

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**PROCESSING OF BCZT POWDERS BY SOL-GEL
METHOD FOR ELECTROCALORIC APPLICATIONS**

HELİN TEMEL
A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

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FEN BİLİMLERİ ENSTİTÜSÜ

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HELİN TEMEL
YÜKSEK LİSANS TEZİ
MALZEME BİLİMİ VE MÜHENDİSLİĞİ
ANABİLİM DALI

THESIS SUPERVISOR
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GEBZE
2023



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SUMMARY

This study discusses the widespread use of piezoelectric materials in converting mechanical pressure forces into electrical signals. It emphasizes that lead-containing piezoelectric ceramics are harmful to the environment and human health due to their high toxicity. Recent studies have shown that lead-free materials such as BZT-BCT solid solution can serve as a good alternative in piezoelectric applications.

Furthermore, the importance of BZT-BCT ceramics in electrocaloric cooling systems is highlighted. The search for environmentally friendly and cost-effective alternatives has increased interest in electrocaloric effects. In this study, lead-free piezoelectric $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x=0.5$) ceramics with critical phase points are investigated indirectly for their electrocaloric behavior.

The lead-free piezoelectric ceramics were produced using the sol-gel method, aiming to obtain more homogeneous structures. Additionally, the effect of different ball-milling processes on particle size and crystallite size variation on the performance of the ceramics was observed. The structural and electrical properties of the produced samples were characterized. Measurements of dielectric constant, polarization-electric field, and electrocaloric effect were conducted for electrical characterization. When compared with the literature, highly significant values of $\Delta T \sim 1.2\text{-}2.5$ K have been successfully achieved for both ceramics. It is considered that BZT-BCT ceramics are a promising candidate in the search for environmentally friendly electrocaloric materials.

Key Words: Lead-free Piezoelectric, BZT-BCT, Electrocaloric Cooling, Electrical Properties.

ÖZET

Bu çalışma, mekanik basınç kuvvetlerini elektrik sinyallerine dönüştürmek için piezoelektrik malzemelerin yaygın kullanımını ele almaktadır. Kurşun içeren piezoelektrik seramiklerin yüksek toksisiteye sahip olması nedeniyle çevre ve insan sağlığı için zararlı olduğuna vurgu yapmaktadır. Son çalışmalar, BZT-BCT katı çözeltisi gibi kurşunsuz malzemelerin piezoelektrik uygulamalar için iyi bir alternatif olabileceğini göstermiştir.

Ayrıca, BZT-BCT seramiklerinin elektrokalorik soğutma sistemlerindeki önemi vurgulanmaktadır. Çevre dostu ve maliyet açısından avantajlı alternatiflerin arayışı, elektrokalorik etkilere olan ilgiyi artırmıştır. Bu çalışmada, kritik faz noktalarına sahip olan kurşunsuz piezoelektrik $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ($x=0.5$) seramiklerinin elektrokalorik davranışı dolaylı olarak incelenmiştir.

Kurşunsuz piezoelektrik seramikler, daha homojen yapı elde etmek amacıyla sol-jel yöntemi kullanılarak üretilmiştir. Ayrıca, seramiklerin performansı üzerinde farklı bilyalı öğütme işlemlerinin parçacık boyutu ve kristal boyutu değişiminin etkisi gözlemlenmiştir. Üretilen örneklerin yapısal ve elektriksel özellikleri karakterize edilmiştir. Dielektrik sabiti, polarizasyon-elektrik alan ve elektrokalorik etki ölçümleriyle elektriksel karakterizasyon yapılmıştır. Literatürle karşılaştırıldığında, her iki seramik için $\Delta T \sim 1.2-2.5$ K gibi oldukça önemli değerler başarıyla elde edilmiştir. BZT-BCT seramiklerinin çevre dostu elektrokalorik malzemeler arayışında umut verici bir aday olduğu düşünülmektedir.

Anahtar Kelimeler: Kurşunsuz Piezoelektrik, BZT-BCT, Elektrokalorik Soğutma, Elektriksel Özellikler.

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LIST OF ABBREVIATIONS AND ACRONYMS

<u>Abbreviations</u>	<u>Explanations</u>
<u>and Acronyms:</u>	
°	: Degree
Å	: Angstrom
°C	: Degrees Celsius
%	: Percentage
Θ	: Bragg angle
ϵ	: Dielectric permittivity
ϵ_0	: Permeability of vacuum
ϵ_r	: Dielectric constant
ϵ_m	: Maximum dielectric constant
$\mu\text{C}/\text{cm}^2$	: Micro coulomb/ square centimeter
μm	: Micrometer
ΔT	: Electrocaloric temperature change
ΔT_m	: Degree of deviation from Curie-Weiss
ΔS	: law
C	: Adiabatic entropy change
cm	: Capacitance
d_{33}	: Centimeters
min	: Piezoelectric charge coefficient
E	: Minute
E_c	: Electric field
t	: Forcing electric field
$\tan \delta$	: Tolerance factor
Gr/cm^3	: Dielectric loss
Hz	: Gram/cubic centimeter
KHz	: Hertz
kV	: Kilohertz
kV/cm	: Kilovolts
	Kilovolt/centimeter

Log	: Logarithm
MPa	: Mega pascal
mm	: Millimeter
pm/V	: Picometer / volt
pC/N	: Pico coulomb / newton
P	: Polarization
P _{max}	: Maximum polarization
P _r	: Residual polarization
P _s	: Self-polarization
T	: Temperature
T _c	: Curie temperature
T _m	: Maximum permeability temperature
T _{T-C}	: Tetragonal-Cubic phase transition temperature
T _{R-T}	: Rhombohedral-Tetragonal phase transition temperature
V	: Volts
ABO ₃	: Perovskite structure
BaTiO ₃	: Barium titanate
BaBi ₄ Ti ₄ O ₁₅ (BaBiT)	: Barium bismuth titanate
Bi ₄ Ti ₃ O ₁₂ (BiT)	: Bismuth titanate
BiNaTiO ₃ (BNT)	: Bismuth sodium titanate
BZT-BCT	: Barium zirconium titanate-barium calcium titanate
Ca	: Calcium
ECE	: Electrocaloric Effect
KNaNbO ₃ (KNN)	: Potassium sodium niobate
MFS	: Morphotrophic phase boundary
PbTiO ₃	: Lead titanate
PbZrO ₃	: Lead zirconate
PNR	: Polar nano region
PT	: Lead titanate
PZT	: Lead zirconate titanate
SEM	: Scanning electron microscope
Ti	: Titanium

TP	: Triple phase limit
XRD	: X-ray diffraction
Zr	: Zirconium
0.5BZT-0.5BCT	: $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-}0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$

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1. INTRODUCTION

Piezoelectric materials are widely used in modern technology and in the production of many electronic devices in daily life, thanks to their ability to convert mechanical pressure forces into electrical signals [1]. Lead-based piezoelectric ceramics such as PZT have been widely used in piezoelectric applications for more than half a century due to their superior properties [2]. However, it is harmful to human health and the environment due to the high toxicity of lead-containing ceramics, which can evaporate at high temperatures ($\sim 550^{\circ}\text{C}$). The use and recycling of lead-based piezoelectric ceramics is of great concern. Therefore, the necessity to develop lead-free materials with piezoelectric properties that can replace PZT has gained importance.

Recent studies show that BaTiO_3 based BZT-BCT solid solution is a good option among lead-free piezoelectric materials. Although this material is in a narrow temperature range, it has a higher piezoelectric coefficient ($d_{33} \sim 620 \text{ pC/N}$) than soft PZT, which increases the importance of BZT-BCT ceramics [2].

The Sol-Gel method is a versatile and inexpensive technique for creating a wide variety of materials. It has advantages such as low-temperature processing, controlled particle size, and the ability to form materials with specific properties. However, the method has disadvantages such as long processing times, limited final product size, limited mechanical properties, and limited purity of the final product. Despite these limitations, Sol-Gel method is an important technique that has found application in many fields of science and technology. It is possible to produce ceramics with a more homogeneous structure with the Sol-Gel method.

When the electric field inside a material changes, the ECE effect results in a change in the substance's temperature. In contrast to the traditional mechanical or magnetic cooling methods, the cooling process can be carried out using the electrocaloric effect in this way that is more energy and environmentally friendly [18]. Recent studies show that ECE is a potential alternative, especially in terms of energy density and conversion efficiency [18]. Within the scope of the thesis study, besides the production and structural-electrical properties of BZT-BCT lead-free ceramics obtained by applying different ball-mill methods, the electrocaloric effect in BZT-BCT ceramics was also investigated.

2. LITERATURE REVIEW

2.1. Piezoelectric Properties

The capacity of some materials to produce an electrical charge when subjected to mechanical stress is known as piezoelectricity. This phenomenon was first discovered by French scientists Jacques and Pierre Curie in 1880, and they observed that certain crystals, such as quartz, produce a small electric charge when they are mechanically deformed. Since then, a wide variety of materials have been found to exhibit piezoelectric properties, including ceramics, polymers, and even some biological materials. Some ceramics, such as lead zirconate titanate (PZT), and some polymers, such as polyvinylidene fluoride (PVDF), are other typical piezoelectric materials [1].

Piezoelectric materials are typically crystalline and have a polar axis, meaning that their atoms are arranged to form a permanent dipole moment. When a mechanical stress is applied to the material, the dipole moments are distorted, resulting in an electric charge. The magnitude of the generated load is directly proportional to the applied voltage, and the direction of the load is determined by the direction of the voltage.

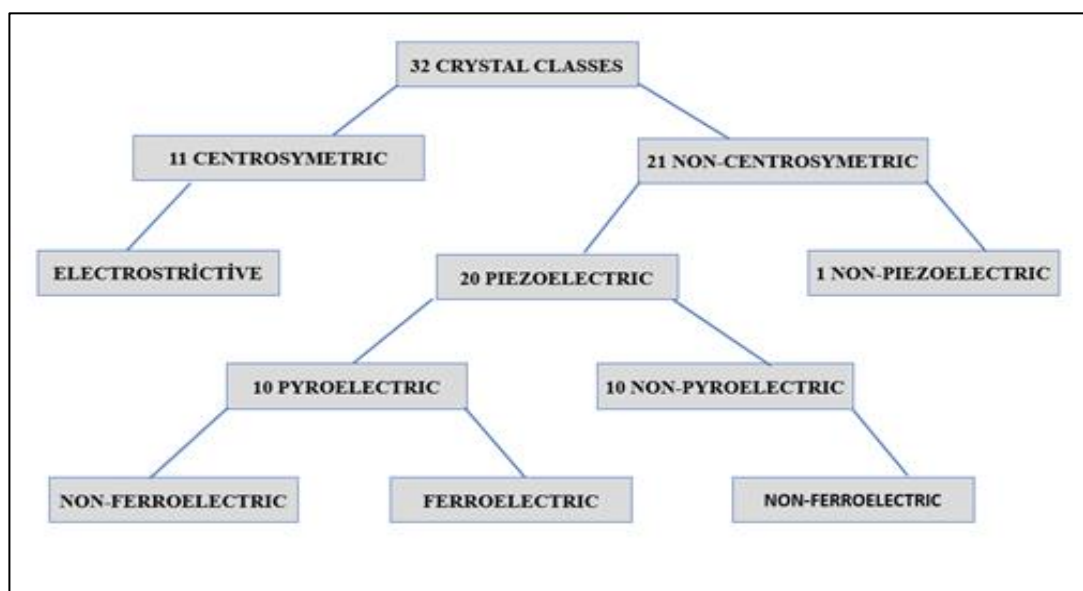


Figure 2.1: Classification of crystal classes according to their ferroelectric, pyroelectric, and piezoelectric properties.

There are 32 crystal classes available. Of these, 11 have centers of symmetry. This means that when subjected to a mechanical force, an electrical dipole moment will not occur since the movements of the ions are symmetrical. Of the remaining 21 classes, 20 have no centers of symmetry and dielectric polarization develops under mechanical stress. These materials are known as 'piezoelectric materials' [2].

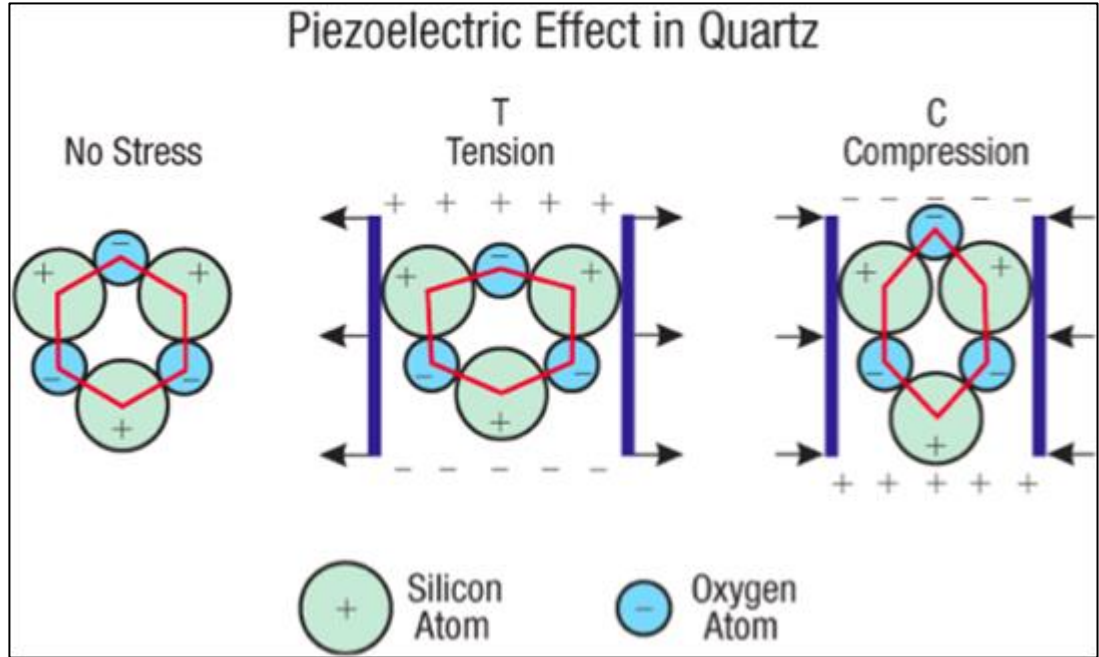


Figure 2.2: Piezoelectric effect resulting from pressure effect in quartz crystal [3].

When a mechanical force is applied to these materials, a potential difference occurs on the material. Thus, the mechanical effect turns into electrical magnitude. This behavior is called direct or motor piezoelectric effect. The linear relationship resulting from this effect can be formulated by equation 2.2. The electrical displacement D_i in the Dijk equation is a third-order tensor, its piezoelectric coefficient, and its unit is C/N [3].

$$D = d X \quad (\text{Flat Piezoelectric Effect}) \quad (2.1)$$

$$\chi = d E = d^t E \quad (\text{Reverse Piezoelectric Effect}) \quad (2.2)$$

In addition to the piezoelectric effect, some materials also have the capacity to change their size or form in response to an applied electric field. This effect is used in actuators and other mechanical devices such as ultrasonic transducers.

It is possible to determine the piezoelectric behavior of the material by its 'piezoelectric coefficient'. The piezoelectric voltage coefficient, denoted by g , is the proportionality coefficient between the electric field produced by the voltage applied to the material (stress, σ) in the case of the direct piezoelectric action [3].

$$E = g \cdot \sigma \quad (2.3)$$

2.2. Ferroelectric Properties

In a ferroelectric material, the atoms are arranged in such a way as to allow the existence of a spontaneous electrical polarization. This polarization can be reversed when an external electric field is applied. The ability of a ferroelectric material to exhibit this reversible polarization is known as the ferroelectric effect.

Ferroelectricity occurs in materials that have a non-centrally symmetrical crystal structure, that is, the crystal structure does not have a center of symmetry. The occurrence of a spontaneous electrical polarization is made possible by this lack of symmetry. Perovskites like barium titanate and lead-based compounds like lead zirconate titanate are examples of common ferroelectric material types.

The relationship between the electric field we apply and the polarization of ferroelectric materials is defined by a hysteresis loop. The area inside this curve gives the energy expended to rotate the electrical dipole moments over a cycle. This energy consumed as heat energy is called dielectric loss.

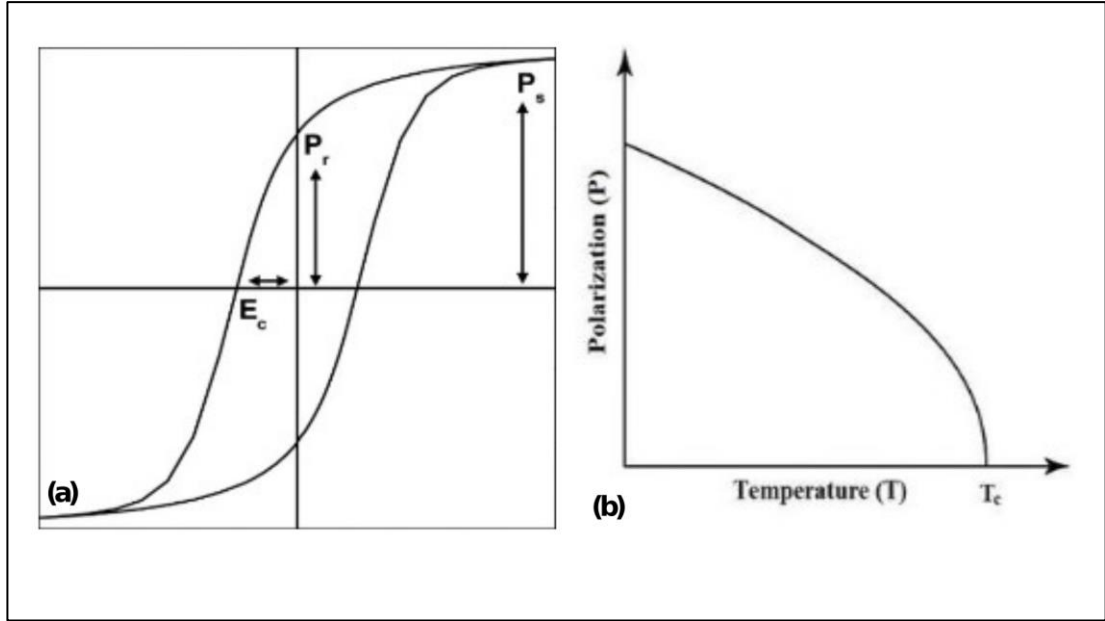


Figure 2.3: a) typical P-E hysteresis loop for a ferroelectric material at TC temperature, and b) a ferroelectric material's change in polarization with temperature.

