

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

**CHARACTERIZATION OF BZT AND BCZT CERAMICS WITH CRITICAL  
PHASE POINTS FOR NEW GENERATION ELECTROCALORIC BASED  
COOLING DEVICES**

**TUBANUR AVCI**  
**A THESIS SUBMITTED FOR THE DEGREE OF**  
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**GEBZE**

**2023**

**T.C.**  
**GEBZE TEKNİK ÜNİVERSİTESİ**  
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**YENİ NESİL ELEKTROKALORİK ESASLI SOĞUTMA**  
**CİHAZLARI İÇİN KRİTİK FAZ NOKTALARINA SAHİP BZT**  
**VE BCZT SERAMİKLERİNİN KARAKTERİZASYONU**

**TUBANUR AVCI**  
**YÜKSEK LİSANS TEZİ**  
**MALZEME BİLİMİ VE MÜHENDİSLİĞİ ANABİLİM DALI**

**DANIŞMANI**  
**PROF. DR. EBRU MENŞÜR ALKOY**

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## SUMMARY

Barium titanate-based ceramics, one of the most widely used lead-free ferroelectric materials, exhibit lower electrical properties compared to lead-based materials, although they show relatively high dielectric constants, polarization, piezo and electrocaloric effects. To solve this problem, solid solutions of barium zirconium titanate (BZT) and barium calcium zirconium titanate (BCZT) were formed by adding  $\text{Ca}^{2+}$  and  $\text{Zr}^{4+}$  into barium titanate (BT).  $\text{BaTiO}_3$  ceramics for BZT are doped with  $\text{Zr}^{4+}$ . For BCZT,  $\text{Ca}^{2+}$  and  $\text{Zr}^{4+}$  replace  $\text{Ba}^{2+}$  and  $\text{Ti}^{4+}$  in the  $\text{BaTiO}_3$  crystal lattice, respectively. In this thesis's study  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  ( $x=0.15$  &  $x=0.20$ ) [BZT], and  $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  ( $x=0.32$  &  $x=0.50$ ),  $(1-x)\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-x(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$  ( $x=0.20$ ) [BCZT] composition ceramics with critical phase points were prepared by solid-state calcination and produced by the dry press method. The structural, electrical, and electrocaloric properties of the produced ceramics were investigated. In this study, the electrocaloric effect, which is one of the promising solid-state cooling techniques is used essentially. Temperature-dependent polarization measurement was done under different electric fields which is called as indirect method.  $\Delta T$  values were calculated using the temperature-dependent polarization results from Maxwell's equations. Within this master thesis, a TÜBİTAK 1002 project was completed and the second-best poster presentation award was received in "V. International Ceramic, Glass, Porcelain, Enamel, Glaze and Pigment Congress". Additionally, two SCI articles are being prepared from this thesis. TÜBİTAK #1002BF-01 and AFOSR #FA9550-18-1-0450 financially supported the thesis work.

**Keyword: Lead-Free Electroceramics, Electrocaloric Effect, Solid-State Method, Critical Point.**

## ÖZET

En yaygın kullanılan kurşunsuz ferroelektrik malzemelerden Baryum titanat bazlı seramikler, nispeten yüksek dielektrik sabitleri, polarizasyonları, piezo ve elektroklorik etkileri gösterse de kurşun bazlı malzemelere kıyasla daha düşük elektriksel özellikler sergiler. Bu sorunu çözmek için Baryum titanat (BT) içerisinde  $\text{Ca}^{2+}$  ve  $\text{Zr}^{4+}$  katılarak baryum zirkonyum titanat (BZT) ve baryum kalsiyum zirkonyum titanat (BCZT) katı eriyikleri oluşturulmuştur. BZT için  $\text{BaTiO}_3$  seramikleri  $\text{Zr}^{4+}$  ile katkılandırılmıştır. BCZT için  $\text{BaTiO}_3$  kristal kafesinde  $\text{Ca}^{2+}$  ve  $\text{Zr}^{4+}$  sırasıyla  $\text{Ba}^{2+}$  ve  $\text{Ti}^{4+}$ 'nın yerini alır. Bu tez çalışmasında kritik faz noktalarına sahip  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  ( $x=0.15$  &  $x=0.20$ ) [BZT] ve  $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  ( $x=0.32$  &  $x=0.50$ ),  $(1-x)\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-x(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$  ( $x=0.20$ ) [BCZT] kompozisyonlu seramikler, katı hal kalsinasyonu ile sentezlenip, kuru pres yöntemi ile üretilmiştir. Üretilen seramiklerin yapısal, elektriksel ve elektroklorik özellikleri incelenmiştir. Bu çalışmada gelecek vaat eden katı hal soğutma tekniklerinden biri olan elektroklorik etki temel alınmıştır. Dolaylı yöntem olarak adlandırılan farklı elektrik alanları altında sıcaklığa bağlı polarizasyon ölçümü yapılmıştır.  $\Delta T$  değerleri, Maxwell bağıntılarından sıcaklığa bağlı polarizasyon sonuçları kullanılarak hesaplanmıştır. Bu yüksek lisans tezi kapsamında bir TÜBİTAK 1002 projesi tamamlanmış ve "V. Uluslararası Seramik, Cam, Emaye, Sır ve Boya Kongresi"nde en iyi ikinci poster sunum ödülü alınmıştır. Ayrıca bu tezden iki SCI makale hazırlanmaktadır. Tez çalışmasını TÜBİTAK #1002BF-01 ve AFOSR #FA9550-18-1-0450 mali olarak desteklemiştir.

**Anahtar Kelimeler:** Kurşunsuz Elektroseramikler, Elektroklorik Etki, Katı Hal Yöntemi, Kritik Nokta.

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## LIST of ABBREVIATIONS and ACRONYMS

| <u>Abbreviations</u><br><u>and Acronyms</u> | <u>Explanations</u>                  |
|---------------------------------------------|--------------------------------------|
| $\text{\AA}$                                | : Angstrom                           |
| $\Delta E_b$                                | : Energy Barrier                     |
| $\Delta S$                                  | : Adiabatic Entropy Change           |
| $\Delta T$                                  | : Electrocaloric Temperature Change  |
| $\lambda$                                   | : X-ray Wavelength                   |
| $\mu\text{C}/\text{cm}^2$                   | : Microcoulomb per Centimeter Square |
| $\mu\text{m}$                               | : Micrometer                         |
| $C_p$                                       | : Heat Capacity                      |
| $Di$                                        | : Electrical Displacement            |
| $d_{ijk}$                                   | : Piezoelectric Coefficient          |
| $d_{33}$                                    | : Piezoelectric Charge Coefficient   |
| $E$                                         | : Electric Field                     |
| $E_c$                                       | : Coercive Field                     |
| $K$                                         | : Kelvin                             |
| $\text{kHz}$                                | : Kilohertz                          |
| $\text{kV}/\text{cm}$                       | : Kilovolt per Centimeter            |
| $L$                                         | : Average Crystallite Size           |
| $\text{mm}$                                 | : Milimeter                          |
| $\text{MPa}$                                | : Megapascal                         |
| $\text{ms}$                                 | : Millisecond                        |

|                |                                                             |
|----------------|-------------------------------------------------------------|
| nm             | : Nanometer                                                 |
| P              | : Polarization                                              |
| $\rho$         | : Density                                                   |
| pC/N           | : Picocoulomb per Newton                                    |
| $P_{\max}$     | : Maximum Polarization                                      |
| $P_r$          | : Remnant Polarization                                      |
| $P_s$          | : Spontaneous Polarization                                  |
| r              | : Ionic Radius                                              |
| t              | : Tolerance Factor                                          |
| $\tan\delta$   | : Loss Tangent                                              |
| $T_c$          | : Curie Temperature                                         |
| $T_m$          | : Maximum Transition Temperature                            |
| $x_{ij}$       | : Strain                                                    |
| $X_{jk}$       | : Applied Stress                                            |
| $ABO_3$        | : Perovskite Structure                                      |
| $BaTiO_3$ (BT) | : Barium Titanate                                           |
| $BaZrO_3$ (BZ) | : Barium Zirconate                                          |
| BCT            | : Barium Calcium Titanate                                   |
| BCZT           | : Barium Calcium Zirconium Titanate                         |
| BZT            | : Barium Zirconium Titanate                                 |
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|          |                                                           |
|----------|-----------------------------------------------------------|
| 0.15 BZT | : $\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3$ |
| 0.20 BZT | : $\text{Ba}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$ |
| DC       | : Direct Current                                          |
| DSC      | : Differential Scanning Calorimetry                       |
| ECE      | : Electrocaloric Effect                                   |
| ICP      | : Invariant Critical Point                                |
| KNN      | : Potassium Sodium Niobate                                |
| MPB      | : Morphotropic Phase Boundary                             |
| PNR      | : Polar Nanoregion                                        |
| PLZT     | : Lead Lanthanum Zirconate Titanate                       |
| PMN      | : Lead Magnesium Niobate                                  |
| PVDF     | : Polyvinylidene Fluoride                                 |
| PZN      | : Lead Zinc Niobate                                       |
| PZT      | : Lead Zirconate Titanate                                 |
| PPT      | : Polymorphic Phase Transition                            |
| rpm      | : Revolutions per Minute                                  |
| SEM      | : Scanning Electron Microscope                            |
| TCP      | : Tricritical Point                                       |

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# 1. INTRODUCTION

In advanced electronic technology, miniaturization necessitates recent thermal management solutions to reduce or avoid overheating during their usage. The traditional cooling technology, based on vapor compression, has been replaced by the environmentally friendly "solid-state cooling" technology. Solid-state cooling systems are divided into three parts and mainly used thermoelectric, magnetocaloric, and electrocaloric effects. The electrocaloric effect (ECE), which is the more environmentally friendly method, has higher energy efficiency. The devices based on the EC effect can be miniaturized compared to existing cooling devices and have recently attracted attention.

When an electric field is applied to a dielectric material, the change in the polarization and thus entropy ( $\Delta S$ ) and temperature ( $\Delta T$ ) in the material is called as the electrocaloric effect. Although the electrocaloric effect has been recognized for a while, it wasn't thought to have any practical uses due to the low-temperature variation ( $\Delta T < 1$  K) in previously known materials. The giant electrocaloric effect in Lead Zirconate Titanate (PZT) and Polyvinylidene Fluoride (PVDF) has revived interest in this area of study. Lead-based ferroelectrics such as  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT),  $\text{Pb}(\text{Mg}, \text{Nb}, \text{Ti})\text{O}_3$  (PMN-PT), and  $\text{Pb}(\text{La}, \text{Zr}, \text{Ti})\text{O}_3$  (PLZT) show excellent electrocaloric properties, but interest in  $\text{K}(\text{Na}, \text{Nb}, \text{Sr}, \text{Ti})\text{O}_3$  (KNN-STO) ceramics and  $\text{BaTiO}_3$ (BT)-based lead-free ferroelectrics has increased as lead's toxicity causes health and environmental problems.  $\text{BaTiO}_3$  exhibits low electrical properties (dielectric, piezoelectric charge coefficient, etc.) compared to lead-based materials. This problem has been solved by doping  $\text{BaTiO}_3$  ceramics.

For  $\text{Ba}(\text{Zr}, \text{Ti})\text{O}_3$  (BZT),  $\text{BaTiO}_3$  ceramics are doped with  $\text{Zr}^{4+}$ . For  $\text{Ba}(\text{Ca}, \text{Zr}, \text{Ti})\text{O}_3$  (BCZT),  $\text{Ca}^{2+}$  and  $\text{Zr}^{4+}$  replace with  $\text{Ba}^{2+}$  and  $\text{Ti}^{4+}$  in the  $\text{BaTiO}_3$  crystal lattice, respectively. Thus, BZT and BCZT exhibit high piezoelectric, dielectric, ferroelectric, and electrocaloric performances.

In the thesis study, the production, structural-electrical characterization, and electrocaloric properties of BZT and BCZT lead-free ceramics with different compositions were investigated.

## 1.1. Purpose of Thesis

- This study, it is aimed to develop materials that can be used in the cooling systems of micro-scale electronic circuits and work in extreme conditions for a long time with electrocaloric cooling, which is one of the promising solid-state cooling techniques.
- The primary aim of this thesis is to produce lead-free ferroelectric ceramic systems with a wide phase transition range and high polarization direction in critical point compositions and to investigate the effect of polarization number on ECE.
- The critical points chosen for the BZT are the normal ferroelectric  $x=0.15$  composition, which operates at the quaternary critical invariant point, and the  $x=0.20$  composition, which is the relaxor ferroelectric.
- The critical points chosen for the BCZT are the  $x=0.32$  and  $x=0.20$  compositions operating at the triple critical invariant points and the  $x=0.50$  composition operating at the MPB (morphotropic phase boundary).
- Ferroelectric, dielectric, and electrocaloric properties of ceramic samples produced at critical points by the dry pressing method were examined and the effect of multiple polarization conditions on these properties was evaluated.

## 2. LITERATURE REVIEW

### 2.1. Electroceramics

Electroceramic is a ceramic material specially produced for specific electrical, magnetic, or optical properties. Electroceramics, a subclass of advanced ceramics, are used in a wide variety of electrical, optical, and magnetic applications such as batteries, fuel cells, varistors, thermistors, capacitors, and ferroelectric memories due to their high dielectric and piezoelectric constants properties. Although electroceramics have been used since the latter decades of the 20th century and the percentage of use is low, it has an extensive market share in the ceramic industry because of its significant added value. Piezoelectric ceramics and dielectric ceramics are common types of electroceramics due to their properties of high electrical resistivity and high dielectric strength. Capacitors, piezo transformers, ultrasonic motors, heaters, electrodes, gas detectors, varistors, thermistors, sonars, buzzers, hydrophones, accelerometers, surface acoustic wave filters, positioners with high precision for scanning probe analysis (XPM) systems, and touch controls are just a few examples of the widest range of applications for piezoelectric ceramics, which are typically based on PZT compositions [1],[2]. Figure 2.1 shows the classification of electroceramics.

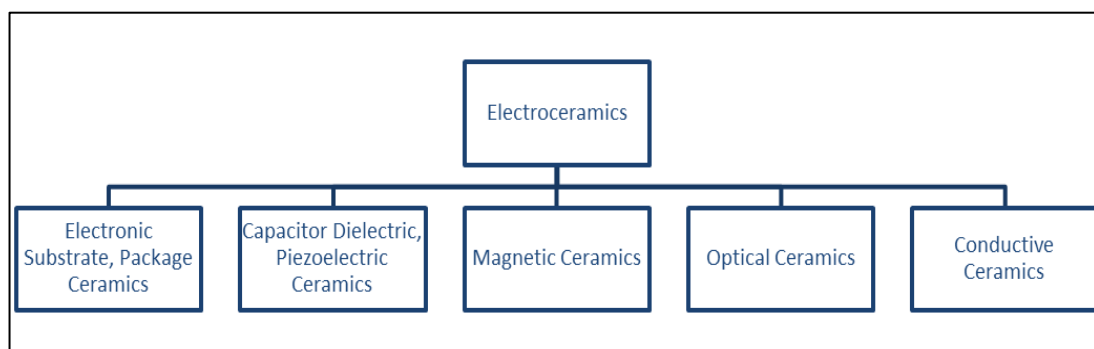


Figure 2.1: Classification of electroceramics.

## 2.1. Piezoelectricity

The Greek word "piezien," which means pressure, is the origin of the term "piezo." Piezoelectric materials are materials that change shape with the applied electric field and produce electricity with the applied pressure. This property was found in 1880 by Jacques & Pierre Curie in crystals such as quartz, tourmaline, and Rochelle salt [3].

In most kinds of crystals non-centrosymmetric, the applied stress can create electric dipole moments, leading to the piezoelectric effect. Due to their polar structure in their crystal lattices, all ferroelectric materials have piezoelectric capabilities [4],[5].

The direct piezoelectric effect, which is used in device applications such as sensors and energy harvesting, is the formation of electrical orientation as a result of applying mechanical stress to a piezoelectric material [4]. The mathematical expression of the direct piezoelectric effect:

$$D_i = d_{ijk}X_{jk} \quad (2.1)$$

In Equation 2.1,  $D_i$  is the electrical displacement and  $d_{ijk}$  is the piezoelectric coefficient, which is a third-order tensor and its unit is C/N.  $X_{jk}$  is the applied stress, which is a second-order tensor [4].

The converse piezoelectric effect, employed in actuator applications, experiences strain or displacement in proportion to an electric field applied to the material [4]. The mathematical expression of the converse piezoelectric effect:

$$x_{ij} = d_{ijk}E_k \quad (2.2)$$

In Equation 2.2, the strain ( $x_{ij}$ ) is the second order tensor and the electric field ( $E_k$ ) is the first order tensor. The converse piezoelectric coefficient is also a third-order tensor [4]. Figure 2.2 shows the direct and converse piezoelectric effect.

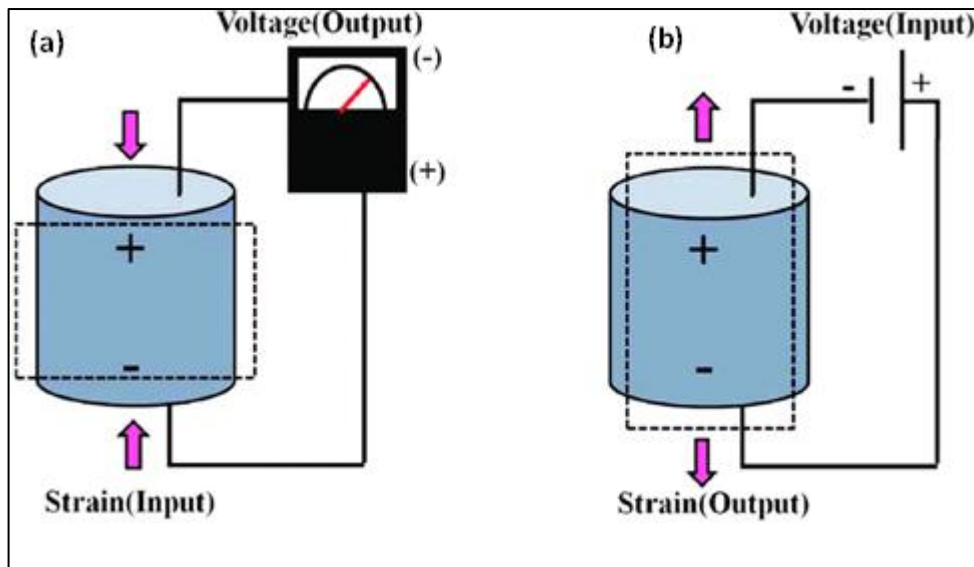


Figure 2.2: (a) Direct and (b) converse piezoelectric effect.

## 2.3. Ferroelectricity

Ferroelectrics are dielectric materials that have spontaneous permanent polarization without exposure to the influence of an external electric field. Spontaneous polarization results from the central atom in the unit cell being non-centrosymmetric and can be increased or decreased by the electric field applied in the polarization directions [6],[7]. Ferroelectric materials are polar crystals. Crystal materials are divided into 7 basic crystal systems: triclinic, monoclinic, orthorhombic, trigonal, hexagonal, tetragonal, and cubic. These crystal systems can also be referred to as "point groups" since each one of them exhibits symmetry with regard to a point. There are 32-point groups for each of the 7 crystal classes, as shown in Figure 2.3. Among the 32-point groups, 11 of them cannot show ferroelectric properties because they are centromeric. With the application of the electric field, these materials are linearly polarized and exhibit dielectric polarization. The remaining 21-point groups are piezoelectric crystals except for one. In these materials, applying mechanical stress causes an electric current to flow in a particular direction. 10 of the 20 non-centrosymmetric point groups have pyroelectric properties because they have a single polar axis per unit cell. These point groups exhibit spontaneous polarization,

which depends on temperature. Because spontaneous polarization occurs, a charge flow may be seen with temperature dependency. Positive and negative charges can be reoriented via reversible spontaneous polarization. This characteristic is known as "ferroelectricity" [8],[9].

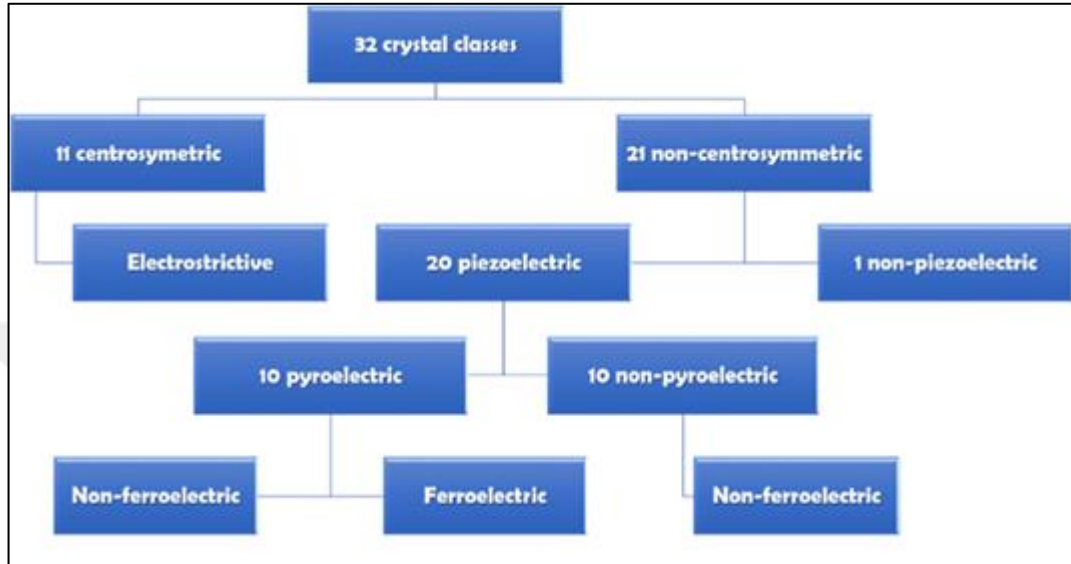


Figure 2.3: Categorization of crystal classes based on ferroelectric, pyroelectric, and piezoelectric characteristics.

