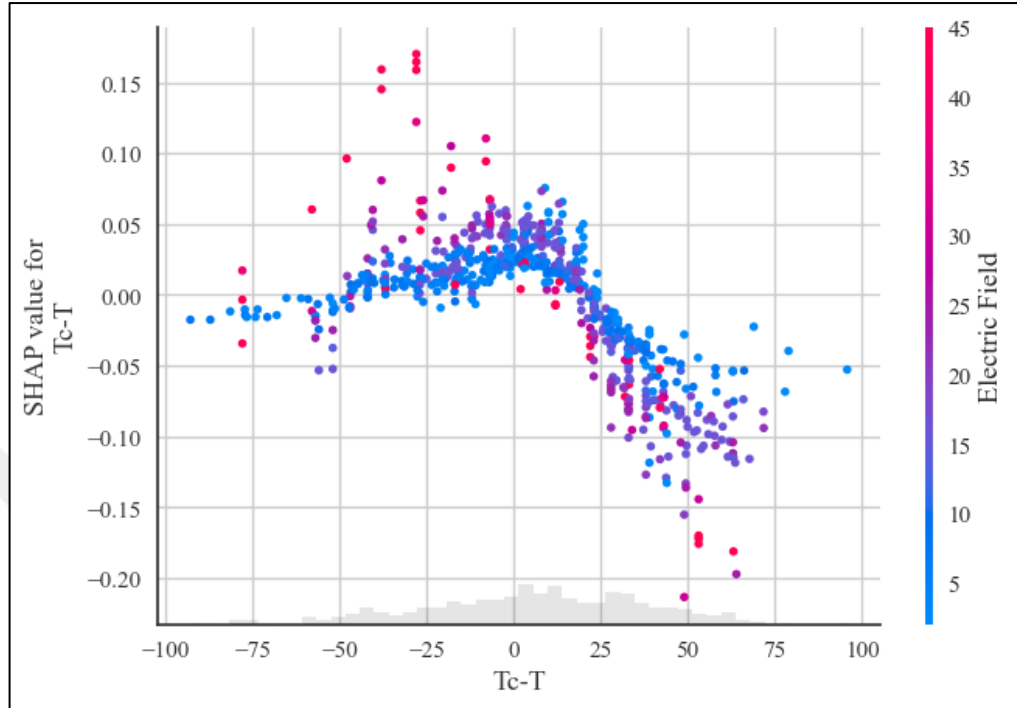


Figure 4.25: SHAP dependency plot for Curie temperature offset in BCZT dataset.

Other important variables from the SHAP analysis are sintering conditions. This highlights the important influence of processing parameters on the temperature change. The SHAP values are indicating that the ΔT_{EC} reaches to its maximum when the sintering temperatures between 1350 and 1400°C and times of 4 to 8 hours. These values are aligning with the studies in the literature and characterized with the densification level, domain structure and grain connectivity. It is known that the dipolar reorientation is blocked by the high porosity or possibly also due to not developed perovskite phase which can be reasoned from low sintering temperatures. On the other hand, excessively aggressive sintering can cause ferroelectric properties to weaken due to increased grain growth, loss of domain wall density, or volatilization of A-site cations like Ba [67], [115], [124], [125]. The important descriptors such as grain size, porosity, or XRD phase linked to the sintering are not involved to this study, but model is still able capture the critical characteristics related with the sintering.

Measurable effects are also shown by the measurement mode and method, which are frequently ignored in model design. Maxwell-based extrapolations tend to

overestimate the electrocaloric response, particularly when dielectric losses and field-induced heating are not appropriately taken into account. SHAP values showed that methods impact the ΔT_{EC} predictions and similar to this, there are small asymmetries introduced by the measurement mode (cooling vs. heating), with cooling mode typically producing lower SHAP values. This is probably due to thermal inertia in bulk ceramics, hysteresis, and delayed dipole relaxation upon cooling. In order to create reliable predictive frameworks for materials data derived from literature, the model must have internalized both physical phenomena and methodological limitations, as evidenced by the fact that it captures these systematic biases.

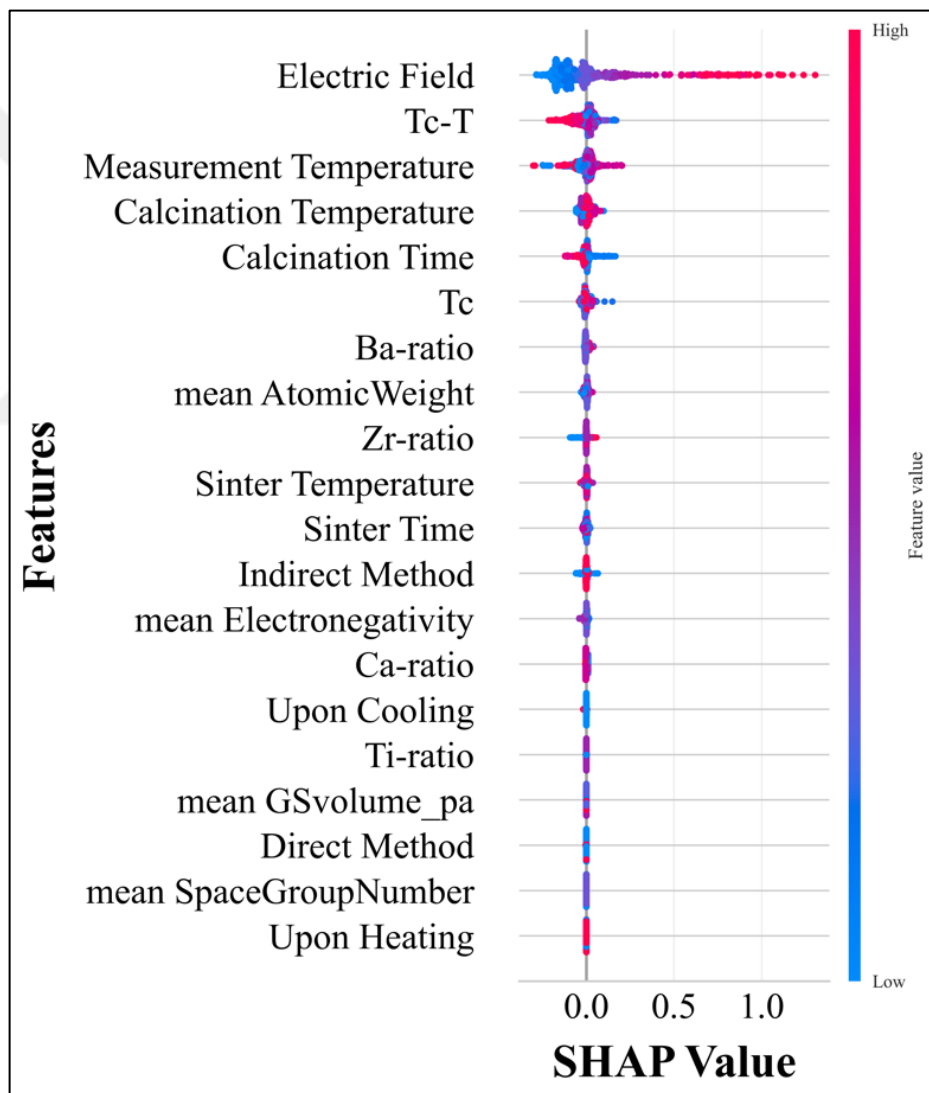


Figure 4.26: SHAP value ranges of the features within the BCZT dataset.

SHAP interaction patterns given in **Figure 4.27** provide important information about the multivariate structure of electrocaloric performance, going beyond single-feature effects. The model shows that only when other conditions are met, especially favorable sintering and thermodynamic proximity to T_C , does a high electric field positively contribute to ΔT_{EC} . Similar to this, conditional thermodynamic alignment is also reflected in the SHAP values for T_C increasing only when paired with measurement temperatures that are close to T_C . It is known that a combination of composition, process, and measurement conditions is critical for the best electrocaloric behavior, and these evolving patterns reflect their domain knowledge. Ensemble tree models are specifically made to learn and take advantage of this type of interaction, which is frequently too intricate to represent using traditional statistical techniques.

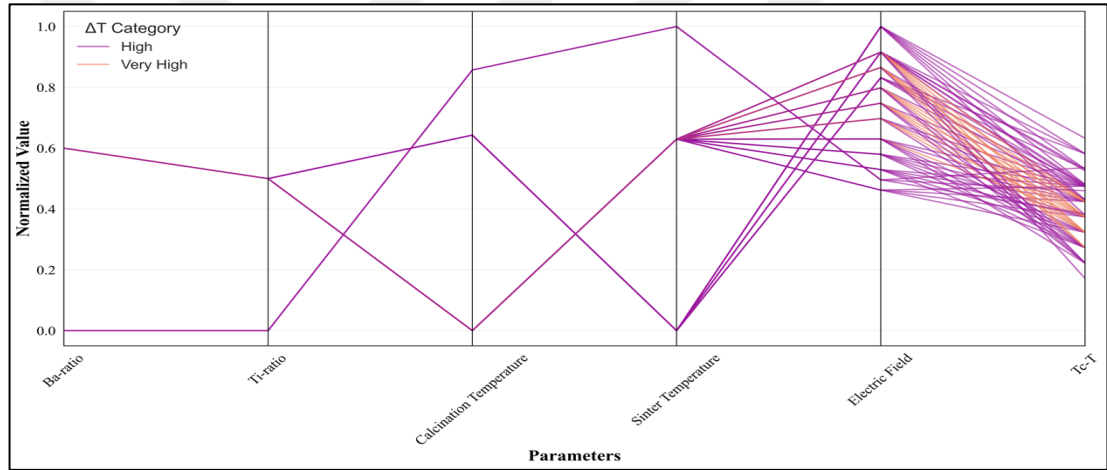


Figure 4.27: Parallel coordinates plot of the samples with high electrocaloric temperature change.