Ferroelectricity refers to the phenomenon in which a spontaneous polarization state exists below a certain temperature known as the transition temperature (T_c), often called the Curie temperature. A phase transition from a crystalline polar state to a non-polar state takes place at T_c . Reversible polarization, anomalous properties, and nonlinearity are three prominent characteristics of ferroelectrics.

When the crystal is in a paraelectric state above T_c , it behaves similarly to paramagnetic materials, showing a rapid decrease in dielectric constant (ϵ) with increasing temperature [4],[5]. The dependence of the dielectric constant on the temperature above the Curie point can be explained by the Curie-Weiss law:

$$\epsilon = \epsilon_0 + \frac{C}{T - T_c} \quad (2.4)$$

Here ϵ_0 represents the temperature independent component of the dielectric constant, C is the Curie constant, T_0 is the Curie-Weiss temperature. Due to the presence of electronic polarization, T_0 differs from the Curie point T_c . Both first order and higher (second order) phase transitions are possible for T_c . For a second-order phase transition, $T_0 = T_c$ in the case of a first-order phase transition, and $T_0 < T_c$

otherwise. Since T is near to T_0 and much less than the $C(T-T_0)$ component, the temperature-independent term can typically be omitted [8].

Ferroelectric materials have distinctive electrical properties that have uses in numerous potential technological applications. Among these applications, non-volatile memory devices called ferroelectric random access memory (FeRAM) come to the fore. FeRAM represents a valuable form of computer memory that can maintain data integrity even when there is no power, and replaces traditional volatile memory solutions.

Apart from permanent memory devices, ferroelectric materials are also used in sensors and actuators. Ferroelectric materials can also be used as piezoelectric materials. This means that they can convert mechanical tension into electrical charge and vice versa. This property makes ferroelectric materials useful for many sensor applications. Ferroelectric materials are also used in actuators, which are devices that can convert electrical charge into mechanical motion [4].

Another potential application of ferroelectric materials is energy storage. Ferroelectric capacitors, also called "ferroelectric energy storage devices", have a high energy density and can be used in applications such as electric vehicles and renewable energy systems [4].

Ferroelectricity, then, is the ability of some materials to spontaneously produce an electrical polarization that is reversible by an externally applied electric field. Ferroelectric materials have a centrally non-symmetrical crystal structure and are found in many types of materials such as perovskites and lead-based materials. Ferroelectric materials have many potential applications, such as non-volatile memory devices, sensors, actuators, and energy storage.

2.2.1. Perovskite Structure

Perovskite is a special crystal structure found in many types of materials, as well as in ferroelectric materials. The perovskite structure can be characterized by the presence of a metal cation surrounded by a group of anions located in a certain order in the center of the crystal. Additionally, ferroelectric perovskites have the ability to change their spontaneous electric polarization in response to an external electric field [9].

The perovskite structure derives its name from the perovskite mineral first discovered in the Ural Mountains of Russia in 1839. The basic structure of perovskite is that in the center of the crystal there is a metal cation surrounded by a group of anions in a certain arrangement. The most common type of perovskite is ABX_3 where A is a metal cation, B is a metal or metalloid cation, and X is an anion. 'type. The metal cation at the center of the crystal is typically a transition metal such as titanium or niobium. Anions are typically oxygen or halide ions. With the inclusion of doping atoms, the phase transition properties and transition temperature of ferroelectrics replaceable [9]-[10]-[16].

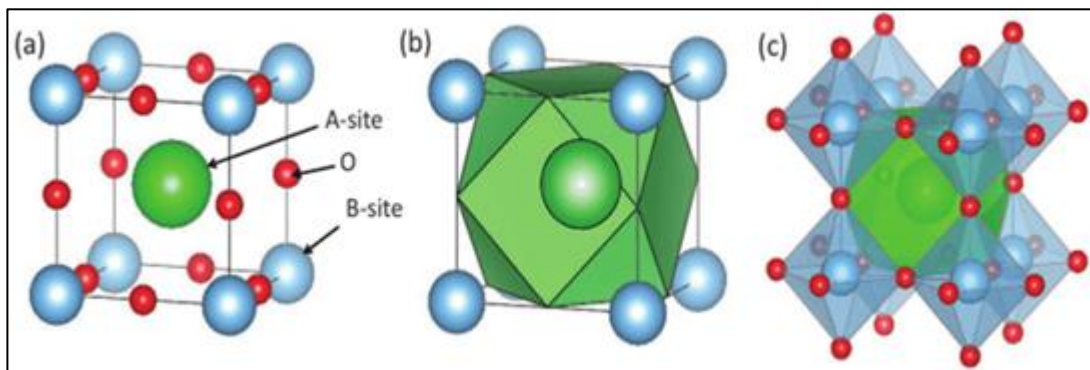


Figure 2.4: An ideal cubic perovskite structure of ABO_3 , (a) Unit cell (the smaller region B is chosen as the origin of the unit cell, while in Figure 1.2a the larger region A is an origin); (b) coordination of the A-site ion; and (c) coordination of the B-site ion.

The perovskite lattice arrangement is shown in figure 2.4. The most common type of ferroelectric perovskite is a special type of perovskite called a relaxor ferroelectric, with the chemical formula $(1-x)ABO_3$, where A and B are metal cations and x is a small fraction. Barium titanate ($BaTiO_3$), which is widely employed in a variety of electronic applications, is the most well-known ferroelectric perovskite.

2.2.2. Phase Transition and Curie (T_c) Temperature

A phase transition can be defined as a change in the physical state of a material, such as a transition from solid to liquid or liquid to gas. A well-known type of phase transition is the ferroelectric phase transition that occurs in ferroelectric materials.

By using an external electric field, it is possible to reverse the spontaneous electrical polarization of ferroelectric materials. These materials exhibit a remarkable ability to change the direction of their polarization when exposed to an applied electric field.

Curie temperature, or T_c , is defined as the temperature at which a ferroelectric material spontaneously loses polarization. Above the Curie temperature, the material is in the paraelectric phase and therefore does not exhibit ferroelectric properties. The substance is in the ferroelectric phase and exhibits spontaneous polarization below the Curie temperature. Curie temperature can vary depending on the particular ingredient and the way it's prepared. As the Curie temperature is increased, the permeability decreases according to the “Curie-Weiss” law given in Equation 2.5 [11]-[14].

$$\epsilon_r = \frac{A}{T - \theta_c} \quad (2.5)$$

The temperature at which the crystal switches from one ferroelectric phase to another might be referred to as the transition temperature if there are many ferroelectric phases. One of the main goals of research on the properties of barium titanate has been to understand the mechanism of ferroelectricity. BaTiO_3 has a cubic structure above the Curie temperature (120°C). The Curie temperature depends on the lattice parameters of this temperature point, which is the beginning of self-polarization as the temperature drops. The lattice constants can be reduced by hydrostatic pressure and therefore the Curie temperature point can be changed accordingly. It has been determined that the Curie temperature of the BaTiO_3 crystal shifts linearly to lower temperature values at increasing pressure values (Merz, 1950) [11]-[12]-[13].

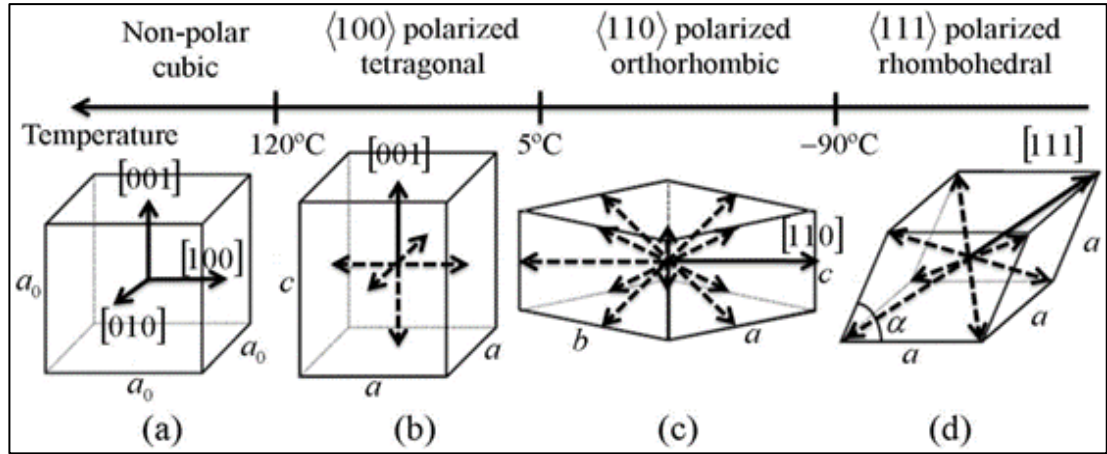


Figure 2.5. Crystal structure change of BaTiO₃ crystal with temperature.

In the literature, the Curie temperature for the BaTiO₃ crystal is 120°C. Above this temperature, the crystal has a cubic structure (Figure 2.5). Between 120°C and 5°C the structure is quadrilateral and the direction of self-polarization is along the c -axis of the quadrangular structure. Quadrangular unit cell at about 5°C. This structure remains stable between 5°C and -90°C. Similarly, as the unit cell lengthens in the direction of the volume diagonals at approximately -90°C, the rectangular structure turns into a rhombic structure [13].

2.2.3. Domain and Domain Wall Movement

A unique category of materials known as ferroelectric materials exhibits self-polarization, or the ability to maintain a dipole moment even in the absence of an external electric field. This characteristic results from the alignment of electric dipoles, or fields, within the substance. The domains are the areas of the material where the dipoles are oriented in the same plane.

In a ferroelectric material, there are generally multiple fields with different dipole orientations. The area wall can be called as the boundary between two areas. These walls separate regions with different polarization. It can be moved or prevented from moving by applying an external electric field [16].

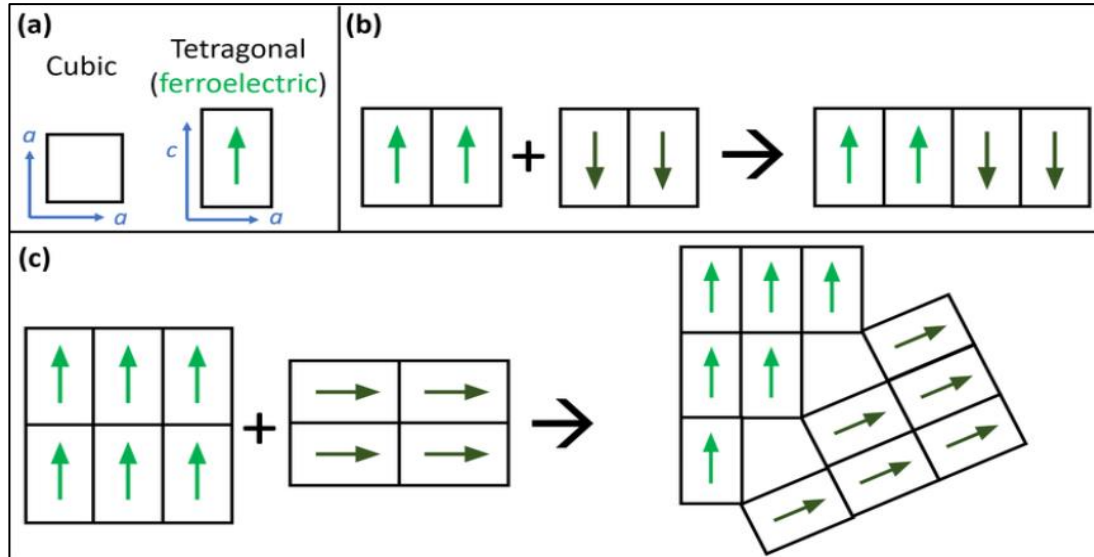


Figure 2.6: Ferroelectric field wall formation in PbTiO_3 with polarization parallel to (a): c . (b): for 180° DW (c): for 90° DW [15].

2.2.4. Hysteresis Cycle

The capacity of ferroelectric materials to alter their polarization state in response to an externally applied electric field is one of their most significant recognized features. The term "ferroelectric" or "polarization switching" refers to this quality.

When an external electric field is applied to a ferroelectric material, the fields within the material will move or be redirected in response to the field, causing the material's polarization to change. This phenomenon is known as the hysteresis loop. The hysteresis loop is a graph of the polarization state of the material as a function of the applied electric field.

The hysteresis loop is generally represented by a loop on a graph with the x-axis representing the applied electric field and the y-axis polarization. The loop starts at the origin where the polarization and electric field are zero. When the electric field increases, the polarization of the material increases and the loop moves upward. At a certain point called the coercive field, the polarization reaches its maximum value and the loop reaches the top of the loop [6].

If the electric field continues to increase, the polarization of the material begins to decrease. The loop moves to the right. At a certain point, called the permanent field, the polarization becomes zero and the loop reaches the far right point of the loop. Here the residual electric field is removed and the material returns to its original state.

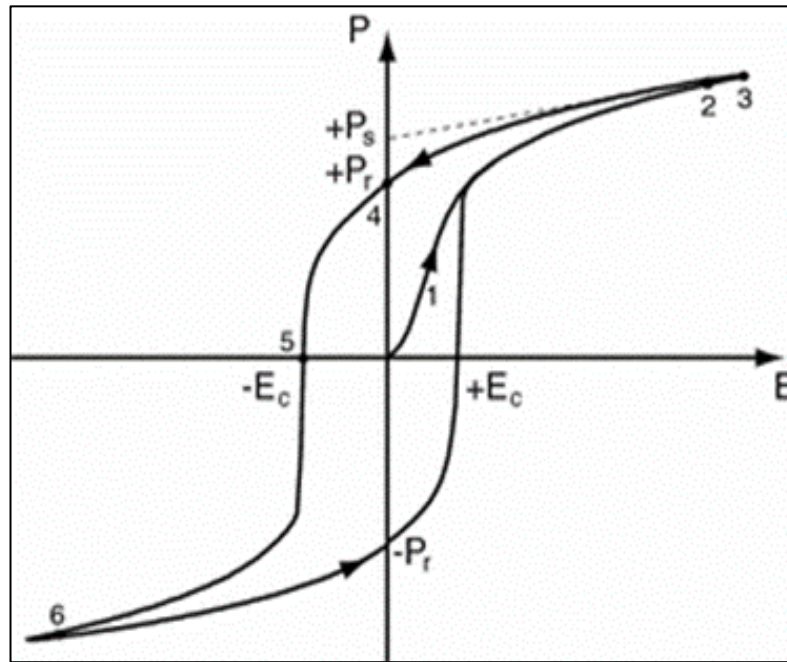


Figure 2.7 Ideal hysteretic behavior of ferroelectric polarization in an applied electric field at macroscopic scale. [Original picture by N. Stucki]

As can be seen in Figure 2.7, the total polarization corresponds to all unit cells that are oriented consistently with the field as the field is raised in the direction (1), starting from the origin ($P=0, E=0$, macroscopically possible if there are multiple fields counterbalancing, for example), and gradually increasing towards the saturation value (2). Due to dielectric charge, the polarization intensifies with increasing electric field (3). This polarization value attained at $E = 0$ is known as permanent polarization and is denoted as $+P_r$. After reducing the field to zero, the total polarization undergoes a tiny reduction but stays non-zero [6],[17].

As the electric field intensifies in the opposite direction, it undergoes a sudden transition at a given field intensity, known as the polarization coercive field, denoted as $-E_c$. With further increase in field, the polarization eventually saturates. Afterwards, a simple dielectric reaction takes place again (6). When the electric field is reversed, this behavior is frequently seen. It also creates a symmetrical hysteresis loop characterized by switching events occurring at $\pm E_c$.

The extrapolation of the polarization value in the zero field at high fields, where the tiny decline in polarization is caused by the charge, is how self-polarization, or P_s , is typically characterized. P_r and P_s should be equal in a perfect world. In practice, P_s

can be quite near in single crystals but is typically higher in polycrystalline materials [17].

The hysteresis loop is dependent in shape, on the microstructure of the material, the presence of defects or impurities, temperature, and a number of factors. The coercive field and the permanent field are also affected by these factors. This is used to describe the properties of the material.

2.3. Ferroelectric Materials

2.3.1. Lead-Free Ferroelectric Materials

Lead-free ferroelectrics are a new group of materials developed as an alternative to the most well-known lead-based ferroelectric materials such as lead zirconate titanate (PZT). Ferroelectrics are known for their ability to have a natural electric polarization that can be reversed by an externally applied electric field. However, the presence of lead element in ferroelectric materials has raised concerns in the field of toxicity and environmental impact. Lead is a toxic metal that can harm many vital systems in humans and animals. At the same time, its persistence in the environment is long and it is known to pose a significant environmental hazard due to its accumulation in the food chain [2],[6].

Due to these disadvantages, researchers are investigating lead-free ferroelectric materials as an alternative to PZT. Examples of lead-free piezoelectric materials include BaTiO_3 (BT), BiNaTiO_3 (BNT), BiKTiO_3 (BKT), KNaNbO_3 (KNN), and other perovskite compounds. In addition, non-perovskite bismuth layered structures (BLSF) and tungsten-bronze type ferroelectrics are also seen as suitable alternatives. Bismuth ferrite, a class of lead-free ferroelectric materials, has been shown to have ferroelectric properties similar to PZT. It is also known to be non-toxic and environmentally friendly. Another class of lead-free ferroelectric materials are known as strontium-based compounds such as strontium bismuth tantalate ($\text{SrBi}_2\text{Ta}_2\text{O}_9$). $\text{SrBi}_2\text{Ta}_2\text{O}_9$ was also found to have similar or even more advanced ferroelectric properties when compared to PZT. One of the most researched materials among lead-free materials is BaTiO_3 . BaTiO_3 is a ferroelectric material with a perovskite structure. BaTiO_3 has a highly polarized character and is also known to have high dielectric strength [18].

Lead-free ferroelectric materials have many potential advantages over conventional lead-based ferroelectric materials. They are environmentally friendly, making them a more sustainable material for applications where toxicity and environmental impact are concerned. They are also more stable and have higher temperature tolerance. This allows the device to operate more robustly and reliably. In addition, lead-free ferroelectric materials can be synthesized from lower cost and more readily available raw materials, which provides the advantage of reducing the cost of equipment in production [18],[19].