### 2.3.1. Perovskite Structure

$\text{ABO}_3$  perovskite structure is the usual unit cell type for a typical ferroelectric material [11]. Generally, the A cations are at the corners of the cubic structures, the B cations are at the oxygen octahedral center spaces, and the oxygen atoms are at the surface centers of the cubic structure. In ferroelectric materials, the "A" cation is usually large atoms such as  $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Bi}^{3+}$  or  $\text{Na}^+$ , and the "B" cation is small atoms such as  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  [10],[11]. When barium titanate, one of the ferroelectrics formed in the perovskite structure, is taken as an example, barium atoms are found at the corners of the crystal lattice (Figure 2.4). The unit cell has a symmetrical cubic structure with  $\text{Ti}^{4+}$  ions at the center of the volume.  $\text{Ba}^{2+}$  (ion radius  $\sim 1.43 \text{ \AA}$ ) and  $\text{Ti}^{4+}$  (ion radius  $\sim 0.72 \text{ \AA}$ ) ions are in octahedral lattice form with  $\text{O}^{2-}$  ions. Differences in cation sizes cause some structural distortions. This affects the stability

of the perovskite structure. For the perovskite structure, there is a tolerance factor defined as “t” that determines the properties of perovskite-type oxides [3],[12].

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (2.3)$$

In a perfect cubic perovskite structure would be  $t=1.0$ , and  $r_A$ ,  $r_B$ , and  $r_O$  represent the ionic radius of the large and small cation, and anion, respectively. Generally, cubic for  $t \approx 1$ , orthorhombic or rhombohedral symmetries for  $t < 1$ , and tetragonal for  $t \geq 1$  are the most stable structures in ferroelectric  $ABO_3$  [13].

The perovskite structure is significant because the majority of them have high dielectric constants, ferroelectric, and piezoelectric characteristics. The perovskite structure's elasticity and compatibility with a variety of cation combinations provide a great framework for the development of novel material systems as well as the investigation of the effect of crystal chemistry on physical properties. When additives are made to barium titanate, new properties are achieved with atoms going to A or B positions. Lead zirconium-titanate and lead magnesium titanate-lead titanate compositions are ferroelectric ceramics widely produced for commercial purposes [14].

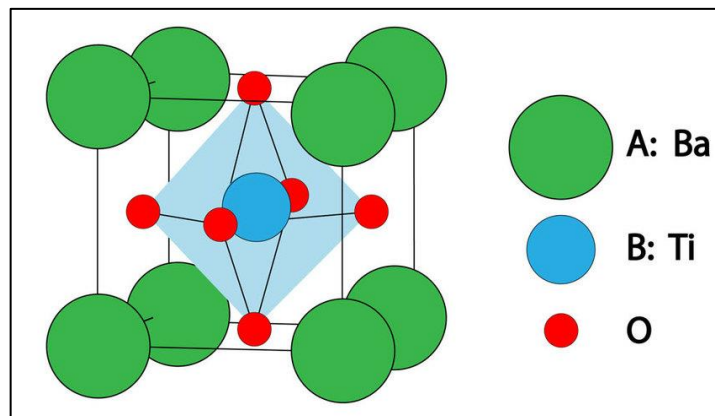


Figure 2.4: BaTiO<sub>3</sub> perovskite structure.

### 2.3.2. Phase Transitions

The most essential property for numerous ferroelectric materials is phase transitions. The most obvious phase transition occurs between the high-temperature paraelectric phase and the low-temperature ferroelectric phase and is called the Curie temperature ( $T_c$ ) [15]. During this phase transition, the material runs out of its ferroelectric property and reveals normal dielectric behavior, known as the paraelectric phase [16].

At temperatures under  $T_c$ , ferroelectric materials often behave non-polarly, and the dielectric constant reaches its highest value, especially in regions near  $T_c$ . As the  $T_c$  is exceeded, the dielectric constant decreases according to the “Curie-Weiss” law given in Equation 2.4. In this case, where the ferroelectric behavior is lost, the material acquires a perovskite crystal structure. Dimensional changes are caused by phase transitions in the crystal structure's unit cell. The electrical characteristics of crystals depend on their dimensional variations [3].

$$\epsilon_r = \frac{A}{T - \theta_c} \quad (2.4)$$

A: The coefficient depending on the material,  $\theta_c$ : A temperature near to the  $T_c$ ,  $\epsilon_r$ : Dielectric constant. Figure 2.5 shows the variations in the lattice parameter, spontaneous polarization, and dielectric constant in the various phases of  $\text{BaTiO}_3$  (BT). Since the tetragonal phase is stable at room temperature and above room temperature, the tetragonal phase of BT has been the focus of most research. Macroscopic spontaneous polarization does not occur without the presence of a DC electric field because of the existence of the  $90^\circ$  and  $180^\circ$  domains.

With the application of the DC field, the domains combine to form monodomain crystals. Orientation of all domains along the applied external DC field

is not possible for BaTiO<sub>3</sub> ceramic. Therefore, ceramic samples have lower saturation polarization and remnant polarization compared to single crystals [4],[17],[18].

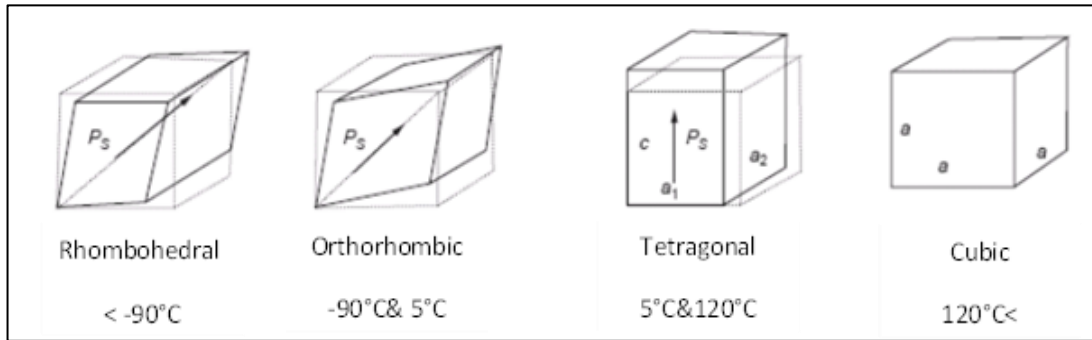


Figure 2.5: Crystal structure change of BaTiO<sub>3</sub> crystal with temperature.

### 2.3.3. Domains

Aligning all dipoles in one direction in ferroelectric materials under an external field raises the energy of the system, which causes instability. To decrease the system's energy and minimize the electrical and mechanical limitations of the material, dipoles oriented in the same direction form regions with the same polarization direction called "domains". These domains are separated by domain walls [3],[6]. A ferroelectric material exhibits domain growth and domain wall motion when an electric field is applied in a direction that is parallel to the direction of the electric field applied [19]. Domain walls separating mutually vertically polarized regions are divided by 90° walls, whereas domain walls separating oppositely polarized parts are separated by 180° walls. The material is ferroelectric since the walls with an angle of 180° differ in the orientation of the polarization vector. Because the orientation of the polarization vector and the spontaneous strain tensor differs, walls with a 90° angle are both ferroelectric and ferroelastic [6].

Figure 2.6 shows that a ferroelectric hysteresis cycle occurs as a result of domain wall movement. When the polarization-electric field hysteresis plot of the ferroelectric material against the electric field is examined, the polarization increases linearly under low electric fields. Because the electric field applied is not strong enough to polarize the domain structure (between OA). The polarization increases non-linearly with an increasing electric field (between AB). Here, the domains begin

to orient with the effect of the electric field. The polarization reaches saturation due to the high electric field effect between the BC. Here, most of the domains are oriented in the same direction as the electric field. If the electric field is reduced, some domains get back and the polarization will follow the path indicated by the CBD. In the zero electric fields, as shown at point D, the polarization is not zero. The spontaneous polarization of the material in a zero electric field is called "remnant polarization" ( $P_r$ ). To reach the zero polarization state, the field is reversed, the electric field value required for this is called the "coercive electric field" ( $E_c$ ). With the increasing negative electric field, reverse polarization occurs until it reaches saturation in the E-F range. If the electric field is reversed again, the polarization is reduced to zero along the F-G-H path and completes the cycle [3],[7],[20].

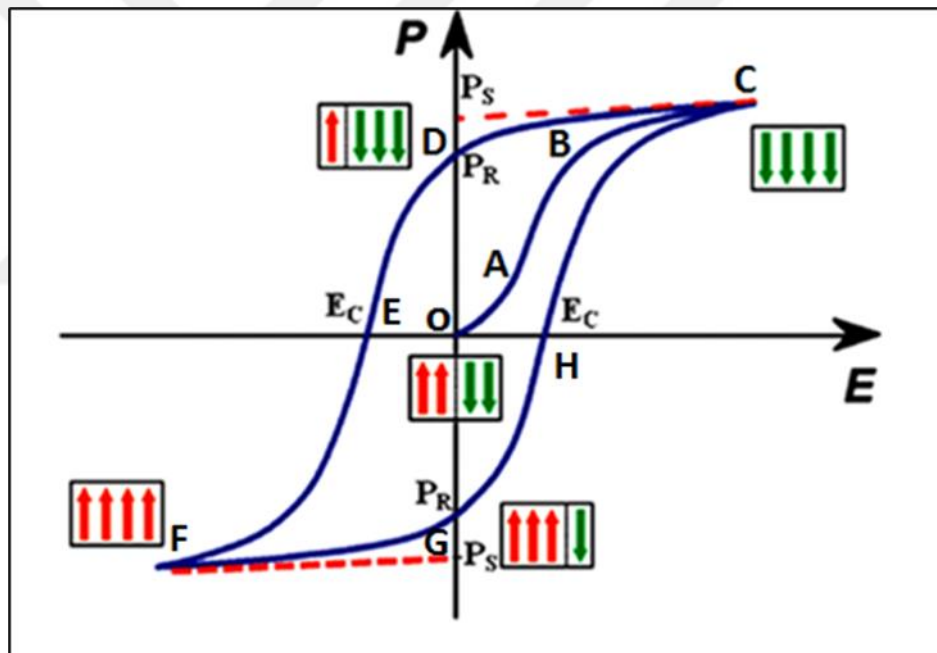


Figure 2.6: Hysteresis curve in ferroelectric materials.

## 2.4. Relaxor Ferroelectrics

Distortions in the lattice occur as a result of the chemical substitution of ions with valence different from the valence of the host ions in the matrix of the ferroelectric material and the ferroelectric domains are divided into polar nano regions (PNRs) with randomly distributed dipole moment directions [21]. The relaxor

state is formed by the appearance of polar nano regions in the material under a certain temperature, which is called the “Burns temperature” [22]. Relaxors are a special class of ferroelectric materials that contain local inhomogeneities known as polar nano regions (PNR). The difference between relaxor ferroelectrics and normal ferroelectrics is a wide phase transition range, a frequency-dependent and high dielectric constant at around  $T_c$  [23].

Normal ferroelectrics have large remnant polarization and coercive fields with the contribution of macro-sized ferroelectric domains and exhibit strong hysteretic properties. But they lose their polarization at the  $T_c$ . Any polar domains or spontaneous polarization in the material are absent above the  $T_c$ . In contrast, the polarization of a relaxor decreases slowly above the  $T_m$  transition temperature due to the presence of nanodomains (Figure 2.7) [19].

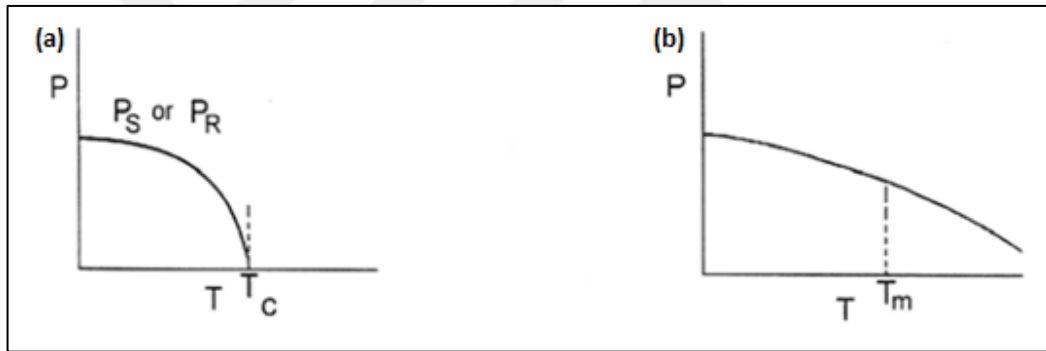


Figure 2.7: Temperature dependent variations of polarization of (a) Normal ferroelectric and (b) Relaxor ferroelectric.

The electric field-polarization curves of relaxor ferroelectrics are also different from normal ferroelectrics. Relaxors have thin hysteresis curves. It is possible to achieve high saturation polarization under a sufficient electric field. However, with the removal of the electric field, the PNRs return to their random state, resulting in minor remnant polarization. The induced polarization of the material gradually decreases at the Curie temperature (Figure 2.8) [19].

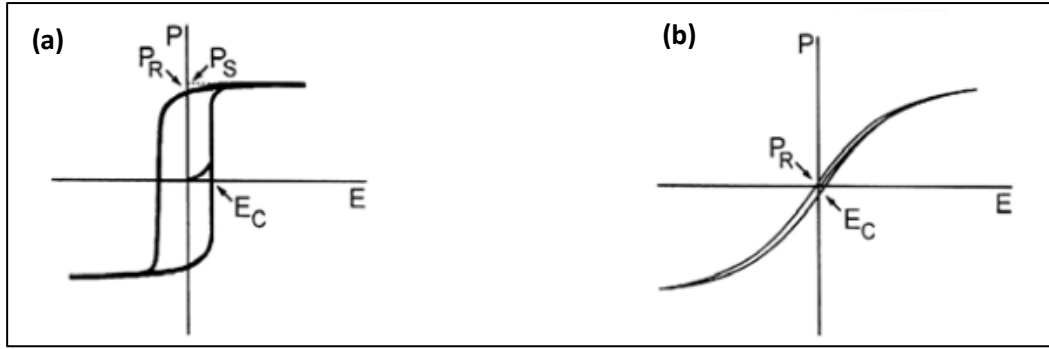


Figure 2.8: Typical P-E hysteresis cycle for (a) Normal ferroelectric and (b) Relaxor ferroelectric.

Normal ferroelectric material has a sharp phase transition, while relaxors have a diffuse phase transition. Because there are long nano regions with different ferroelectric phase transition temperatures in relaxors, the exact temperature at which the phase transition occurs is not exactly clear and changes with frequency [19],[22]. Normal ferroelectrics reach the dielectric maximum with a sharp transition and they have no frequency dependence. Relaxor ferroelectrics show a frequency-dependent dielectric behavior over a broad temperature range and depending on the frequency, the dielectric maximum shifts to higher temperatures (Figure 2.9) [19].

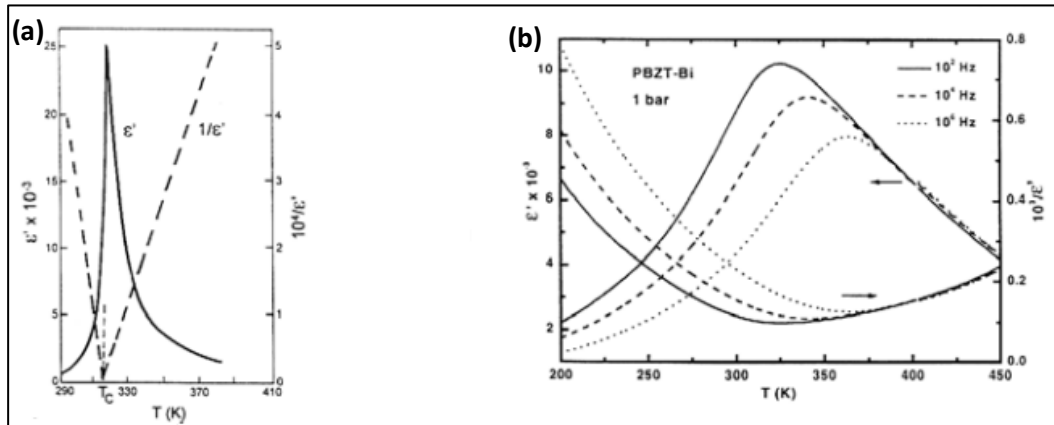


Figure 2.9: Temperature-dependent dielectric properties (a) Normal ferroelectric and (b) Relaxor ferroelectric.

The high permittivity is due to the two ions in the B position in the perovskite structure having different values and different sizes. As shown in Figure 2.10, these two ions of different sizes are located in the B position in an irregular manner. The

motion of small ions inside the lattice is helped by large ions that cause the lattice structure to widen. The B ions with a large field of motion have a very high dielectric constant because of their ease of movement when an electric field is applied to the irregular perovskite structure. There are also some small regular regions (2-5 nm) with less range of motion in the crystal lattice. In structures where regular and irregular regions coexist, a diffusion is observed in the phase transition, since each region acts as if it has a distinct  $T_c$  [22],[23].

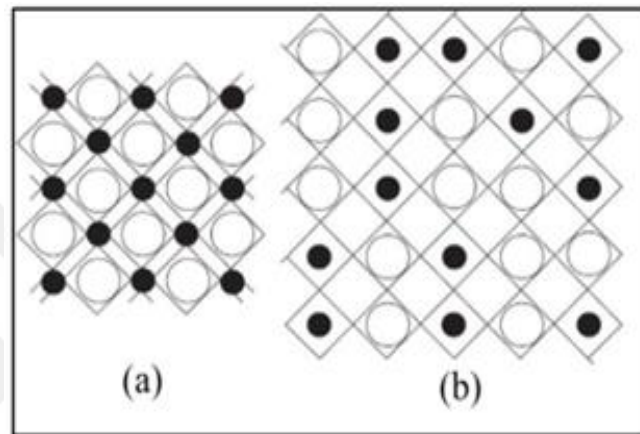


Figure 2.10:  $ABO_3$  crystal of the perovskite-type (a) the small movable hollow regular structure, (b) the big movable hollow irregular structure.

At the same time, relaxor materials offer additional degrees of freedom due to their nanoscopic structure, which can be converted to a ferroelectric state by applying an electric field. The resulting large entropy changes provide an increase in the electrocaloric effect (ECE) [9].

## 2.5. Electrocaloric Properties

The continuous expansion of the industry, the increase in the standard of living, and climate change have led to an increase in the place of the cooling market in energy consumption. Therefore, it has led to excessive energy consumption, which leads to the depletion of non-renewable energy sources and thus the deepening of the greenhouse effect [22]. In advanced electronic technology, miniaturization necessitates recent thermal management solutions to reduce or avoid overheating

during their usage [24]. ECE is an attractive method because, in addition to being used in standard cooling and heating devices, it can be adapted to almost any application in microelectronics such as chips, sensors, electronic devices, and micro-robotics [27]. It could be used as a substitute for the current vapor compression method since it is easier and cheaper to manufacture, and additionally environmentally friendly due to its capacity for energy conversion and savings [25],[26].

### **2.5.1. History of Electrocaloric Effect**

The earliest experimental studies of the electrocaloric effect were conducted on single-crystal Rochelle salt by Kurchatov and Kobenko in 1930, and measured by Hautzenlaub in 1943. Although the electrocaloric effect has been recognized for a while, it wasn't thought to have any practical uses due to the low-temperature variation ( $\Delta T < 1$  K) in previously known materials. Instead of the electrocaloric effect, the magnetocaloric effect was used. Electrocaloric effects research has been revived with the discovery of huge electrocaloric response in some inorganic and organic materials (70°C P(VDF – TrFE) – 25°C P(VDF – TrFE – CFE) and 222°C PZT thin film). Since 2006, research in the field of electrocaloric materials has intensified [27].

### **2.5.2. Mechanism of Electrocaloric Effect**

The electrocaloric effect is that when an electric field is applied to a dielectric material, the change in polarization causes a change in entropy and temperature in the material [25]. As shown in Figure 2.11, It is the inverse of the pyroelectric response, in which the total electric polarization changes with temperature [28]. In addition to large polarization to achieve a large electrocaloric effect, ferroelectric materials must be able to operate close to room temperature. This requires them to have a suitable ferroelectric-paraelectric phase transition point because ECE is maximized just above the Curie temperature [25].

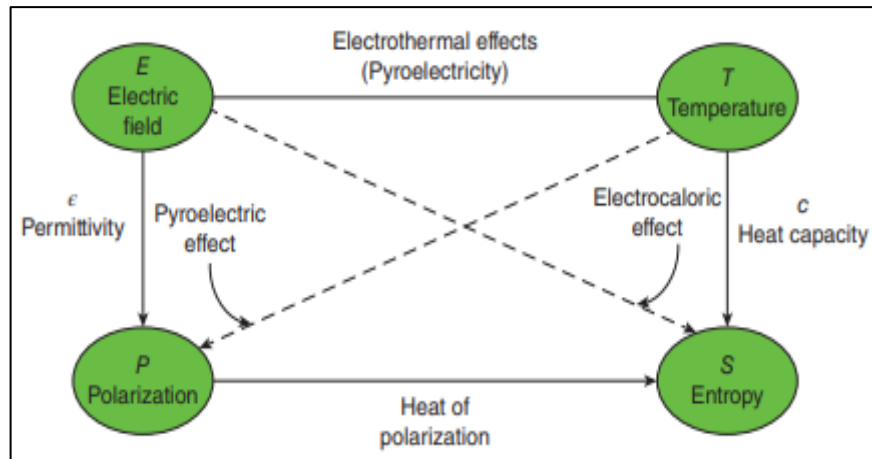


Figure 2.11: Expanded pyroelectric zone showing pyroelectric and electrocaloric effects.

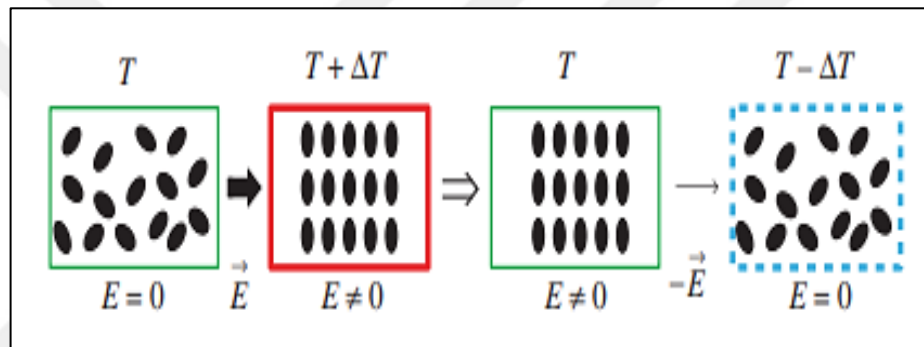


Figure 2.12: Schematic illustration of the electrocaloric effect.