One limitation of the dataset is the absence of direct microstructural descriptors. Grain boundary density, domain wall mobility, and internal stress distributions all significantly affect the electrocaloric response, and while sintering parameters are useful approximations, they are not accurate. Making these latent variables available through data or SEM image analysis could significantly improve the model's explanatory power. Additionally, the dataset lacks dynamic properties like fatigue behavior, temperature ramp rate, and field cycling frequency that affect device performance in the real world. Despite being challenging to integrate on a large scale, these dimensions mark the cutting edge of informatics for physically enriched materials. On the other hand, it is well known that due to the diversity on the reporting

of the experimental results, it is not an easy challenge to bring these descriptors into the dataset. The current model offers useful design insights in spite of these drawbacks. The best electrocaloric response, for example, requires electric fields >40 kV/cm, T_C between 95 and 105 °C, sintering temperature around 1375°C, and sintering time of 6 to 7 hours, according to an analysis of the SHAP values across the top 5% of predicted ΔT_{EC} values. These conditions are promising targets for experimental validation because they not only produce high ΔT_{EC} but also show low model uncertainty and fall within densely sampled training regions. Furthermore, the compositional patterns linked to high SHAP values specifically, Ba close to 0.85 and the slight Zr enrichment, indicate that even within the BCZT family, there is potential for improving performance by fine-tuning the phase behavior and lattice dynamics.

Overall, the model's performance is a statistical optimization success but also it shows that machine learning can encode thermodynamic relationships, reflect physical intuition, and act as a scaffold for experimental investigation when set up and interpreted correctly.

4.2.4. Optimization Results

By identifying points of maximum electrocaloric temperature change and demonstrating how particular regions in the composition–process–measurement space combines to produce conditions of amplified entropy reordering, the Bayesian optimization results reported in this study provide an engaging window into these relationships. As a result, the optimization outputs are data-driven reconstructions of the fundamental physical principles governing electrocaloric behavior in BCZT ceramics rather than just design suggestions.

Table 4.2: Optimization history of the BCZT electrocaloric system.

Trials	Ba	Zr	T_{calc}	t_{calc}	T_{sint}	t_{sint}	E	T	Method	Cycle	ΔT_{EC}
1000	0.73	0.28	1077	5	1384	10	87	106	Direct	Heating	2.14
2000	0.78	0.29	1058	5	1385	10	88	105	Direct	Heating	2.15
5000	0.78	0.29	1058	5	1385	10	88	105	Direct	Heating	2.15
1000	0.51	0.34	1019	3	1371	3	39	24	Direct	Heating	1.14
2000	0.51	0.34	1062	3	1359	2	38	24	Direct	Heating	1.14
5000	0.86	0.37	1024	3	1352	2	38	24	Direct	Heating	1.14
1000	0.85	0.39	1090	3	1300	2	40	24	Direct	Heating	1.03
2000	0.85	0.39	1090	3	1300	2	40	24	Direct	Heating	1.03
5000	0.85	0.39	1090	3	1300	2	40	24	Direct	Heating	1.03

First set of optimizations were done with unrestricted exploration space just the optimization study in PMN-PT. The unconstrained optimization regime, in which neither the electric field nor the measurement temperature were limited, demonstrated a maximum ΔT_{EC} of 2.15°C after just 2000 trials. The consistency of this result between the 2000 and 5000-trial levels demonstrates the stability of the model and the clarity of the search space's performance peak. This processing set combined the optimal microstructural development with high-field, near-transition conditions. Its main components were selected as $\text{Ba}=0.78$, $\text{Zr}=0.29$, calcination at 1058°C for 5 hours, sintering at 1385°C for 10 hours, and measurement at 105°C under 88 kV/cm . It is particularly remarkable that this arrangement meets several physical requirements at the same time. First, the measurement temperature is near the Curie point of many BCZT systems, where dipolar entropy reordering is maximized by the collapse of long-range ferroelectric order. Second, the extended sintering likely supports a highly connected grain structure with mobile domain walls, which are necessary for a large and reversible electrocaloric response. Meanwhile, the high electric field acts to induce full polarization alignment, which improves the thermal output and entropy gradient.

However, there are real-world limitations to the outstanding performance anticipated in this unrestricted regime. It is difficult to maintain an electric field of 88 kV/cm in bulk ceramics without running the risk of dielectric breakdown or field-induced mechanical failure, even though it is possible in thin films or multilayer stacks. To better reflect real-world conditions, the subsequent optimization phase imposed stringent operational constraints. These included setting the measurement temperature at 24°C , which is representative of room temperature operation, and limiting the electric field to levels that are practical within standard dielectric strengths as 40 kV/cm . The optimization quickly came to a new local maximum within these limitations: $\text{Ba}=0.51$, $\text{Zr}=0.34$, calcination at 1019°C , sintering at 1371°C for 3 hours, yielding $\Delta T_{EC}\approx 1.14^{\circ}\text{C}$ under an electric field of 39 kV/cm . Under practical circumstances, the performance is still a significant electrocaloric output, even though it is less than in the unconstrained case. Under restricted circumstances, this transition from Ba-rich to Ba-deficient compositions is especially interesting. It implies that compositions containing more Zr may contribute to local field enhancement through polar nanoregions, broadened phase transition behavior at lower field strengths, or even relaxor-like behavior that preserves partial dipolar reconfigurability at room

temperature. These processes are in line with earlier findings that Zr-rich perovskites show prolonged dielectric activity over a broad temperature range, frequently with diffuse phase transitions and frequency dispersion [126]. The optimization framework's ability to reach these compositions without being specifically aware of relaxor physics implies that phase transition thermodynamics has been successfully internalized by the underlying surrogate model, which the optimizer has used to identify entropy-rich regimes under external constraints.

The third optimization phase set the electric field at 40 kV/cm and the measurement temperature at 24 °C, which are values commonly found in the literature and safely below dielectric strength thresholds, in order to replicate realistic experimental conditions and referring to usual commercial device limitations. The optimization framework found a configuration with an 81PMN-19PT pellet sample that supposed to be sintered for seven hours at 1280 °C and calcined for 3 hours at 810 °C under these more tough restrictions. The expected ΔT_{EC} stayed at a reasonable 1.40 °C despite these restrictions. This result simply can be defined as an important finding. First of all, it shows that even at moderate electric field application, PMN-PT ceramics have latent potential. Secondly, it shows the compositional resilience of formulations that are adjacent to MPB despite a slight increase in the PT ratio (from 15 to 19%), the performance is still strong and promising, suggesting some margin in composition tuning for applications with limited field. Third, the higher sintering temperature of the processing route implies that full densification and defect mitigation are required to guarantee effective thermal exchange and field propagation. The interesting part of this output is a returning to the pellet form. Even though the multilayers perform best in high-field regimes this architecture-field coupling seems to be internalized by the optimizer, which exhibits both statistical optimization and embedded physical sensitivity.

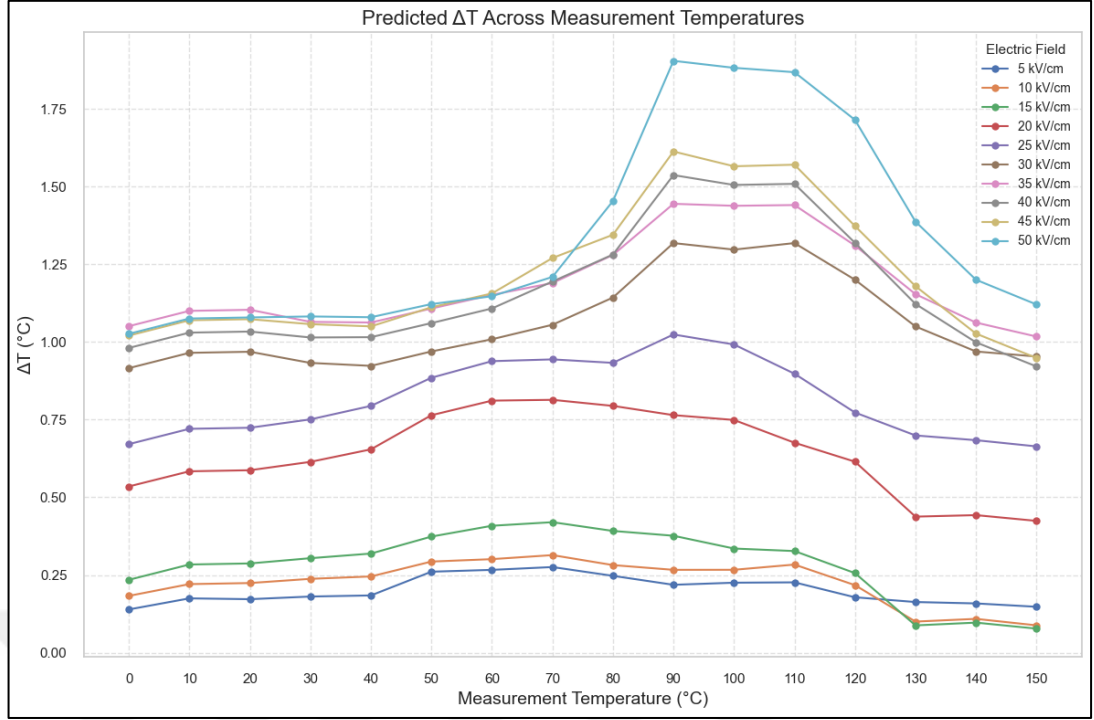


Figure 4.28: Predictive ΔT_{EC} versus T plot for the optimized processing parameters for BCZT.

ΔT_{EC} vs. temperature mapping given in **Figure 4.28** was created by using the ideal 40 kV/cm, 24 °C composition in order to further validate the configurations that were found and broaden their applicability. There are important takeaways from the plot to consider. ΔT_{EC} stays low over the entire temperature range if electric field level is below 15 kV/cm, which is again highlighting the necessity of a minimum driving field to produce an entropy change. ΔT_{EC} value have peaks between 20 and 40 °C, where it increases. This is consistent with the thermodynamic explanations of the electrocaloric effect as the electric field increased, the temperature change is also increasing after the threshold. There is a spike around 70–80 °C which could be a sign of data sparsity in that area of the dataset or underlying relaxor-to-ferroelectric transitions [115]. These peaks are interesting, but they need careful interpretation and experimental validation.