In addition to these advantages, there are some problems that must be overcome before lead-free ferroelectric materials can fully replace PZT in all applications. For example, these materials are generally known to have lower dielectric constants, which may limit their performance for some applications. Also, having lower Curie temperatures makes them less stable at higher temperatures. In addition, research on these materials is still ongoing and it is a known fact that more studies are needed to fully understand their properties and potential applications [19].

2.3.2. BaTiO₃ Type Ferroelectrics

BaTiO₃ is a particularly interesting material due to its high Curie temperature. BaTiO₃'s high Curie temperature provides an advantage, allowing it to retain its ferroelectric properties at elevated temperatures. This makes it suitable for use in a wide variety of applications.

BaTiO₃ is a piezoelectric material, meaning it has the ability to generate an electric charge when it is mechanically deformed. This property makes it an ideal lead-free ferroelectric material for use in pressure sensors, accelerometers and other types of sensors based on the piezoelectric effect.

Another usage area of BaTiO₃ is actuators, which are devices that convert electrical energy into mechanical energy. BaTiO₃ actuators are known to be used in a wide variety of applications, including the control of microelectromechanical systems (MEMS) and optical systems. BaTiO₃ actuators are suitable for operation at high temperatures due to the high Curie temperature, making them suitable for use in harsh conditions [1],[6].

One application area of BaTiO₃ is data storage. Since BaTiO₃ is a ferroelectric material, it has the ability to maintain electrical polarization even when the external

applied electric field is removed. This property makes it an ideal material for use in ferroelectric random access memory (FeRAM), a type of non-volatile memory that can retain data even when the power is turned off. It can be said that BaTiO₃ has a highly polarized character. It is also known to have a high dielectric strength. Therefore, it is a potential material candidate for electrocaloric cooling, another important use. One of the major advantages of the perovskite structure is its ability to accommodate doping in both the A and B sites. This property provides significant advantages for introducing dopant atoms and tailoring the material's properties to meet specific requirements [1]-[6]-[10].

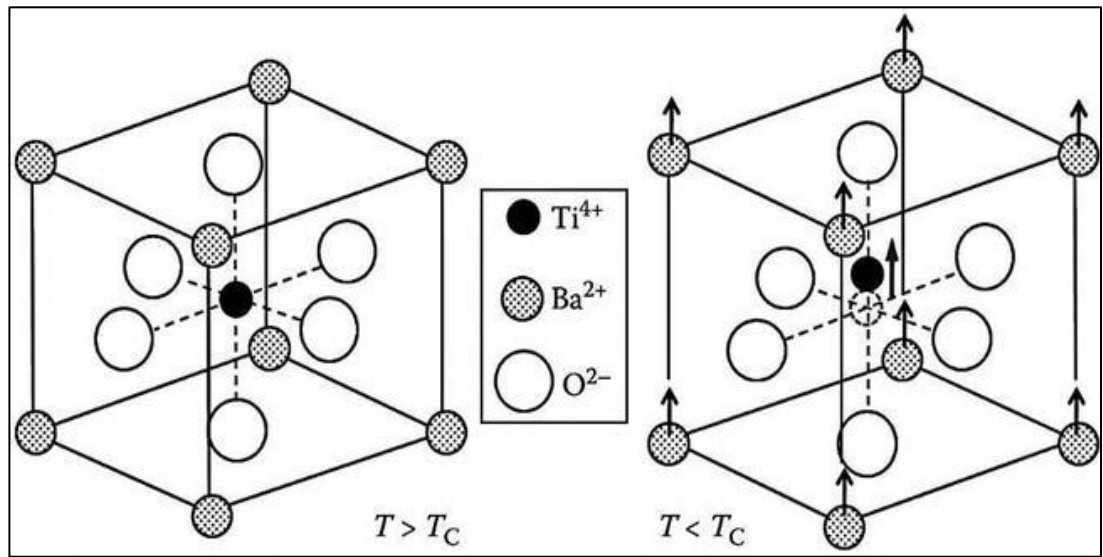


Figure 2.8. Structures of BaTiO₃.

Although it has many advantages, it is known that there are some disadvantages of using BaTiO₃ as a ferroelectric material. One of the main challenges is controlling the crystal structure of BaTiO₃. It can be said that BaTiO₃ exists in several different crystal structures, including perovskite structure, tetragonal structure and cubic structure. Each of these crystal structures has different properties and there are difficulties in controlling the crystal structure during the synthesis process [2].

It is known as a result of researches that the temperature change (ΔT) values of lead-free materials for electrocaloric (EC) applications are not yet sufficient for use in cooling technologies. In conclusion, extensive research has been carried out to investigate the EC properties of materials through the development of various doping strategies, and these studies have focused on unraveling the mechanisms that can

increase the electrocaloric effect in materials. By understanding these mechanisms, the researchers aim to improve the performance and efficiency of electrocaloric materials for potential advances in cooling technologies.

2.3.3. Effect of Doped for Piezoceramics

Piezoceramics is a type of ceramic material that exhibits piezoelectric properties, that is, they can convert mechanical stress into electrical energy and vice versa. Doping, the process of adding impurities to a material, affects the piezoelectric properties of piezoceramics.

One way that doping affects piezoceramics is by making changes in the crystal structure of the material. For example, doping of piezoceramics with certain elements can induce a phase transition from a non-piezoelectric state to a piezoelectric state. This can greatly improve the piezoelectric properties of the material and can be predicted to become more efficient at converting mechanical energy to electrical energy.

Another way in which doping can affect piezoceramics is by modifying the electrical conductivity of the material. Doping of piezoceramics with elements such as lithium or sodium increases the electrical conductivity of the material, which contributes to its performance in devices based on the material's piezoelectric properties.

In addition, doping can also affect the mechanical properties of piezoceramics. Doping with elements such as titanium increases the hardness and strength of the material, which can make the material more resistant to mechanical stress.

However, doping can have both positive and negative effects on piezoceramics. For example, the incorporation of impurities into the material can result in the formation of defects in the crystalline structure that can adversely affect the piezoelectric properties of the material. In addition, doping can reduce the overall quality of the material and its performance may be impaired in certain applications.

In general, it can be said that doping has both positive and negative effects on the properties of piezoceramics. While it can be used to improve the performance of the material in certain applications, if it is not done properly, it can lead to a decrease in quality and performance. Careful selection of additive elements and precise control of doping levels are key considerations to optimize the properties of piezoceramics.

2.3.4. Zr Doped BaTiO₃ ((1-x)Ba(Zr_{0.2}Ti_{0.8}) O₃) Ceramic System(BZT)

Ba(Zr_{0.2}Ti_{0.8})O₃, also known as barium zirconium titanate, is known as an extraordinary ferroelectric and piezoelectric material. Changes can be made on its structural and electrical properties by applying doping and sintering processes. It has been observed in studies that with increasing Zr⁴⁺ doping concentration, it exhibits remarkable changes in material properties. Specifically, the dielectric constant increases as the Curie temperature and dielectric loss decrease. These changes contribute to the material's improved performance and improved efficiency in a variety of applications requiring ferroelectric and piezoelectric properties [20].

Zr-doped BaTiO₃ ceramic materials are well suited for a wide range of applications due to their distinctive characteristics. For instance, they have high piezoelectric coefficients and dielectric constants, which make them perfect materials for use in sensors and capacitors, among other electrical devices. In addition, they have high thermal stability and low dielectric loss, making them the ideal material for use in high temperature applications.

It is possible to synthesize Zr-doped BaTiO₃ ceramic systems by various methods such as solid state reaction, sol-gel and hydrothermal methods. The effects of zirconium (Zr) additives on the structure of Barium Titanate (BaTiO₃) ceramics may vary depending on the additive level used and the synthesis method [20].

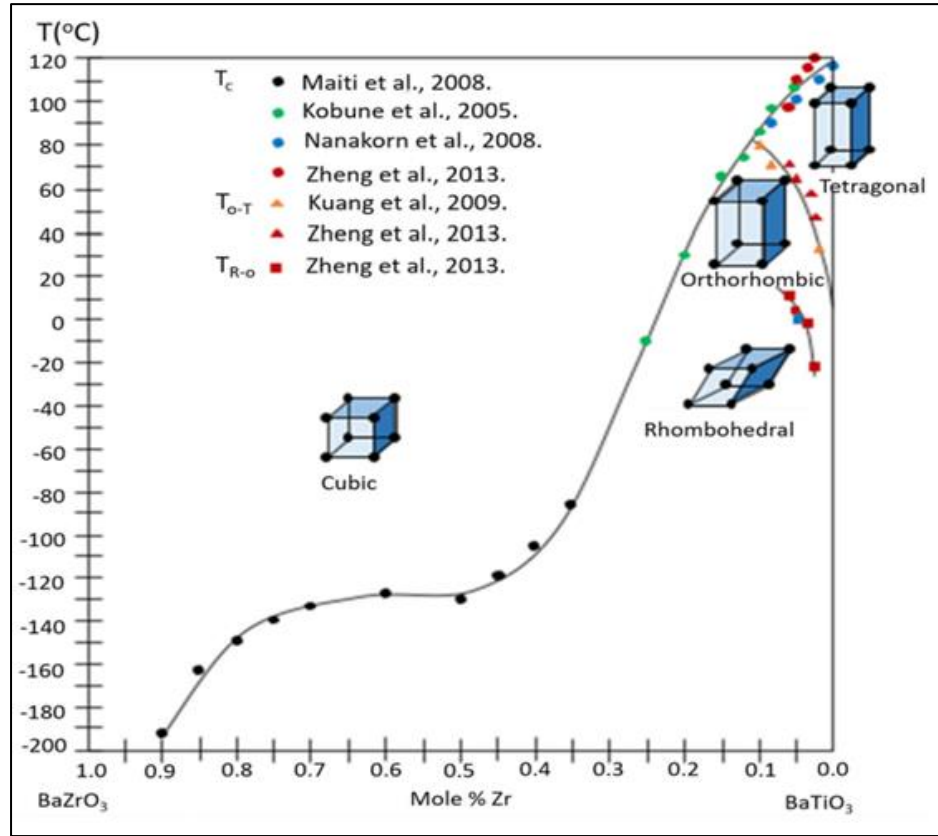


Figure 2.9. Phase transition of $\text{BaZr}_x\text{Ti}(1-x)\text{O}_3$ based on dielectric permittivity measured at 1 kHz (composition vs. temperature).

In BaTiO_3 ceramics, Zr doping causes a phase change from the tetragonal to the cubic phase, which may have an impact on the material's piezoelectric capabilities. In addition, it also changes the symmetry of the crystal structure. This may have some effect on the properties of the material. Zr doping can affect the microstructure of BaTiO_3 ceramics while causing the formation of small, homogeneously dispersed Zr-rich areas in the ceramic matrix. This can lead to improved piezoelectric properties as well as increased mechanical strength and thermal stability [20]-[21]-[22].

Zr doping can also affect the porosity of BaTiO_3 ceramics by causing a decrease in the amount of pores in the ceramic matrix. This results in the formation of a more dense and homogeneous microstructure, which can improve the properties and performance of the material in certain applications. By encouraging the diffusion of titanium ions into Zr-rich regions and vice versa, Zr doping can also have an impact on the diffusion characteristics of BaTiO_3 ceramics.

2.3.5. $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ - $x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ Ceramic System (BCZT)

$((1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3)$ - $x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramic system is composed of two perovskite type oxides $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ and $\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$. is a solid solution. It is possible to replace the composition with the value of x ranging from 0 to 1. The crystal structure of this system can be said to be perovskite structure characterized by a repeating array of vertex-sharing oxygen tetrahedron surrounding a metal ion [26,27,28]. The $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ component has a quadrangular crystal structure with $P4mm$ space group symmetry. $\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ component is known to have a cubic crystal structure with $Pm3m$ space group symmetry. Since the composition of the system is changed by changing the value of x , the crystal structure of the system will also change by being affected [23].

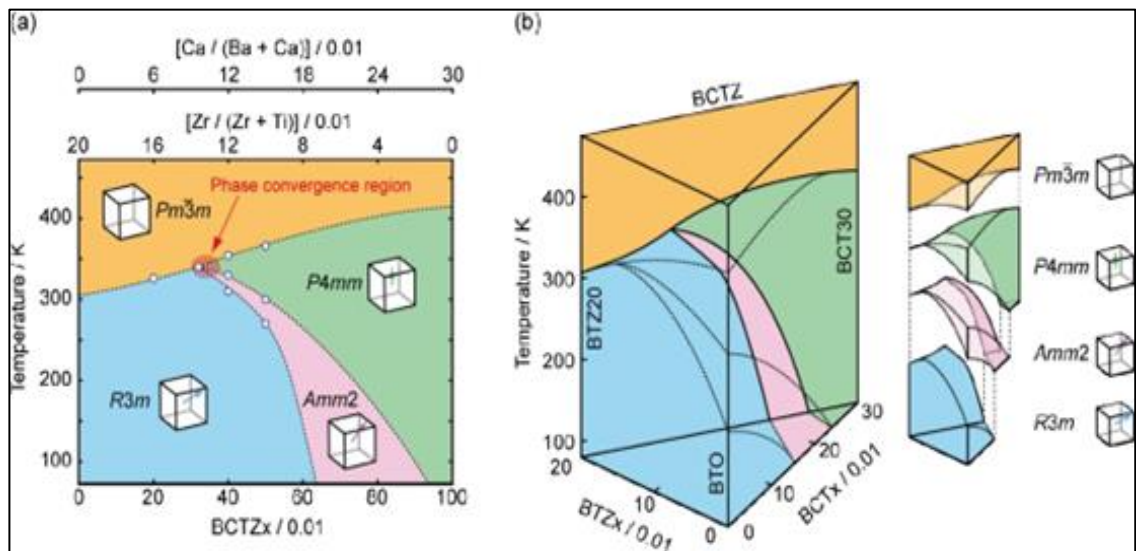


Figure 2.10. (a) Phase diagram of BCTZ. (b) 3D phase diagram of the BCTZ [23].

The structural properties of this ceramic system can be characterized by the crystal structure and composition of the system. The lattice constants, unit cell volume, and coordination environment of metal ions will change, influenced by the composition change. It can be said that the dielectric properties, piezoelectric properties and ferroelectric properties of the system will also be affected by the crystal structure and composition.

Recent research has focused on the exceptional piezoelectric properties of solid solution $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$, abbreviated as 0.5BZT–0.5BCT or BCZT. These ceramics show a high piezoelectric coefficient of 620 pC//. It is known that compositions close to the polymorphic phase boundary exhibit superior properties. However, it might be required to mention that the BCZT material's temperature stability is generally poor as a result of the polymorphic phase border between the rhombic and quadrangular phases' steepness [9]. The greatest values of the piezoelectric coefficient d_{33} are only observed in a small temperature range around room temperature, according to earlier studies. It has been discovered that even a slight departure from room temperature of 10–20 °C results in large drops in d_{33} of up to 40% [28].

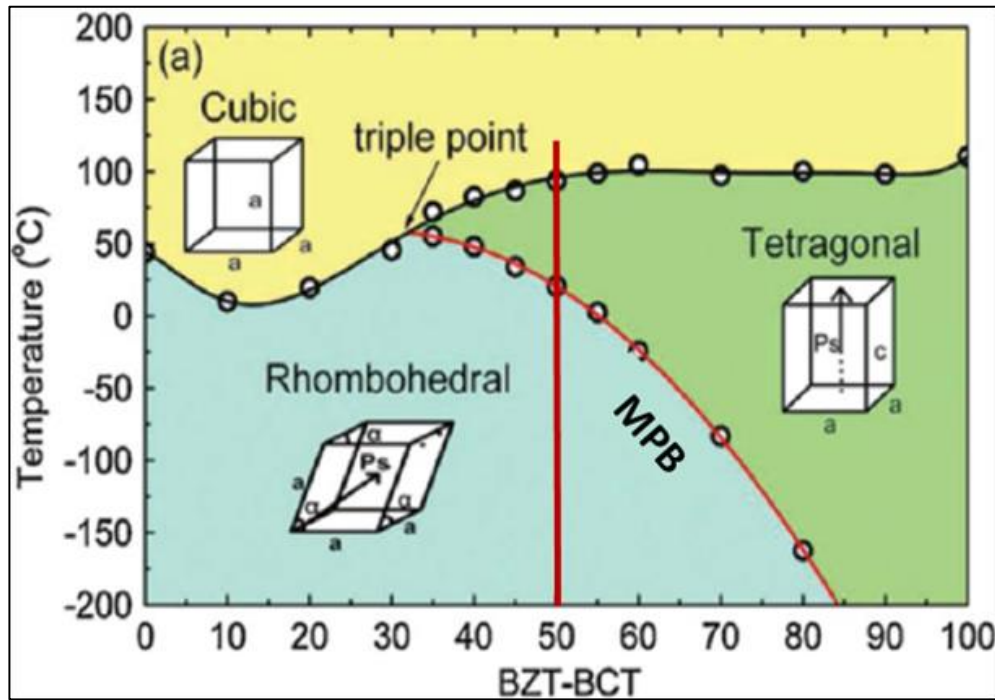


Figure 2.11: Phase diagram of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ composition.

As can be seen from the diagram in Figure 2.11, this composition corresponds to a point at the morphotrophic phase boundary (MPB) at room temperature [2]. There are 6 possible polarization directions for the quadrilateral structure and 8 for the rhombic structure in the MPB composition. As phase combinations will happen around the MPB, a total of 14 potential polarization orientations are available. This causes the

material to polarize easily and exhibit high piezoelectric and dielectric properties under an electric field [2].

Within the scope of the thesis study, $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$, $x=0.5$ composition was investigated due to its morphotropic phase boundary.

2.4. Electrocaloric Effect

2.4.1. History of Electrocaloric Effect

The electrocaloric effect (ECE) can be defined as the temperature change experienced by a material when exposed to an electric field. Although first observed in the early 1900s, it wasn't studied extensively until the 1950s, when researchers began investigating its intricacies. ECE can be said to hold promise to revolutionize the field of refrigeration by providing a tool for developing energy efficient and environmentally sustainable refrigeration systems. By taking advantage of this effect, it is aimed to design new cooling technologies that offer significant improvements in energy saving and ecological impact.