The schematic illustration of the electrocaloric effect given in Figure 2.12 shows the rearrangement of the dipoles by causing a change in temperature and entropy of the applied electric field. Cooling is done through adiabatic depolarization. Since the total entropy in adiabatic systems is the sum of thermal and dipolar entropy, they behave in a way that they balance each other [29]. When the electric field is applied, the dipolar subsystem entropy decreases, and the lattice vibration causes the temperature to rise of the material to compensate for the decreasing entropy. On the contrary, the reduction in lattice vibration entropy caused by the adiabatic removal of the electric field balances out the rise in dipolar subsystem entropy and causes the material's temperature to drop [24],[27]-[29].

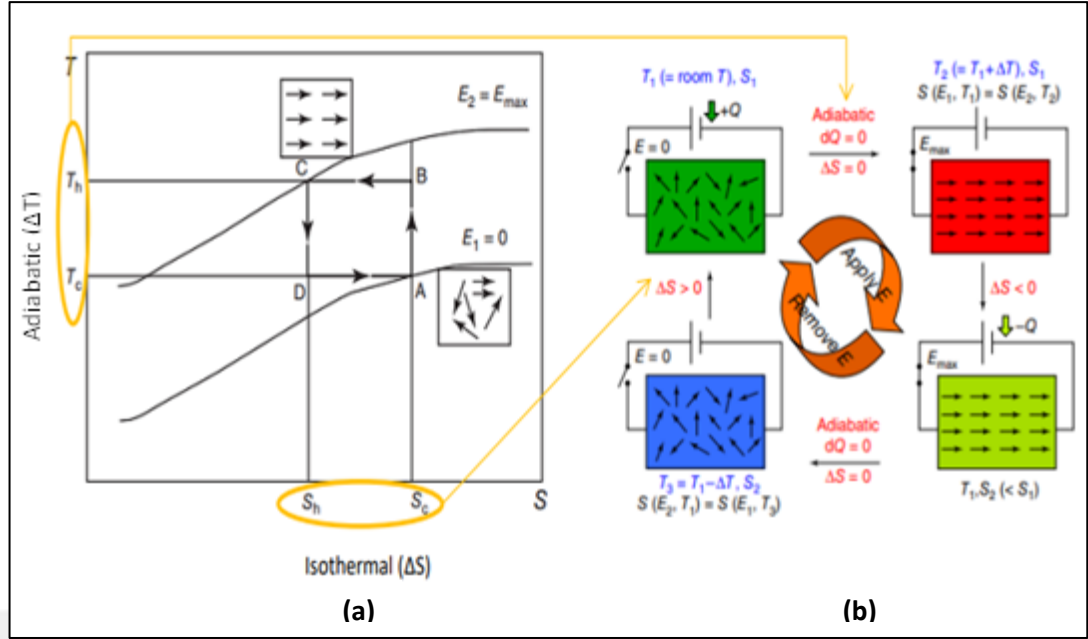


Figure 2.13: (a) Schematic diagram of the ECE cycle, similar to a Carnot cycle (b) cycles of both positive and negative EC cooling.

According to the schematic representation of the ECE cycle given in Figure 2.13, from A to B, an applied electric field increases from  $E_1$  to  $E_2$ , and  $\Delta T$  experiences an adiabatic temperature change. The temperature increases.

From B to C, the electric field is constant, the crystal is allowed to cool slowly, and the entropy  $\Delta S$  changes. The entropy decreases. Through the A-B and then the B-C path, an applied electric field is amplified from  $E_1$  to  $E_2$ , which induces a polar ordered phase.

From C to D, the adiabatic removal of the electric field causes the material to cool. The D state EC material cooled by adiabatic depolarization absorbs heat from the load and heats up to its original A state.

This electric field (cooling) loop has a very low potential for electrical loss and as a result, cooling devices based on the ECE have the potential to achieve extreme effectiveness [25],[30].

### 2.5.3. ECE Measurement Methods

There are basically two methods for measuring ECE: the "direct method" and the "indirect method." The "direct method" involves using differential scanning calorimetry (DSC), infrared (IR) sensors, thermocouples, etc. to detect temperature changes in the EC material.

The other is the "indirect method" in which the electrocaloric effect is approached in terms of thermodynamic relations [31]. In Figure 2.14, devices and graphics used in direct and indirect methods are given. To the extent of the thesis, the indirect measurement method was used.

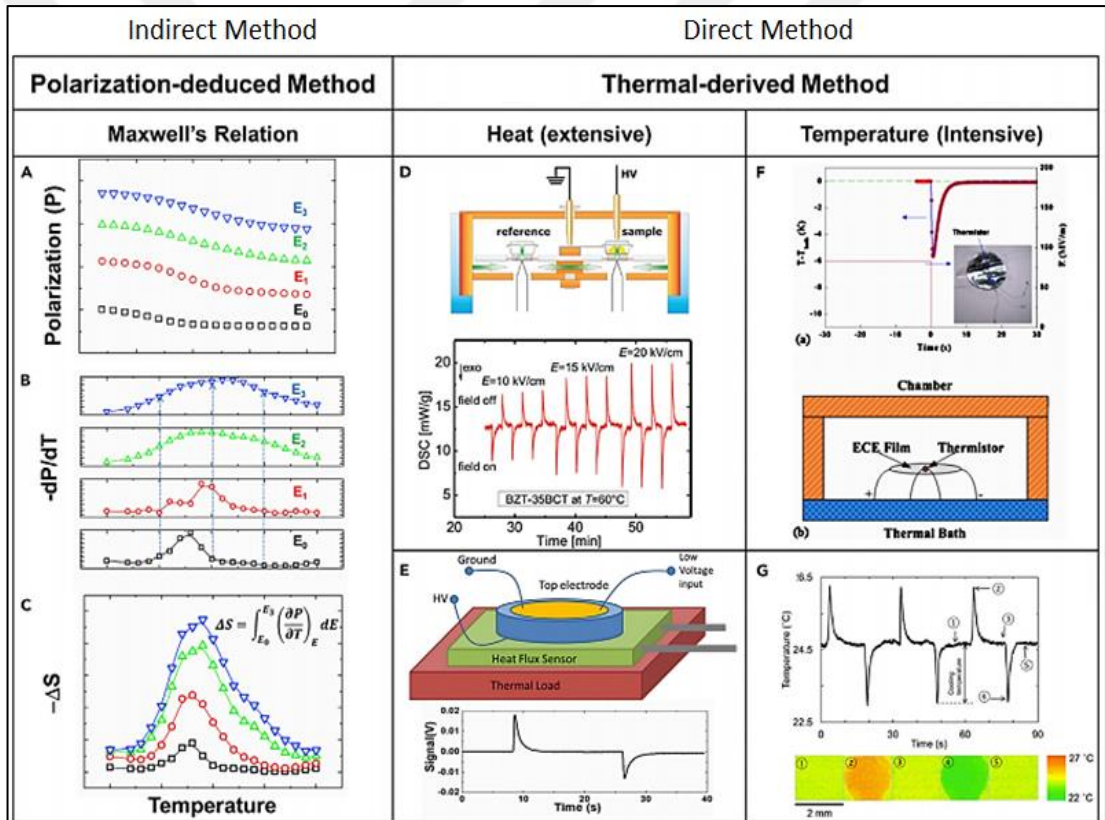


Figure 2.14: (a) Temperature-dependent polarization, (b) graph of polarization derivative according to temperature, (c)  $\Delta S$ , (d) DSC, (e) on-site calibration method, (f) Thermistor, (g) infrared camera.

### 2.5.3.1. Indirect Method

In the indirect method, the calculation is made using the heat capacity of the material and the pyroelectric coefficient. In terms of thermodynamic relations of the electrocaloric effect, two different approaches are used in the indirect method: (a) Maxwell's approach and (b) Landau's phenomenological approach. The Landau-Devonshire (L-D) phenomenological theory, in which the Gibbs free energy of the ferroelectric material is written as an expansion of polarization, is widely used to describe macroscopic phenomena near phase transitions that occur in polar materials [32]. In this thesis, polarization change is measured as a function of temperature under a constant electric field, Maxwell relation is used for temperature change  $\Delta T$  and entropy change  $\Delta S$  calculation [27],[32]. The relationship between  $\Delta S$  and  $\Delta T$  is given in Equation 2.5 and Equation 2.6.

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

$$\Delta T = T_f - T_o = - \int_{E_1}^{E_2} \frac{T}{C_p} \left( \frac{\partial P}{\partial T} \right)_E dE, \quad (2.6)$$

In this formula,  $P$  polarization,  $E_1$  and  $E_2$ , respectively, the first and last of the applied electric field,  $\rho$  the density of the ceramic sample,  $C_p$  the heat capacity,  $\Delta S$  the adiabatic entropy change, and  $\Delta T$  electrocaloric temperature changes represent. Although the direct method gives more reliable results than the indirect method, it is difficult to achieve perfect adiabatic conditions in practice. Therefore, the indirect method with fast and easy processing is often used to measure ECE [31],[33].

### 2.5.3.2. Direct Method

Thermocouples, IR sensors, DSC, and adiabatic calorimeters are typically used for direct ECE measurement. The direct method can be divided into two subgroups:

measuring the entropy change due to the application of an electric field (extensive) or measuring the temperature change (intensive). DSC and adiabatic calorimeters are in the "extensive" group, while thermocouples and IR sensors are in the "intensive" group.

In the adiabatic calorimeter, the sample in the heat-insulated container is exposed to the electric field, and the ECE is measured as a function of both temperature and polarization.

In the DSC system, equal heat fluxes are applied to the sample, and the temperature change due to the electrocaloric effect caused by the absorption or diffusion of heat in the material is recorded with sensitive temperature sensors.

In a calorimeter using a heat flow sensor, the heat produced by the ECE of the sample is calibrated using the heat produced by a standard reference heater from which  $\Delta S$  is obtained. Replacing the heat flow sensor with a thermocouple or IR sensor allows adiabatic temperature variation using the same calorimeter [30],[31],[34].

#### **2.5.4. Electrocaloric Materials**

Electrocaloric materials should be chosen from materials that exhibit a strong electrocaloric effect in the presence of a relatively low electric field at room temperature, are chemically stable and non-toxic, offer minimal economic expenses, and are easy to reproduce. Electrocaloric materials are classified according to their structural composition (Single crystals, Ceramics, Polymers) and production forms (Thin and Thick films, Bulk samples).

Single crystals are produced in bulk form, and although they give high electrocaloric responses, ease of fracture due to electric field stress, and difficulty in fabrication are the major restrictions. Therefore, smaller electric field changes can be applied compared to thin films.

Polymers are organic materials produced in the form of thick or thin films. They give high electrocaloric responses in a high electric field. However, it has been investigated whether there are ways to generate large ECE with less necessary electric fields. Therefore, interest in ceramics has increased.

Ceramics with electrocaloric properties are inorganic materials produced in the form of bulk ( $> 100 \mu\text{m}$ ), thick ( $\sim 10 \mu\text{m}$ ), and thin ( $< 1 \mu\text{m}$ ) films. Although higher electric fields can be applied to the films compared to the bulk form, the bulk form which has ease of manufacture, characterization, and measurement is more convenient than films. Because the films can only cool small areas. In addition, the low electrical conductivity and high thermal conductivity of ceramics completely meet the requirements for an electrocaloric material to be regarded as a suitable solid-state refrigerant.

Perovskite lead-based ferroelectrics such as PZT, PMN-PT, PZN-PT, and PLZT have high electrical properties. Zr: Ti $\sim$ 53:47 PZT, one of the most commercially used compounds, works at room temperature at the morphotropic phase boundary (MPB) where Ti (Tetragonal) and Zr (Rhombohedral) phases coexist. The rhombohedral phase has 8 possible domains, the tetragonal phase has 6 possible domains, and there are 14 possible polarization directions in which dipoles can move in the MPB where the R-T phases coexist. The high number of polarization directions provides high piezoelectric, dielectric, and electrocaloric properties. In addition, lead-based systems have high electrical properties because they have high polarizability by having  $6s^2$  lone-pair in  $\text{Pb}^{2+}$  ions. However, interest in KNN-STO ceramics and BT-based lead-free ferroelectrics has increased, as lead toxicity causes health and environmental problems, especially during its manufacture and recycling. Another reason to work on lead-free materials is that lead's volatility degrades stoichiometry and thus functional properties (such as polarization, piezoelectric constants, and elastic constants) [27]-[29],[35],[43]-[45].

One of the first ferroelectric materials to be commercially available among these lead-free materials is barium titanate ( $\text{BaTiO}_3$ ), which doesn't include any harmful or volatile components [26].  $\text{BaTiO}_3$  has a perovskite structure and has three structural phase transitions, from rhombohedral to tetragonal at around  $-80^\circ\text{C}$ , from orthorhombic to tetragonal at around  $5^\circ\text{C}$ , and from tetragonal to cubic at around  $125^\circ\text{C}$ .  $\text{BaTiO}_3$  has a highly polarizable character and high dielectric strength with its phase transitions [18]. Because of these properties, it is a potential candidate for electrocaloric cooling. However,  $\text{BaTiO}_3$  exhibits lower dielectric properties compared to lead-based materials, and its dielectric constant below the Curie

temperature drops rapidly due to the tetragonal/cubic phase transition. This problem is solved by doping additives to  $\text{BaTiO}_3$  ceramics [26].

In the BCZT system,  $\text{Ca}^{2+}$  and  $\text{Zr}^{4+}$  are incorporated into the  $\text{BaTiO}_3$  crystal lattice to replace  $\text{Ba}^{2+}$  and  $\text{Ti}^{4+}$ , respectively. In the BZT system,  $\text{Zr}^{4+}$  replaces  $\text{Ti}^{4+}$ . BZT and BCZT have perovskite crystal structures. This process leads to improving the relaxor behavior and dielectric constant of barium titanate materials, expanding the maximum at the Curie point [26],[36],[37].

In Table 2.1, the electrocaloric properties of BZT and BCZT ceramics are compared with other lead-based and lead-free materials in different forms given in the literature.



Table 2.1: Electrocaloric properties of BZT and BCZT ceramics.

|                        | Material                                                         | T [K] | $\Delta T_c$ [K] | $\Delta E$ [kJ/c m] | $\Delta T_c/\Delta E$ [K.mm/kV] | Tspan. | Method   |
|------------------------|------------------------------------------------------------------|-------|------------------|---------------------|---------------------------------|--------|----------|
| Lead-based / Inorganic | PbZr <sub>0.95</sub> Ti <sub>0.05</sub> O <sub>3</sub> Thin Film | 768   | 12               | 7150                | 0.017                           | -      | Indirect |
|                        | Pb <sub>0.8</sub> Ba <sub>0.2</sub> ZrO <sub>3</sub> Thin Film   | 563   | 45.3             | 5980                | 0.076                           | -      | Indirect |
|                        | 0.90 PMN-0.10PT Bulk                                             | 313   | 0.7              | 40                  | 0.175                           | 70     | Indirect |
|                        | PMN-30PT Bulk                                                    | 418   | 2.6              | 90                  | 0.29                            | -      | Direct   |
|                        | 0.72PMN - 0.28PT Bulk                                            | 405   | 0.48             | 60                  | 0.08                            | 80     | Indirect |
| Polymer / Organic      | P(VDF-TrFE) Thin Film                                            | 306   | 35               | 1800                | 0.194                           | 50     | Direct   |
|                        | P(VDF-TrFE-CFE) Thin Film                                        | 303   | 15.7             | 1500                | 0.105                           | 50     | Direct   |
|                        | Polymer / BST Composite                                          | 572   | 32               | 15000               | 0.021                           | -      | Indirect |
| Lead-Free / Inorganic  | BaTiO <sub>3</sub> Single Crystal                                | 402   | 0.7              | 12                  | 0.583                           | 5      | Direct   |
|                        | BZT (x = 0.2) Bulk                                               | 312   | 4.5              | 145                 | 0.31                            | > 30   | Direct   |
|                        | BZT (x = 0.2) Bulk                                               | 311   | 1.1              | 21                  | 0.52                            | > 30   | Direct   |
|                        | BZT (x = 0.15) Bulk                                              | 342   | 4.2              | 150                 | 0.28                            | > 30   | Direct   |
|                        | 0.3BZT-0.7BCT Bulk                                               | 403   | 0.47             | 28                  | 0.17                            | -      | Indirect |
|                        | 0.4BZT-0.6BCT Bulk                                               | 403   | 0.59             | 28                  | 0.21                            | -      | Indirect |
|                        | 0.5BZT-0.5BCT Bulk                                               | 393   | 0.49             | 28                  | 0.18                            | -      | Indirect |
|                        | 0.68 BZT-0.32 BCT Bulk                                           | 336   | 0.97             | 60                  | 0.162                           | 63-68  | Indirect |
|                        | 0.80 BZT-0.20 BCT Bulk                                           | 348   | 0.85             | 55                  | 0.155                           | 75     | Indirect |

#### 2.5.4.1. BZT Properties and Phase Diagram

Zr<sup>4+</sup> ions in the B region are substituted into BaTiO<sub>3</sub>-based ceramics which have perovskite structure (ABO<sub>3</sub>). The Zr/Ti ratio has a strong effect on the crystal

structure, microstructure, and dielectric properties. The phase transition behavior is highly influenced by  $\text{Zr}^{4+}$  concentrations, as can be seen, in the phase diagram of the  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  ( $x=0-0.30$ ) system in Figure 2.15 [24],[51]. An increase in the concentration of  $\text{Zr}^{4+}$  ( $\sim 0.98 \text{ \AA}$ ) which has a higher ionic radius than  $\text{Ti}^{4+}$  ( $\sim 0.72 \text{ \AA}$ ), weakens the bonding strength between the B-site ions and oxygen ions, thus the lattice constant increases. Due to the slower diffusion of  $\text{Zr}^{4+}$ , it inhibits grain growth in BZT and a decrease in grain size occurs. Therefore, the Curie temperature decreases, the phase transition temperatures are shifted, occurs spontaneous polarization. The reason for the Curie temperature decrease is that when the B-O bonds are weakened, the B-site ion can only maintain its position in the lower-temperature tetragonal ferroelectric state [53],[54]. With increasing  $\text{Zr}^{4+}$  addition ( $x \leq 0.20$ ), tetragonality decreases, and  $90^\circ$  domain formation increases to minimize internal stress, therefore  $\epsilon_r$  increases. Chemically, the host  $\text{Ti}^{4+}$  ion which has multiple valence states is less stable than the  $\text{Zr}^{4+}$  ion. Substitution of Ti by Zr reduces electron-hopping conduction between  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$  ions and thus dielectric loss [51],[52].

When the Zr ions content  $x > 0.08$ , BZT ceramics exhibit a broad permittivity near the temperature of the maximum dielectric constant because of the inhomogeneous solute distribution into the B regions and the internal stresses on the grains [50],[52].

When  $x \leq 0.10$ , normal ferroelectric behavior has been observed in BZT ceramics, but they also display anomalies in their dielectric properties that are related to the cubic-tetragonal, tetragonal-orthorhombic, and orthorhombic-rhombohedral phase transitions [55]. As the Zr content in the system increases ( $x < 0.20$ ), the phase transition temperatures approach each other and pinched phase transition occurs. When this amount is around  $x = 0.20$ , only a single phase transition is observed in the structure [52].

BZT ceramics exhibit a diffuse phase transition in the range of  $0.1 < x < 0.2$  due to compositional inhomogeneity and internal stresses in the microstructure. The composition  $x \sim 0.15$  operates at an invariant critical point (ICP) where four phases (paraelectric cubic, tetragonal, orthorhombic, and rhombohedral) coexist. It exhibits normal ferroelectric behavior with 26 possible polarization directions in which the dipoles can move. The energy barriers for phase transformations near the ICP are

very low. The entropy change that occurs as a result of dipole motion and the near-zero energy barrier makes a great contribution to ECE [39],[50].

The composition of  $x \geq 0.20$  shows relaxor ferroelectric properties by dividing the macrodomains in  $\text{BaTiO}_3$  into microdomains with an increased Zr ion contribution [54]. As relaxor-like characteristics start to become effective, the peak of the electrocaloric temperature change expands and moves to lower temperatures. Therefore, it has a higher dielectric permittivity. Since, they have structurally polar nano regions, as mentioned in the chapter on relaxor ferroelectrics, they provide additional degrees of freedom on which the dipoles can move. This situation enhances the electrocaloric effect [28],[37],[39].

Although the  $0.2 < x < 0.5$  composition exhibits relaxor ferroelectric properties, the  $T_c$  shifts to lower temperatures for the  $x \geq 0.27$  compositions, which causes a usage restriction [50],[55].

The increase in Zr concentration causes phase transition behavior from the first to the second order. Latent heat is related to first-order transitions. Since there is no latent heat in second-order transitions, there is no change in entropy during the transition. The decreasing contribution of the latent heat of the second order leads to a decrease in the electrocaloric temperature change [24].

For these reasons, the critical points that  $x=0.15$  (abbreviated as 0.15 BZT) normal ferroelectric and  $x=0.20$  (abbreviated as 0.20 BZT) relaxor ferroelectric, which are the most suitable compositions, were used in the thesis study for  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ .

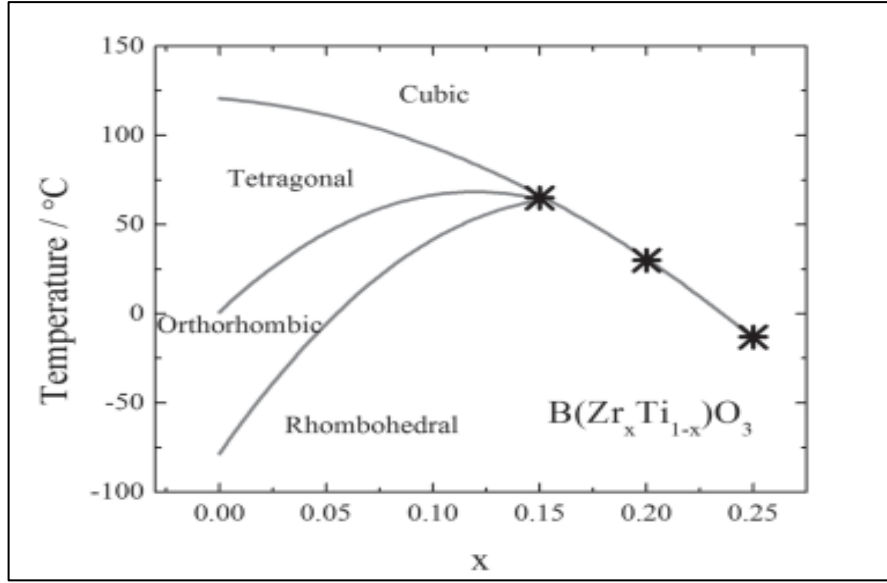


Figure 2.15: Phase diagram of the  $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$  ( $x=0-0.30$ ) system.