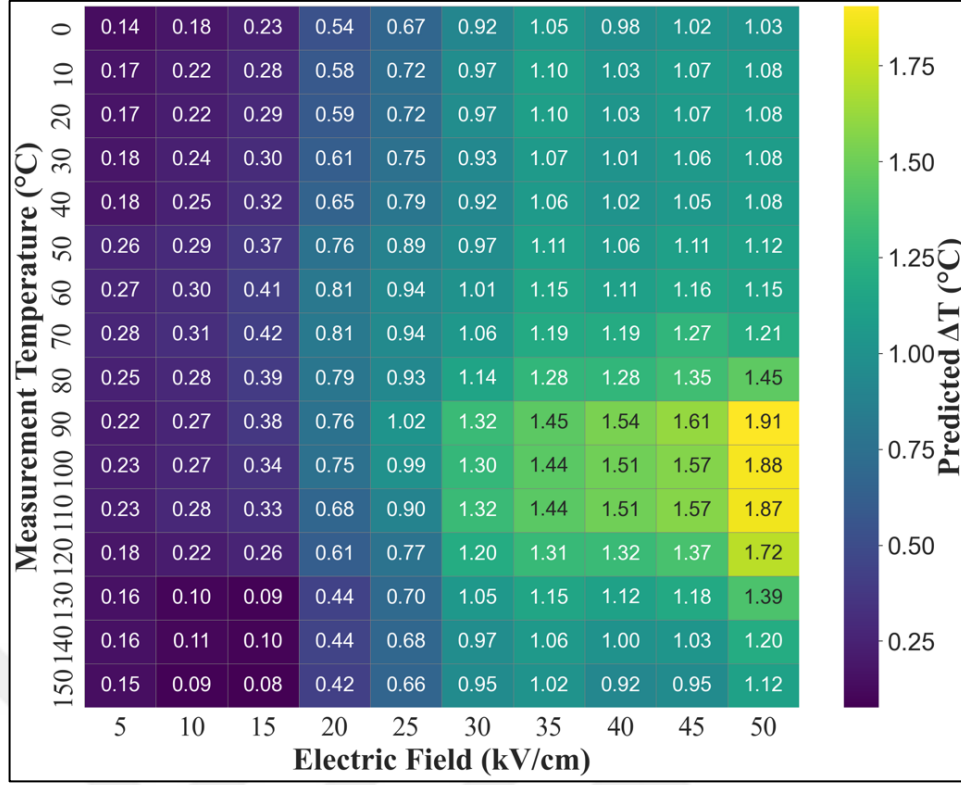


Figure 4.29: Heatmap of predicted ΔT_{EC} values as a function of measurement temperature and electric field strength.

Further information is provided by the field–temperature heatmap given in **Figure 4.29**, which is linked to the optimized configuration. For fields below 15 kV/cm, the ΔT_{EC} surface is flat at room temperature and responds very little, independent of composition. This shows that there is a minimum field threshold below which there is not enough energy input to overcome thermal damping or drive domain reorientation. However, ΔT_{EC} increases sharply above 30 kV/cm, indicating the start of strong field–entropy coupling. High spatial resolution mapping of this threshold behavior is crucial for practical device engineering since it establishes the activation field needed for feasible cooling, which directs the choice of materials and the design of the circuit for electrocaloric modules. From a methodological perspective, the substitute model's credibility is validated by the optimizer's quick convergence, the stability of optima across trials, and the results' physical plausibility. Despite being trained only on data from the literature, the XGBoost regression reproduces known phase behaviors, thermodynamic extrema, and structure–property–process interactions without the need for hard-coded physics. This demonstrates how powerful machine learning is as a tool for emergent mechanistic inference as well as a prediction engine. Additionally,

Bayesian optimization enables active decision-making: future implementations could actively prioritize experimental regions with high predictive variance by integrating uncertainty estimates (for example, through quantile regression forests or Gaussian process models), turning the optimizer into an independent experimental guide.

In conclusion, high-performance and practically feasible BCZT configurations for electrocaloric applications were successfully found using the Bayesian optimization framework in conjunction with a physically coherent machine learning surrogate. The findings clarify the multi-parametric structure of performance and show how composition, field, thermal proximity, and process interact to produce regions of enhanced entropy change, rather than just pointing to numerical maxima. Crucially, the discovery of field thresholds, the existence of multiple optima, and the thermal flattening at subcritical regimes all work together to provide a better understanding of the electrocaloric design space. Instead of searching for a single solution, optimization is a thermodynamic cartographic technique that maps the topography of entropy, field, and polarization across a challenging terrain of design opportunities and physical constraints.

4.2.5. Virtual Dataset Prediction and Predictive Mapping

The creation of a virtual dataset with 100,000 entries that covers a multidimensional design space of BCZT compositions and processing-measurement conditions provides an effective overview for analyzing the material system's learned electrocaloric behavior. The application of a trained, physically meaningful model to predict expected ΔT_{EC} values across composition, temperature, electric field, and processing parameters is what makes this synthetic dataset different.

Three critical territories in the BCZT phase diagram are represented by the three Ba content regimes chosen (Ba=0.72, 0.85, and 0.90). The ΔT_{EC} contour map given in **Figure 4.30** displays a weak and comparatively diffuse electrocaloric response at Ba=0.72. A broad maximum of $\sim 0.75^\circ\text{C}$ only appears near 100°C , indicating that ΔT_{EC} is modest even at high field strengths ($>40\text{ kV/cm}$). A signature of relaxor-like behavior, where local dipolar entities contribute small, distributed entropy changes instead of a sharp first-order transition, is the field-temperature landscape's flatness, which suggests limited thermodynamic sensitivity. This is in line with the high Zr and

Ca content at this Ba ratio, which is known to enhance spatial heterogeneity in polarization and suppress long-range ferroelectric order [127], [128]. Due to the lack of collective domain reorientation, these materials naturally limit peak ΔT_{EC} , even though they are advantageous for thermal stability and wide operating ranges.

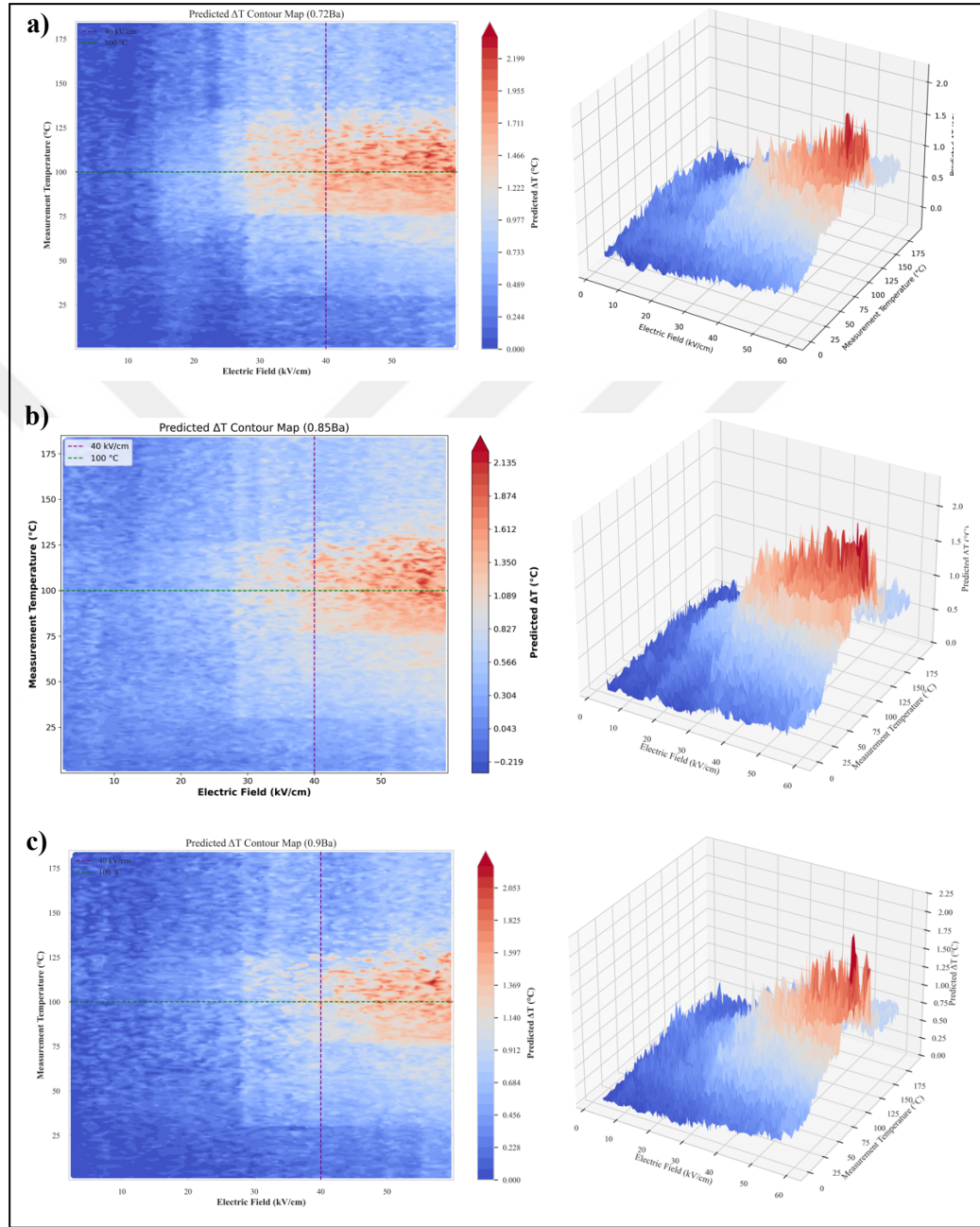


Figure 4.30: Contour plots and 3D-surfaces of the virtual dataset predictions for various Ba-content as (a) 0.72, (b) 0.85, (c) 0.90.