The history of ECE can be said to date back to the early 20th century, when scientists first observed the phenomenon in ferroelectric materials. In 1917 B.E. Spicer noted that he observed a change in temperature in a barium titanate ceramic when an electric field was applied. However, this effect was not studied in detail until the 1950s, when researchers began investigating it more deeply [32],[33].

In the early days of ECE research, scientists primarily spent time understanding the physical mechanisms underlying the effect. They observed that ECE is closely related to the ferroelectric phase transition that occurs in certain materials when an electric field is applied. ECE is also known to be related to the piezoelectric effect, which is the change in electric potential due to mechanical stress [33].

In the 1980s and 1990s, researchers began examining ECE for more practical applications such as refrigeration. They discovered that ECE could be used to create a new type of cooling system known as an electrocaloric refrigerator. This type of refrigerator uses ECE to cool a material instead of using conventional refrigerants like Freon.

In the last few years, researchers have made significant achievements in understanding and optimizing ECE in a variety of materials. It has been observed that

the most promising materials for practical applications of ECE are ceramic and polymeric materials with relaxant-ferroelectric properties. These materials have a high electrocaloric effect and can also be used at room temperature.

In recent years, the development of new materials and new manufacturing techniques has led to the creation of new devices that can use ECE for cooling. This includes solid state cooling devices that are compact, efficient and environmentally friendly. ECE also continues its research in other applications such as thermal management and energy harvesting.

2.4.2. Mechanism of Electrocaloric Effect

The electrocaloric effect (ECE) can be defined as the temperature change experienced by a material when exposed to an applied electric field. The ferroelectric phenomena, which calls for some materials to be able to have a permanent electric polarization that may be reversed by an external electric field, is known to be strongly related to this effect. Additionally, the piezoelectric phenomenon, which is the ability of some materials to produce an electric potential in response to mechanical stress, is connected to ECE. These interrelated phenomena contribute to the understanding and exploration of the electrocaloric effect in various materials [33],[34].

ECE is a phenomena that happens when a ferroelectric material experiences an electric field, changing the substance's electrical polarization. It is possible to say that this change in polarization is accompanied by a change in the alignment of the material's dipoles, which causes a change in the entropy of the substance. The substance absorbs or releases heat as a result of the change in entropy, which also affects temperature [33],[34].

It is known that there are two main mechanisms contributing to ECE in ferroelectric materials: direct and indirect electrocaloric effects. The direct electrocaloric effect occurs due to the reorientation of the dipoles in response to the applied electric field. The indirect electrocaloric effect can be said to result from the change in the entropy of the material due to the change in electrical polarization.

In the direct electrocaloric effect, the dipoles in the material change direction again in response to the applied electric field, resulting in a change in the heat capacity of the material. This change in heat capacity is accompanied by a change in

temperature as heat is absorbed or released by the material. The direct electrocaloric effect is typically observed in materials with a high ferroelectric transition temperature.

In the indirect electrocaloric effect, the change in the electrical polarization of the material leads to a change in the entropy of the material. This change in entropy is accompanied by a change in temperature as heat is absorbed or released by the material. The indirect electrocaloric effect can typically be observed in materials with low ferroelectric transition temperature [34].

The piezoelectric effect also has an important effect on ECE. In piezoelectric materials, the application of mechanical stress creates an electric potential. This effect can be used to change the temperature of the material. This is called the piezoelectric electrocaloric effect [34].

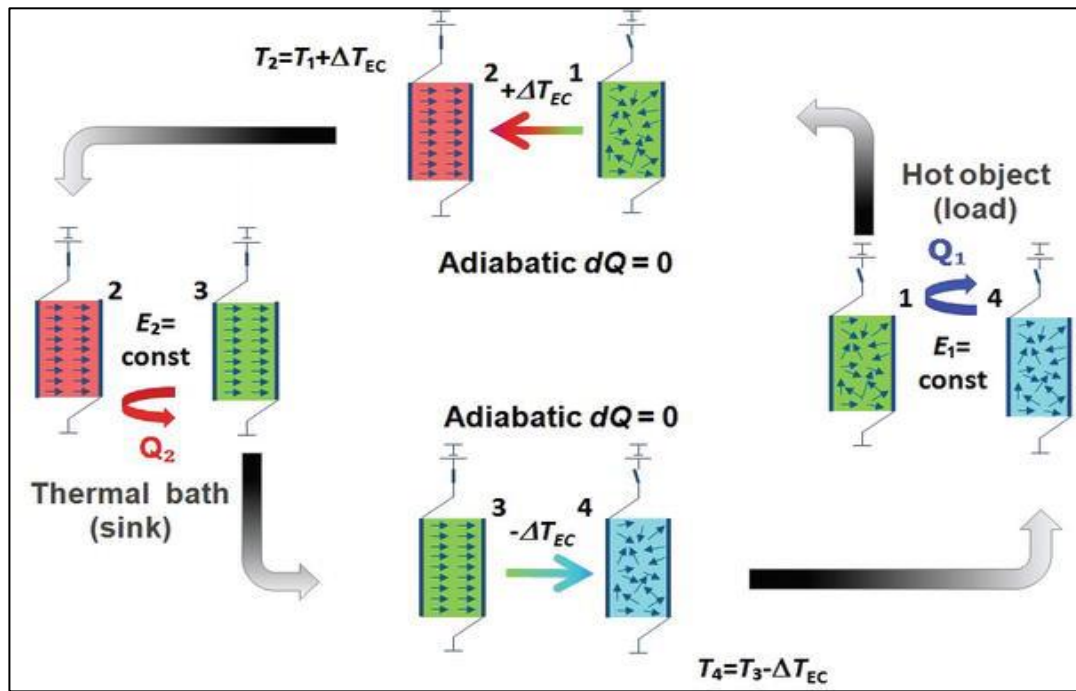


Figure 2.12. Cooling cycle based on electrocaloric effect.

2.4.3. Electrocaloric Materials and Their Properties

Electrocaloric materials are known as materials that exhibit a change in temperature in response to an applied electric field. These materials can be used in a wide variety of potential applications, including cooling, thermal management and energy harvesting. The properties of electrocaloric materials are related to their crystal structures, compositions and microstructures.

One of the most important properties of electrocaloric materials can be said to be their electrocaloric coefficient, which is a measure of the magnitude of the temperature change in response to an applied electric field. In its simplest definition, the electrocaloric coefficient can be expressed in units of temperature per electric field. It can be said that materials with high electrocaloric coefficients are more suitable for cooling applications as they can produce a greater temperature change for a given electric field.

Table 2.1 provides a comparison of different lead-containing and lead-free materials. It can be said that lead-containing materials generally exhibit higher ΔT values than lead-free materials. However, this inconsistency may result from the application of very high electric fields. It is more accurate to take into account the temperature change per unit electric field (T/E), or electrocaloric efficiency, when comparing materials with and without lead.

Researching the electrocaloric effect is mostly done to create more eco-friendly refrigeration solutions. As a result, research efforts in this area have focused primarily on lead-free materials. By discovering the electrocaloric properties of lead-free materials, researchers have made the development of efficient and sustainable cooling technologies free from environmental concerns related to lead-containing materials as their main goal.

BaTiO₃ is indeed one of the extensively studied lead-free materials and is seen as a viable option for EC (electrocaloric) cooling. They show three structural phase transitions that occur at about -80°C, 5°C and 125°C. These transitions, which are rhombic to orthorhombic, orthorhombic to tetragonal, and tetragonal to cubical alterations, correlate to the polar directions $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 001 \rangle$, respectively, in terms of changes in crystal symmetry. These phase transitions contribute to BaTiO₃'s unique electrical and thermal properties, making it a suitable candidate for electrocaloric applications, including cooling [34].

Since BT's crystal structure is of the perovskite variety, it can be doped with various atoms in both the A and B regions. Thanks to the doping atoms, the structural phase transition temperatures of BT undergo changes.

Table 2.1. The most significant lead-containing and lead-free materials' electrocaloric reactions.

Material	T _c (K)	ΔE (kV/cm)	ΔT (K)	$\Delta T/\Delta E$ (K.mm/kV)	Method	Ref.
PZT (95/05) Thin film	222	776	12	0.15	Indirect	[35]
PZN-PT(92/08) Single crystal	180	12	0.23	0.21	Direct	[36]
PMN-PT(92/08)ceramic	23	15	1.4	0.93	Direct	[37]
PMN-PT(85/15)ceramic	17	16	1.7	1.06	Direct	[38]
PMN-PT (75/25) Single crystal	100	10	0.61	0.61	Direct	[39]
PMN-PT (65/35) Thin film	140	750	31	0.41	Indirect	[40]
P(VDF-TrFE)(55/45) Thin film	80	2090	12.6	0.06	Indirect	[42]
BaTiO ₃ – single crystal	402	12	0.9	0.75	Direct	[41]
BaTiO ₃ - ceramic	398	20	1.11	0.56	Indirect	[13]
Ba _{0.85} Ca _{0.15} Zr _{0.10} Ti _{0.90} O ₃ - ceramic	370	21.5	0.4	0.186	Indirect	[43]
Ba _{0.80} Ca _{0.2} Zr _{0.04} Ti _{0.96} O ₃ - ceramic	386	7.95	0.27	0.340	Indirect	[43]
Ba _{0.80} Ca _{0.20} Zr _{0.08} Ti _{0.92} O ₃ - ceramic	386	7.95	0.22	0.27	Indirect	[43]
Ba _{0.92} Ca _{0.08} Zr _{0.05} Ti _{0.95} O ₃ - ceramic	410	15	0.38	0.253	Indirect	[43]
BaTi _{0.895} ,Sn _{0.105} O ₃ -ceramic	301	20	0.61	0.31	Indirect	[44]
Ba _{0.90} Ca _{0.05} Ti _{0.95} Sn _{0.05} O ₃ - ceramic	386	10.8	0.53	0.49	Indirect	[44]
Ba _{0.85} Ca _{0.15} Ti _{0.94} Hf _{0.06} O ₃ - ceramic	401	21	0.65	0.31	Indirect	[44]

The electrocaloric responses from several investigations on doped and undoped BaTiO₃ are shown in Table 2.1. When compared to the doped BT, it can be seen that the T and P/E values of the undoped BT are quite high. Doping, however, can be utilized to bring down BT's Curie temperature. For applications, a Curie temperature that is close to room temperature is preferable. research have so recently concentrated on doping research [34].

2.4.4. Electrocaloric Effect (ECE) Measurement Techniques

Measurement of ECE is essential to understand the physical mechanisms underlying the effect and to optimize the performance of electrocaloric materials in practical applications. There are two main types of ECE measurement: direct and indirect. Each type of measurement has its own advantages and disadvantages, and these are used to examine different aspects of ECE. In the scope of the thesis study, indirect measurement method was used.

2.4.4.1. Direct Measurement

Direct ECE measurements are used to measure the temperature change of a material directly in response to an applied electric field. The most common direct ECE measurement technique is the temperature versus electric field (T-E) method. In this technique, a sample of the material is placed in a temperature-controlled chamber, and an electric field is applied to the sample using electrodes. The temperature of the sample is then measured as a function of the electric field. This method is simple and easy to implement, but it can be affected by heat loss to the environment and by the non-uniformity of the electric field [45],[34].

The direct measurement method for the electrocaloric effect (ECE) involves the use of an adiabatic calorimeter. In this setup, the sample is placed inside a heat-insulated container and subjected to an electric field. The ECE is then measured as a function of both temperature and polarization. It's important to note that the direct method is not adiabatic, as it requires rapid voltage increases to prevent heat transfer from the surroundings. This approach allows for more accurate measurements of the electrocaloric effect by minimizing external influences on the sample. By employing

the direct method, researchers can obtain precise and reliable data on the ECE characteristics of materials [45].

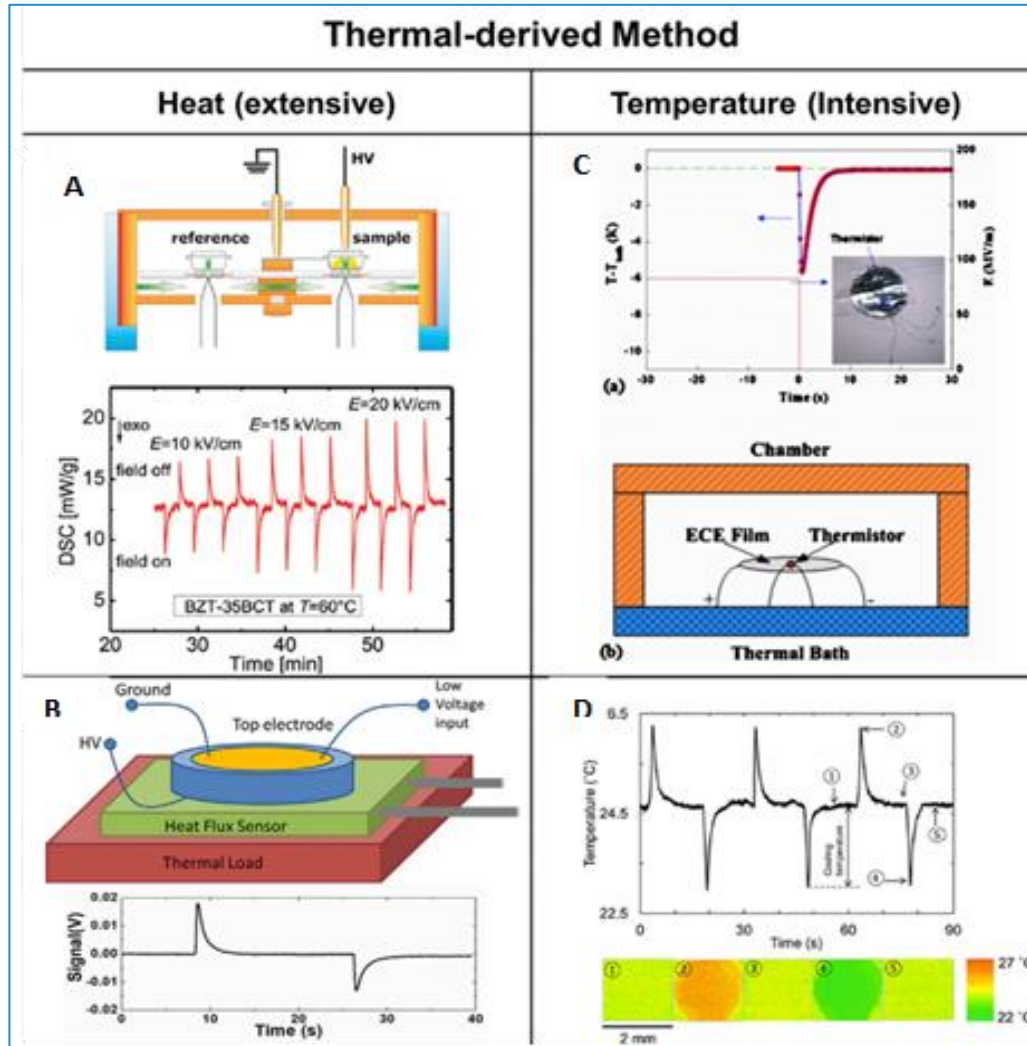


Figure 2.13. (A and B) Typical heat flux measurement of ECE using a modified DSC91 (A) and in situ calibration method (B). (C and D) ECE typical of ECE via thermistor92 (C) and infrared camera93 (D) temperature measurement [45].

2.4.4.2. Indirect Measurement

Indirect ECE measurements are a measurement method used to measure the change in electrical polarization of a material in response to an applied electric field and then calculate the temperature change from the polarization change.

To indirectly predict the temperature change associated with the electrocaloric effect (EC), the change in electrical polarization with temperature under a constant electric field must be determined. This can be achieved by two different computation

methods: the numerical method and the polynomial fitting method. Both methods use analysis of slopes of polarization-temperature (P-T) graphs.

By obtaining the slopes of P-T graphs through numerical calculations or polynomial fitting, it is possible to determine the rate of change of polarization with temperature. This information is necessary to indirectly evaluate the EC temperature change. These calculation methods contribute to the estimation of the EC effect in materials by providing valuable information about the relationship between temperature and polarization. This is based on the Maxwell relation (Equation 2.6) [44],[45].

$$\left(\frac{\partial P}{\partial T}\right)_E = \left(\frac{\partial S}{\partial E}\right)_T \quad (2.6)$$

For the numerical calculation, the slope is calculated using Equation 2.7.

$$\left(\frac{\partial P}{\partial T}\right)_E = \left(\frac{1}{2}\right) * \left(\frac{P_n - P_{n-1}}{T_n - T_{n-1}} + \frac{P_{n+1} - P_n}{T_{n+1} - T_n}\right) \quad (2.7)$$

In the following formulas, P is the macroscopic electrical polarization, E_1 (0 kV/cm) is the first external field and E_2 is the final external field, ρ is the density of the ceramic, C_p is the heat capacity, ΔS is the entropy change, and ΔT is the electrocaloric temperature change.

$$\Delta T = -\frac{T}{\rho C_p} \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T}\right)_E dE \quad (2.8)$$

$$\Delta S = -\frac{1}{\rho} \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T}\right)_E dE \quad (2.9)$$

The indirect method for measuring electrocaloric (EC) temperature change is known to have limitations that affect its applicability. The indirect method's reproducibility is constrained by some materials' low relaxation durations and lack of ergodicity. Furthermore, unless the polarization curve is saturated, it is not recommended to use the indirect technique to determine the EC temperature change of materials with a single field structure. Despite these limitations, the indirect method

is more popular among researchers due to its advantages of being faster and easier to perform compared to the direct method. It is necessary to consider these limitations and select the appropriate method according to the specific requirements of the study [44],[45].