#### 2.5.4.2. BCZT Properties and Phase Diagram

As stated in "2.5.4. Electrocaloric Materials" section, substitutions of  $\text{Zr}^{+4}$  for the A region and  $\text{Ca}^{+2}$  for the B region of  $\text{BaTiO}_3$ -based ceramics with perovskite structure ( $\text{ABO}_3$ ) improve the electrical properties [26]. Within the study of this thesis, the ferroelectric, dielectric, and electrocaloric properties of  $0.68\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.32(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  (abbreviated as 0.32 BCZT) and  $0.8\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-0.2(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$  (abbreviated as 0.20 BCZT) compositions at the rhombohedral, tetragonal and cubic triple phase point, and  $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  (abbreviated as 0.50 BCZT) compositions at the MPB where T-R phases coexist were investigated.

$\text{Ca}^{+2}$  (1.06 Å) with an ionic radius smaller than  $\text{Ba}^{+2}$  (1.43 Å) in region A and  $\text{Zr}^{+4}$  (0.98 Å) in region B with an ionic radius larger than  $\text{Ti}^{+4}$  (0.72 Å) substitutes. Substitution of  $\text{Zr}^{+4}$  with a larger ionic radius than  $\text{Ti}^{+4}$  results in longer (Ti, Zr)-O bonds and hence a higher lattice constant. In addition, the chemically more stable  $\text{Zr}^{+4}$  substitution in the  $\text{Ti}^{+4}$  region can adjust the electrical and structural properties of BT. Increasing the amount of  $\text{Ca}^{2+}$ , which has a smaller ion radius than  $\text{Ba}^{2+}$ , causes shorter (Ba, Ca)-O bonds and higher vibration in the unit cells. Therefore, the lattice constant decreases as the BCT concentration increases. The limited solubility of  $\text{Ca}^{2+}$

in the A region has led to the reporting of some observations of the formation of oxygen vacancies and  $CaTi''$  defects with the substitution of  $Ca^{2+}$  in the  $Ti^{4+}$  region. However, the difference in ionic charge and radius between  $Ca^{2+}$  and  $Ti^{4+}$  ions makes it difficult for  $Ca^{2+}$  to migrate in the Ti region, and thus  $Ca^{2+}$  opts to substitute  $Ba^{2+}$  over  $Ti^{4+}$ . It was previously believed that Ca substitution reduces the Curie temperature. However, according to recent studies, it has been reported that Ca doping can increase the phase transition temperatures depending on the powder preparation method and calcium site occupancy, stabilize the tetragonal phase over a wide temperature range, and lead to a diffuse phase transition curve. In particular,  $Ca^{2+}$  substitution has been shown to be beneficial for multilayer ceramic capacitors and other applications [44],[46]-[48].

There is less homogeneity in  $Ba_{1-x}Ca_xTiO_3$  ( $x=0.20$ ) ceramics than in ( $x=0.30$ ). Compositional fluctuation of different polar microdomains occupied by different ions ( $Ba^{2+}$ ,  $Ca^{2+}$ ,  $Ti^{4+}$ ,  $Zr^{4+}$ ) in the same crystallographic regions in  $ABO_3$  perovskite causes diffusion phase transition in this composition. Structural heterogeneity leads to polar nano-domains, as in relaxor ferroelectric systems, resulting in field-induced transformation and a  $90^\circ$  domain wall movement that contributes to the piezo properties.  $Ba_{1-x}Ca_xTiO_3$  ( $x=0.30$ ) ceramics have higher spontaneous polarization, resulting in higher remnant polarization. BCT ( $x=0.30$ ) ceramics with greater homogeneity and higher tetragonality contribute to better ferroelectric and piezoelectric properties than BCT ( $x=0.20$ ) ceramics [43],[47].

In this study,  $x=0.32$  and  $x=0.50$  compositions were used for  $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3-x(Ba_{0.7}Ca_{0.3})TiO_3$  ceramic system (Figure 2.16).  $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3-x(Ba_{0.7}Ca_{0.3})TiO_3$  ( $x=0.50$ ) system operates at the MPB where T-R phases coexist near the tricritical point at room temperature.  $x=0.40$ - $0.60$  compositions operating in MPB at room temperature have typical rhombohedral and tetragonal domain structures. However, the  $x=0.50$  composition contains the micron-sized domains and nano-domains miniaturized on the domains at room temperature. The presence of miniaturized nano-domains in MPB caused maximum domain wall motion with decreased domain wall energy and easy polarization rotation with a low energy barrier due to structural heterogeneity between  $\langle 001 \rangle_T$  to  $\langle 111 \rangle_R$  states. This

situation results in high piezoelectric ( $d_{33}=620$  pC/N) and high dielectric response [47].

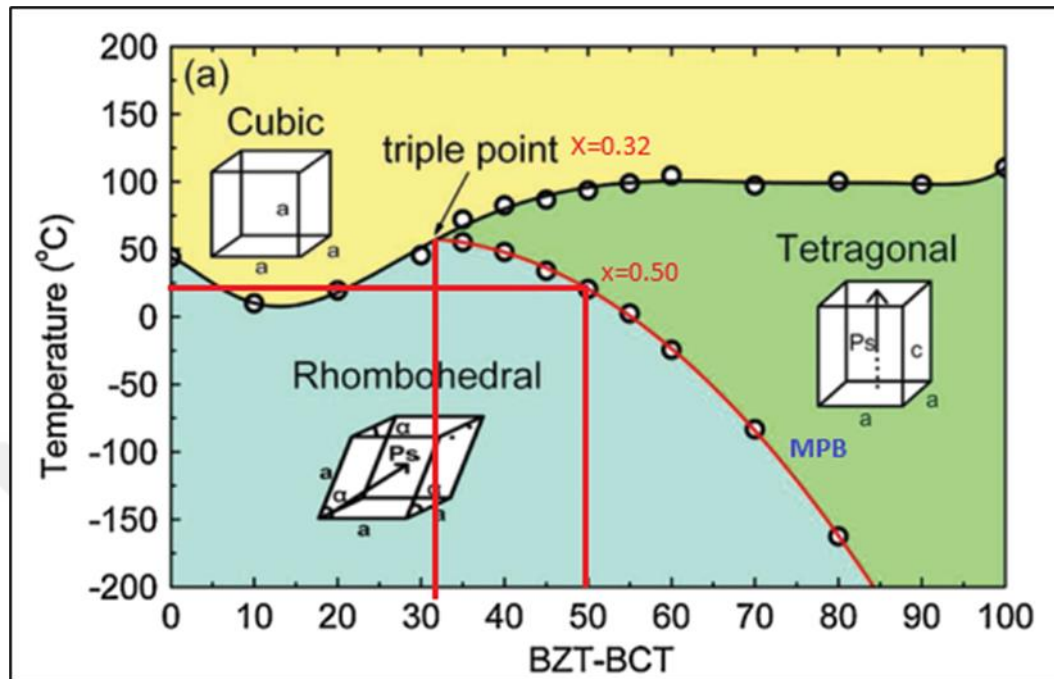


Figure 2.16: Phase diagram of  $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  ceramic system.

The  $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  ( $x=0.32$ ) composition operates at a triple-invariant point with a low Curie temperature ( $T_c$ ), where the MPB and the paraelectric phase intersect. Since this composition is the intersection point of two different ferroelectric phases and non-polar paraelectric phases containing 14 possible polar directions, it is a composition that should be examined especially for ECE applications. The narrow region formed at  $57^\circ\text{C}$  at  $x=0.32$  was initially considered to be MPB. But the temperature dependence of this composition suggests a polymorphic phase transition (PPT-like) nature by definition. Subsequent studies revealed the presence of another PPT and thus a mixed R + T narrow region between the R and T phases. In other words, as seen in Figure 2.17, the MPB region was a separate phase that bridged the polymorphic phase transition between the rhombohedral and tetragonal phases with orthorhombic ( $\text{Amm}2$ ) symmetry. Locally heterogeneous PNRs in the orthorhombic ( $\text{Amm}2$ ) phase allow easier fluctuations of the polarization around the MPB. Large fluctuations in polarization and domain wall movements lead to a low energy barrier between the  $\text{Amm}2$  and  $\text{P4mm}$  ferroelectric

phases, providing easy polarization rotations and hence high piezoelectric and high dielectric properties [43],[44],[47].

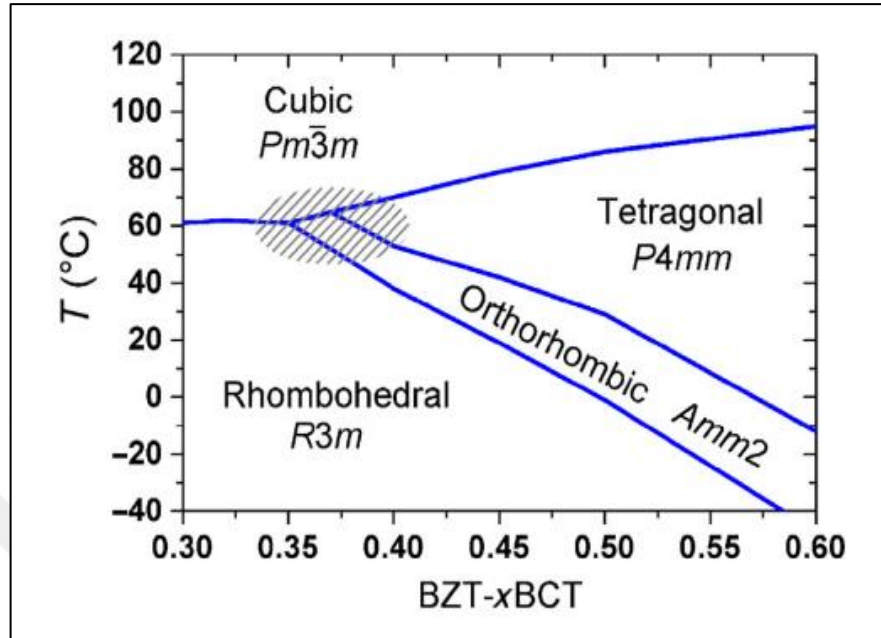


Figure 2.17: Pseudobinary phase diagram of the  $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  system.

In the  $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  [abbreviated as BZ20T-xBC30T] system, compositions operating at the triple point ( $x=0.32$ ) and morphotropic phase boundary ( $x=0.50$ ) exhibit very high piezoelectric properties. However, their application is restricted due to their low Curie temperatures ( $T_c \sim 93^\circ\text{C}$  for 0.50 BCZT exhibiting the largest  $d_{33}$  at room temperature). The rhombohedral (R;  $R3m$ ) phase and the tetragonal (T;  $P4mm$ ) phase are both represented in the BZT-XBCT system's BZT-rich side and BCT-rich side, respectively. In the  $(1-x)\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-x(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$  system [abbreviated as BZ15T-xBC20T], Zr and Ca doping, which are known to decrease the Curie temperature of  $\text{BaTiO}_3$ , are reduced in order to increase the  $T_c$  of the tetragonal and rhombohedral terminals. It is known that the phase transition temperature for the BZ20T is  $51^\circ\text{C}$  and the phase transition temperature for the BC30T is  $101^\circ\text{C}$ . As seen in Figure 2.18, the BZ15T composition transitions from the cubic paraelectric phase to the rhombohedral ferroelectric phase at  $71.8^\circ\text{C}$ , and the BC20T composition transitions from the cubic paraelectric phase to the tetragonal ferroelectric phase at  $122.8^\circ\text{C}$  [49].

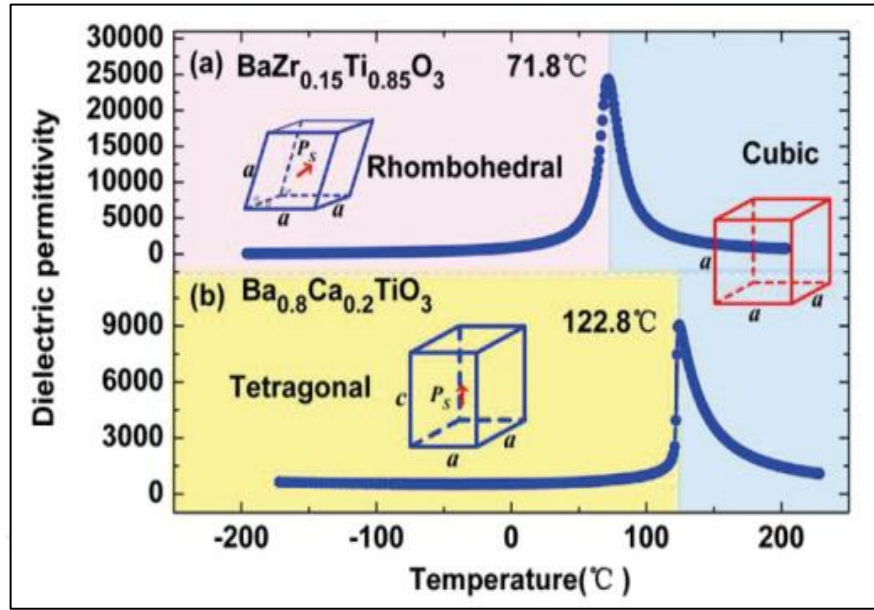


Figure 2.18: The temperature dependence of the dielectric permittivity for the two terminals: (a) rhombohedral BZ15T and (b) tetragonal BC20T.

Thus, in the improved BZ15T–xBC20T system ( $T_c=114^\circ\text{C}$  for  $x=0.53$ ), whose doping is reduced, a higher Curie temperature is obtained than BZ20T–xBC30T ( $x=0.50$ ). In the phase diagram of the BZ15T–xBC20T system, it is clearly seen that it is shifted towards a high temperature of approximately  $20^\circ\text{C}$  compared to the BZ20T–xBC30T system. But the high Curie temperature is accompanied by a low  $d_{33}$  and low dielectric permittivity. ( $d_{33}=450\text{ pC/N}$ ,  $\epsilon \sim 2252$  for  $x=0.53$ ), ( $d_{33}=620\text{ pC/N}$ ,  $\epsilon \sim 3060$  for  $x=0.50$ ) [47],[49].

In the phase diagram of Figure 2.19, it is seen that there is a triple point where cubic-tetragonal–rhombohedral (C–T–R) phases intersect for  $x = 0.20$  compositions around  $82^\circ\text{C}$ .

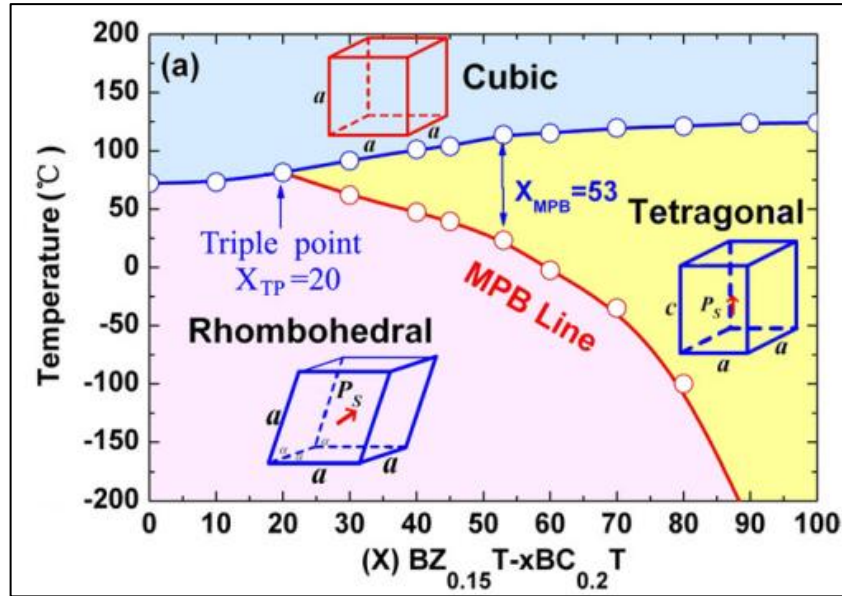


Figure 2.19: Phase diagram of  $(1-x)\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-x(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$  ceramic system.

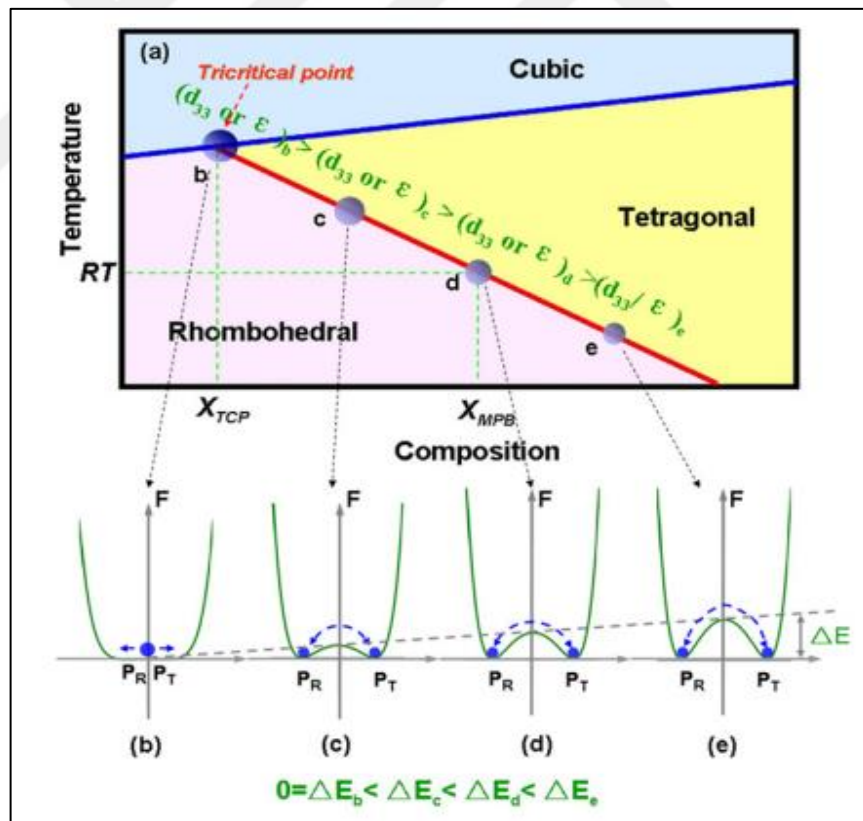


Figure 2.20: On the schematic phase diagram the free energy barriers of the compositions on the TCP (point b) and on the MPB (points c, d and e).

As can be shown in Figure 2.20, since the free energy in the TCP is isotropic in relation to the polarization direction, the energy barrier ( $\Delta E_b$ ) between the  $\langle 001 \rangle_T$  and  $\langle 111 \rangle_R$  phases is zero. Shifting away from the TCP, the energy barrier increases by stages due to an increase in polarization anisotropy, making polarization rotation difficult. Therefore, a gradual weakening of the piezoelectric and dielectric properties is observed as the composition deviates from the triple point along the MPB.  $0.8\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-0.2(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$  composition was studied due to its triple point for obtaining high ECE [49]. In addition, the  $T_c$  of this composition has increased compared to the  $x=0.32$  composition operating at the TP in the 0.20 BZT-0.30 BCT system.

For these reasons, 0.32 BCZT and 0.20 BCZT ceramics operating at the TCP, and 0.50 BCZT ceramic operating at the MPB to investigate the effect of polarization number on ECE in this thesis study.

## 2.6. Conventional Solid-State Reaction Method

One of the most popular methods for producing ceramic powders is the solid-state reaction method, which relies on the solid-solid interaction of oxide and carbonate precursors (Figure 2.21). This environmentally friendly method has some advantages that can be synthesized in large quantities with simple procedures, a relatively short reaction time, and low production cost. However, carrying out the reaction at high temperatures causes agglomeration of the particles and thus a relatively large particle size [56],[57]. The easy control of the synthesis steps is one of the essential reasons why we chose this method for the thesis study. The steps of the method will be explained in the "EXPERIMENTAL STUDY" section.

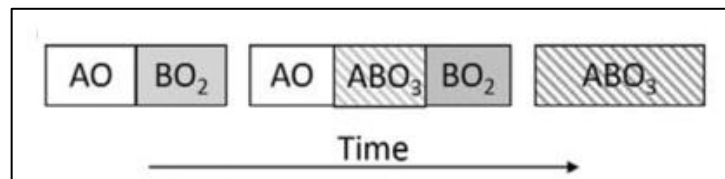


Figure 2.21: Conventional Solid-State Reaction Method.

### 3. EXPERIMENTAL STUDY

In this study, mainly ceramics with following compositions were investigated:  $\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3$  (0.15 BZT),  $\text{Ba}(\text{Zr}_{0.20}\text{Ti}_{0.8})\text{O}_3$  (0.20 BZT),  $0.8\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-0.2(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$  (0.20 BCZT),  $0.68\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.32(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  (0.32 BCZT) and  $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  (0.50 BCZT).

#### 3.1. Synthesis and Processing of BZT and BCZT Powders and Dry-Pressed Ceramics

In this study,  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  ( $x=0.15$  and  $x=0.20$ ),  $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  and  $(1-x)\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-x(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$  ( $x=0.20$ ,  $x=0.32$ , and  $x=0.50$ ) ceramic powders in different compositions were produced by the solid-state reaction method. The raw materials used for powder synthesis are given in Table 3.1.

Table 3.1: Raw materials used for BZT and BCZT powder synthesis and their properties.

| Ceramics |     | Raw Materials   | Commercial References | Purity (%) | CAS No.   |
|----------|-----|-----------------|-----------------------|------------|-----------|
| BCZT     | BZT | $\text{BaCO}_3$ | Alfa Aesar            | 99.8       | 513-77-9  |
|          |     | $\text{ZrO}_2$  | Alfa Aesar            | 99+        | 1314-23-4 |
|          |     | $\text{TiO}_2$  | Alfa Aesar            | 99.5       | 1317-80-2 |
|          |     | $\text{CaCO}_3$ | Alfa Aesar            | 99,5       | 471-34-1  |

The starting powders given in Table 3.1 were weighed in appropriate stoichiometric ratios and ground in a mortar. The powders were mixed in a Nalgene™ bottle in an ethanol medium with zirconia balls in a ball mill at 200 rpm for 24 hours. After that, the slurry was dried on a hot plate at 80°C and kept in an oven for 24 hours approximately at 60°C to prevent the powder from remaining moist. After drying, process the powders were calcined to obtain BZT and BCZT phases. BZT and BCZT powders were calcined at 1150°C for 4 hours and at 1200°C for 3-6 hours,

respectively, with a ramp rate of 5°C/min. The calcined powders were ball-milled again in ethanol medium for 24 hours and then dried. Mixture was the ball milled at 200 rpm for 24 hours, and then was dried on the hot plate at 80°C. The dried powders were ground in a mortar and then granulated with a 425 µm sieve. The pellets were prepared by uniaxial dry press applied to 150 MPa pressure for 3 minutes using a 16 mm diameter disc-shaped steel die.