At ~ 100 °C and electric fields of 40–50 kV/cm, the Ba=0.85 composition, in contrast, shows a well-defined and elevated ΔT_{EC} ridge that peaks close to 1.6°C. The trajectory of the ridge is in line with the intersection of strong field-induced polarization,

indicating a distinct thermodynamic gradient. The coexistence of tetragonal and rhombohedral domains promotes low-energy polarization rotation and enhanced entropy mobility, which is indicative of an MPB-mediated enhancement. As field and temperature approach the critical regime, the ΔT_{EC} surface does, in fact, exhibit a noticeable curvature, increasing quickly from baseline levels ($<0.5^{\circ}\text{C}$) to peak values. The idea that $\text{Ba}=0.85$ represents a sweet spot, where ferroelectric order is strong but still sufficiently destabilized to allow for large entropy changes under external driving, is supported by this behavior.

The contour plot changes once more as the Ba content rises to 0.90. The peak ΔT_{EC} remains constant over a wider range of field values and shifts slightly higher at 105°C . Remarkably, the response surface is flatter and longer than in the $\text{Ba}=0.85$ case, but the magnitude of ΔT_{EC} stays high ($\sim 1.5^{\circ}\text{C}$). This suggests a shift toward a classical ferroelectric regime, where the entropy transition may be less abrupt due to the absence of phase competition, but domain alignment is more complete. Although the ΔT_{EC} values are still strong, their field-temperature dependence lessens, indicating increased stability but possibly less tunability.

An important realization emerges when these three compositions are superimposed: The response surface of ΔT_{EC} is not invariant under compositional scaling, nor is it a monotonic function of Ba content. Rather, composition changes the shape of the field-temperature response topology as well as its thermodynamic magnitude. The $\text{Ba}=0.90$ system is smoother and broader, the $\text{Ba}=0.72$ system is diffuse and low in magnitude, and the $\text{Ba}=0.85$ system is sharply peaked and high in ΔT_{EC} . The model, which was not trained to enforce such behavior but seems to have internalized it from experimental data, naturally produces these distinctions.

Turning to the global contour plot given in **Figure 4.31** which is drawn from the full virtual dataset, we observe a consistent thermodynamic signature across the landscape: ΔT_{EC} increases with both temperature and electric field, but only within a specific diagonal band aligned with the expected Curie temperature region of BCZT systems. Regardless of the measurement temperature, ΔT_{EC} consistently stays below 0.4°C below 20 kV/cm , suggesting a field threshold below which entropy perturbation is not enough to cause a noticeable thermal response. After 35 kV/cm , ΔT_{EC} rises sharply, reaching a peak between 100 and 110°C , and then falling off rapidly after 120°C , where thermal disorder most likely defeats field-induced alignment.

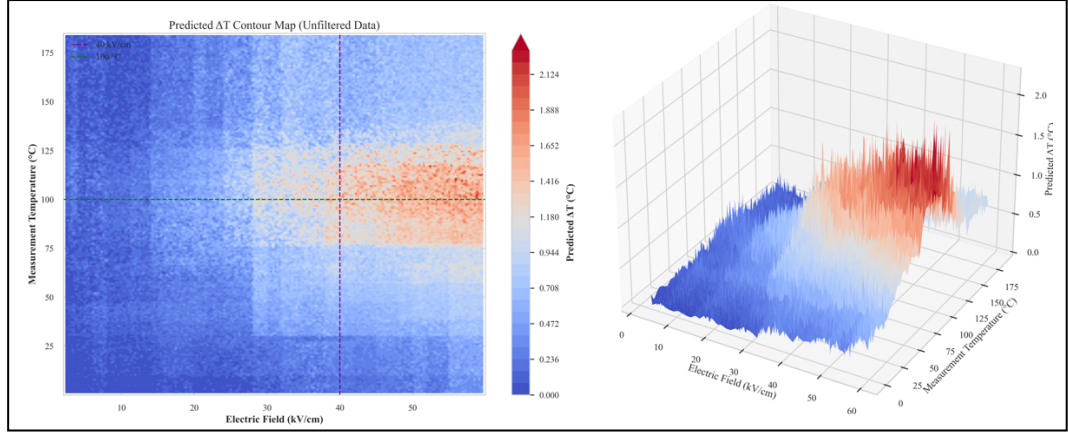


Figure 4.31: Contour plot and 3D-surface of the virtual dataset prediction at global level.

This diagonal ridge which can be understood as an expression of the entropy–field–temperature coupling, is the central component of electrocaloric performance in BCZT. In terms of physics, it shows the path that drives the system closest to the transition zone while sustaining an electric field strong enough to cause dipolar entropy collapse. Crucially, this ridge's location, steepness, and width change with composition and process parameters; this behavior is encoded in the virtual dataset but only becomes apparent through high-resolution mapping. These observations are further quantified by the histogram of ΔT_{EC} predictions over the whole virtual dataset. It is extremely skewed, with a long, thin tail extending toward 2.0°C after a prominent peak at low ΔT_{EC} values ($<0.3^{\circ}\text{C}$). The underlying physics of the design space is reflected in this skewness: only a small, precisely calibrated subset of compositions and conditions produce large entropy-driven effects, whereas the majority produce modest electrocaloric response. The difficulty of designing electrocaloric materials is highlighted by this: there is little chance of finding a high- ΔT_{EC} configuration by random sampling, which emphasizes the necessity of guided search techniques like Bayesian optimization or SHAP-informed ranking.

This has significant consequences. Initially, the model validates that compositional optimization is not enough on its own. Performance is highly dependent on measurement temperature, field strength, and processing history, even in high-potential Ba regimes (such as 0.85–0.90). These factors' high-dimensional coupling explains why brute-force synthesis frequently yields inconsistent results and why, in the wrong circumstances, even promising compositions can produce subpar ΔT_{EC} .

Second, we can assess operational robustness and design tolerance using the virtual dataset. We determine the areas where minor changes in temperature or field cause significant performance declines by looking at the gradient of ΔT_{EC} in E–T space. These zones, which are typical in compositions with Ba=0.85, indicate high tunability but low robustness, necessitating careful device integration control. The ΔT_{EC} plateaus of Ba=0.90 systems, on the other hand, are wider, suggesting a higher tolerance to operational fluctuation but possibly a lower maximum response. These insights are important for application-specific design: Ba=0.85 zone domains may be advantageous for systems that need high-amplitude, precise cooling (like microelectronic spot cooling), while Ba=0.90 zone stability may be preferred for broader thermal management applications (like passive devices). Lastly, the virtual dataset makes inverse querying possible, which involves figuring out which field, temperature, and composition combinations, given a constraint, result in $\Delta T_{EC} > 1^\circ\text{C}$. These features serve as the foundation for materials informatics-driven design, to select experimental candidates prior to synthesis. These predictive maps develop into computational phase diagrams when combined with Bayesian acquisition functions and SHAP feature importance, directing material exploration with thermodynamic intelligence.

Finally, the predictive mapping that was obtained from the 100,000-entry virtual dataset shows both the structural logic and the electrocaloric potential of BCZT. It shows how temperature and field align to cause entropy transitions, how composition shapes the response surface, and how process conditions affect how accessible these behaviors are. This map, which converts machine learning output into scientific knowledge and useful design, is more than just a data product.

4.3. PST System

PST system ($\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$) dataset was relatively smaller than PMN-PT and BCZT dataset due to the reported research studies in the literature. The studies on PST have a wide variety of combinations with other systems such as PZT, PT, PIN. These studies were excluded as they bring too much complexity and high probability resulting in poor generalization due to structure of the dataset.

4.3.1. Dataset Summary and Descriptive Statistics

Even though the dataset was small, the experimental conditions in the dataset were found to be diverse. Also, new features highly related with PST were introduced to the dataset. These features are the crystallographic order degree and annealing parameters that are affecting this order degree. The reported electrocaloric temperature change values showed a wide distribution from 0°C to 4°C. As expected, the distribution of these values is highly skewed to the lower values as it can be seen from **Figure 4.32**.

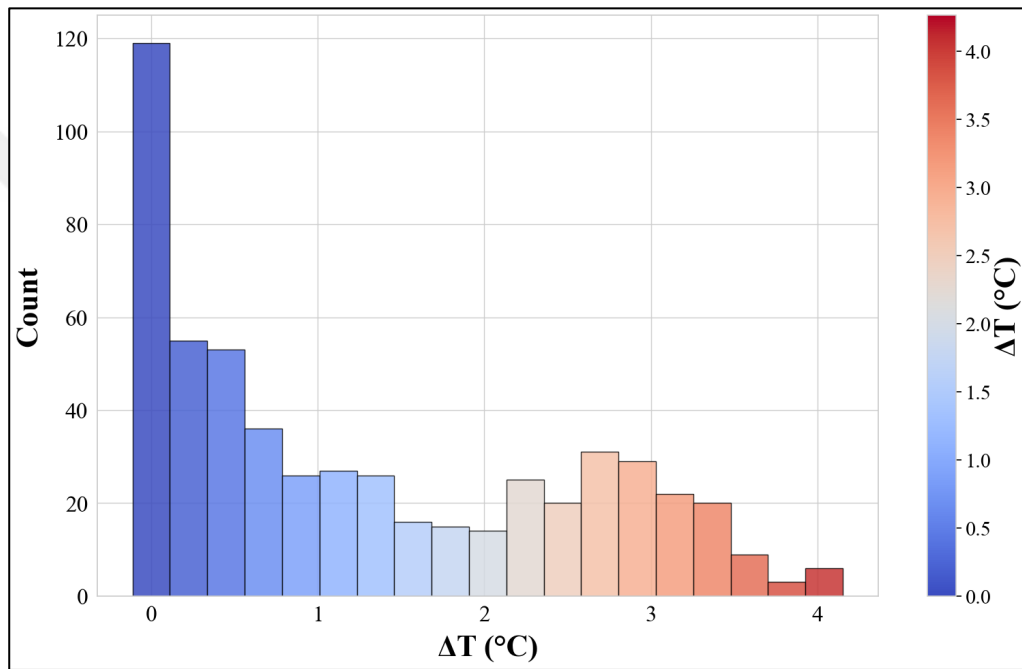


Figure 4.32: Electrocaloric temperature distribution within the PST dataset.