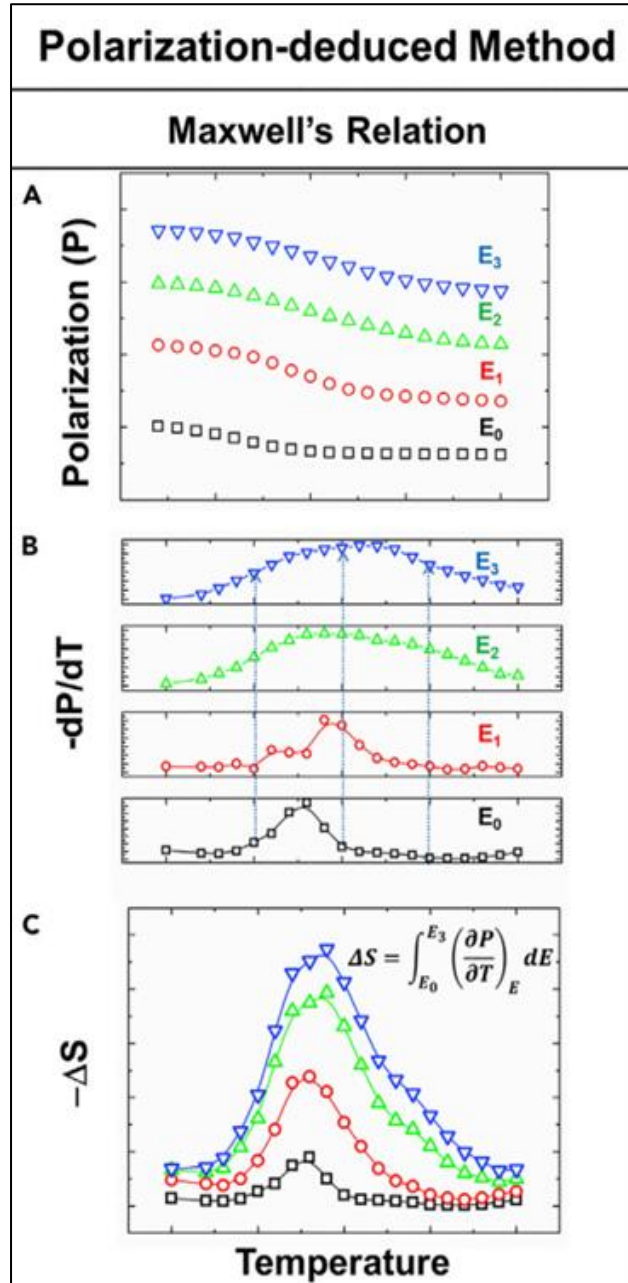


Figure 2.14. (A–C) Polarization-derived method using Maxwell relation where $E_0 < E_1 < E_2 < E_3$ (indirect method). (A) Temperature dependent polarization is plotted, from which (B) polarization versus temperature derivative can be plotted. (C) The entropy change ΔS can be obtained by following the equation shown in addition [45].

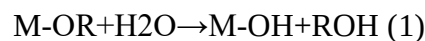
2.5. Sol-Gel Method

Sol-Gel method is known as a versatile technique for the synthesis of inorganic and hybrid materials. The method involves the formation of a precursor solution known as a sol, which is then converted into a solid material through a gelation process. Sol-gel process can be said to be a versatile and cost-effective method used to synthesize a wide variety of materials, including ceramics, glass, metals and semiconductors.

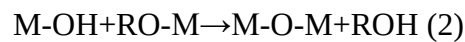
2.5.1. General Principles of Sol-Gel Method

The general principles of the Sol-Gel method can be divided into three main steps: preparation of the precursor solution, gelling the solution, and finishing the gel.

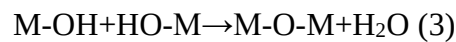
Hydrolysis of metal alkoxides.



Left formation.



Gel formation by polycondensation.



The first step in the Sol-Gel method begins with the preparation of the precursor solution, also known as the sol. Sol is typically formed from metal ions and precursors of the desired oxide or other inorganic material. The metal ions may be in the form of metal alkoxides or metal salts, and the oxide may be in the form of precursors, organic acids or metal alkoxides. Sol is usually prepared by mixing metal ions and oxide precursors in a solvent such as alcohol or water. Solvent selection and reaction conditions depend on the specific materials synthesized [46]-[47]-[48]-[49].

The second step in the Sol-Gel method is the gelation of the solution. Gelation is known as the process by which the sol turns into a gel. This process is typically the addition of a gelling agent such as water, acid or base to the sol. The gelling agent reacts with the metal ions and precursors on the left, causing a chemical bonding network to form between the metal ions and the precursors, and this chemical bonding network provides the gel with its mechanical and chemical stability. It is possible for

the gelation process to take place at room temperature or at high temperatures, depending on the specific materials synthesized [49]. The final step in the Sol-Gel method is post-treatment of the gel. This step involves the removal of the solvent from the gel and the conversion of the gel into the desired solid material. The removal of the solvent can be achieved through evaporation or by heating the gel in an oven. The conversion of the gel into the desired solid material can be achieved through heating the gel at a high temperature. This process is known as sintering. The sintering temperature and time will depend on the specific materials being synthesized [49].

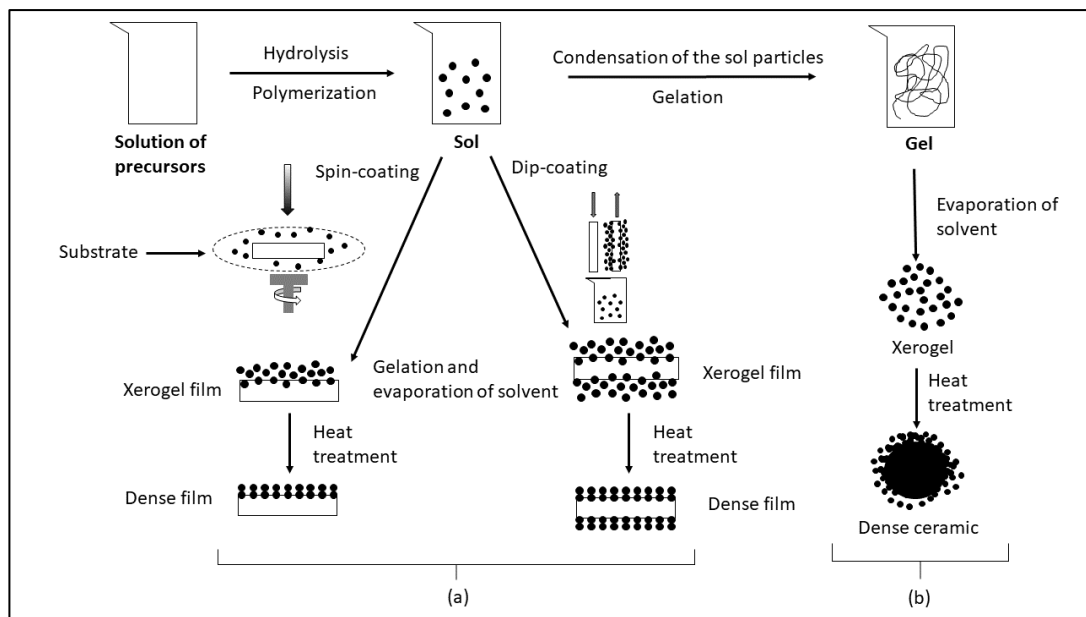


Figure 2.15. Sketch of the sol-gel synthesis process; (a) films from a colloidal left; (b) powder obtained from a gel-converted colloidal sol.

2.5.2. Advantages and Disadvantages of Sol-Gel Method

The sol-gel method is known to have several advantages and disadvantages that make it a useful, but not always ideal, method for creating certain materials [50].

Advantages:

Low-temperature processing: The sol-gel method can be processed at relatively low temperatures, making it to form materials sensitive to high temperatures.

Controlled particle size: The sol-gel method provides precise control of particle size, which can be important for creating materials with particular properties.

Inexpensive: The sol-gel method can be said to be relatively inexpensive compared to other methods of creating similar materials.

Versatile: The sol-gel method has the ability to be used to create a wide variety of materials, including ceramics, glass and even some metals.

Disadvantages:

Long processing times: Sol-gel method can take a long time to complete, which can be seen as a disadvantage in some applications.

Limited size of the final product: The sol-gel method is usually limited by the size of the final product it can produce.

Limited mechanical properties: Materials produced by the sol-gel method tend to have limited mechanical properties such as low strength and brittle structure.

Limited purity: The purity of the final product is usually not high, which can be a disadvantage in some applications.

In general, the sol-gel method is a useful technique for creating materials with certain properties, but it should be noted that it has limitations [47],[49].

3. EXPERIMENTAL STUDY

3.1. Powder Synthesis and Production of Ceramic Samples

In this study, the structural and electrical properties of lead-free piezoelectric ceramics of BCZT($\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ -($\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$) compositions were investigated. First of all, BCZT powders were synthesized by sol-gel method. All source chemicals in the synthesis of powders were given in Table 3.1.

Table 3.1: Chemicals used in powder synthesis

Chemical	Chemical Formula	Brand
Barium acetate	$\text{C}_4\text{H}_6\text{BaO}_4$	Sigma-Aldrich
Titanium(IV) n-butoxide	$\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$	Alfa-Aesar
Zirconium(IV) n-propoxide	$\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$	Alfa-Aesar
Calcium acetate hydrate	$\text{C}_4\text{H}_6\text{CaO}_4$	Sigma-Aldrich
Acetic acid	$\text{CH}_3\text{CO}_2\text{H}$	Sigma-Aldrich
2-Methoxyethanol	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$	Sigma-Aldrich

3.1.1. Synthesis of BCZT Powder

The synthesis of BCZT ceramic powders by the sol-gel method based on the complexation of alkoxides with acetic acid was carried out using analytical-grade chemicals. BCZT powders were formed by mixing BZT($\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$) and BCT($(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$) solutions separately as a single solution. First, 80% acetic acid, 20% 2-methoxy ethanol and barium acetate were mixed at 80°C for 30 minutes to form a solvent solution. After the solvent solution were completely clear, BT and BZ solutions for BZT were divided into 25 ml each, and then BT and BZ solutions were formed for BCT. For BZT, titanium n-butoxide + 25 ml solvent and zirconium n-propoxide + 25 ml solvent separately at 80°C were mixed for 30 minutes. The BZ-BT solution was then mixed and homogenized for 1 hour at 80°C. Beside this, titanium n-

butoxide+ 25 ml solvent and calcium acetate hydrate for BCT solution + 25 ml solvent was mixed again at 80°C for 30 minutes.

The solution was mixed and homogenized for 1 hour at 80°C. The resulting BZT and BCT solutions were mixed for 1 hour at 100°C and turned into a homogeneous gel. The final gel was dried at 100°C for 24 hours and the solidified agglomerates were ground into fine powders.

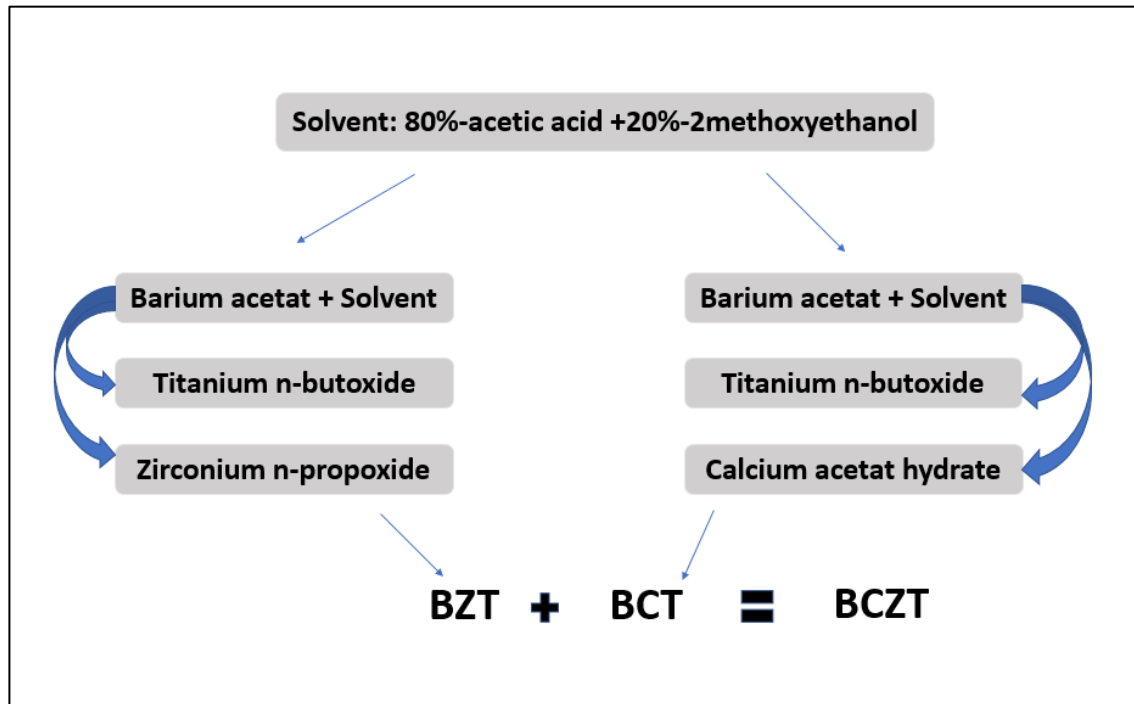


Figure 3.1: The follow chart of BZT-BCT powder synthesis.

3.1.2. Production of BCZT Ceramics Samples

The resulting powder was calcined at 900°C for 2 hours at an incremental rate of 5°C/min. In order to reduce the grain size, after calcination, a ball mill process was applied at two different speeds as 200 rpm and 500 rpm for 24 hours, and the lumps were removed.

The calcined powders were granulated and the disc-shaped ceramic samples were prepared under 150 MPa pressure with the addition of a binder . The obtained BCZT pellets were sintered at 1450°C with a ramp rate of 2°C/min for 4 hours, and during this sintering process, organic content was removed from the green samples with a heating rate of 600°C for 1 hour. The surfaces of the sintered samples were

polished to create parallel surfaces. BCZT ceramic sample production flow chart is shown in Figure 3.2.

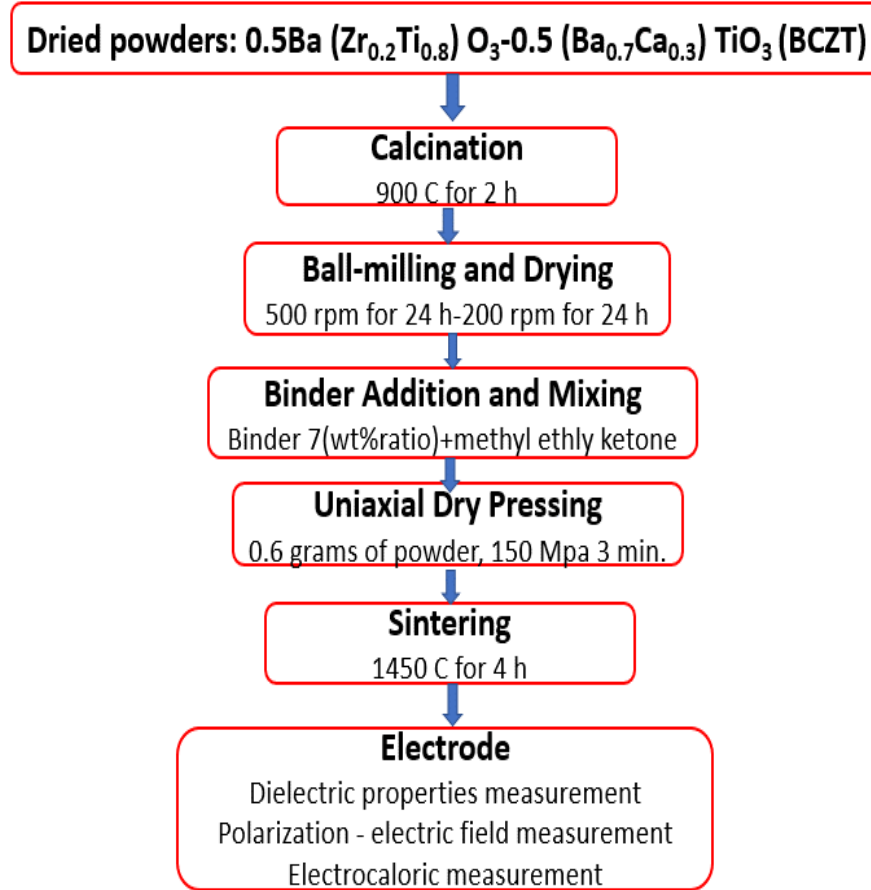


Figure 3.2: The flow chart of BCZT sample production.

3.2. Structural Characterization

3.2.1. X-ray Diffraction (XRD)

The X-Ray Diffraction method (XRD) is known to be a technique based on the principle that X-rays are refracted by crystal structures in a unique pattern determined by their atomic arrangement. This diffraction pattern acts as a fingerprint for each crystal phase. One of the advantages of XRD analysis is that it does not damage the sample, allowing for further analysis or additional experiments. In addition, XRD allows us to obtain information about interatomic distances, interatomic angles and atomic positions in the crystal structure.

In this study, XRD analysis was used to perform phase analysis of both powders and ceramics. The XRD instrument used was the Rigaku DMax 2200 from Tokyo, Japan, using Cu-K α radiation. The scanning range is set from 20° to 70° with a 0.02° step size. By analyzing the diffraction patterns obtained from the XRD measurements, the researchers were able to identify the crystal phases present in the samples and gather valuable information about their atomic arrangements and structural properties.

3.2.2. Scanning Electron Microscope (SEM)

Scanning electron microscope can be defined as a system that uses electrons to take high resolution images on the sample surface. It works thanks to a high-energy electron beam to scan a sample surface and create a detailed image of its topography, composition, and other features.

SEM can be said to consist of several components, including an electron source, an array of electromagnetic lenses, and a detector. The electron source is typically a heated filament that emits electrons, which are then accelerated by voltage applied to an anode. A set of electromagnetic lenses then focus and direct the generated electron beam to the sample surface. Different signals are created when the beam interacts with the sample surface, including secondary electrons, backscattered electrons, and distinctive X-rays. A detector that may be positioned to gather signals from various angles and depths within the sample then detects these signals.

SEM is a method that can produce high resolution images by scanning a focused beam of electrons across the sample surface and detecting emitted secondary electrons. It can be said that this method allows the visualization of surface properties at various scales ranging from micrometer to nanometer.

In addition to the surface topography, SEM helps us gain valuable information about the composition, crystal structure and other properties of the sample. By adjusting the energy and angle of incidence of the electron beam, SEM allows us to obtain details about element composition and chemical mapping, as well as crystallographic orientation and phase identification.

In this study, ceramic samples, whose surface roughness was removed with SiC sandpaper, were polished with alumina paste and felt. It was then thermally etched for 30 minutes at 200°C below the sintering temperature to determine grain boundaries.