BZT and BCZT pellets were sintered at 1400-1440°C for 4-6 hours with a ramp rate of 5°C/min. But firstly, the polymeric-based binder was removed from the green pellet samples at 600°C for 1 hour with a ramp rate of 2°C/min. The flow charts of the ceramic synthesis process for BZT and BCZT are given in Figure 3.1 and Figure 3.2, respectively.

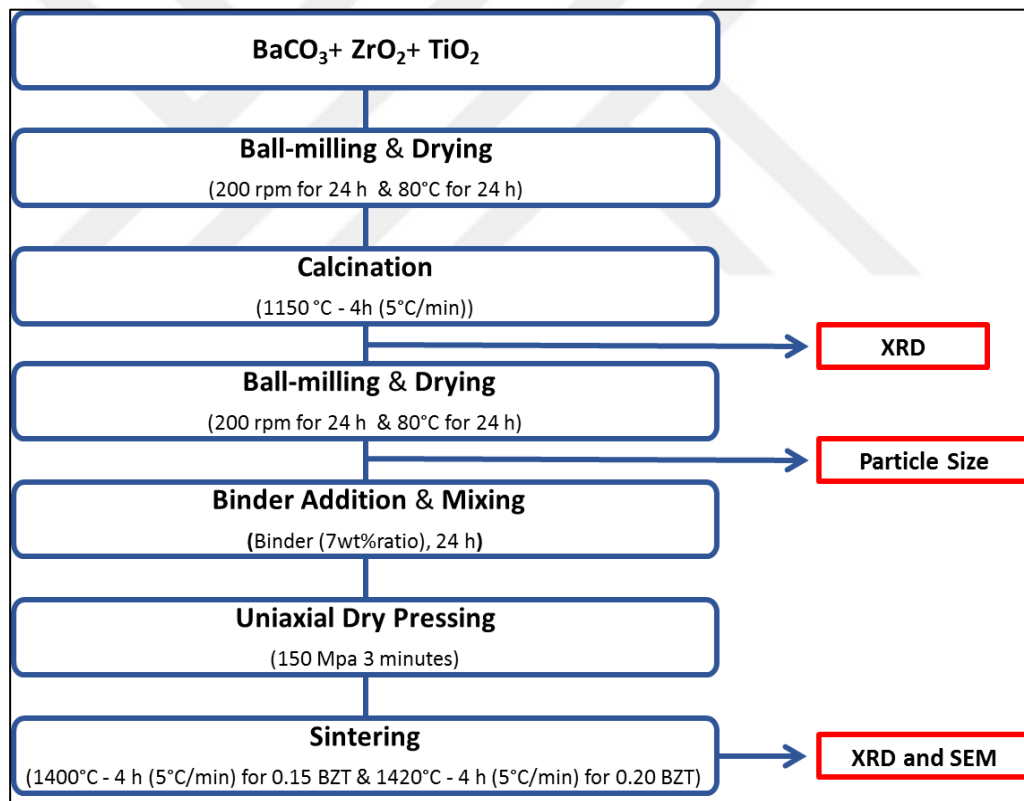


Figure 3.1: The flow chart of BZT powder synthesis and sample production.

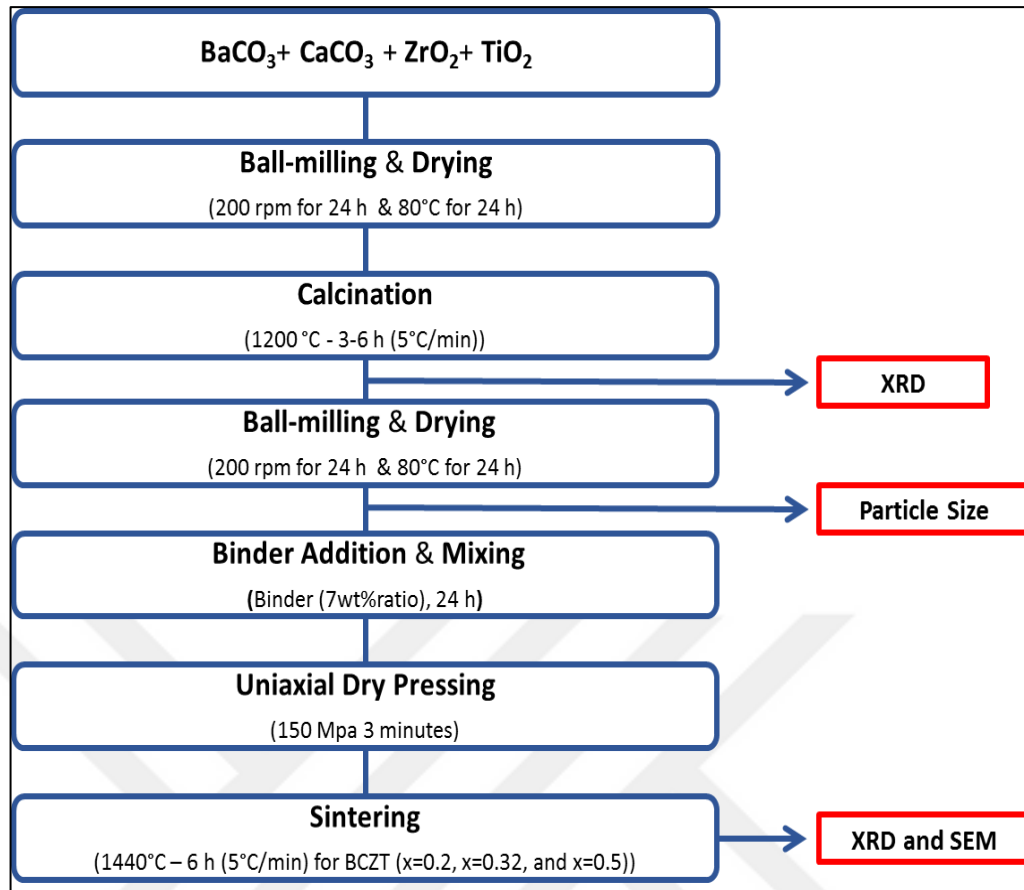


Figure 3.2: The flow chart of BCZT powder synthesis and sample production.

As shown in Figure 3.3, BT and BZ powders were prepared separately by the solid-state method and then BZT phase was obtained by mixing these two powders. It is thought that the formation rate of BaZrO<sub>3</sub> is lower than BaTiO<sub>3</sub> due to the fact that Ti, which has a higher electronegativity than Zr, reacts faster with BaCO<sub>3</sub> and the ionic radius of Zr<sup>4+</sup> (~0.98 Å) is larger than Ti<sup>4+</sup> (~0.72 Å). The morphology of the final product can be controlled by the morphology control of the more slowly formed BZ [58],[59]. The starting powders (Table 3.1) were ball milled in ethanol medium for 24 hours and then calcined separately at 1100°C for 2 hours at a ramp rate of 5°C/min to form single-phase BT and BZ powders. After the calcination process, BT and BZ powders were mixed using a ball milling in an ethanol medium according to their stoichiometric compositions as 0.15 and 0.20. The intermediate steps from calcination to sintering are the same as the BZT and BCZT powder production methods. The BZT pellets were sintered in the furnace at 1380°C for 4 hours, with a ramp rate of 5°C/min.

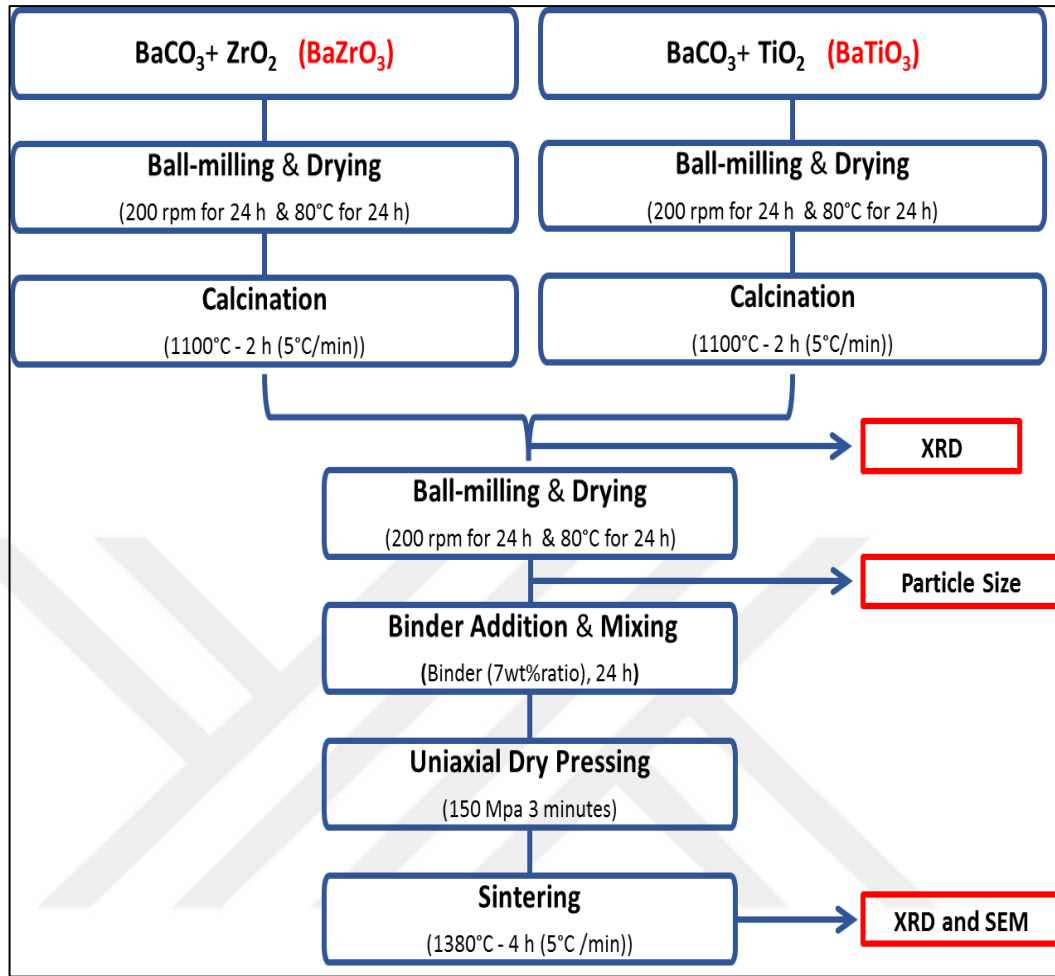


Figure 3.3: The flow chart of BZ-BT powder synthesis and sample production.

### 3.1. Characterization of BZT and BCZT Ceramics

As shown in the flow diagram in Figure 3.4, structural and electrical characterization were done to the sintered samples. Archimedes' technique was used for determining the densities of sintered samples. In this method, the samples' dry weights, hanging weights in water, and complete wet weights were measured and calculated.

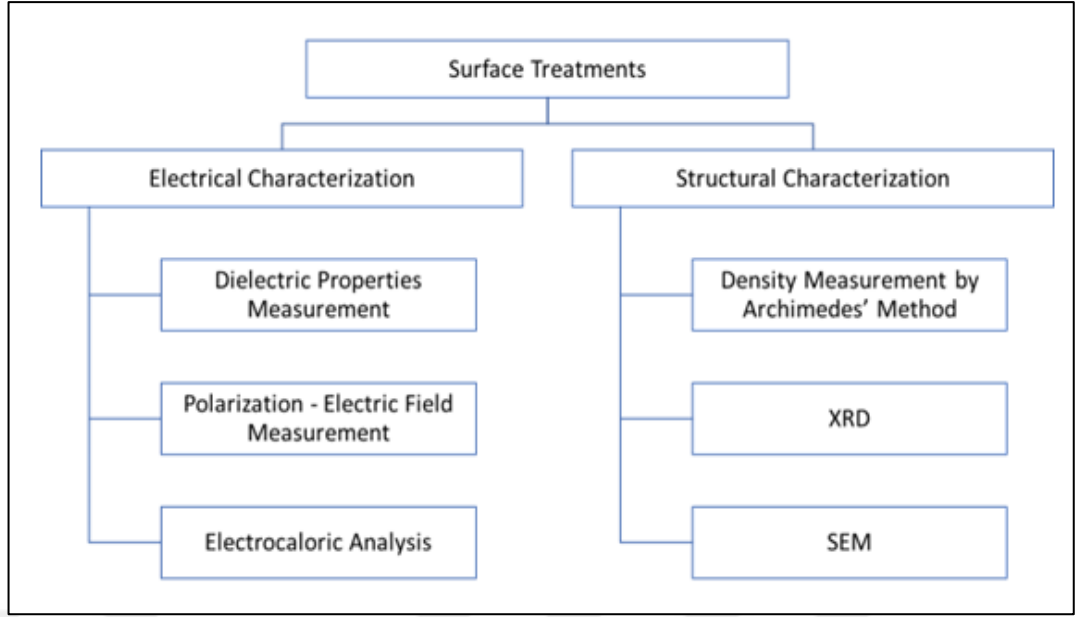


Figure 3.4: The flow chart of the characterization of BZT and BCZT samples.

The phase formation investigation of ceramics was occurred by X-ray diffraction method (XRD) (Rigaku D/max 2200, Tokyo, Japan) by scanning between 20°-70° at a scanning rate of 1°/min at a step size of 0.02° using Cu-Kα ( $\lambda = 1.5405 \text{ \AA}$ ) radiation. Crystallite size results were obtained with Scherrer Equation (3.1) using XRD data.

$$L = \frac{K\lambda}{\beta \cdot \cos \theta} \quad (3.1)$$

where  $L$  is the average crystallite size,  $K$  is a constant related to crystallite shape (~ 0.90),  $\lambda$  is the X-ray wavelength in nanometers (nm),  $\beta$  is the measuring full width at half maximum of peaks and  $\theta$  is the Bragg angle.

The surface roughness of the samples is removed with 1000, 2000, and 2500 mesh SiC abrasives, respectively, and after that polished using a felt and a solution containing diamond particles. Then, thermal etching was performed at 200°C below the sintering temperature of the samples for 30 minutes to make clear the grain boundaries. SEM analyzes of the surface-treated samples were made with Philips XL30 SEM (FEI, USA) device for microstructure investigations.

A silver electrode was applied to the surface of sintered samples for electrical measurements. Electrodes were fired at 600°C for 30 minutes at a ramp rate of 5°C/min to adhere to the surface. Temperature dependence of capacitance and loss tangent ( $\tan\delta$ ) were measured using an LCR meter (Hioki 3532-50, Japan) from room temperature (RT) to 180°C in the frequency range of 1-100 kHz.

Measurements of polarization under applied electric field (P-E) were done in a ferroelectric measurement system (Precision LC, Radiant Inc., Albuquerque, NM) to determine the maximum polarization ( $P_{\max}$ ), remnant polarization ( $P_r$ ), and coercive electric field ( $E_c$ ) values of ceramics. Measurements were carried out at RT under an electric field between 10-50 kV/cm and a period of 1000 ms.

For the electrocaloric analysis of the ceramics, polarization-electric field (P-E) cycles at different temperatures under a certain electric field were measured again using the ferroelectric measurement system (Precision LC, Radiant Inc., Albuquerque, NM). Starting from above the Curie temperature of the composition, the temperature was decreased to 0°C by reducing the temperature by 10 degrees. Polarization-electric field measurements were done in certain electric fields by waiting for 10 minutes at each temperature. These measurements were analyzed (called as indirect method) using Maxwell relations (Equation 2.6) to determine the electrocaloric temperature change ( $\Delta T$ ).

## 4. RESULTS and DISCUSSION

### 4.1. BZT Ceramics

In this section, the structural and electrical results of  $\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3$  compositions operating at an invariant critical point where four phases coexist and  $\text{Ba}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$  compositions with relaxor ferroelectric properties will be investigated. In addition, BZT results obtained from BZ-BT will also be discussed. They will be abbreviated  $\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3$  composition as 0.15 BZT,  $\text{Ba}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$  composition as 0.20BZT,  $0.15\text{BaZrO}_3\text{-}0.85\text{BaTiO}_3$  composition as 0.15 BZ-BT,  $0.20\text{BaZrO}_3\text{-}0.80\text{BaTiO}_3$  composition as 0.20 BZ-BT.

#### 4.1.1. Phase Analysis of BZT Powders

Figure 4.1(a) and Figure 4.2(a) show the XRD patterns of 0.15 BZT and 0.20 BZT powders calcined at  $1150^\circ\text{C}$  with a ramp rate of  $5^\circ\text{C}/\text{min}$  for 4 hours. Figure 4.1(b) and Figure 4.2(b) show the particle size of the calcined powders subjected to the ball milling process has a narrow and homogeneous size distribution, with an average particle size of 0.15 BZT ( $d_{0.5}$ )  $0.185\ \mu\text{m}$  and 0.20 BZT ( $d_{0.5}$ )  $0.188\ \mu\text{m}$ .

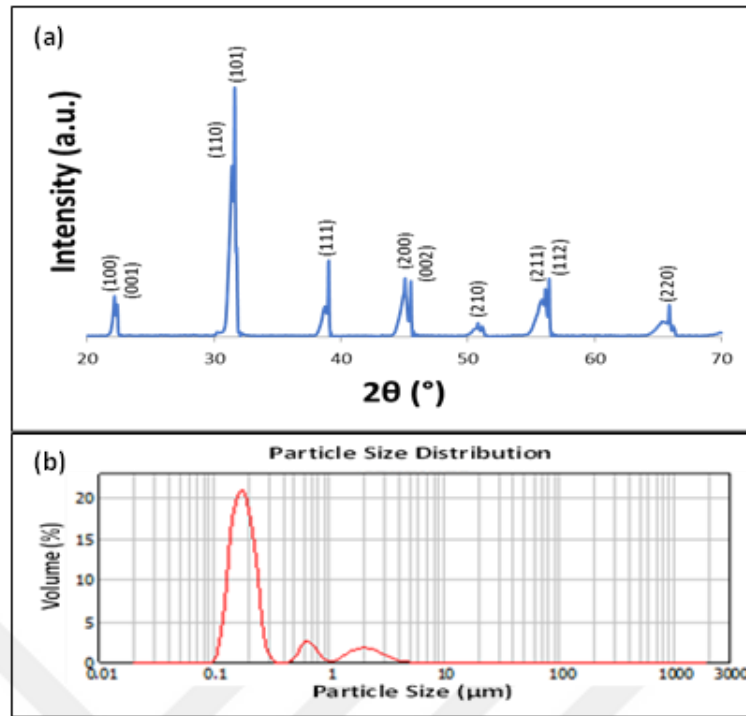


Figure 4.1: (a) The XRD pattern and (b) particle size distribution measurement of  $\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3$  powder.

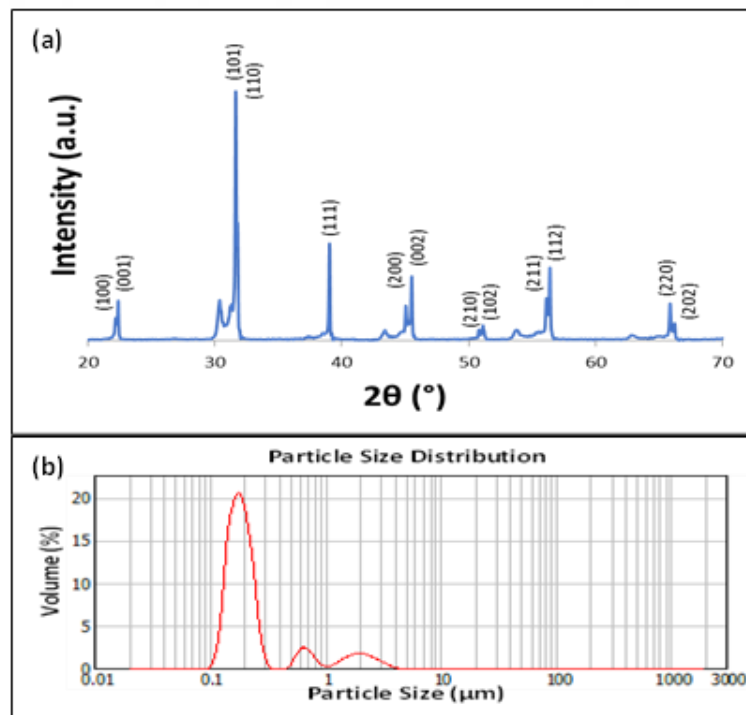


Figure 4.2: (a) The XRD pattern and (b) particle size distribution measurement of  $\text{Ba}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$  powder.

In Figure 4.3, the XRD result of BZ and BT powders calcined for 2 hours at 1100°C with a ramp rate of 5°C/min is also given, separately.

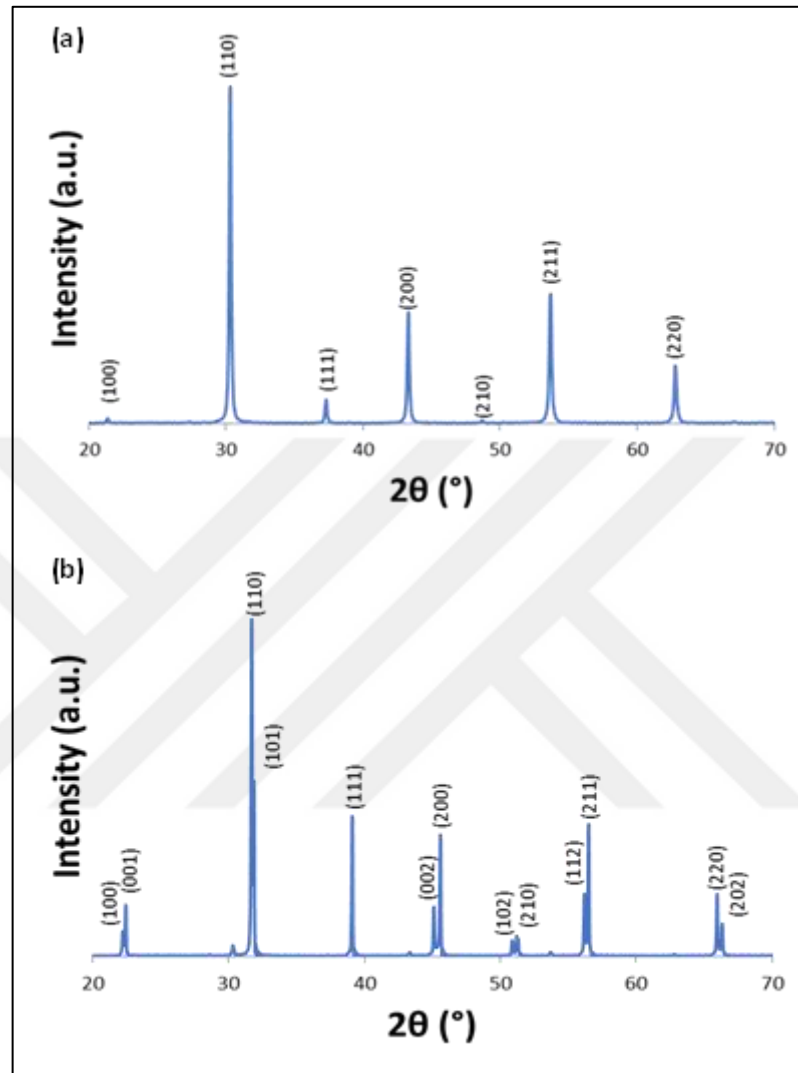


Figure 4.3: The XRD patterns of (a)  $\text{BaZrO}_3$  and (b)  $\text{BaTiO}_3$  powder.