An important metric, order degree of the PST is reasoned from its relaxor character, and it is captured in the dataset. Order degree values are distributed from 0.75 to 1.0, which reflects that fully ordered and partially ordered samples are covered. As this metric is directly related with the annealing process after sintering, annealing temperature and time parameters were also included. The value of annealing temperature shows a quite tight distribution with only 900°C to 1000°C. On the other hand, the duration of the annealing shows a wider distribution with 30 to 190 hours. The dataset shows that the duration for calcination and sintering is mostly fixed between 2 to 4 hours as standard values.

The dataset has a lack of compositional variety with a single ratio of Sc to Ta. Therefore, it is expected that there will be no information gain to the model to empower the predictions. Measurement related variables have enough variety that can support to model learning. Most of the measurements are taken between 0°C to 60°C as the transition temperature of the PST expected to be around 27°C. Electric field spans from low levels until 200 kV/cm, which is a multilayer sample.

4.3.2. Correlation Analysis

Correlations within the dataset are showing recognizable patterns. The first and the most clear relation is with electric field as expected. It can be seen from **Figure 4.33**, it shows a strong positive correlation with the temperature change, up to 50 kV/cm levels. After this region, the temperature change still increases but with slower increments. This is aligning with the previous discussions made for PMN-PT and BCZT, supporting the saturation of domain alignment idea. As the entropy-driven dipolar realignment saturates at certain high electric field, the additional field yields weakening thermodynamic gains. The trend also shows that PST samples are mostly measured between 20 to 50 kV/cm as a measurable region with minimized dielectric breakdown risk.

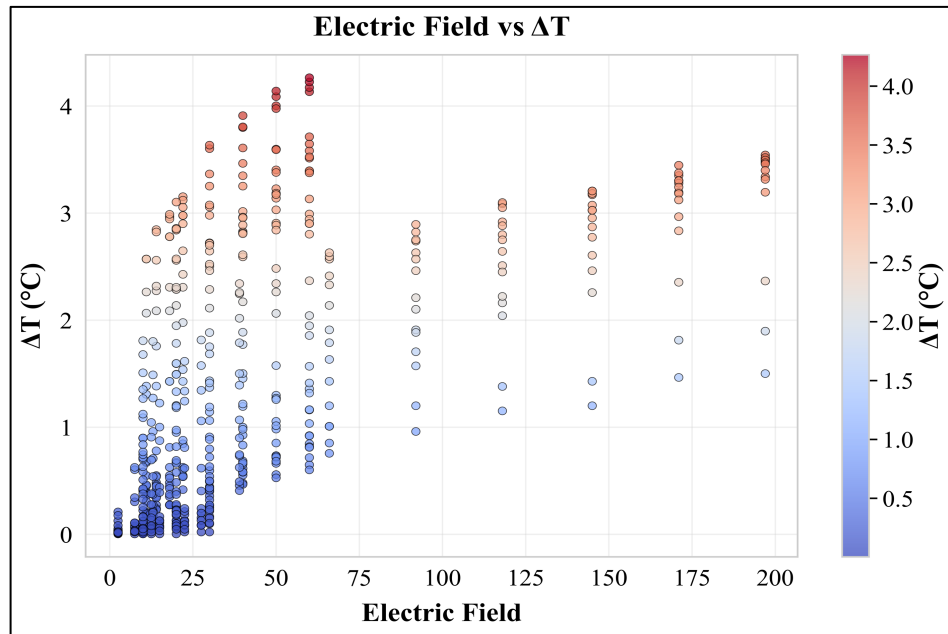


Figure 4.33: Electrocaloric temperature change values depending on the electric field level.

Order degree of the PST doesn't seem to be strongly affecting the electrocaloric response as all different degree levels shows comparable span of response values. The temperature offset from Curie temperature again shows up as an important feature. A wide trend is visible in **Figure 4.34**. The maximum ΔT_{EC} value is slightly above Curie temperature as referring to the maximized entropy change near the transition point, well aligned with the thermodynamic phenomenon. Electric field induced and intrinsic thermal fluctuations always contribute to the electrocaloric response, and this align with the relaxor character as entropy decrease does not occur in a narrow temperature range but distributed over a wider window.

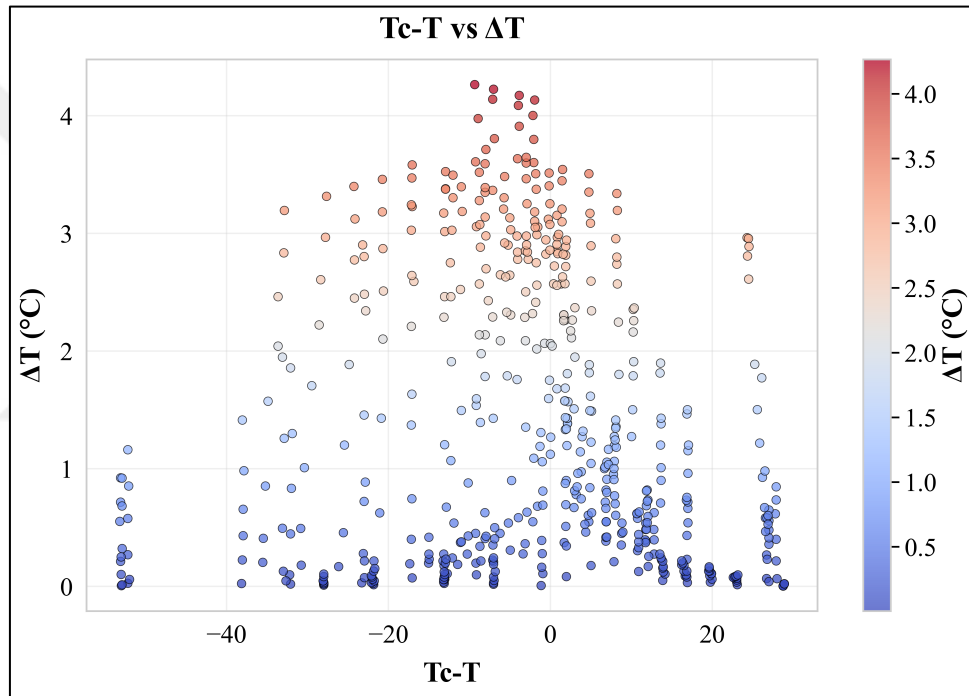


Figure 4.34: Electrocaloric response depending on the proximity to Curie point.

4.3.3. Machine Learning Performance

XGBoost regression model trained with the PST dataset resulted with important metrics that are highlighting that model is able to recognize patterns even within a small dataset. The test set performance was found as R^2 value of 0.91, MSE of 0.11, and MAE of 0.22 °C. The results indicates that there is a high reliability in modeling the electrocaloric response within the existing data and the prediction errors and the residuals shows that model generalizes the task with a good performance.

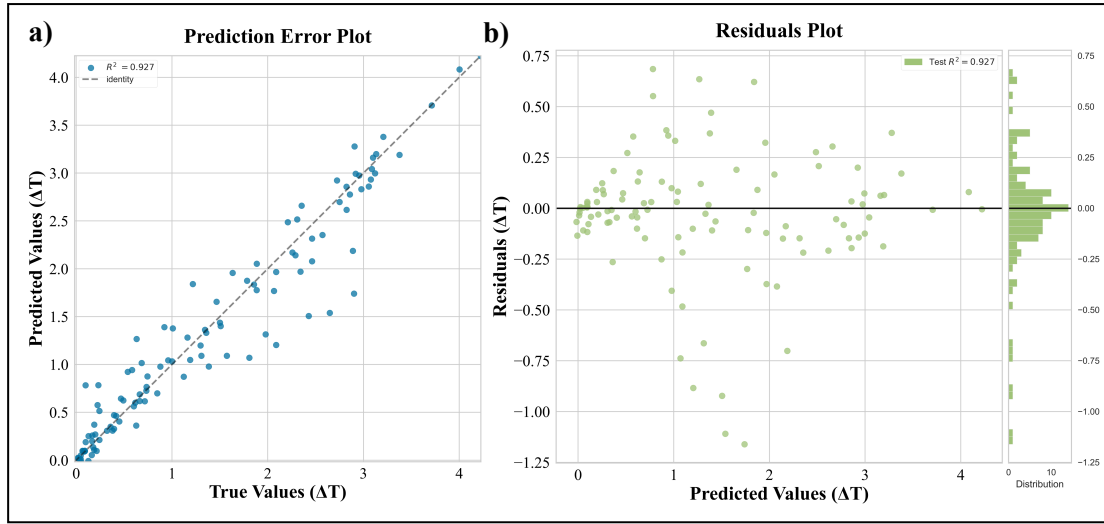


Figure 4.35: Prediction Error and Residual values plot of the XGBoost algorithm tested against the test subset in PST system; (a) Prediction Error Plot, (b) Residuals Plot.

Figure 4.35 shows the prediction errors and the residuals plot for the test subset. The prediction accuracy of the model is powerful, but it should be also noted that there are some prediction regions especially for 1.5 to 3 °C indicating that the model is more open to predict the value lower. This can be explained by the under representation of these regions in the dataset as it was given in Figure 4.32. There is a consistency between the train and test subsets showing that the model is robust and especially performing much better in regions closer to the mean of the ΔT_{EC} values.