Surface microstructure properties of ceramics were investigated by scanning electron microscope (SEM) (Philips XL30 FEI Co., USA).

3.3. Electrical Characterization

In this section, the dielectric, polarization-electric field, and electrocaloric measurements of the samples and the techniques which used are explained. The surfaces of the samples with a certain diameter and thickness were coated with silver electrodes and then the electrodes were baked at 600°C for 30 minutes, and then electrical measurements were taken.

3.3.1. Dielectric Constant Measurements

The dielectric constant of a substance can be determined using a number of techniques, including an LCR meter. An electronic device that measures a circuit's inductance (L), capacitance (C), and resistance (R) is known as an LCR meter. It is frequently employed in the electronics sector to gauge the characteristics of electronic parts like capacitors and inductors.

When measuring the dielectric constant of a material using an LCR meter, the material is placed between two parallel plates that act as electrodes. An AC voltage is then applied to the electrodes and the resulting capacitance is given by the LCR meter. It can be said that the measured capacitance depends on the dielectric constant of the material between the electrodes. After obtaining the capacitance value, the dielectric constant of the materials is calculated using Equation (3.1), which is the parallel plate capacitor equation given below. In the equation, ϵ_r is the dielectric constant of the sample, A is the area of the sample, d is the distance between the plates, and ϵ_0 is the dielectric constant in space. ($\epsilon_0 = 8.85 \times 10^{-12}$ F/m). The accuracy of the measurement depends on several factors, such as the frequency of the applied voltage and the geometry of the electrodes.

$$\epsilon_r = \frac{Cd}{A\epsilon_0} \quad (3.1)$$

The dielectric properties of the ceramics in this study were measured using an LCR meter (Hioki 3532-50 LCR meter, Japan). The tests were made in the 1 kHz to 100 kHz frequency range. With a heating rate of 2°C per minute, the temperature was adjusted and ranged from ambient temperature to 180°C.

3.3.2. Polarization-Electric Field Measurements

Polarization-electric field measurements are used to investigate the properties of materials and their response to external stimuli. This technique allows us to apply an electric field to a sample and measure the resulting polarization. It helps us to have an idea about the structure and behavior of the material by examining the relationship between polarization and the applied field.

A common method of performing polarization-electric field measurements is to use a ferroelectric capacitor. This device consists of two electrodes separated by a thin layer of ferroelectric material. When an electric field is applied, the material becomes polarized with positive and negative charges accumulating at opposite ends of the capacitor. By measuring the resulting charge or voltage, it is possible to determine the polarization of the material. A ferroelectric test equipment (Precision LC; Radiant Technologies, Inc., Albuquerque, NM) is used to measure electric field induced polarization (P-E), which ranges from 50 to 80 kV under a frequency of 1 Hz. It is measured in / cm.

3.3.3. Electrocaloric Measurements

The measurement of a material's temperature change in response to an applied electric field is the definition of the indirect method for measuring the electrocaloric effect (ECE). This method is based on the assumption that the observed temperature change is predominantly due to the electrocaloric effect itself. The indirect method provides a practical way to study ECE, although it is known that it is important to consider the potential contributions of other factors that may affect the temperature change.

Electrocaloric measurements were made indirectly by examining the temperature dependent evolution of the P-E cycle of samples cooled from 90°C to 0°C. After P-E cycles were obtained with a ferroelectric test device, adiabatic temperature

change (ΔT) analyzes were performed by the Sabancı University collaborative working group.

4. RESULTS AND DISCUSSION

In this section, the structural and electrical analyses of dry-pressed ceramics with a detailed composition of $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ - $0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$, abbreviated as BCZT located at the morphotropic phase boundary, will be discussed. Structural changes due to the difference in grinding speed were observed on the ceramics after applying two different grinding speeds of 200 rpm and 500 rpm to the starting ceramic powders. Consequently, their effects on the electrical properties will be examined.

4.1. Phase and Microstructure Analysis of BCZT Powders

XRD examination was performed on the synthesized BCZT powder that had been sol-gel calcined at 900°C for two hours with a heating rate of $5^\circ\text{C}/\text{min}$. Figure 4.1(a) shows the XRD pattern of the powder belonging to the composition of 0.5BZT-0.5BCT. It is clearly seen from Figure 4.1 that it exhibits a pure perovskite phase.

The particle size distribution of the 0.5BZT-0.5BCT powder after the grinding process is also given in Figure 4.1(b). The average particle size of the powder is measured as $d_{0.5} \cong 0.181 \mu\text{m}$. It is observed that the powder has a homogeneous particle size distribution.

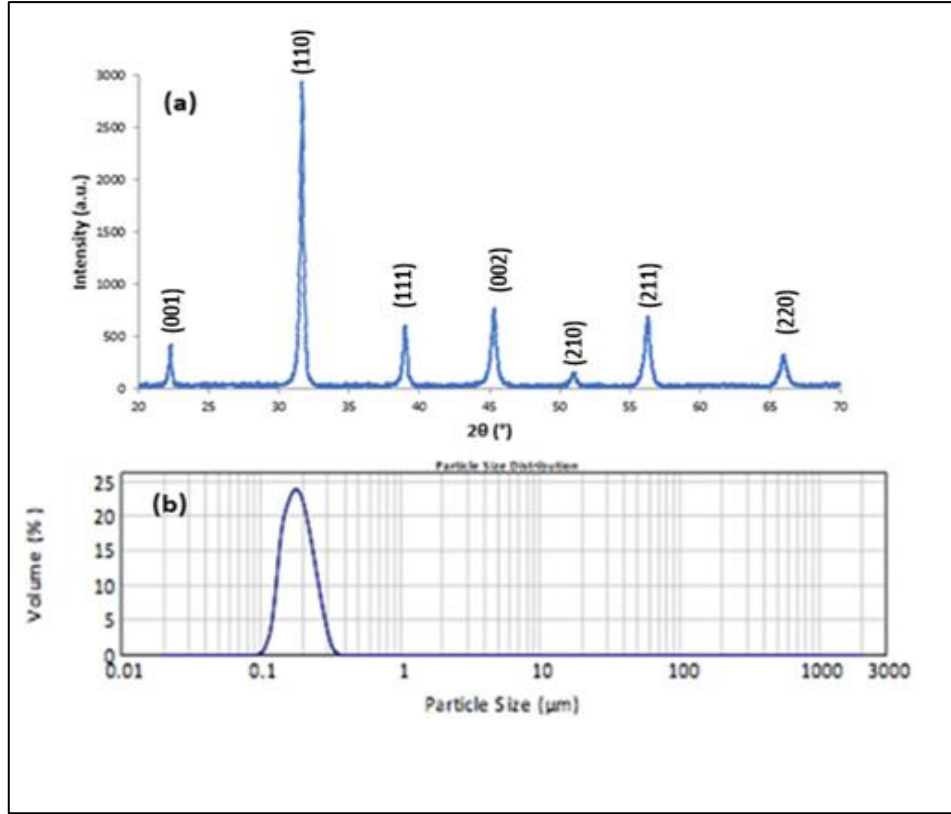


Figure 4.1: (a) XRD pattern and (b) particle size distribution of BCZT powder.

4.2. Study of BCZT Ceramics with Fabricated From Powder-1

In this section, the structural and electrical properties of the dry pressed $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramic, which was subjected to 24 hours of ball-milling at 200 rpm, will be discussed. From now on, the ceramic sample will be referred as BCZT-SG.

4.2.1. Structural Analysis of BCZT-SG Ceramic Samples

The XRD pattern between 20° and 70° 2θ angle of the 0.5BZT-0.5BCT dry pressed sample, which was subjected using Powder-1 and sintered at 1450°C for 4 hours, is given in Figure 4.2. When the XRD pattern was examined, it was observed that all the ceramics were crystallized in perovskite structure. The average crystalline size was determined from XRD peak analysis using the Scherrer equation (Eq.4.1) given below:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (4.1)$$

The crystalline size D is calculated as 64.076 nm using the Scherrer equation, where K is the Scherrer constant, λ is the wavelength of the emitted X-rays, β is the full width at half maximum, and θ is the peak position.

SEM micrographs of the cross-section and surface of the samples are presented in Figure 4.3. SEM analysis indicates that the sample has a dense microstructure.

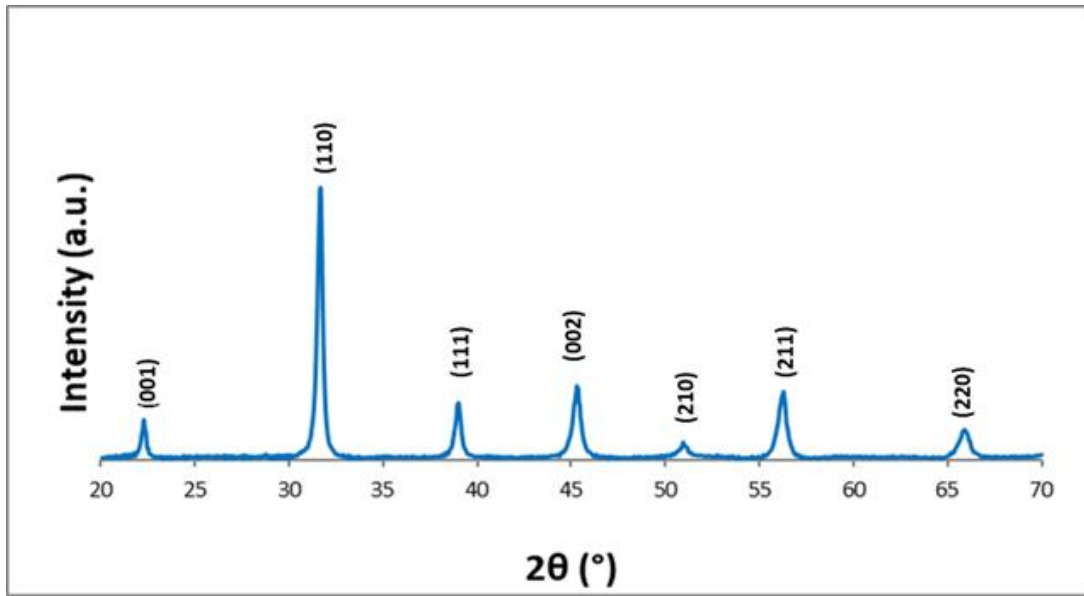


Figure 4.2: XRD pattern of the BCZT-SG ceramic.

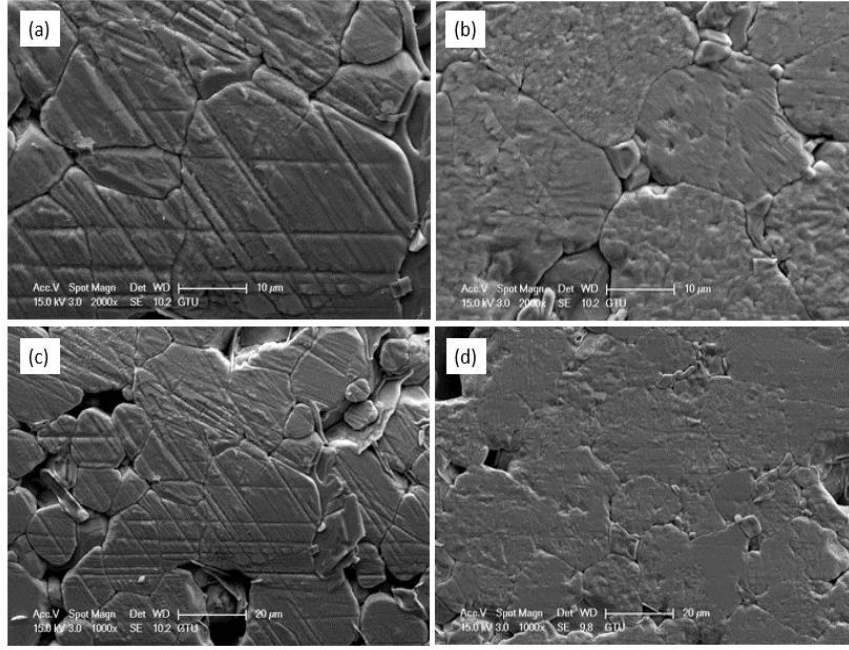


Figure 4.3: SEM micrographs of the BCZT-SG a)cross section and b) surface x2000 magnification and, c) cross section and d) surface x1000 magnifications.

4.2.2. Dielectric Measurements of BCZT-SG Ceramics

The dielectric constant(ϵ_r) of the BCZT-SG ceramic at room temperature was measured as 1366 at a frequency of 1 kHz. At a frequency of 1-100 kHz, the dry-pressed ceramic's Curie temperature (T_c) was also discovered to be 91°C. Table 4.3 provides a detailed breakdown of the data. Figure 4.4 displays, for the BCZT ceramic subjected to a 24-hour 200 rpm ball-mill treatment, the temperature dependence of the dielectric constant and loss tangent determined at various frequencies. It can be seen that the ceramic exhibits a wide transition from the ferroelectric tetragonal phase to the paraelectric cubic phase at around 90°C. As shown in Figure 4.4(a), it can be said that the BCZT ceramic exhibits relaxor ferroelectric properties, such as diffuse phase transition behavior due to microinhomogeneity and frequency-dependent dielectric constant.

For ferroelectrics, dielectric properties above the T_c are generally in accordance with the Curie-Weiss law:

$$\frac{1}{\epsilon_r} = \frac{(T-T_0)}{C(T>T_c)} \quad (4.2)$$

where T_0 is the Curie-Weiss temperature and C is the Curie constant. Figure 4.4(c) shows deviation from Curie-Weiss behavior as the inverse ϵ_r dependence on temperature. The degree of deviation can be expressed as $\Delta T_m = T_{CW} - T_m$, where T_{CW} is the temperature at which the reciprocal ϵ_r value begins to deviate from the Curie-Weiss law. The ΔT_m value for this sample is 46°C .

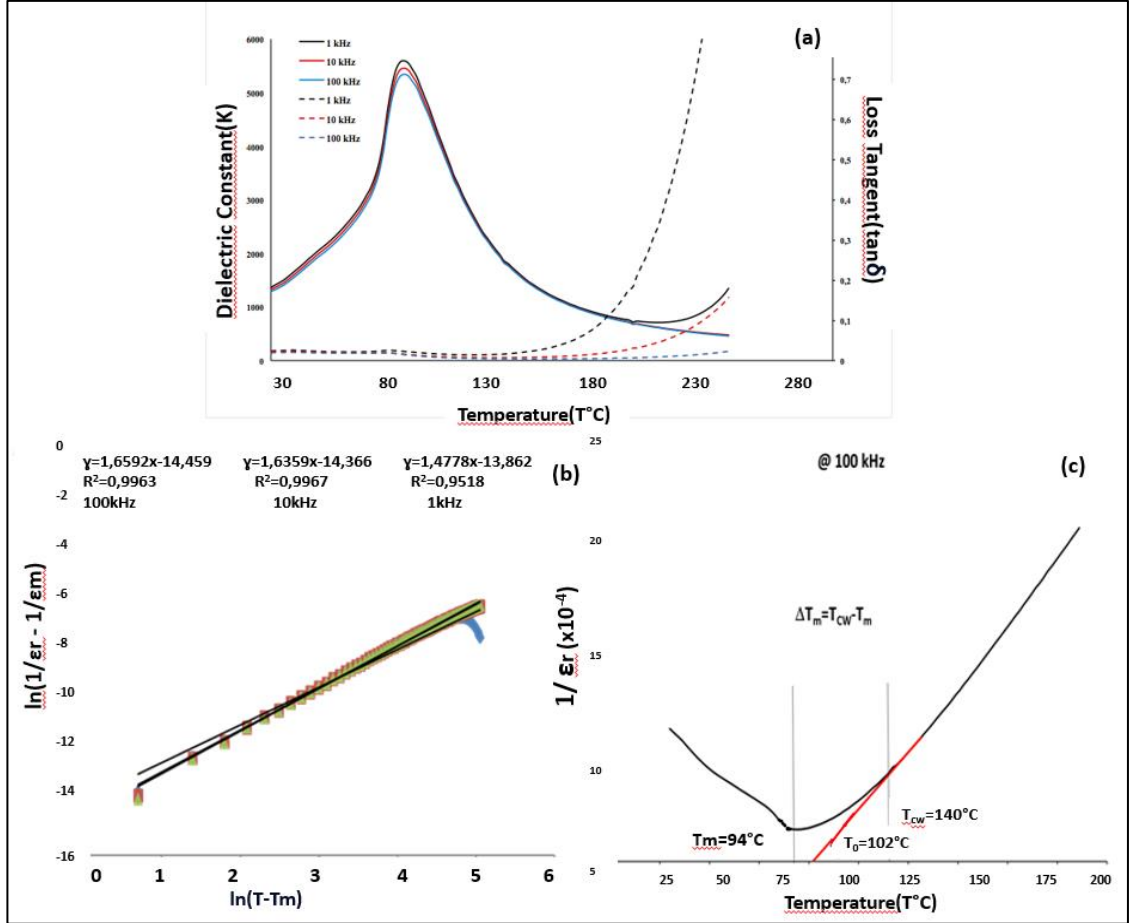


Figure 4.4: Temperature-dependence of (a) dielectric constant and loss tangent, (b) $\ln(1/\epsilon_r - 1/\epsilon_m) - \ln(T - T_m)$ plots at various frequencies and (c) the inverse of the measured dielectric permittivity at 100 kHz.

The following modified Curie-Weiss law is used to investigate the normal and relaxant-like phase transition behavior of ceramics:

$$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_m} = \frac{(T - T_m)^\gamma}{C'} \quad (4.3)$$

The dielectric behavior of the material is described by a number of parameters in the given equation. The material's capacity to retain electrical energy when exposed to an electric field at a particular temperature, denoted as "T," is indicated by the dielectric constant, abbreviated as " ϵ_r ". The temperature at which this highest value occurs is represented by T_m , whereas ϵ_m is the greatest value of the observed dielectric constant. The Curie constant, denoted as C, is a material-specific constant that influences the dielectric behavior. The degree of propagation of the phase transition is described by the parameter γ , which varies depending on the composition and structure of the material. For an ideal relaxor ferroelectric, γ is equal to 2, while for a normal ferroelectric, γ takes a value of 1.