After the calcination process BZ and BT powders are mixed according to their composition (0.15 BZ-BT and 0.20 BZ-BT) using the ball-mill process. Figure 4.4 shows a homogeneous size and a narrow distribution and the average particle sizes are measured as ( $d_{0.5}$ ) 0.195  $\mu\text{m}$  for 0.15 BZ-BT and ( $d_{0.5}$ ) 0.188  $\mu\text{m}$  for 0.20 BZ-BT.

The XRD results of all calcined powders show a perovskite structure with peak separations.

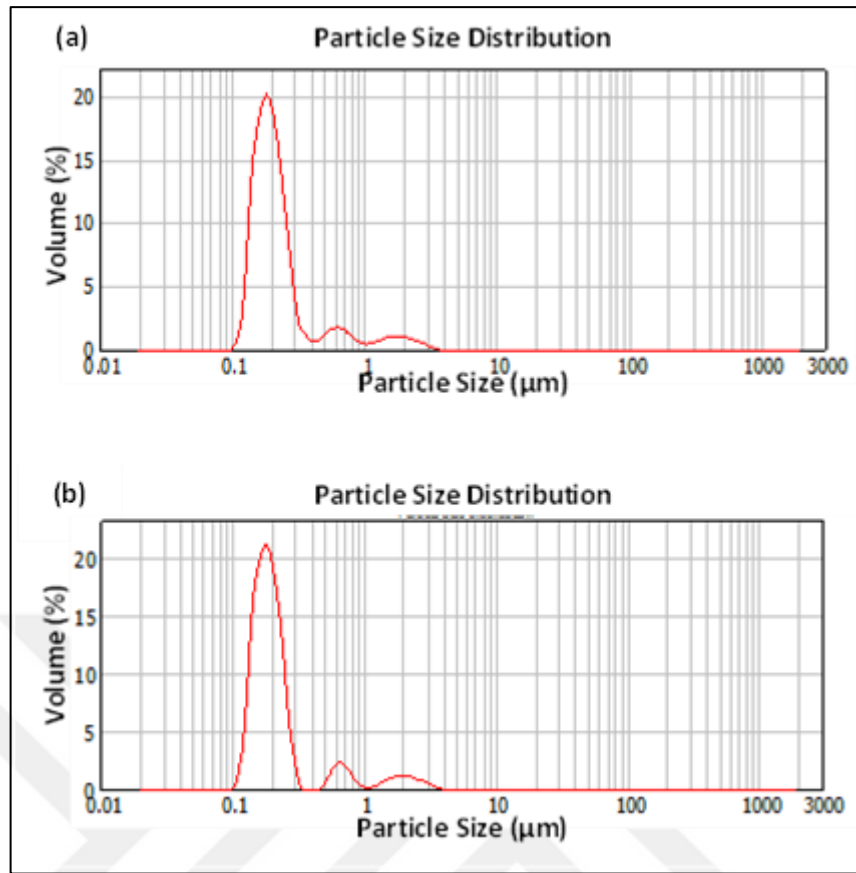


Figure 4.4: The result of particle size distribution analysis of (a) 0.15 BZ-BT and (b) 0.20 BZ-BT powder.

#### 4.1.2. Structural Analysis of BZT and BZ-BT Ceramics

The comparison of XRD patterns of 0.15 BZT sintered at 1400°C for 4 h, 0.15 BZ-BT sintered at 1380°C for 4 h, 0.20 BZT sintered at 1420°C for 4 h, and 0.20 BZ-BT sintered at 1380°C for 4 h are shown in Figure 4.5. When the XRD results are investigated, it is shown that all compositions are sintered at the optimum temperature and time, after the same trials; and crystallized in a pure perovskite structure without any secondary phase as desired. The average crystallite size obtained from the X-ray diffraction data is calculated as 130 nm for the 0.15 BZT, 97 nm for 0.15 BZ-BT, 46 nm for the 0.20 BZT, and 55 nm for 0.20 BZ-BT. As the ratio of  $Zr^{4+}$  ( $0.98 \text{ \AA}$ ) in the structure, which has an ionic radius larger than  $Ti^{4+}$  ( $0.72 \text{ \AA}$ ), increases, the diffusion rate decreases. This results as in a decrease in the grain size in BZT and therefore crystallite size. It is thought that as the crystallite size decreases,

the polar nanodomains and grain boundary scattering will increase in the structure. These situations provide additional degrees of freedom through which the dipoles could move and an increase in electrical resistance. Thus, the decrease in the crystallite size positively affects the electrical properties.

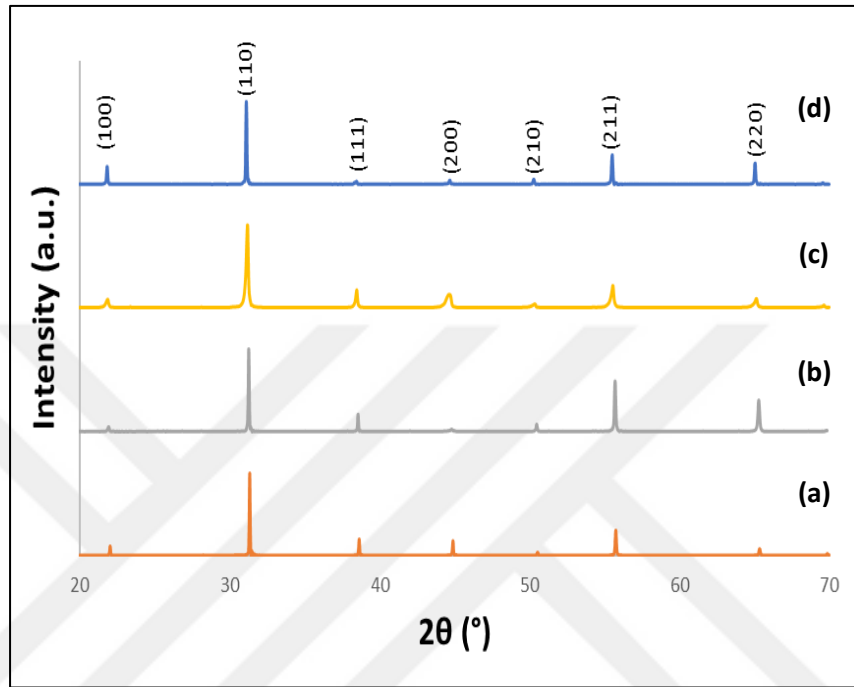


Figure 4.5: The XRD patterns of (a) 0.15 BZT, (b) 0.15 BZ-BT, (c) 0.20 BZT and (d) 0.20 BZ-BT ceramics.

In Figure 4.6, SEM micrographs taken from the polished and thermally etched surfaces and cross-sections are given in order to investigate the microstructure of the samples. SEM images show that all samples have relatively dense morphology with clear visible grain boundaries. According to Archimedes' method, density was calculated as 95-97% for the 0.15 and 0.20 BZT samples and calculated as 90-92% for the 0.15 and 0.20 BZ-BT samples.

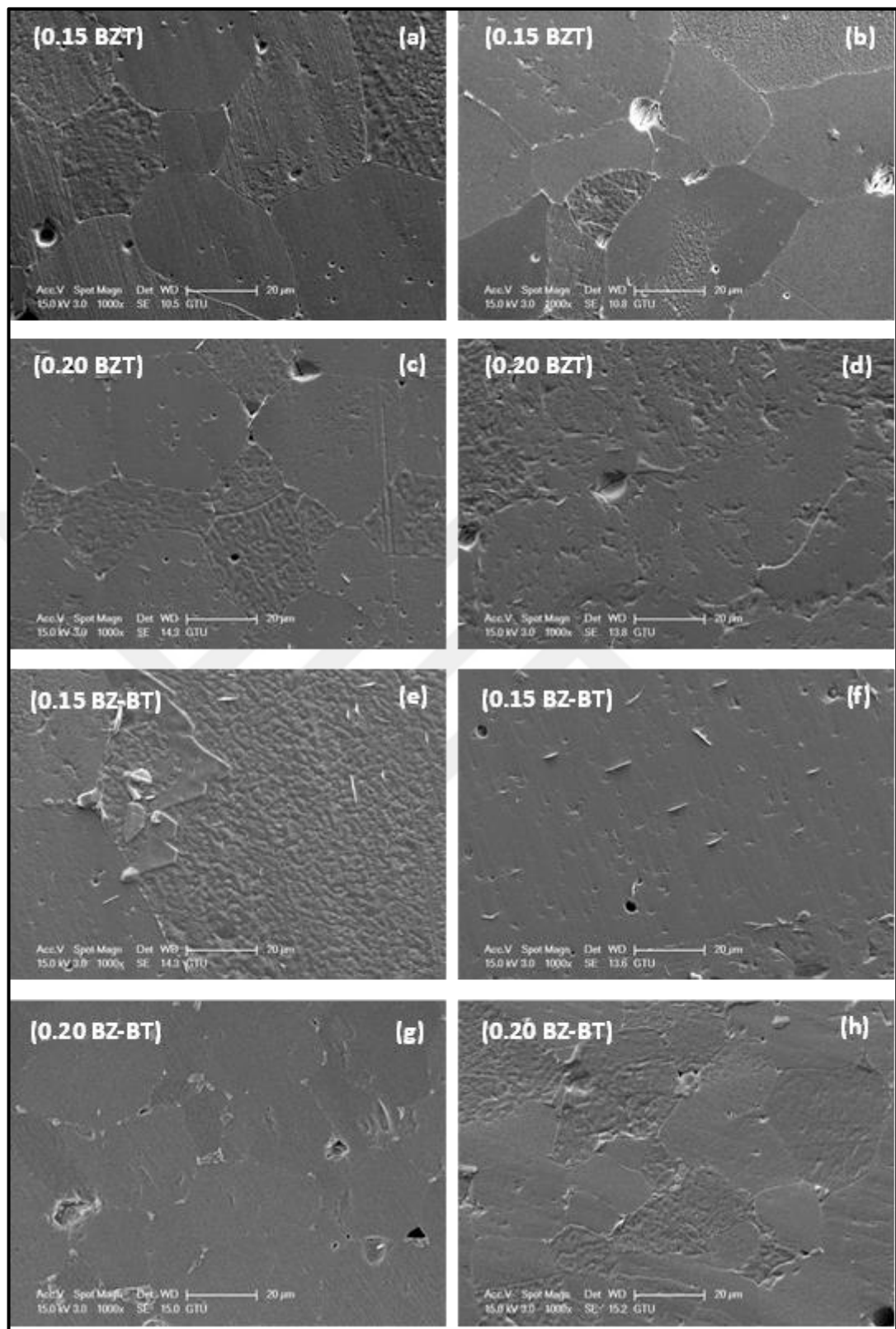


Figure 4.6: SEM micrographs of (a), (c), (e) and (g) cross-sectional and (b), (d), (f) and (h) surfaces of the ceramics.

### 4.1.3. Electrical Characterization of BZT and BZ-BT Ceramics

#### 4.1.3.1. Temperature-Dependent Dielectric Measurements

The dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) measurements of BZT and BZ-BT (0.15 & 0.20) ceramics taken at different frequencies depending on the temperature in the range of 1-100 kHz frequency are given in Figure 4.7.

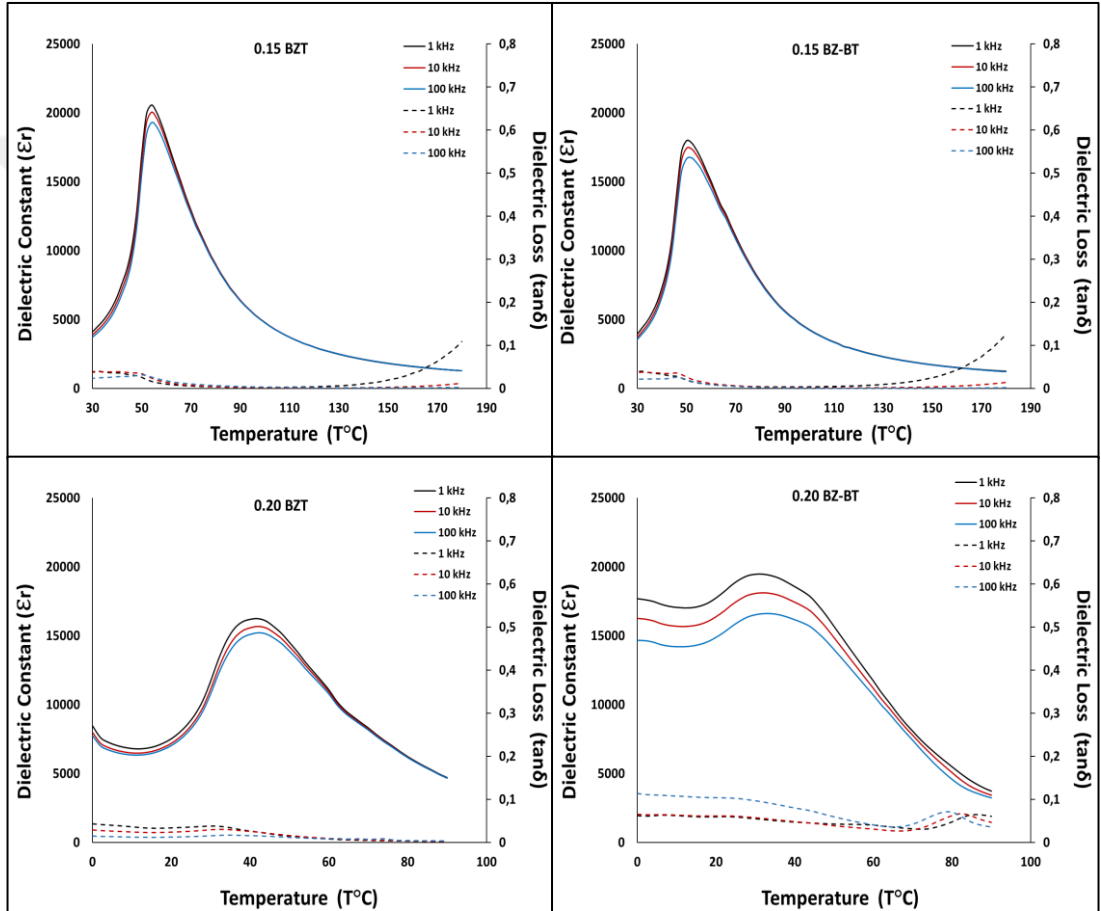


Figure 4.7: Temperature dependence of dielectric loss and dielectric constant of 0.15 BZT, 0.15 BZ-BT, 0.20 BZT, and 0.20 BZ-BT samples.

For ceramics with composition of  $x=0.15$ , measurements were taken from room temperature (RT) to 180°C with a ramp of 2°C/min. The measurements of the  $x=0.20$  composition ceramics, which are known from the literature to have a lower Curie temperature, were taken from room temperature to 90°C with a ramp rate of

2°C/min.  $T_c$ ,  $\epsilon_r$  and  $\tan\delta$  values of 0.15 BZT, 0.15 BZ-BT, 0.20 BZT and 0.20 BZ-BT ceramics at 1 kHz frequency are given in Table 4.1.

Table 4.1:  $T_c$ , dielectric coefficient, and dielectric loss value of ceramics at room temperature.

| Sample     | $T_c$ (°C) | $\epsilon_r$<br>[RT, @1 kHz] | $\tan\delta$<br>[RT, @1 kHz] |
|------------|------------|------------------------------|------------------------------|
| 0.15 BZT   | 56         | 3640                         | 0.04                         |
| 0.15 BZ-BT | 50         | 3084                         | 0.04                         |
| 0.20 BZT   | 42         | 9288                         | 0.04                         |
| 0.20 BZ-BT | 32         | 19088                        | 0.06                         |

As seen in the Table 4.1, ceramics with a composition of  $x=0.20$  have a lower Curie temperature and a broader phase transition than ceramics with a composition of  $x=0.15$ . The frequency dependence of the dielectric properties and the broad phase transition are the relaxor ferroelectric properties. Increasing the zirconium ratio causes the development of relaxor behavior. Increasing the relaxor properties improves the dielectric properties.

#### 4.1.3.2. Ferroelectric Measurements

In Figure 4.8, polarization-electric field (P-E) hysteresis loops of ceramics were measured under the electric fields between 10-40 kV/cm, at room temperature and at 1 Hz period.

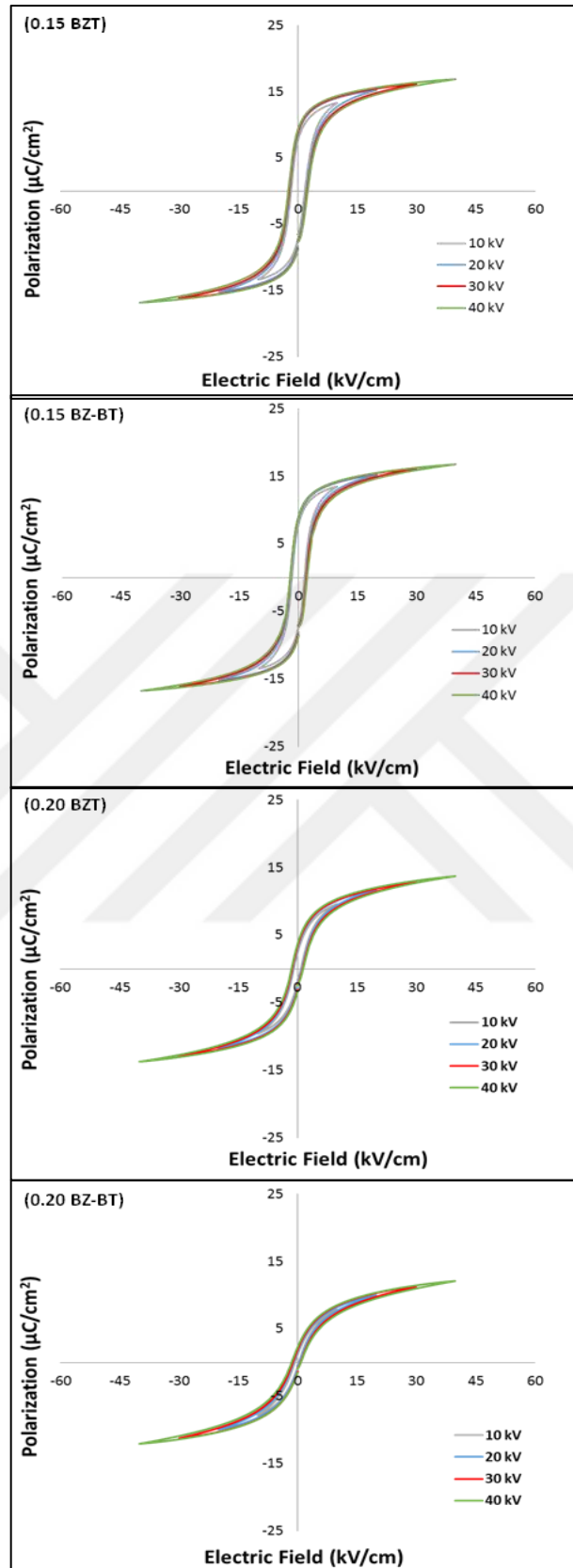


Figure 4.8: The P – E hysteresis loops of 0.15 BZT, 0.15 BZ-BT, 0.20 BZT, and 0.20 BZ-BT ceramics.

The remnant polarization ( $P_r$ ), maximum polarization ( $P_{max}$ ) and coercive electric field ( $E_c$ ) values of the ceramics are given in Table 4.2.

Table 4.2:  $P_r$ ,  $P_{max}$  and  $E_c$  values of the ceramics.

| Sample     | $P_{max}$<br>( $\mu\text{C}/\text{cm}^2$ ) | $P_r$<br>( $\mu\text{C}/\text{cm}^2$ ) | $E_c$<br>(kV/cm) |
|------------|--------------------------------------------|----------------------------------------|------------------|
| 0.15 BZT   | 16.86                                      | 9.45                                   | 2.32             |
| 0.15 BZ-BT | 16.78                                      | 9.32                                   | 2.31             |
| 0.20 BZT   | 13.70                                      | 3.93                                   | 1.27             |
| 0.20 BZ-BT | 12.10                                      | 2.43                                   | 0.96             |

In Figure 4.9, polarization-electric field hysteresis loops of ceramics under 40 kV/cm electric field are given comparatively for all samples.