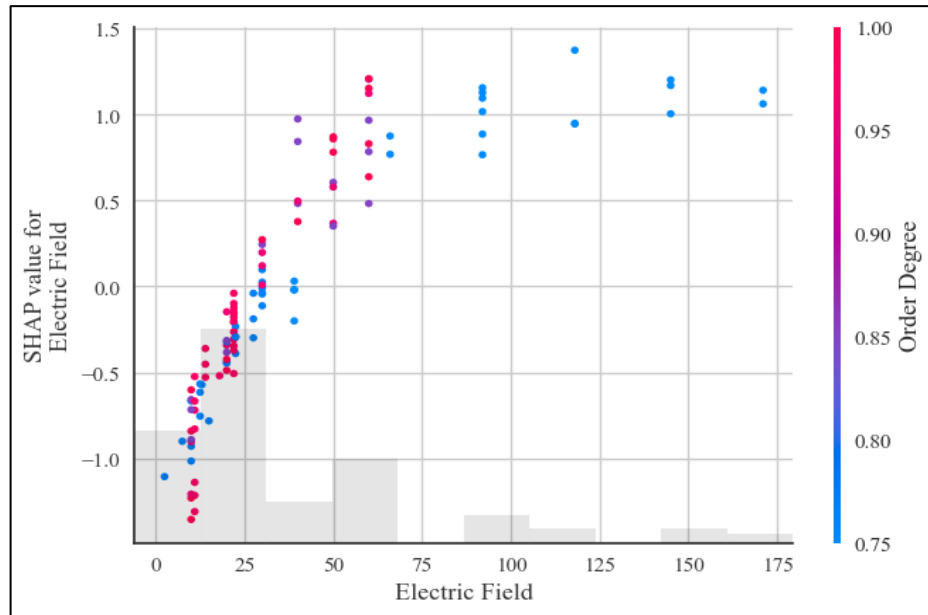


Figure 4.36: SHAP values of electric field for XGBoost predictions.

Feature importance analysis with the SHAP module again shows that the most dominant feature is electric field. The SHAP value profile of electric field increases sharply between 10 kV/cm to 50 kV/cm, and after 50 kV/cm it saturates especially for the samples with lower order. The histogram within the **Figure 4.36** indicates that most of the samples are operating near this field level efficiently, which is also important for the practical applications. Another important and impactful feature is the offset from the Curie temperature. It was discussed in the previous sections that this feature has a clear correlation with the electrocaloric response. Moderate level of SHAP values of calcination, sinter, and annealing temperatures indicates that they are not as dominant as electric field and thermodynamic descriptors.

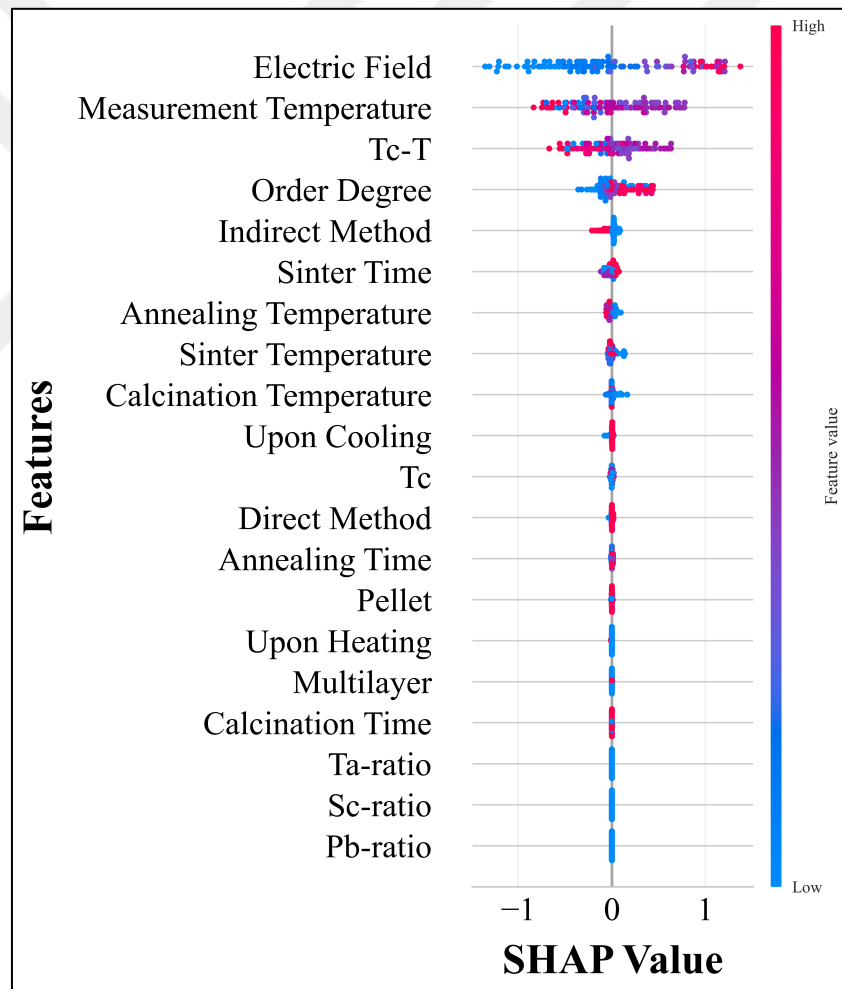


Figure 4.37: SHAP values for the features in PST dataset.

4.3.4. Potential Applications for Electrocaloric Cooling

During the conceptional stage of the thesis, one of the main ideas was developing an integrated cooling device having a triboelectric nanogenerator (TENG) as power source and an electrocaloric material for the cooling. The motivation was harvesting the wasted energy from the environment and using it to drive the electrocaloric component. Even though the experimental study was not fulfilled, simulations were performed for TENG by using COMSOL Multiphysics.

COMSOL was used to analyze the electrostatic behavior of TENGs under different operational conditions and these simulations were constructed to understand if the electrocaloric component can be operated with a TENG sourced electric potential and charge transfer.

Three main simulations were performed under different operating conditions. The boundary conditions, material selections, and mesh refinements were also done. Simulation parameters are given in **Table 4.6**. Lastly, open circuit and short circuit electrical behaviors were compared to assess voltage and charge transfer behavior.

Table 4.6: Simulation input parameters for TENG design.

	Sliding	Single Electrode	Contact-Separation
Temperature (K)	293.15	293.15	293.15
Pressure (atm)	1	1	1
Medium	Air	Air	Air
Component Size	100mm x 0.22mm x 0.1m	5mm x 0.1mm x 0.005m	5mm x 0.1mm x 0.005m
Materials	ϵ_r 4 for top, ϵ_r 2 for bottom	ϵ_r 2 for dielectric (5mm x 0.1mm)	ϵ_r 2 for dielectric (5mm x 0.1mm)
Electrode	No	Copper (5mm x 0.001mm)	Copper (5mm x 0.001mm)
First Gap	0.1 mm	5×10^{-7} mm	5×10^{-7} mm
Circuit Type	Open and Short	Open and Short	Open and Short
Parametric Sweep	Range (0.1, 2, 100)	Range (5×10^{-7} , 0.001, 0.02)	Range (5×10^{-7} , 0.001, 0.02)

For sliding mode of TENG, large planar structures were simulated (100 mm x 0.22 mm, depth: 0.1 mm) using asymmetric dielectric constants and varying interface gaps. The simulation resulted with voltage buildup over 2 kV and charge displacement across millimeter scale. These outputs might approach the magnitude to trigger a

measurable electrocaloric temperature change, especially for well-engineered systems and under sharp voltage spikes.

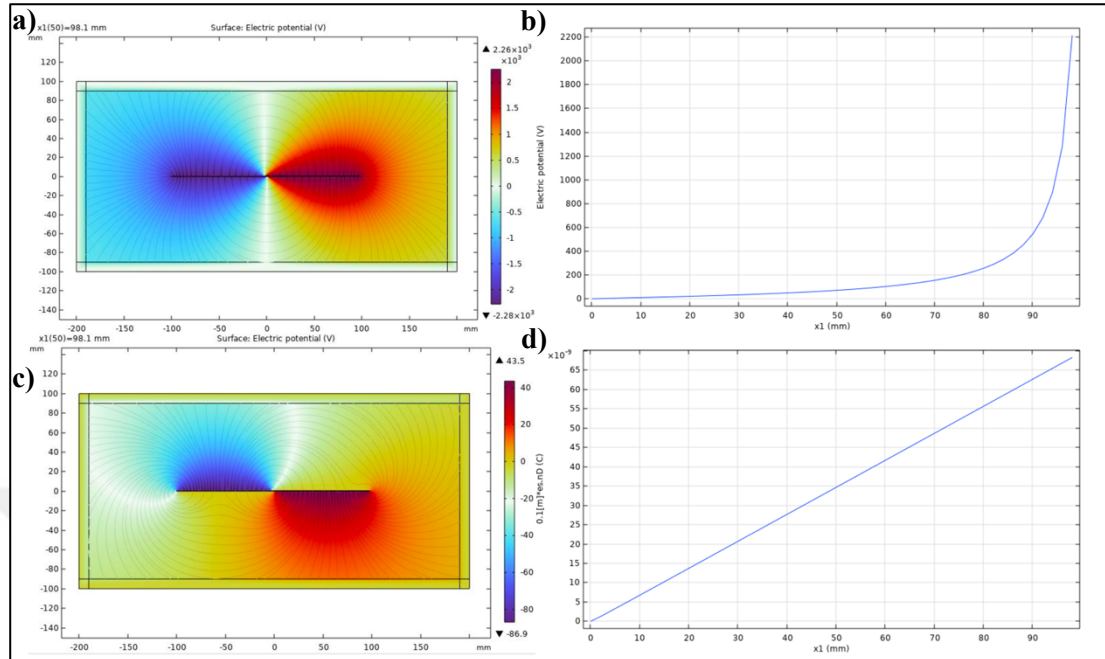


Figure 4.38: COMSOL modeling for sliding mode input parameters (a) surface electric potential for open-circuit, (b) electric potential for open-circuit, (c) surface electric potential for short-circuit, (d) electric potential for short-circuit.

For single electrode mode, much smaller TENG was designed (5 mm x 0.1 mm, depth 0.005 m) with nanometer level air gaps. The electrodes were chosen as copper. Even though the geometry was basic, open circuit potential showed 300 V and charge displacements were found to be in pico-coulomb range. This system was specifically simulated for any miniaturized, integrable system.