Figure 4.4(b) illustrates the determination of the γ parameter by analyzing the relationship between $\ln(1/\epsilon_r - 1/\epsilon_m)$ and $\ln(T - T_m)$ through curve fitting using Equation 4.2. The obtained γ value at a frequency of 100 kHz is found to be 1.66. This analysis helps characterize the dielectric properties and behavior of the material under study.

Table 4.1: Comparison of the electrical properties of BCZT ceramics.

	BCZT-SG (Powder-1)	BCZT-SGH (Powder-2)
Sintering Temperature(°C)/time(h)	1450 C-4h	1450 C-4h
Crystallite Size(nm)	64.0	43.0
T_c(°C)	94	98
P_{max} (μC/cm²) @40kV	11.8	23.21
P_{max} (μC/cm²) @60kV	-	11.66
P_{max} (μC/cm²) @80kV	-	55.10
P_r (μC/cm²) @40kV	5.34	21.86
P_r (μC/cm²) @60kV	-	6.15
P_r (μC/cm²) @80kV	-	35.56
E_c (kV/cm) @40kV	9.8	14.6

Table 4.1(continue): Comparison of the electrical properties of BCZT ceramics.

Ec (kV/cm) @60kV	-	11.68
Ec (kV/cm) @80kV	-	19.12
Er (RT) @1 kHz	1366	2874
tanδ, (RT) @1 kHz	0.023	0.02
ΔTm (°C)	46	58
Tcw (°C)	140	156
T₀(°C)	102	100
γ @100 kHz	1.66	1.85

4.2.3. Ferroelectric Measurements of BCZT-SG Ceramics

Figure 4.5 shows the temperature-dependent hysteresis loop (P-E) of the 0.5BZT-0.5BCT ceramic, under 40 kV/cm electric field, between 0°C and 90°C without any hysteresis. After sintering, the thickness of the sample, which was 0.76 mm, was reduced to 0.48 mm by lepping process for measurement. The measurements were taken every 10 degrees from 90°C to 0°C. As seen in Figure 4.5, while P_{max}, P_r, E_c values were measured as 16.5 μC/cm², 5.3 μC/cm², 5.98 kV/cm, respectively at 90°C, these values were obtained as 8.69 μC/cm², 1.12 μC/cm², 6.63 kV/cm.

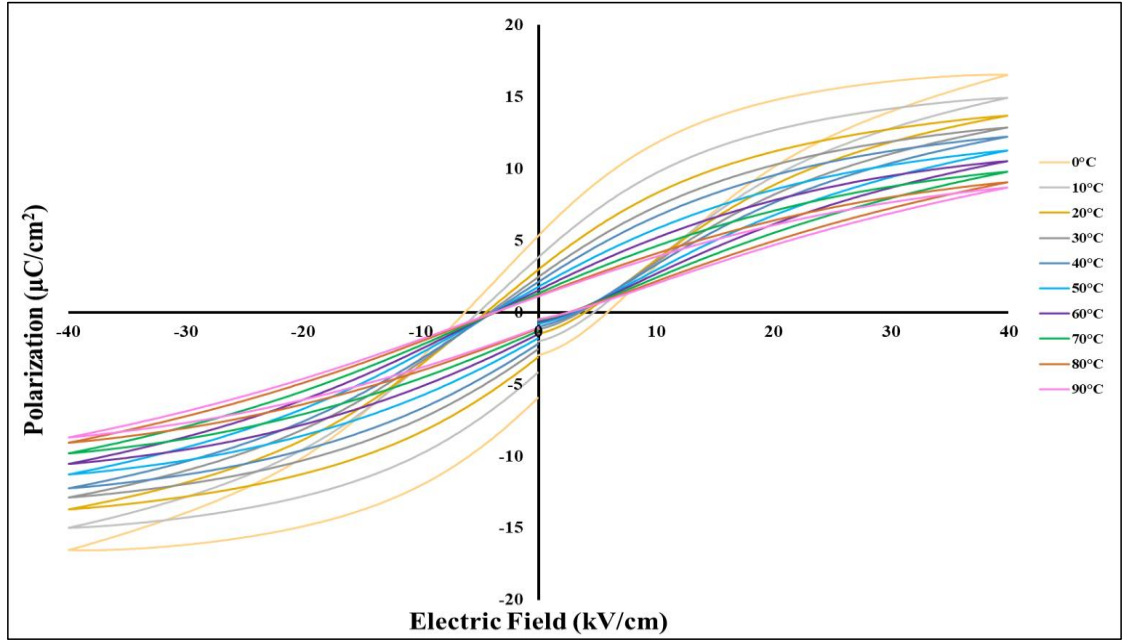


Figure 4.5: Polarization hysteresis loops of the BCZT-SG ceramic at different temperatures.

4.2.4. Evaluation of Electrocaloric Measurement Results of BCZT-SG Ceramics

The three-dimensional temperature-dependent P-E curves and ΔT -T graph of the 0.5BZT-0.5BCT ceramic, under an electric field of 40 kV/cm, are given in Figure 4.6. The measured coercive field, (E_c), residual polarization, (P_r), and maximum polarization (P_{max}) values of the ceramic are given in Table 4.1. It was observed values have decreased with increasing temperature. This is how ferroelectric materials typically behave. The dipoles become more sensitive to the electric field as the temperature rises. In this situation, polarization of the material is possible with a reduced electric field, which lowers the applied field. The Curie temperature of the ceramic is $\sim 94^\circ\text{C}$ and the highest ΔT (K) value is 1.2 K.

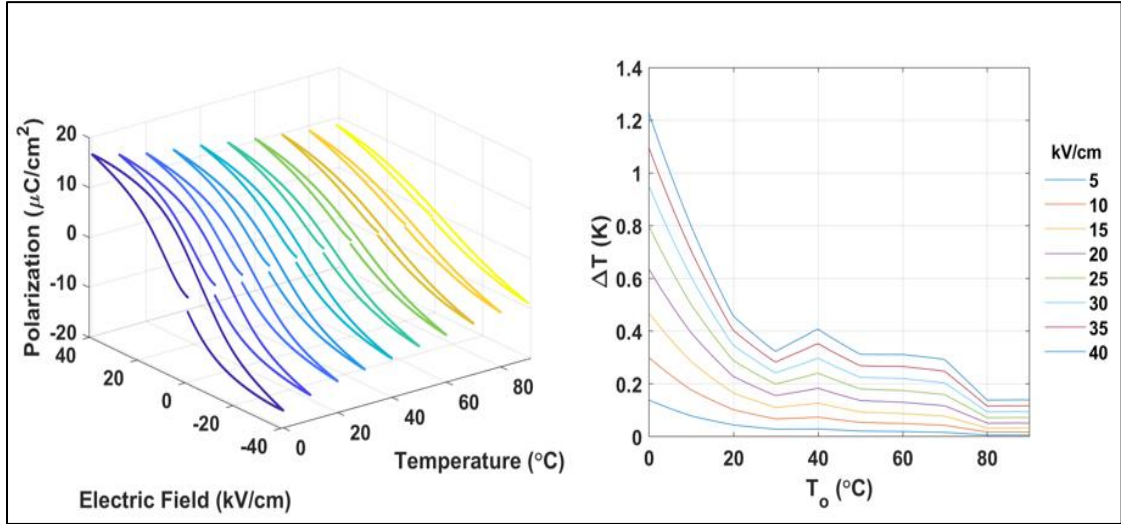


Figure 4.6: Three-dimensional of P-E curves of BCZT-SG ceramic and b) ΔT -T graph of BCZT-SG ceramic.

4.3. Study of BCZT Ceramics with Fabricated From Powder-2

In this section, the structural and electrical properties of 0.5BZT-0.5BCT ceramics fabricated from powder-2 will be discussed. In the following sections, this ceramic sample will be abbreviated as BCZT-SGH.

4.3.1. The Structural Analysis of BCZT-SGH Ceramis

The XRD pattern of the BCZT-SGH sample, is seen in Figure 4.7. The XRD analysis shows that the ceramic crystallized in a pure perovskite structure. Using the Scherrer Equation, the average crystallite size was calculated from the XRD peak analysis (Equation 4.1). By using the Scherrer equation, the crystallite size was calculated as 42.96 nm. Finer crystal sizes were obtained when the grinding speed increased.

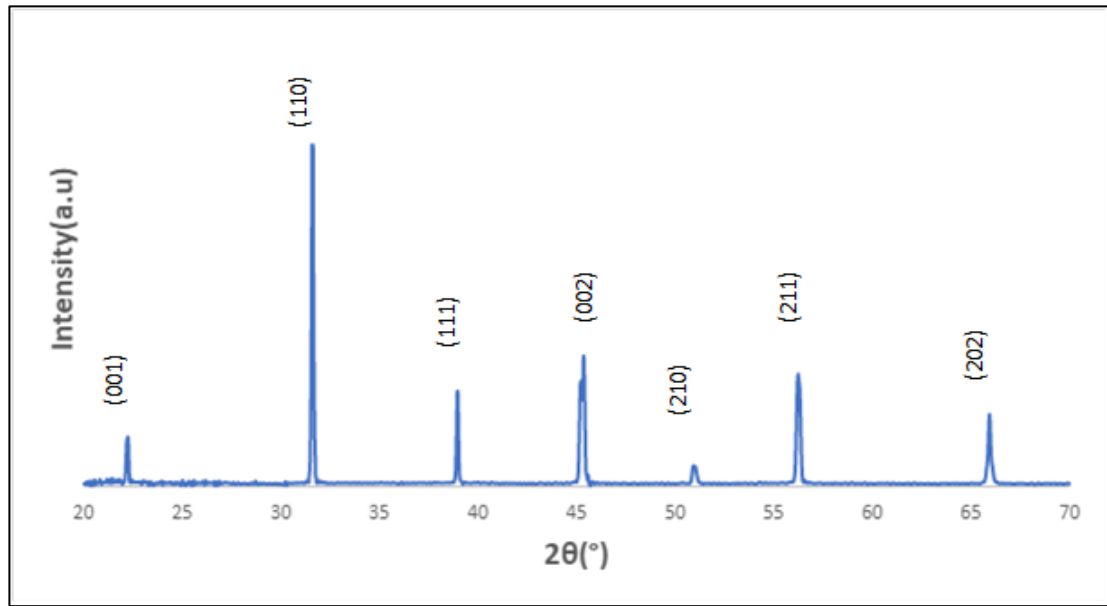


Figure 4.7: XRD pattern of the BCZT-SGH sample.

SEM micrographs of the cross-section and surface of the BCZT-SGH sample are presented in Figure 4.8. SEM analysis revealed that similar to the BCZT-SG sample, the sample also had a dense microstructure.

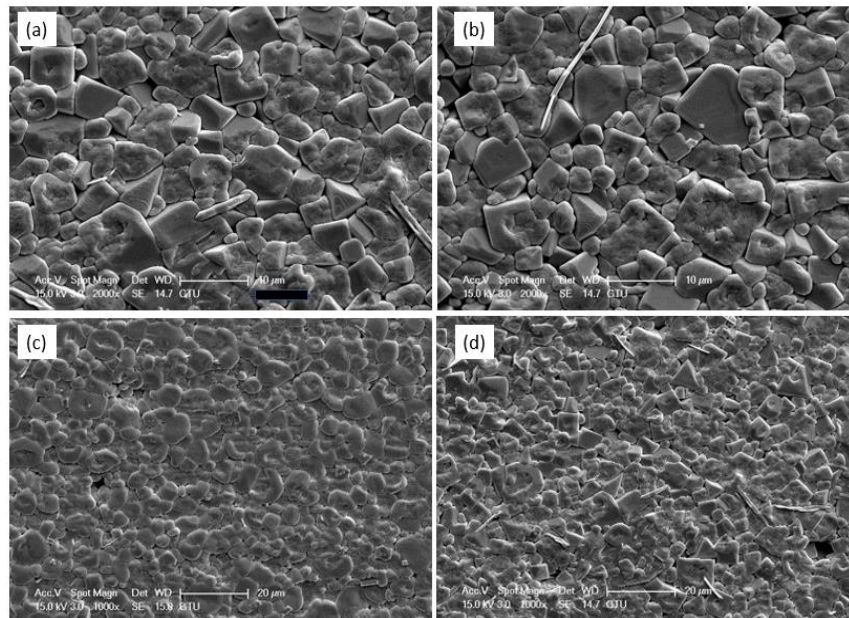


Figure 4.8: SEM micrographs of the BCZT-SGH a) cross section and b) surface at x2000 magnification and, c) cross-section and d) surface at x1000 magnifications.

4.3.2. Dielectric Measurements of BCZT-SGH Ceramics

The dielectric constant of BCZT-SGH ceramic was measured as 2856 at 1 kHz frequency at room temperature. The Curie temperature(T_c) was found to be 98°C for this ceramic at 1-100 kHz frequency. The values are given in detail in Table 4.1. Figure 4.9 illustrates the BCZT-SGH ceramic's dielectric constant and loss tangent temperature dependences at various frequencies. Around 100°C, the BCZT-SGH ceramic may be seen to exhibit a broad transition from the ferroelectric tetragonal phase to the paraelectric cubic phase. As shown in Figure 4.9(a), the BCZT sample exhibits relaxor ferroelectric properties such as diffuse phase transition behavior due to microinhomogeneity and frequency-dependent dielectric constant. The ΔT_m value for this sample is 58°C. It can be seen that the relaxation behavior increases compared to the BCZT-SG sample. The γ value was determined as 1.86 at 100 kHz. It is clearly seen that the increase in diffuse phase transition and γ values in the graphs is inversely proportional to the crystallite size. In this context, as the crystallite size decreases in BCZT ceramics, the relaxation behavior increases.

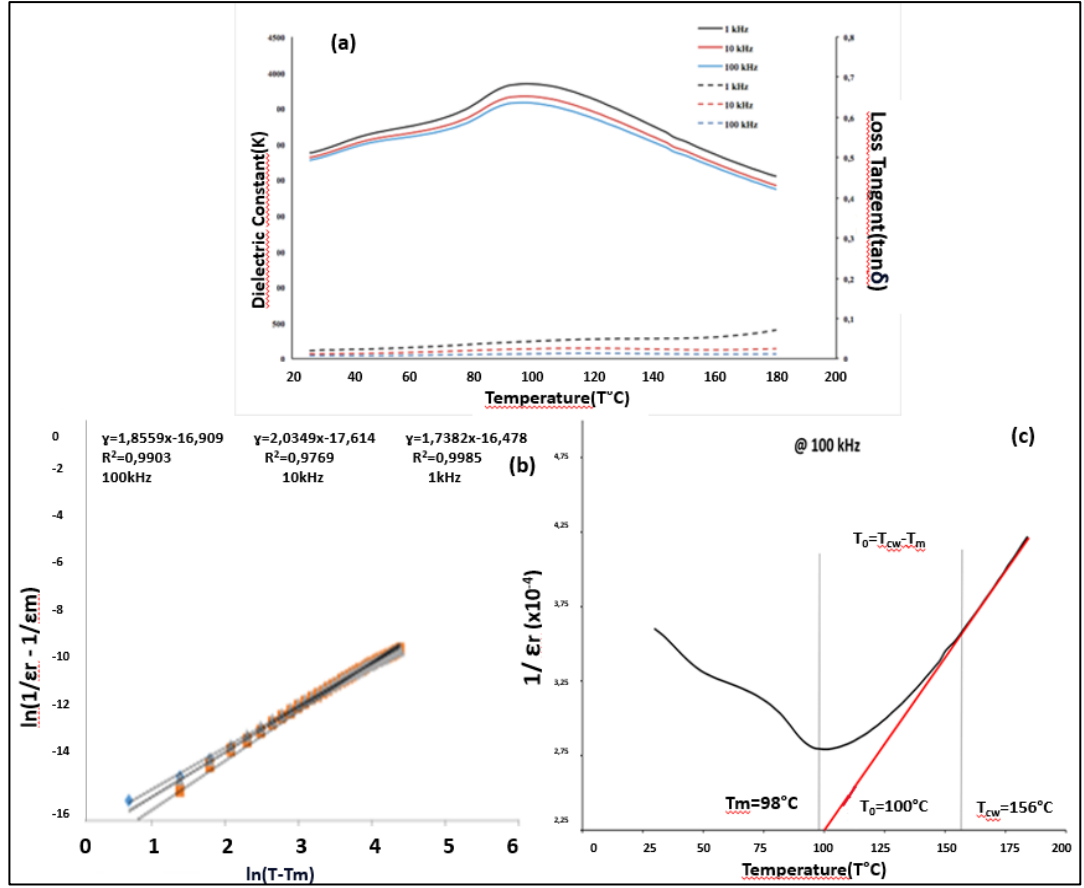


Figure 4.9: Temperature dependent dielectric properties of BCZT-SGH ceramic. (a) Dielectric constant and loss tangent - temperature, (b), $\ln(1/\epsilon_r - 1/\epsilon_m) - \ln(T - T_m)$ graphs at various frequencies, (c) Temperature dependence of the inverse of permeability measured at 100 kHz.

4.3.3. Ferroelectric Measurements of BCZT-SGH Ceramics

Figure 4.10 shows the electric field induced hysteresis loop (P-E) of the BCZT-SGH ceramic under an electric field of 40 kV/cm in various temperature. The sample thickness was measured 0.33 mm and measurements were taken every 10 degrees Celsius from 90°C to 0°C. As seen in Figure 4.10, while P_{max} , P_r , E_c values were measured as 15.7 $\mu\text{C}/\text{cm}^2$, 10.1 $\mu\text{C}/\text{cm}^2$, 8.58 kV/cm, respectively at 90°C, these values were obtained as 13.5 $\mu\text{C}/\text{cm}^2$, 6.9 $\mu\text{C}/\text{cm}^2$, 6.97 kV/cm.