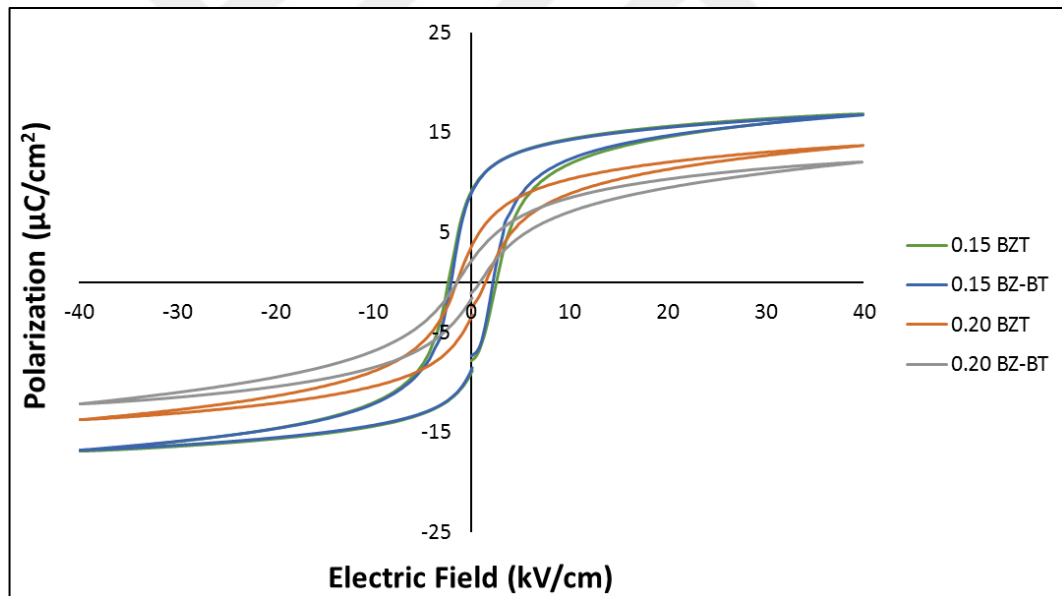


Figure 4.9: Comparison of the polarization vs electric field hysteresis loops of 0.15 BZT, 0.15 BZ-BT, 0.20 BZT, and 0.20 BZ-BT samples.

The Figure 4.9 shows that all samples exhibit slim and saturated hysteresis loops. Slim hysteresis loops indicate the presence of a low coercive electric field ( $E_c$ ). This means that these samples have already no defects where the domain boundaries move easily [62]. However, the fact that the  $x=0.20$  composition exhibits a slimmer hysteresis loops compared to the  $x=0.15$  compositions. This indicates the relaxor

ferroelectric property. The ordering of polar nano regions in the structure of relaxor ferroelectrics causes more difficult movement than normal ferroelectric ones [60]. Therefore, as seen in Table 4.2, normal ferroelectrics ( $x=0.15$  compositions) usually have larger  $P_{\max}$ ,  $P_r$ ,  $E_c$ , and hysteresis loss values.

#### 4.1.3.3. Temperature-Dependent Hysteresis Measurement and Electrocaloric Analysis

Temperature-dependent polarization measurements of all ceramics were shown in Figure 4.10 and Figure 4.11, and results were given in Table 4.3. The measurements were made under 50-60 kV/cm electric field, 70°C to room temperature, and at 1 Hz period.

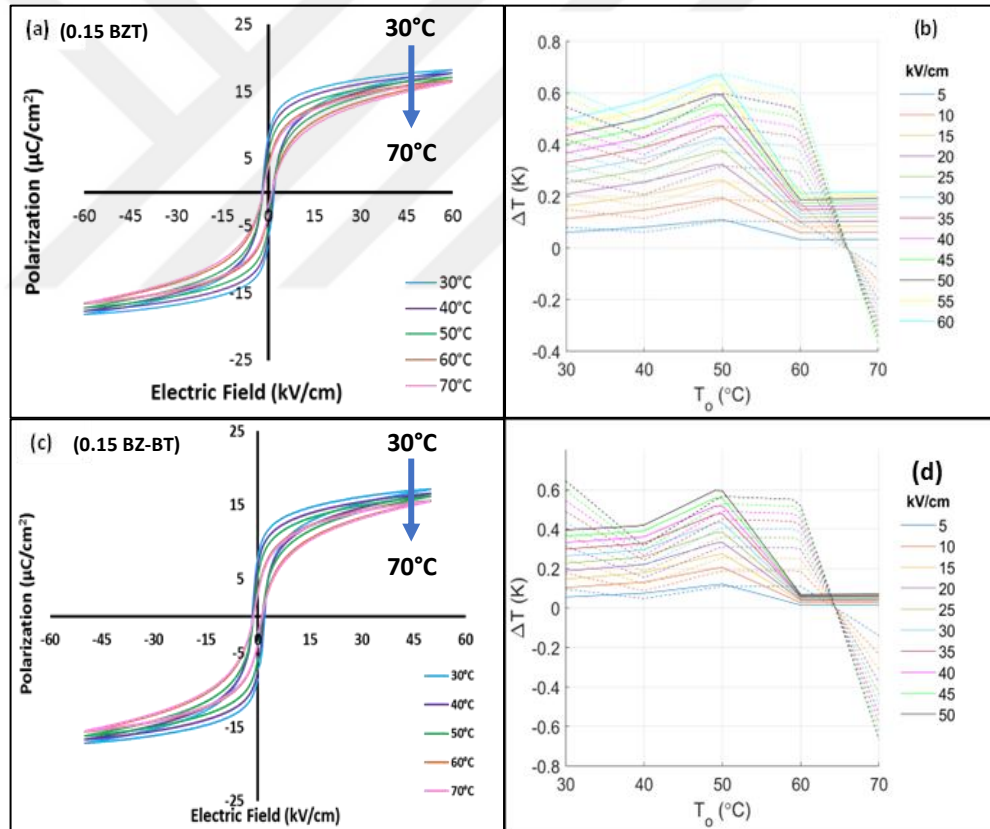


Figure 4.10: (a) and (c) P-E curves at different temperatures, (b) and (d)  $\Delta T$ - $T_0$  plots at different electric fields for 0.15 BZT and 0.15 BZ-BT ceramics.

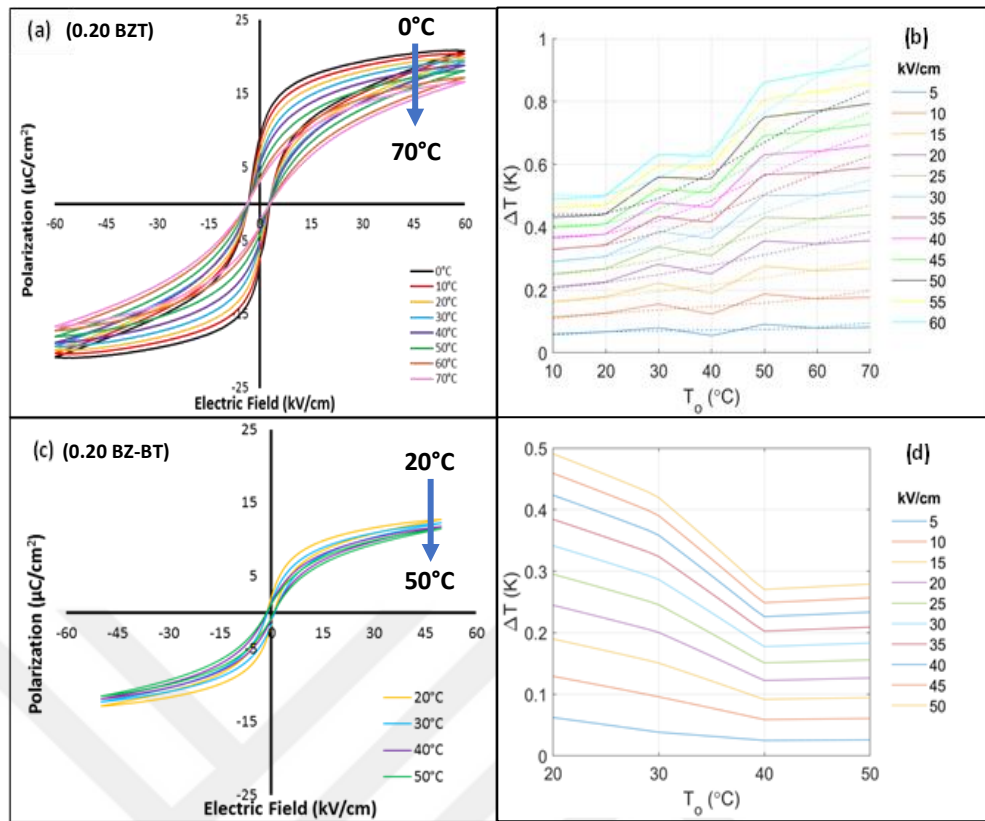


Figure 4.11: (a) and (c) P-E curves at different temperatures, (b) and (d)  $\Delta T$ - $T_0$  plots at different electric fields for 0.20 BZT and 0.20 BZ-BT ceramics.

Table 4.3: Electrocaloric results of BZT and BZ-BT compositions.

| Sample              | 0.15 BZT     |      | 0.15 BZ-BT   |      | 0.20 BZT        |      | 0.20 BZ-BT   |      |
|---------------------|--------------|------|--------------|------|-----------------|------|--------------|------|
| $\Delta E$ (kV/cm)  | 60           |      | 50           |      | 60              |      | 50           |      |
| Temperature         | 30°C         | 70°C | 30°C         | 70°C | 20°C            | 70°C | 20°C         | 50°C |
| $P_{\max}$ (μC/cm²) | 18.2         | 16.4 | 17.1         | 15.5 | 19.9            | 16.6 | 12.8         | 11.5 |
| $P_r$ (μC/cm²)      | 8.2          | 3.7  | 7.9          | 3.2  | 7.1             | 3.1  | 2.1          | 1.1  |
| $E_c$ (kV/cm)       | 2.0          | 1.4  | 2.1          | 1.2  | 2.8             | 2.5  | 0.9          | 0.8  |
| $T_c$               | ~56°C        |      | ~50°C        |      | ~42°C           |      | ~32°C        |      |
| $\Delta T(K)$       | 0.65 K ~50°C |      | 0.60 K ~50°C |      | 0.85 K ~50-70°C |      | 0.45 K ~30°C |      |

As it is known from the literature, the change in entropy is giant near the phase transition region [25]. Therefore, the highest value of  $\Delta T$  is near the  $T_c$  for ferroelectrics.

Since a lower electric field is applied to BZ-BT ceramics than to BZT ceramics, their electrical results are inferior. The reason for taking measurements under a lower electric field than BZT ceramics is that the samples cannot withstand high periods and high electric fields at the same time and the samples break down. In other words, the breakdown strength of BZ-BT's is lower than BZT's.

In Figures (4.12 & 4.13), (4.14 & 4.15), (4.16 & 4.17) and (4.18 & 4.19) electrocaloric results of 0.15 BZT, 0.15 BZ-BT, 0.20 BZ-BT, and 0.20 BZT ceramics, respectively, in different electric fields and different frequencies are shown as comparative. In Table 4.4 is compared electrocaloric coefficients [ $\Delta T_c/\Delta E$ ,  $\Delta S/\Delta E$ ] to establish the effects of applied electric field and frequency in critical compositions on ECE results.

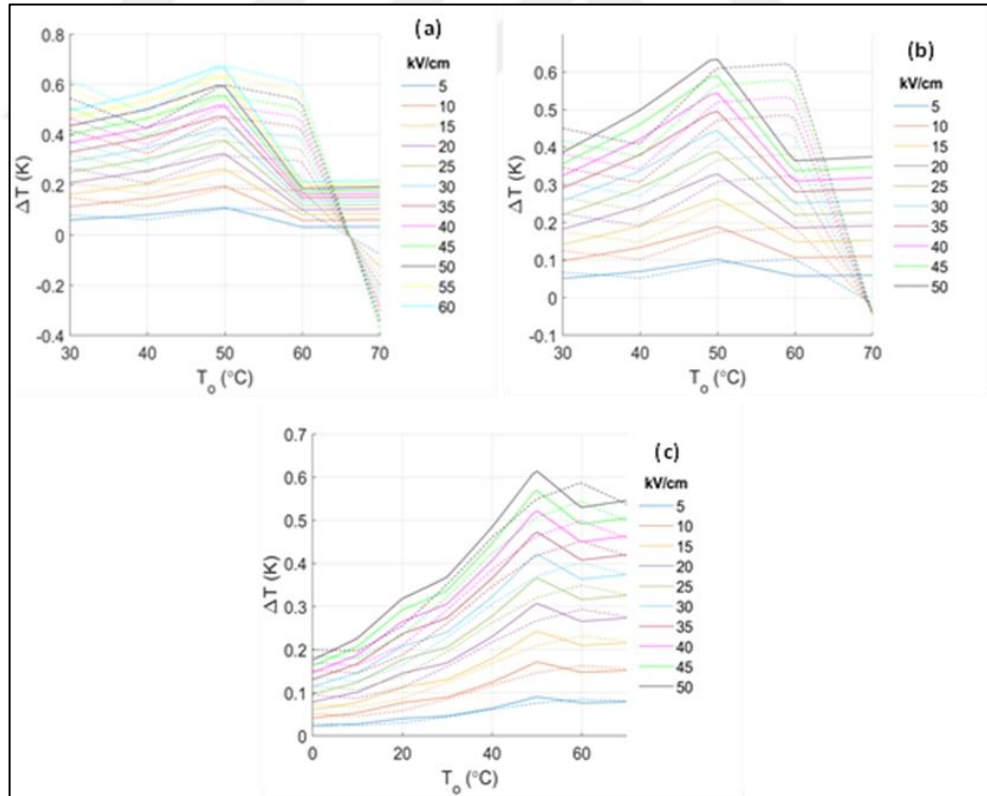


Figure 4.12:  $\Delta T$ - $T_0$  plots of 0.15 BZT ceramics at various frequencies and electric fields. (a) 1000 ms-60kV/cm, (b) 1000 ms-50kV/cm, (c) 500 ms-50kV/cm.

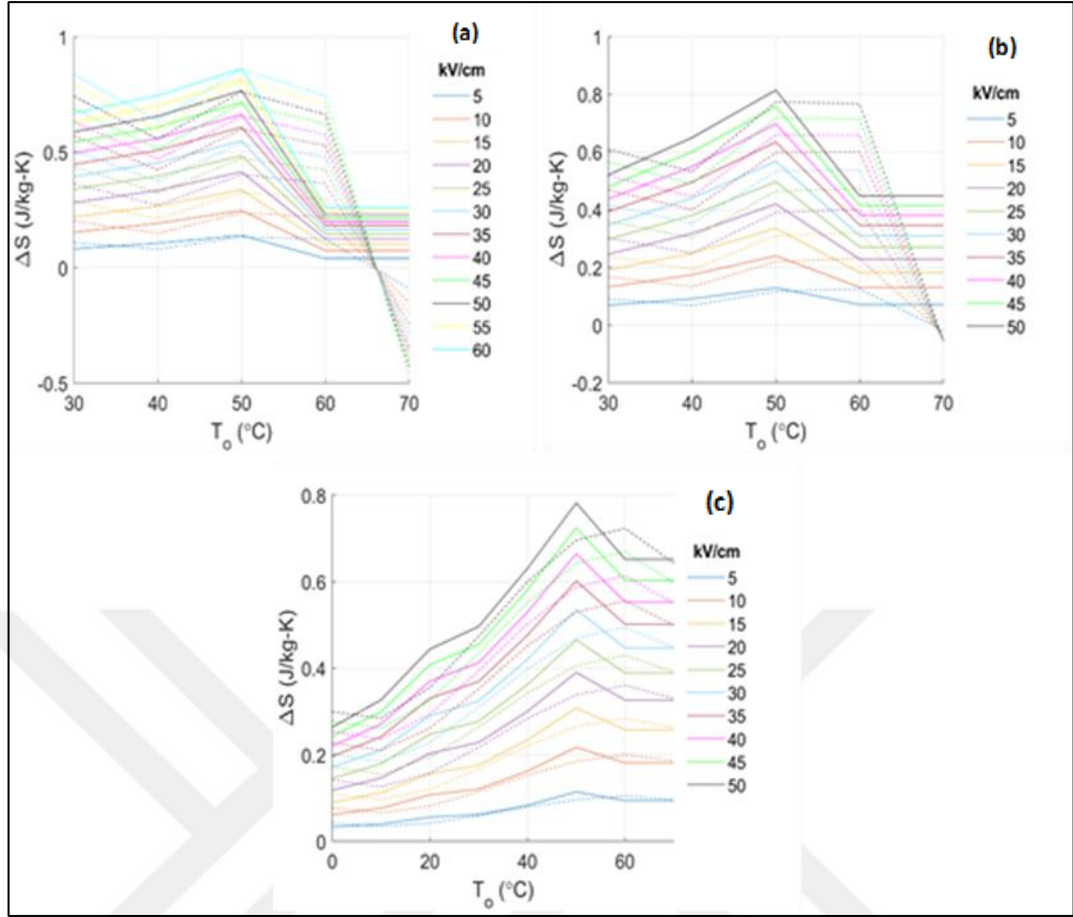


Figure 4.13:  $\Delta S$ - $T_0$  plots of 0.15 BZT ceramics at various frequencies and electric fields (a) 1000 ms-60kV/cm, (b) 1000 ms-50kV/cm, (c) 500 ms-50kV/cm.

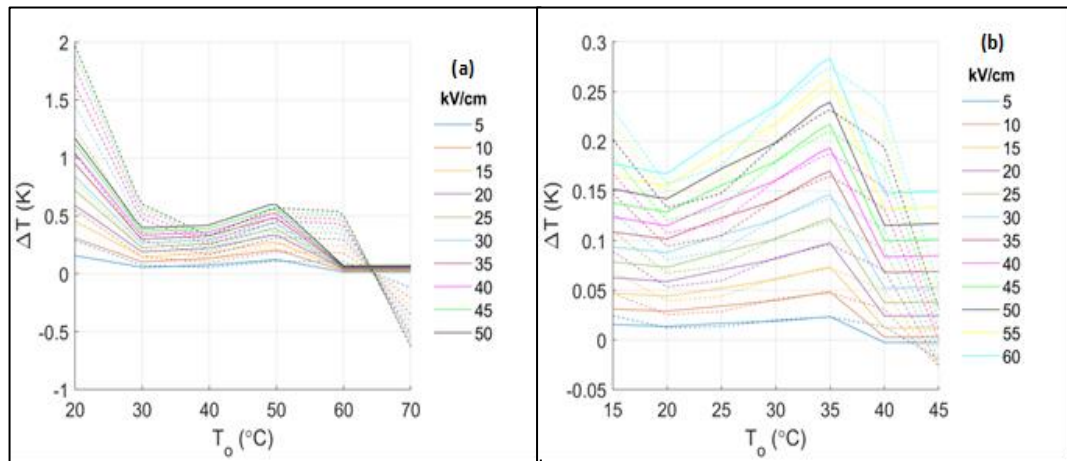


Figure 4.14:  $\Delta T$ - $T_0$  plots of 0.15 BZ-BT ceramics at various frequencies and electric fields (a) 1000 ms-50kV/cm, (b) 500 ms-60kV/cm.

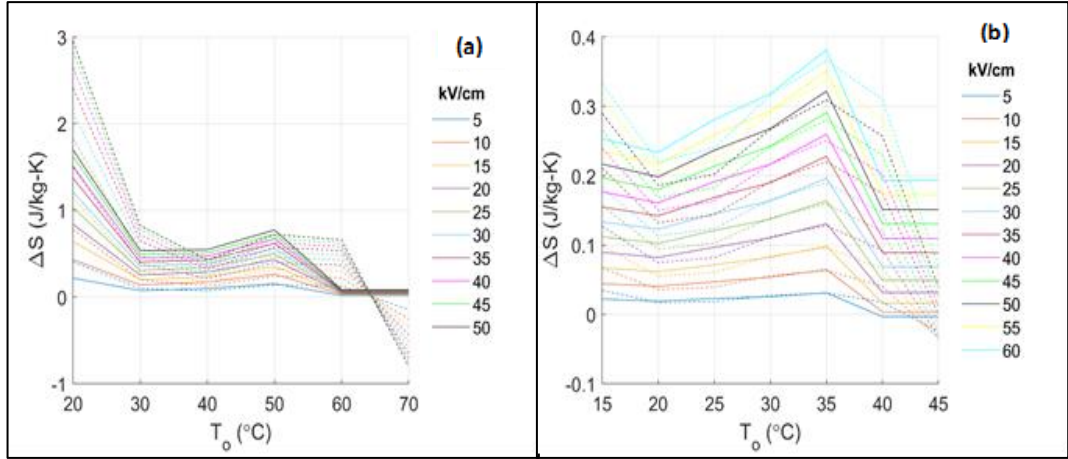


Figure 4.15:  $\Delta S$ - $T_0$  plots of 0.15 BZ-BT ceramics at various frequencies and electric fields (a) 1000 ms-50kV/cm, (b) 500 ms-60kV/cm.

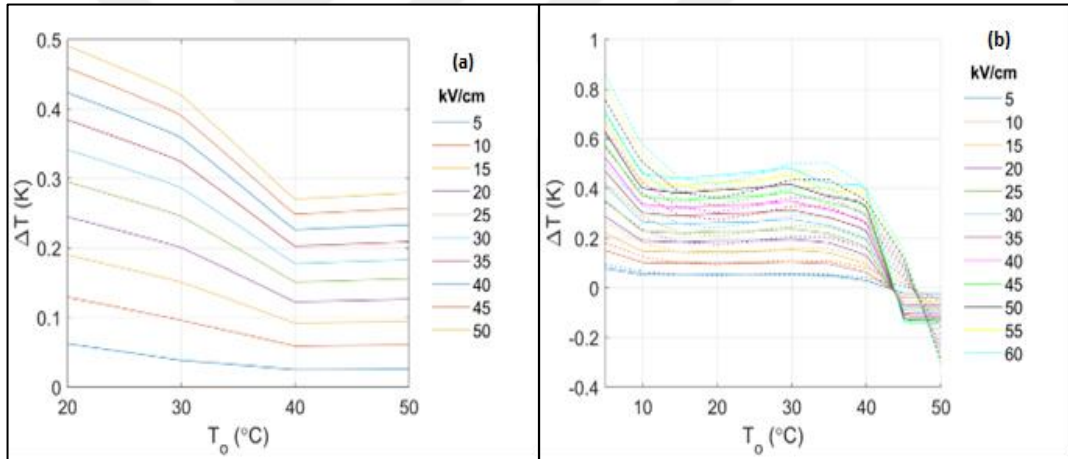


Figure 4.16:  $\Delta T$ - $T_0$  plots of 0.20 BZ-BT ceramics at various frequencies and electric fields (a) 1000 ms-50kV/cm and (b) 500 ms-60kV/cm.