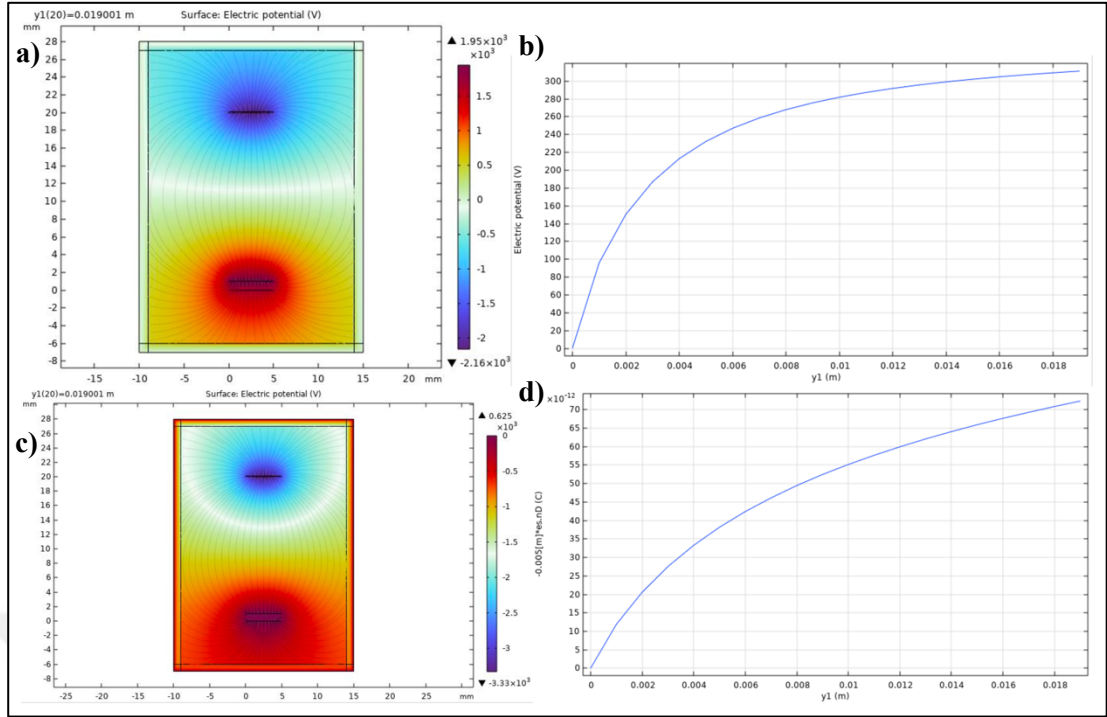


Figure 4.39: COMSOL modeling for single electrode mode input parameters (a) surface electric potential for open-circuit, (b) electric potential for open-circuit, (c) surface electric potential for short-circuit, (d) electric potential for short-circuit.

Finally, contact-separation mode was simulated. The geometry was same with single electrode configuration but this time the simulation was performed with symmetric electrodes. The results have shown that there is an increase in the charge transfer up to 4.5 nC and voltage exceeding 3.5 kV across narrow separations. These values are theoretically suitable to trigger the electrocaloric effect. However, there are important challenges to be addressed such as circuit matching and thermal synchronization.

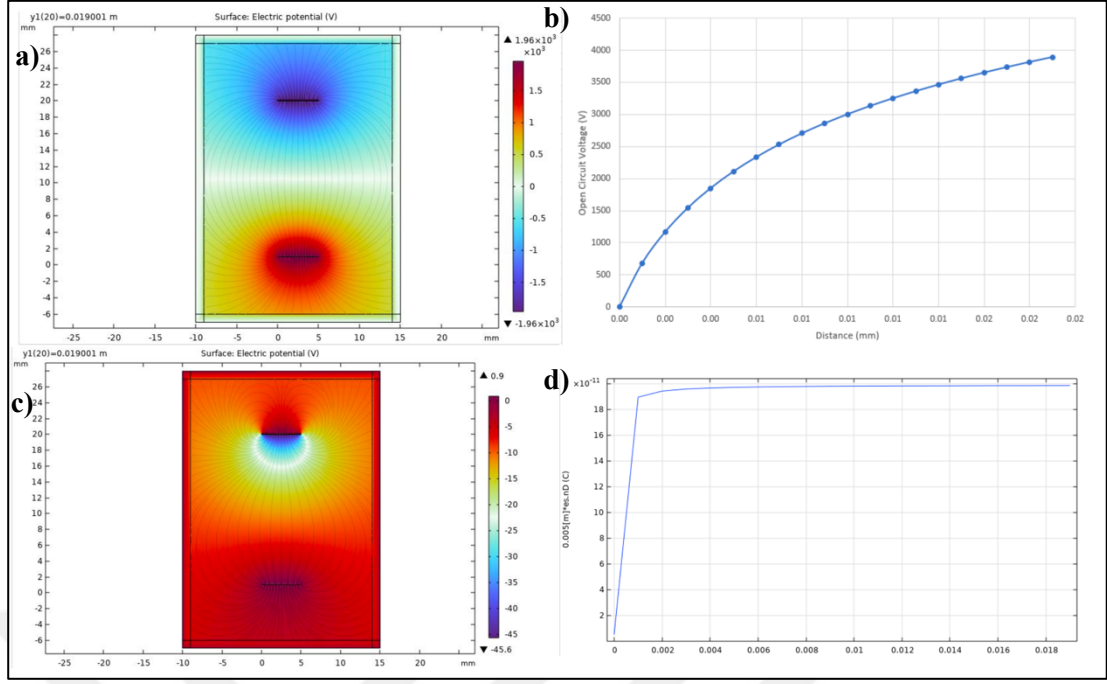


Figure 4.40: COMSOL modeling for contact-separation mode input parameters (a) surface electric potential for open-circuit, (b) electric potential for open-circuit, (c) surface electric potential for short-circuit, (d) electric potential for short-circuit.

Even though the modeling is preliminary and excludes important aspects such as fatigue, dielectric loss, mechanical dissipation, it stands as a conceptual base for future studies where it can be extended to dynamic simulations, thermal-electrical coupling. The voltage levels low however they can trigger the electrocaloric effect while the charge transfer values are within the levels of low capacitance ferroelectrics.

4.4. Cross-System Analysis and Comparative Discussion

Using the knowledge gained from in-depth dataset exploration, machine learning interpretation, and Bayesian optimization, this section offers a comparison of the PMN-PT and BCZT electrocaloric systems. Despite being electrocaloric ceramics based on perovskites, the two systems' crystal chemistry, phase transition characteristics, and structure–property relationships are different. The comparison is made for three analytical point: feature importance trends, model robustness and transferability, and optimization behavior in order to derive both general design principles and system-specific optimization strategies.

4.4.1. Feature Importance Trends Across Systems

Electric Field is the most dominant feature across PMN-PT and BCZT. The electrocaloric is related with the degree of dipolar reordering and domain switching. The SHAP plots shows that there is a threshold effect, and this directly related with the domain dynamics, which are not sufficiently activated at low levels. Above the threshold ΔT_{EC} rises sharply in both systems, plateauing or reaching a saturation zone at about 50–70 kV/cm. Polarization saturation, domain alignment completion, or, in certain situations, the start of harmful effects like dielectric breakdown or Joule heating are all reflected in this region. Despite these parallels, PMN-PT exhibits a wider field-response curve, particularly multilayer configurations. This is explained by PMN-PT's relaxor nature, which allows entropy reorganization over a wider stimulus window by allowing polar nano-regions to persist and reconfigure over a broad field range. On the other hand, BCZT shows a narrower optimal field region, especially close to the morphotropic phase boundary (MPB), due to its sharper phase transitions and more classical ferroelectric behavior.

In both systems, temperature offset from Curie point, or $T - T_C$, is also crucial. For $T - T_C$, BCZT displays a bell-shaped SHAP curve that is comparable, but it has a narrower peak that is usually centered between 0 and +15 °C. The entropy reordering is tightly localized around the transition point, indicating a displacive-type phase transition. For the best electrocaloric behavior, BCZT requires exact temperature alignment, whereas PMN-PT can withstand a wider thermal deviation from T_C .

Processing parameters play a significant role, especially in BCZT, even though their influence is second order when compared to field and thermodynamic features. Sintering time and temperature in both systems show non-monotonic SHAP behavior, peaking in the 4–8 h and 1350–1420°C ranges, respectively. These windows allow for effective domain wall motion without causing excessive grain coarsening or compositional drift because they align with ideal conditions for grain growth and densification. The performance of PMN-PT is notably less susceptible to processing variables. Comparatively lower model SHAP values for calcination temperature or sintering time suggest that intrinsic relaxor behavior, rather than extrinsic microstructure, governs the entropy landscape. Processing becomes more crucial for high-field applications or multilayer formats, though, because these architectures need

high density and flawless interfaces to withstand extreme fields. Grain size, porosity, and domain wall density are all affected by processing. Even though this study doesn't have the microstructural features the model successfully captured some of the relationships.

The measurement technique (direct and indirect) is another similarity. Indirect approaches have a tendency to overestimate ΔT_{EC} in both datasets, particularly in high-field and high- T_C regions. This overestimation results from field-induced loss neglect and assumptions in Maxwell relation integration. When indirect method flags are active, the models learn to downweight such predictions, according to SHAP analysis, effectively internalizing a bias correction mechanism.

The design of experiments depends on these emergent rules. For example, under moderate fields, a robust route to high ΔT_{EC} close to room temperature is provided by the use of multilayers in the 85PMN–15PT composition range in PMN-PT. The best entropy change in BCZT is obtained from slightly Zr-enriched compositions sintered for 6 hours at ~ 1375 °C.

4.4.2. Algorithm Robustness and Transferability

Even though the absolute predictive performance metrics (R^2 , MAE, and MSE) indicate that both systems have excellent statistical reliability, a closer look at algorithmic robustness and transferability shows that these models react very differently to domain shifts, compositional diversity, and sparse data.