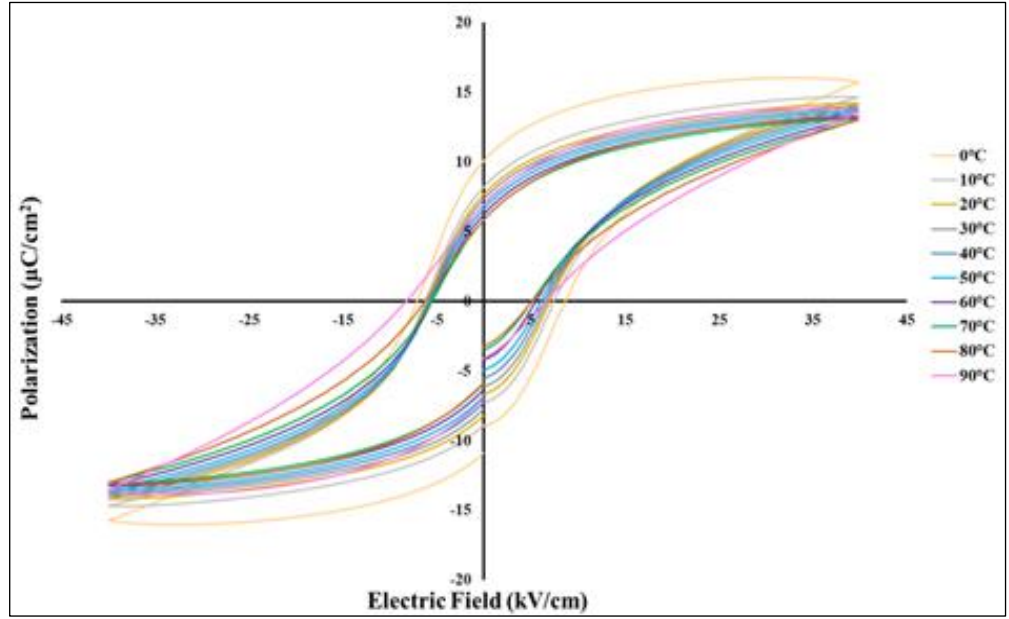


Figure 4.10: Polarization loops of the BCZT-SGH ceramic under 40 kV/cm at various temperatures.

The same sample is measured under 60 kV/cm and 80 kV/cm electric field. The graphs were given in Figure 4.11 and Figure 4.12, respectively. Measurements were generally done at room temperature under a 40 kV/cm electric field, where all samples could be measured without any damage. However, due to structural differences resulting from the increase in milling speed, measurements could also be taken at 60 kV/cm and 80 kV/cm from the BCZT-SGH sample. As can be seen from the graphs in Figures 4.10, 4.11, and 4.12, thinner and more saturated P-E hysteresis loops were obtained with increasing applied electric field. As seen in Figure 4.11, while P_{max,Pr,E_c} values were measured as $11.91 \mu\text{C}/\text{cm}^2$, $6.51 \mu\text{C}/\text{cm}^2$, $11.68 \text{ kV}/\text{cm}$, respectively at 90°C , these values were obtained as $10.28 \mu\text{C}/\text{cm}^2$, $4.94 \mu\text{C}/\text{cm}^2$, $10.00 \text{ kV}/\text{cm}$.

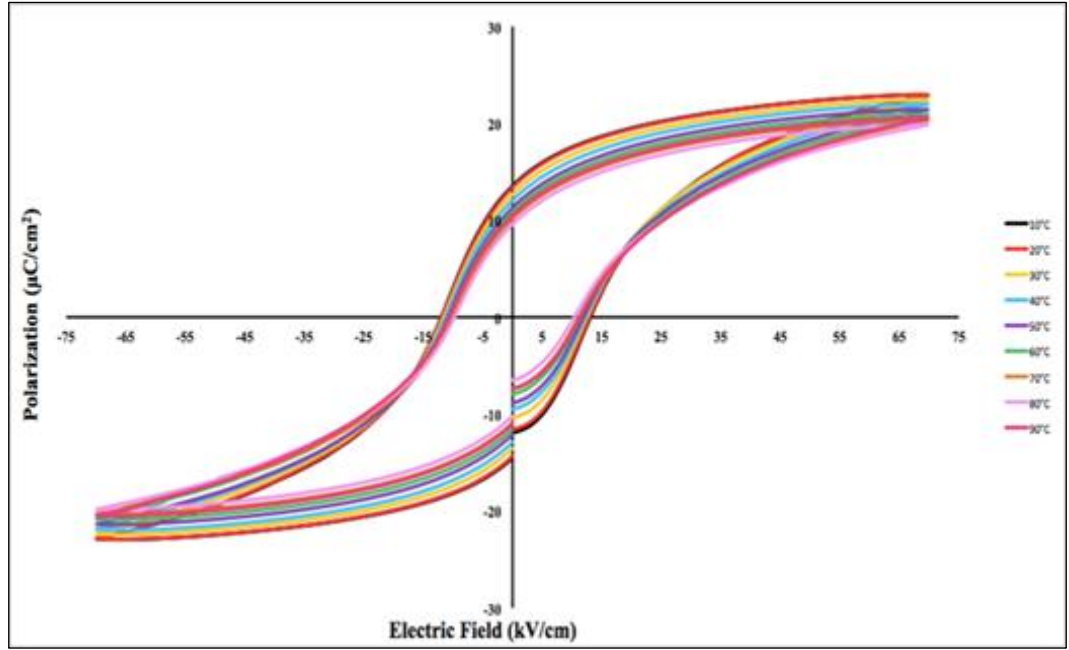


Figure 4.11: Polarization loops of the BCZT-SGH ceramic under 60 kV/cm at various temperatures.

As seen in Figure 4.12, while P_{max} , P_r , E_c values were measured as 57.78 $\mu\text{C}/\text{cm}^2$, 38.16 $\mu\text{C}/\text{cm}^2$, 18.53 kV/cm, respectively at 90°C, these values were obtained as 48.00 $\mu\text{C}/\text{cm}^2$, 25.32 $\mu\text{C}/\text{cm}^2$, 12.04 kV/cm.

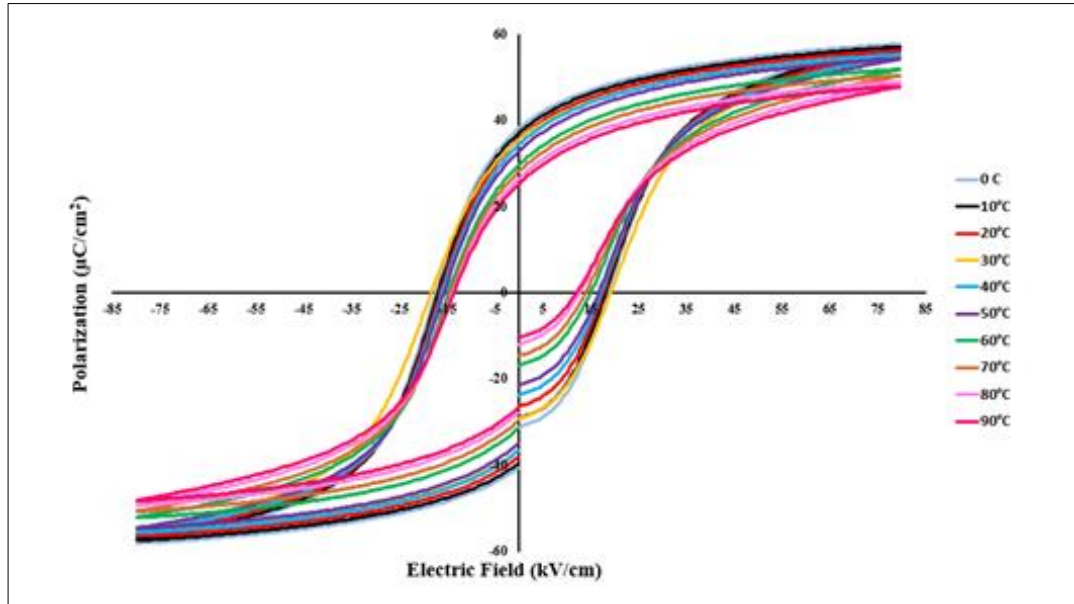


Figure 4.12: Polarization loops of the BCZT-SGH ceramic under 80 kV/cm at various temperatures.

Table 4.2: Comparison of Pmax, Pr and Ec values of BCZT ceramics.

	0° K			90°K		
	Pmax($\mu\text{C}/\text{cm}^2$)	Pr($\mu\text{C}/\text{cm}^2$)	Ec(kV/cm)	Pmax($\mu\text{C}/\text{cm}^2$)	Pr($\mu\text{C}/\text{cm}^2$)	Ec (kV/cm)
BCZT-SG-40kV	16,5	5,3	5,9	8,7	1,1	6,6
BCZT-SGH-40kV	15,7	10,1	8,6	13,5	6,9	6,9
BCZT-SGH-60kV	12,0	6,5	11,7	10,3	4,9	10,0
BCZT-SGH-80kV	57,8	38,2	18,5	48,0	25,3	12,0

4.3.4. Evaluation of Electrocaloric Measurement Results of BCZT-SGH Ceramics

Figure 4.13 presents the three-dimensional graphs of P-E curves and ΔT -T graph dependent on temperature between 0°C and 90°C for BCZT-SG ceramics with a thickness of 0.33 mm under 40 kV/cm electric field. It was observed that ferroelectric values decrease with increasing temperature as seen in Table 4.1.

As a result of the increase in milling speed, a smaller crystallite size was obtained as expected. The domain size and domain wall density are predicted to be impacted by the change in grain size, which will also have an impact on the electrical characteristics.

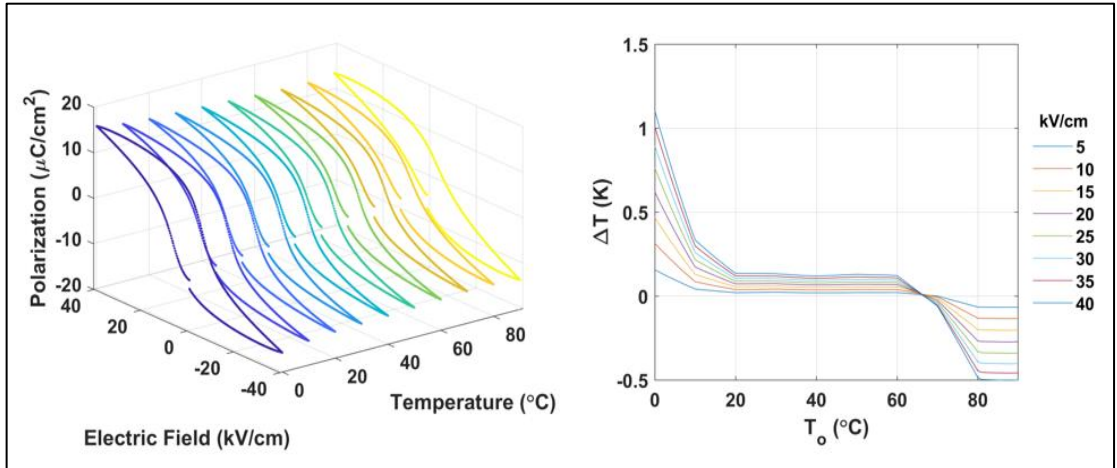


Figure 4.13: a) Three-dimensional P-E curves, b) ΔT -T graph BCZT-SGH.

Table 4.2 show the comparison of the electrocaloric coefficients [$\Delta T_c/\Delta E$, $\Delta S/\Delta E$], crystallite size, and γ values. As the crystallite size decreases, the relaxor behavior increases, and as a result of the increasing polar nano-regions in the structure provide additional degrees of freedom for the movement of dipoles. Moreover, since the dielectric strength increases with the smaller the crystallite size, a high electric field could be applied to the BCZT-SGH sample. The increase in relaxor properties and the application of a high electric field to the BCZT-SGH sample resulted in obtaining very high electrocaloric results.

Figure 4.14 and Figure 4.15 shows the P-E loops and $\Delta T/T_0$ results for the measurements taken under 60 kV/cm and 80 kV/cm, respectively.

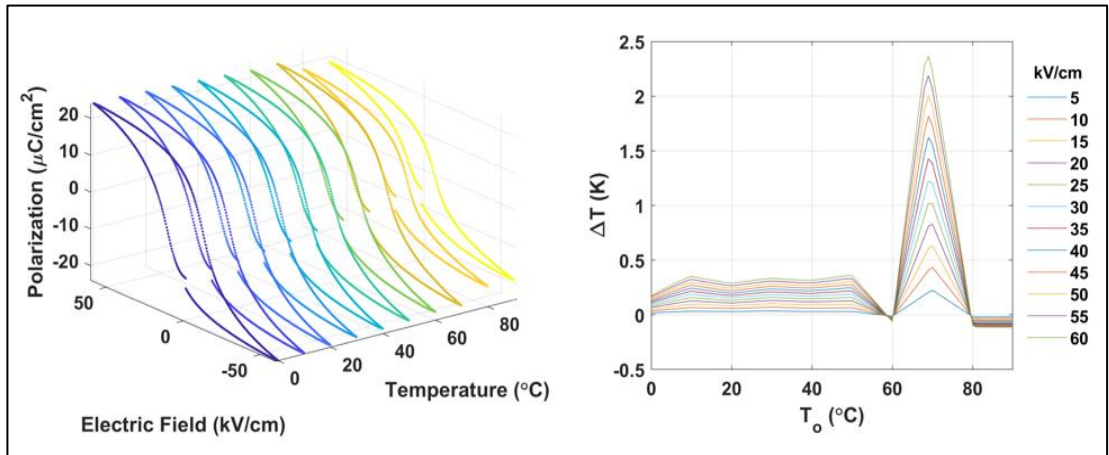


Figure 4.14: a) Three-dimensional P-E curves, b) ΔT -T graph BCZT-SGH.

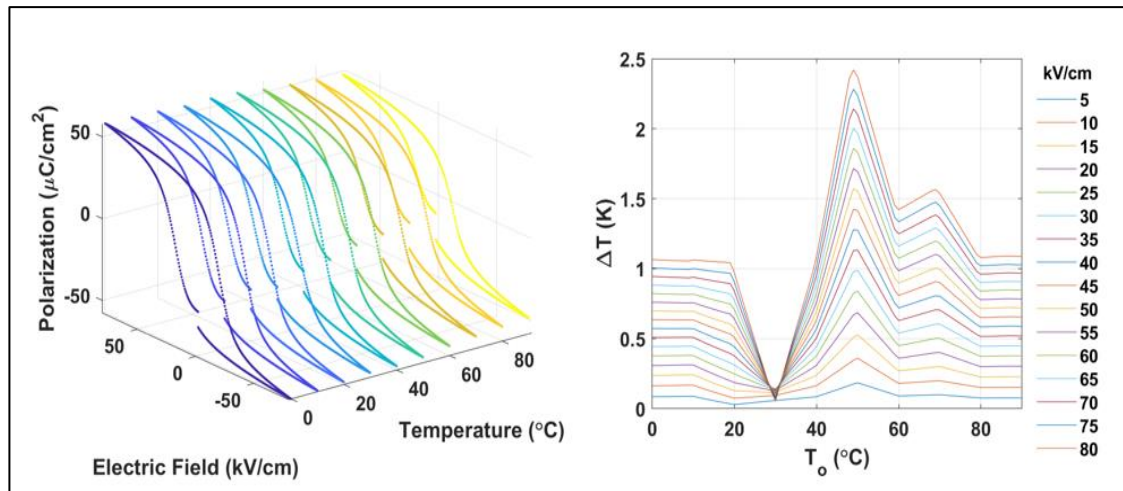


Figure 4.15: a) Three-dimensional P-E curves, b) ΔT -T graph BCZT-SGH

Table 4.3: Comparison of electrocaloric properties according to relaxor behavior.

	T_c ($^{\circ}\text{C}$)	Crystallite Size (nm)	γ @100 kHz	ΔE [kV/cm]	ΔT (K)	$\Delta T / \Delta E$ (10^6K mV^{-1})	$\Delta S / \Delta E$ ($10^{-6} \text{J mkg}^{-1} \text{K}^{-1} \text{V}$)
BCZT-SG	94	64	1.66	40 kV	1.2	0.375	0.40
BCZT-SGH	98	43	1.85	40 kV	1.2	0.375	0.40
				60 kV	2.5	0.357	0.44
				80 kV	2.5	0.313	0.44

5. CONCLUSIONS

Within the scope of a thesis study, ceramic powders with a composition of 0.5BZT- 0.5BCT were synthesized via the sol-gel method, containing rhombohedral and tetragonal phases at the morphotropic phase boundary. The obtained ceramic powders were ground using a ball mill for 24 hours at two different speeds: 200 rpm and 500 rpm. Structural and electrical characterizations of the ceramic pellet samples obtained by dry pressing were performed. With increasing temperature from 0°C to 90°C, a decrease in the values of P_{max} , P_r , and E_c were observed.

The powders synthesized using normal ball milling at 200 rpm and high-energy ball milling at 500 rpm were used to investigate mainly the effects of mechanical milling on the crystal size and electrocaloric properties. A decrease in particle size was observed depending on the grinding speed. Electrical measurement results showed that changes in particle size had an impact on area size and domain wall density. When looking at the P_{max} and P_r values of BCZT-SG and BCZT-SGH samples, it can be seen that crystal size and density are important parameters for electrical properties, and that the BCZT-SGH sample with smaller crystal size and denser structure reaches higher P_{max} and P_r values. As the particle size decreases, the area density increases. As the area density increases, the orientational polarization caused by area-wall vibrations and the ionic polarization caused by cage vibrations increase. In this way, decreasing the particle size causes the area size to decrease and the permeability to increase.

We aimed to investigate the normal and relaxing phase transition behavior of ceramics in Equation 4.3. γ is the degree of diffusion of the phase transition. The value of γ , a material constant dependent on the composition and structure of the material, is $\gamma = 2$ for an ideal relaxing ferroelectric and $\gamma = 1$ for a normal ferroelectric. γ value is 1.66 for BCZT-SG at 100 kHz and it was determined as 1.86 for BCZT-SGH. It is clearly seen that the diffuse phase transition and the increase of γ values in the graphs are inversely proportional to the crystallite size. In this context, while the crystallite size decreases in BCZT ceramics, the relaxing behavior increases.

In addition, the electrocaloric effects of BZT-BCT ceramics were investigated using an indirect method. ΔT - T curves were obtained based on P-E curves depending on temperature. Additionally, it was observed that as the crystallite size decreased, the

relaxor behavior increased, and the increasing polar nano regions in the structure provided additional degrees of freedom for dipole movement. However, high electric fields could be applied to the BCZT-SGH sample with smaller crystallite size since the dielectric strength increased with decreasing crystallite size. When compared with the literature, $\Delta T \sim 1.2\text{-}2.5$ K values, which are quite high for both ceramics. And it is considered that these BZT-BCT ceramics are good candidates for environmentally friendly electrocaloric materials.

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