The XGBoost model produced balanced residuals across performance regimes and an R^2 of 0.969 for PMN-PT. The data density is uneven, though, and clearly skewed toward compositions that are rich in PMN (about 86% mean PMN content). The model's performance held up well over a wide $T-T_C$ and field space, and it showed good generalization in both pellet and multilayer formats. This implies a high degree of interpolation flexibility across regions with different structures and temperatures. However, at the expense of less compositional diversity, BCZT exhibits even greater predictive accuracy (R^2 of 0.994). $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}$ dominates the dataset, with only 6–7 different values per composition axis. Consequently, the model performs exceptionally well in local interpolation but shows reduced dependability in

extrapolation situations. In datasets derived from the literature, where statistical density does not ensure physical generalizability, this trade-off is common.

In PMN-PT, residual analysis demonstrates equal variance error behavior with a symmetric distribution around zero. Underrepresented regions have slightly higher errors, particularly those with extreme field-temperature conditions and compositions doped with BT/ST. However, there is no discernible systematic bias, suggesting that the ensemble model handles data heterogeneity well. Within the dominant compositional regimes of BCZT, residuals are closely clustered; however, outside of these boundaries, they sharply increase, especially in systems that are Ba-deficient or Zr-rich.

An important test of the model's robustness is how well it can learn across different types of structures and ways of measuring. PMN-PT has an appropriate combination of pellet and multilayer samples, which lets the model use binary flags to remember how form factor affects. Physical effects such as field confinement and anisotropic thermal conductivity are encoded by the SHAP values for "Multilayer" and "Textured," which are reflected in precise ΔT_{EC} predictions across device formats. The lack of architectural diversity in BCZT results in less feature learning for behavior that depends on geometry. However, the model makes up for this by using process proxies (sintering parameters) to infer effects related to microstructure. This brings to light an important realization: if the dataset encodes consistent structure–property–process relationships, informative proxy variables can be used in place of missing experimental metadata.

Another sign of a model's strength is that the importance of features stays similar across different training subsets. When training on classified portions of data in PMN-PT, SHAP ranks remain consistent, indicating feature robustness and low sensitivity to sample permutation. Conversely, especially in small training subsets, BCZT demonstrates slight fluctuation in mid-ranking features. This has an effect on transfer learning, and the broader structural and compositional sampling of PMN-PT could make it easier to utilize models in other systems that are similar, like PMN-PZT or BT-modified relaxors. BCZT's fine tailored performance may make it less transferable, but it has predictive capability in recognized areas.

In summary, while both models are high performing, they serve different optimization philosophies. For PMN-PT model, exploratory, tolerant to structural and thermal domain shifts, ideal for hypothesis generation and for BCZT model, precision-tuned, optimal for narrow-window design and high-fidelity predictions within MPB-centered domains.



5. CONCLUSIONS

This thesis developed a data-driven approach for the prediction and the optimization of electrocaloric effect in ferroelectrics. Two lead-based (PMN-PT and PST), and one lead-free (BCZT) system was covered and the study aimed to reveal complex relations between the composition, thermal processing, measurement variables, and finally modelling the electrocaloric temperature change by using the literature data, selection of meaningful features, application of machine learning algorithms. The following key conclusions have been drawn:

Through analysis of over 5000 data points from different electrocaloric systems, it is clearly shown that the electrocaloric performance doesn't respond in a monotonic way to any single parameter. The behavior mostly emerges from the interplay between electric field strength, proximity to transition temperature, and structural configurability. In PMN-PT, the maximum temperature change cluster in the relaxor-ferroelectric boundary where high entropy reconfiguration is possible without complete domain stabilization. The Curies offset showed a peak in 10-60°C window, reflecting the entropy gradient behavior around phase transition.

The correlation and SHAP results shows that sintering parameters have a measurable and often nonlinear effect on the electrocaloric performance. In BCZT, optimal electrocaloric response was strongly linked to sintering around 1375°C for 4-8 hours, where microstructural homogeneity and domain mobility are favored. Deviations from these conditions, either due to under-sintering or over-sintering led to performance degradation.

The thesis also contributed to the literature through its quantitative modeling of experimental context. Direct measurements systematically yielded higher predictions than indirect ones, in line with the literature. Heating cycles tend to show larger entropy change than cooling due to delayed dipole relaxation and thermal hysteresis. These biases, traditionally handled as experimental noise, are here encoded into the model, improving both prediction quality and interpretability.

Bayesian optimization and virtual dataset predictions mapped and guided experimental studies while not only confirming the known physics but generating novel, testable cases. It was seen that BCZT requires precise process tuning for optimal values due to lower spontaneous polarization and higher process sensitivity. PMN-PT benefits more

from structural flexibility, yielding broader design windows for field-induced entropy change. This implies that transfer learning across systems is nontrivial.

5.1. Summary of Contributions

This thesis is one of the first studies to apply machine learning based systematic modeling and optimization to the electroceramic materials. The pre-processing, standardization and collection of data points scattered in the literature and compiling them in a single modeling study creates an important base for data-driven materials science.

The models trained on these datasets resulted with highly accurate predictions for each of the material systems. This results clearly showed that the machine learning models are capable to reveal complex relations within the materials science if the data is given in a meaningful format. On the other hand, SHAP analysis explained the interactions between the input parameters and output properties. These analyses were found to be in line with physical phenomenon. The material systems with different structural and functional characteristics proved that the generalizability and flexibility of the study. Another contribution of the thesis is that providing a systematic recommendation to future works by understanding the existing data and resulting with clear insights on process optimization and measurement condition. Bayesian optimizations were used to identify the highest performance for a given condition. This tool is an important output of the study that can guide the experimental design loop and reduce the trial-and-error efforts.

The virtual dataset concept was created and used in the trained model to have detailed performance maps of electrocaloric cooling performance distribution in temperature, electric field, and composition space. These maps provide a roadmap for the research and visual and numerical prediction of the conditions that are resulting with higher performance.

One of the important contributions of the thesis is providing principles on how to supply the energy need of an electrocaloric component in a system. The triboelectric nanogenerator (TENG) modeling in COMSOL has shown a conceptual start for self-powered systems. Even though the experimental validation and extension of the study is essential, the idea of self-powered cooling systems are potentially feasible.

As conclusion, this thesis did not only provide insights for specific material systems but a methodological direction for the materials science research. Data-driven learning, physics-based explainability and optimization strategies presented in this study are promising for the future studies.

5.2. Opportunities for Future Work

Even though the concept of the study has resulted with strong insights, there are important aspects that should be investigated in the future. First, the datasets can be extended to cover more microstructural information such as grain size, porosity, texture ratio, as they are strongly related with the electrocaloric performance of the material. The challenges of gathering this information in a meaningful structure remains valid. However, lack of this information influence model itself.

The model in this study is focused on achieving higher electrocaloric performance of the electroceramics systems. However, it should be noted that the single objectives might not be enough for a practical application. Therefore, other factors that are influencing the electrocaloric effect should be also addressed.

Finally, as being one of the first optimization study of electroceramics by using machine learning, the study requires to be verified by experimental research as it is guiding. This is essential for the reinforcement of the physical accuracy of the models.

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BIOGRAPHY

Mustafa Çağrı BAYIR received his Bachelor's Degree in Metallurgical and Materials Engineering from Kocaeli University in 2017 with main research area of physical metallurgy and failure analysis in steels. Afterwards, he achieved his Master's Degree in Materials Science and Engineering from Gebze Technical University in 2019 with a thesis on electro-optic thin films. His current main research areas include electrocaloric materials, electro-optic thin films and the application of machine learning to materials science. He is currently working as Quality Assurance Engineer at European Organisation for the Exploitation of Meteorological Satellites (EUMETSAT) in Darmstadt, Germany.



PUBLICATIONS AND PRESENTATIONS FROM THE THESIS

Bayir, M. C., Mensur, E. XGBoost-Based Modeling of Electrocaloric Property: A Bayesian Optimization in BCZT Electroceramics. *Materials* 2025, 18(12), 2682.

Bayir, M. C., Mensur, E. Electrocaloric Property Optimization of PMN-PT Ceramics Using Predictive Modeling. *Journal of Materials Science: Materials in Electronics* 2025, 35, 1097.

Bayir, M. C., Temizel, R. C., Mensur, E. Harnessing Machine Learning for Process Optimization in Lead-Based Electroceramics, MSE Congress 2024, Darmstadt. (Poster Presentation)



APPENDICES

APPENDIX-A: Dataset portion as representation

Pseudo-Ratio	90	10	Stratio	Bt-ratio	Point	Random	Textured	MultiLayer	Upon Coding	Upon Heating	Direct Measurement	Indirect Measurement	Calculation Time/Measurement	Calculation Time/Calculation Time	Sinter Temperature/Size	mean Atomic/mole	mean Electronic/molar	mean Molecular/molar	mean Unfilled	mean (near-superficial) Electric Measurements	T/c	Data#						
90	90	10	0	0	0	1	0	0	0	1	1	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	10	326	-22.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	12	326	-20.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	16	326	-18.6	0.17
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	18	326	-16.6	0.8
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	20	326	-14.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	22	326	-12.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	24	326	-10.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	26	326	-8.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	28	326	-6.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	30	326	-4.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	4	32	326	-2.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	12	326	-20.6	0.47
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	14	326	-18.6	0.41
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	16	326	-16.6	0.4
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	18	326	-14.6	0.4
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	20	326	-12.6	0.27
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	22	326	-10.6	0.2
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	24	326	-8.6	0.18
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	26	326	-6.6	0.17
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	28	326	-4.6	0.16
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	30	326	-2.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	32	326	-0.6	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	34	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	36	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	38	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	40	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	42	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	44	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	46	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	48	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	50	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	52	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	54	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	56	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	58	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	60	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	62	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	64	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	66	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	68	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	70	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	72	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	74	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	76	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	78	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	80	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	82	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	84	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	86	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	88	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	90	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	92	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	94	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	96	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	98	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	100	326	0.4	0
90	90	10	0	0	0	1	0	0	0	1	0	0	0	0	4	1280	2	640000456	23134	0.88	3	149738	95.2	8	102	326	0	