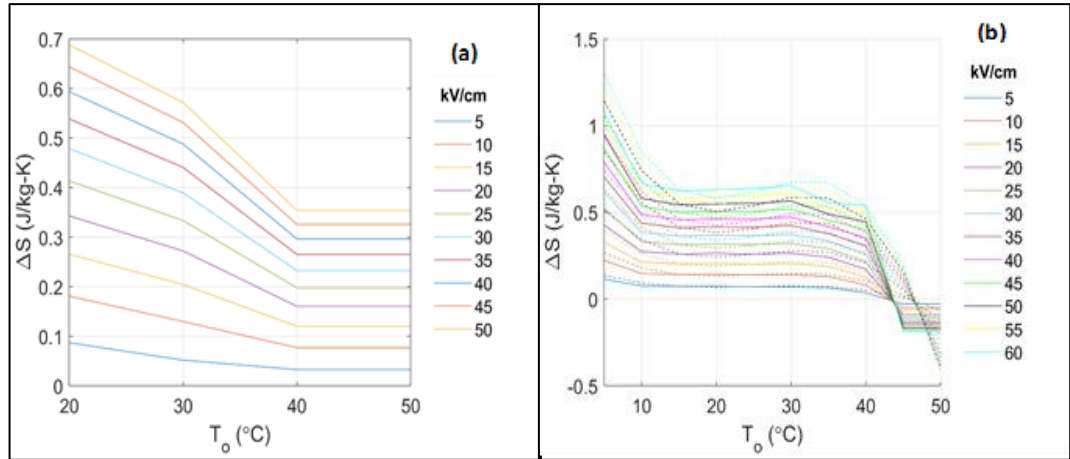


Figure 4.17:  $\Delta S$ - $T_0$  plots of 0.20 BZ-BT ceramics at various frequencies and electric fields (a) 1000 ms-50kV/cm and (b) 500 ms-60kV/cm.

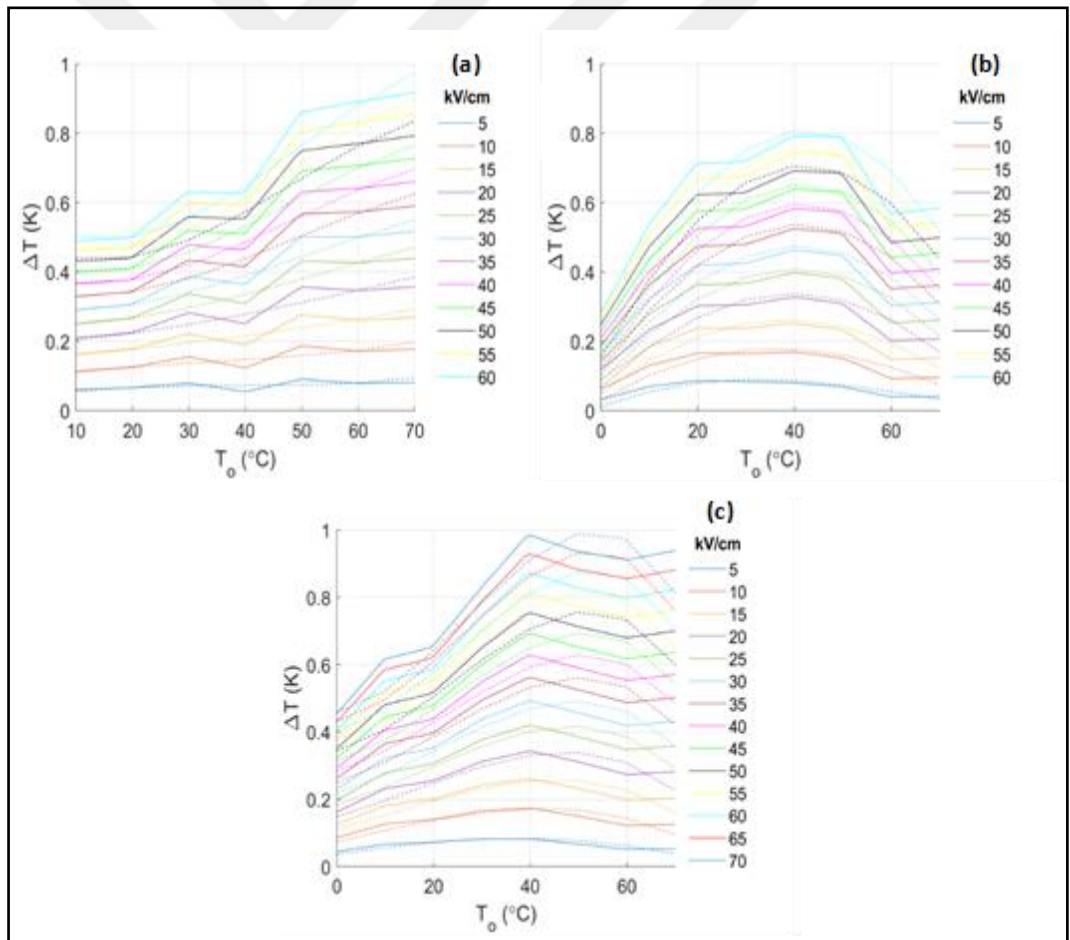


Figure 4.18:  $\Delta T$ - $T_0$  plots of 0.20 BZT ceramics at various frequencies and electric fields (a) 1000 ms-60 kV/cm, (b) 500 ms-60 kV/cm and (c) 500 ms-70 kV/cm.

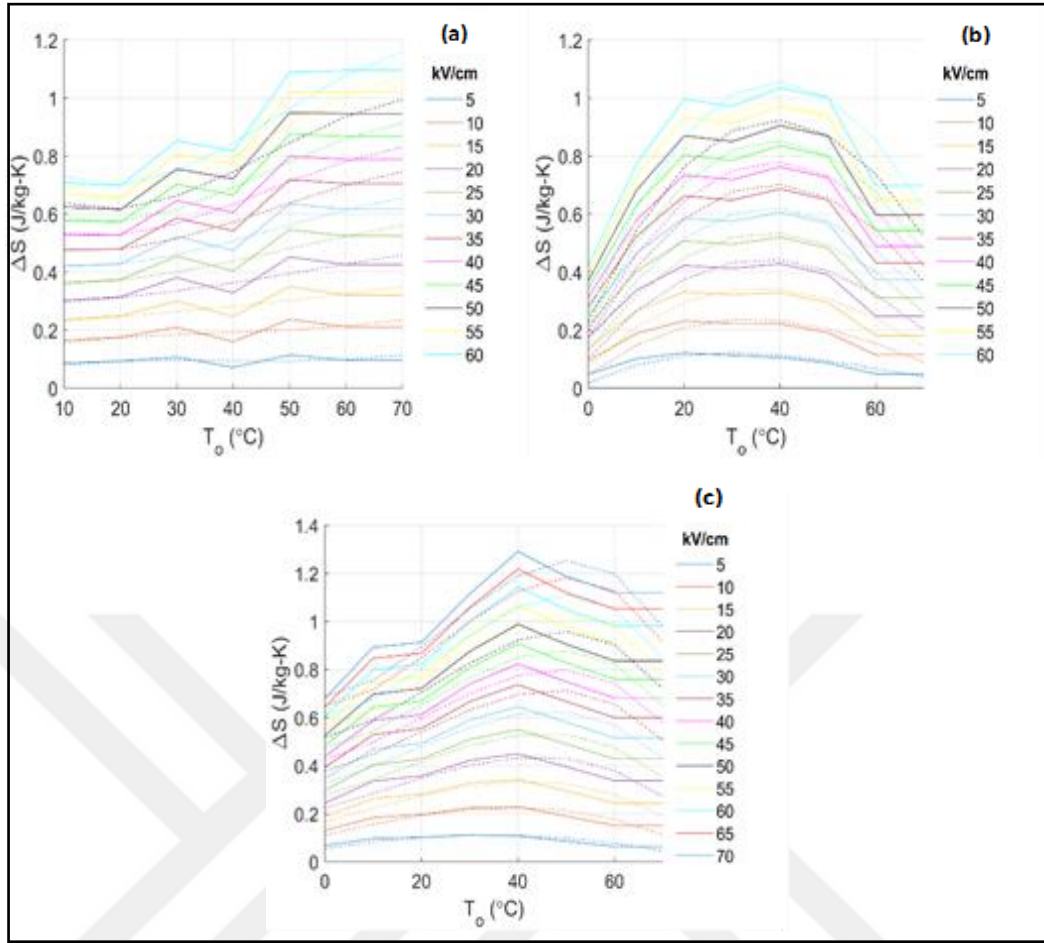


Figure 4.19:  $\Delta S$ - $T_0$  plots of 0.20 BZT ceramics at various frequencies and electric fields (a) 1000 ms-60 kV/cm, (b) 500 ms-60 kV/cm, and (c) 500 ms-70 kV/cm.

As shown in Table 4.4, with increasing the applied electric field, all compositions exhibit a rise in  $\Delta T$  and  $\Delta S$  values and a reduction in the electrocaloric coefficients [ $\Delta T_c/\Delta E$ ,  $\Delta S/\Delta E$ ].

For the  $\Delta T$  value, the frequency affects the  $x=0.15$  compositions more than the  $x=0.20$  compositions. As the applied electric field increases, the  $\Delta T$  results for all compositions increase. However, for the  $x=0.20$  compositions, the electric field's influence is stronger than the  $x=0.15$  compositions. At the same time, the increase in frequency generally favorably affects  $T_{span}$  in all compositions.

Table 4.4: Comparison of EC properties of BZT and BZ-BT (x= 0.15 & 0.20).

| Material   |                    | T <sub>c</sub><br>(°C) | $\Delta T$ [K] |          |          |          | $\Delta S$ [Jkg <sup>-1</sup> K <sup>-1</sup> ] |          |          |          | $\Delta T/\Delta E$<br>[10 <sup>-6</sup> KmV <sup>-1</sup> ] |          |          |          | $\Delta S/\Delta E$<br>[10 <sup>-6</sup> Jmkg <sup>-1</sup> K <sup>-1</sup> V] |          |          |          | T span |
|------------|--------------------|------------------------|----------------|----------|----------|----------|-------------------------------------------------|----------|----------|----------|--------------------------------------------------------------|----------|----------|----------|--------------------------------------------------------------------------------|----------|----------|----------|--------|
|            |                    |                        | 40 kV/cm       | 50 kV/cm | 60 kV/cm | 70 kV/cm | 40 kV/cm                                        | 50 kV/cm | 60 kV/cm | 70 kV/cm | 40 kV/cm                                                     | 50 kV/cm | 60 kV/cm | 70 kV/cm | 40 kV/cm                                                                       | 50 kV/cm | 60 kV/cm | 70 kV/cm |        |
| 0.15 BZT   | 500 ms - 50 kV/cm  | 56                     | 0.52           | 0.61     | -        | -        | 0.65                                            | 0.78     | -        | -        | 0.13                                                         | 0.12     | -        | -        | 0.16                                                                           | 0.16     | -        | -        | 50     |
|            | 1000 ms - 50 kV/cm |                        | 0.55           | 0.65     | -        | -        | 0.70                                            | 0.80     | -        | -        | 0.14                                                         | 0.13     | -        | -        | 0.18                                                                           | 0.16     | -        | -        | 50-52  |
|            | 1000 ms - 60 kV/cm |                        | 0.45           | 0.60     | 0.65     | -        | 0.60                                            | 0.70     | 0.80     | -        | 0.11                                                         | 0.12     | 0.11     | -        | 0.15                                                                           | 0.14     | 0.13     | -        | 50     |
| 0.15 BZ-BT | 500 ms - 60 kV/cm  | 50                     | 0.19           | 0.24     | 0.27     | -        | 0.25                                            | 0.31     | 0.38     | -        | 0.05                                                         | 0.05     | 0.05     | -        | 0.06                                                                           | 0.06     | 0.06     | -        | 35     |
|            | 1000 ms - 50 kV/cm |                        | 0.50           | 0.52     | -        | -        | 0.50                                            | 0.60     | -        | -        | 0.13                                                         | 0.10     | -        | -        | 0.13                                                                           | 0.12     | -        | -        | 50     |
| 0.20 BZT   | 500 ms - 60 kV/cm  | 42                     | 0.60           | 0.70     | 0.80     | -        | 0.70                                            | 0.90     | 1.05     | -        | 0.15                                                         | 0.14     | 0.13     | -        | 0.18                                                                           | 0.18     | 0.18     | -        | 40-50  |
|            | 500 ms - 70 kV/cm  |                        | 0.60           | 0.70     | 0.85     | 0.95     | 0.80                                            | 1.00     | 1.10     | 1.30     | 0.15                                                         | 0.14     | 0.14     | 0.14     | 0.20                                                                           | 0.20     | 0.18     | 0.19     | 40     |
|            | 1000 ms - 60 kV/cm |                        | 0.60           | 0.70     | 0.85     | -        | 0.80                                            | 0.90     | 1.10     | -        | 0.15                                                         | 0.14     | 0.14     | -        | 0.20                                                                           | 0.18     | 0.18     | -        | 50-70  |
| 0.20 BZ-BT | 500 ms - 60 kV/cm  | 32                     | 0.35           | 0.43     | 0.50     | -        | 0.45                                            | 0.55     | 0.65     | -        | 0.09                                                         | 0.08     | 0.08     | -        | 0.11                                                                           | 0.11     | 0.11     | -        | 25-30  |
|            | 1000 ms - 50 kV/cm |                        | 0.35           | 0.45     | -        | -        | 0.50                                            | 0.58     | -        | -        | 0.09                                                         | 0.09     | -        | -        | 0.13                                                                           | 0.12     | -        | -        | 30     |

When 0.15 and 0.20 compositions are compared at the same electric field and different frequencies (50 kV/cm-1000 ms and 500 ms), it is seen that there is more change in the electrocaloric results of x=0.15 than x=0.20.

When the same frequency and different electric fields (1000 ms-40 kV/cm, 50 kV/cm, and 60 kV/cm) are applied to ceramics, a higher electrocaloric response is observed at x=0.20 compositions, especially for  $\Delta E > 50$  kV/cm.

When compared for the same frequency and the same electric field, it is seen that the electrocaloric results of x=0.20 compositions are higher than x=0.15 compositions. The fact that x=0.20 compositions are a relaxor ferroelectric with nanodomains that require less energy to align causes the applied electric field to be more effective.

BZ-BT results are significantly lower than BZT results, though compositionally coherent with the observations. It is thought that although BZ-BTs provide relaxor properties, they shift from critical points due to the production method has separation of BZ and BT.

In this thesis, 0.20 BZT is considered more appropriate in terms of the advantage of composition and production method, since a wide operating temperature is requested with high electrocaloric results.

## 4.2. BCZT Ceramics

In this section, the structural and electrical results of the compositions of  $0.68\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.32(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  operating at the triple point and  $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  operating at the morphotropic phase boundary in the BZ20T–xBC30T system, and  $0.8\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-0.2(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$  operating at the triple point in the BZ15T–xBC20T system will be examined.  $0.68\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.32(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  composition will be abbreviated as 0.32 BCZT,  $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  composition as 0.50 BCZT and  $0.8\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-0.2(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$  composition as 0.20 BCZT, respectively.

### 4.2.1. Phase Analysis of BCZT Powder

Figure 4.20, Figure 4.21 and Figure 4.22 show the XRD result of 0.32, 0.50 and 0.20 BCZT powders calcined at 1200°C with a ramp rate of 5°C/min for 3-6 hours, respectively. The XRD results of all calcined powders show a perovskite structure. The particle size of these powders exhibits a narrow and homogeneous size distribution, with an average particle size of ( $d_{0.5}$ ) 0.176  $\mu\text{m}$  for 0.32 BCZT, ( $d_{0.5}$ ) 0.180  $\mu\text{m}$  for 0.50 BCZT and ( $d_{0.5}$ ) 0.177  $\mu\text{m}$  for 0.20 BCZT.

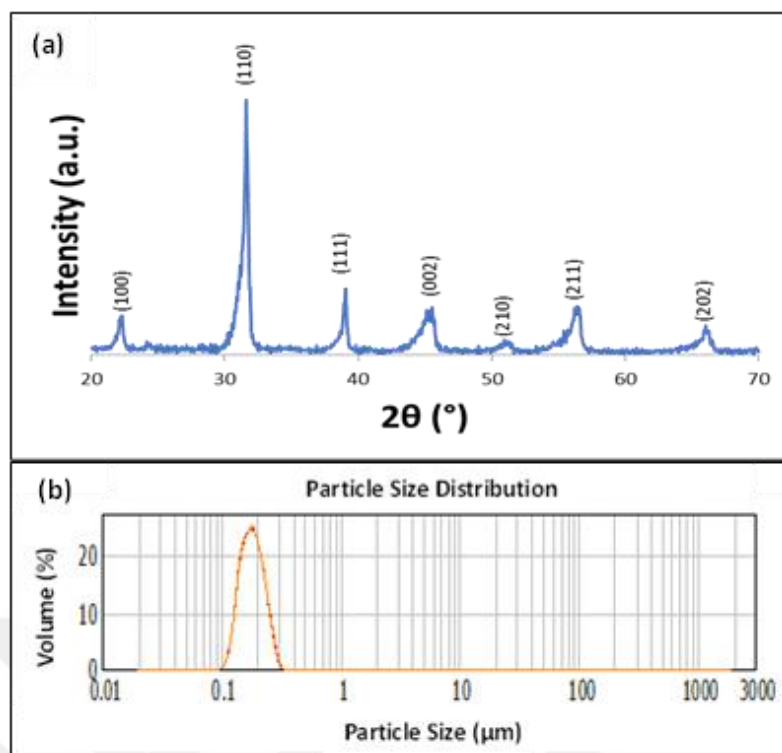


Figure 4.20: (a) XRD pattern and (b) particle size distribution measurement of 0.32 BCZT powder calcined at 1200°C for 3 h.

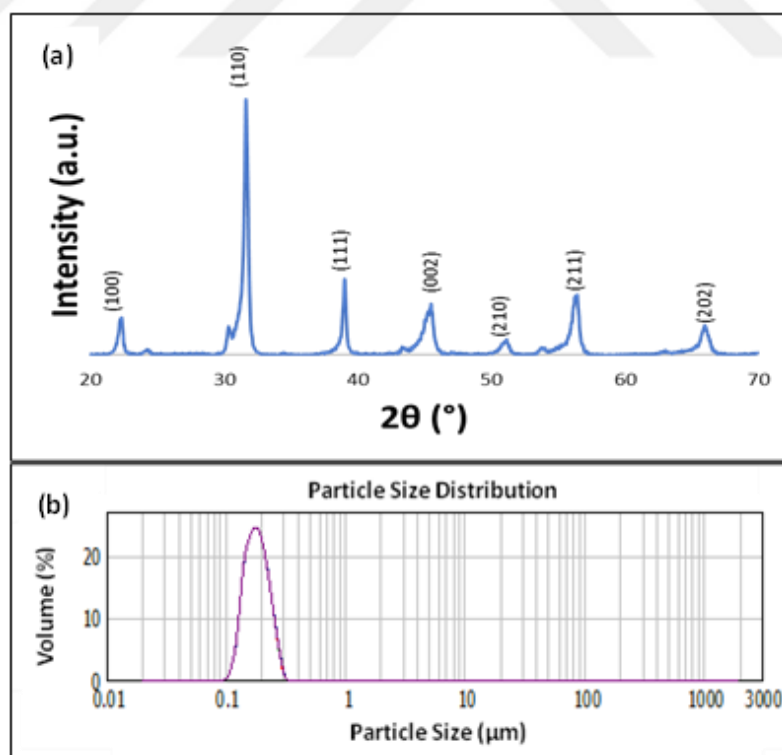


Figure 4.21: (a) XRD pattern and (b) particle size distribution measurement of 0.50 BCZT powder calcined at 1200°C for 6 h.

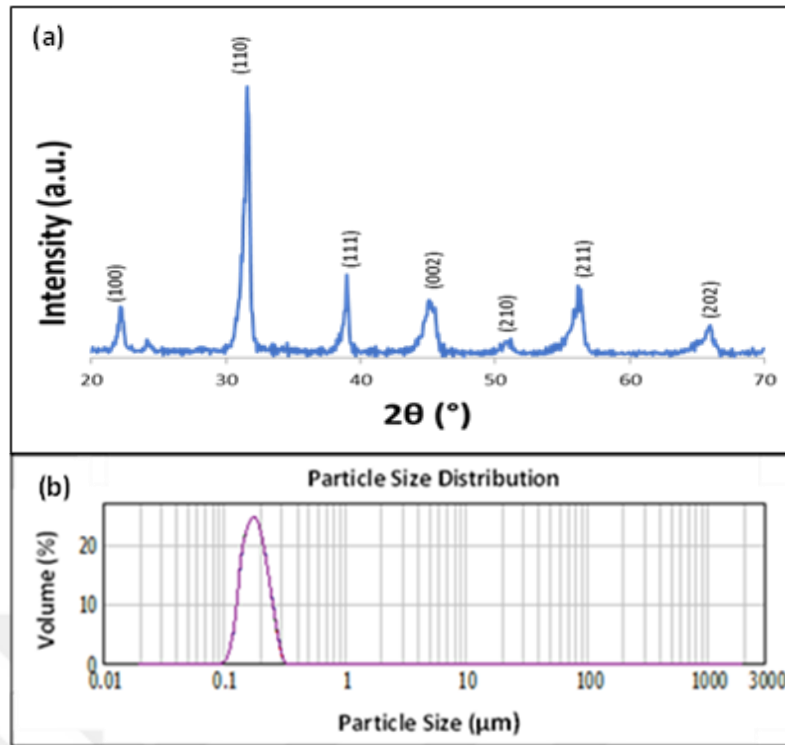


Figure 4.22: (a) XRD pattern and (b) particle size distribution measurement of 0.20 BCZT powder calcined at 1200°C for 3 h.

#### 4.2.2. Structural Analysis of BCZT Ceramics

Figure 4.23 shows comparative XRD patterns of 0.32, 0.50, and 0.20 BCZT sintered at 1440 C° for 6 hours. The XRD results have shown that all compositions are sintered at the optimum temperature and time, and ceramics are crystallized in a pure perovskite structure without any secondary phase.

The average crystallite size obtained from the X-ray diffraction data is 82.3 nm for the 0.32 BCZT, 68.8 nm for the 0.50 BCZT, and 102 nm for the 0.20 BCZT. In BCZT,  $\text{Ca}^{+2}$  (1.06 Å) with a smaller ionic radius is substituted instead of  $\text{Ba}^{+2}$  (1.43 Å), and  $\text{Zr}^{+4}$  (0.98 Å) with a larger ionic radius is substituted instead of  $\text{Ti}^{+4}$  (0.72 Å). A decrease in the concentration of BCT and an increase in the concentration of BZT reduce the diffusion rate. This situation causes the grain size and therefore the crystallite size to decrease. As mentioned in the BZT part, crystallite size reduction increases polar nanodomains and grain boundary scattering in the structure. Thus, the additional degrees of freedom with which dipoles can move and the increased electrical resistance positively affect the electrical properties.

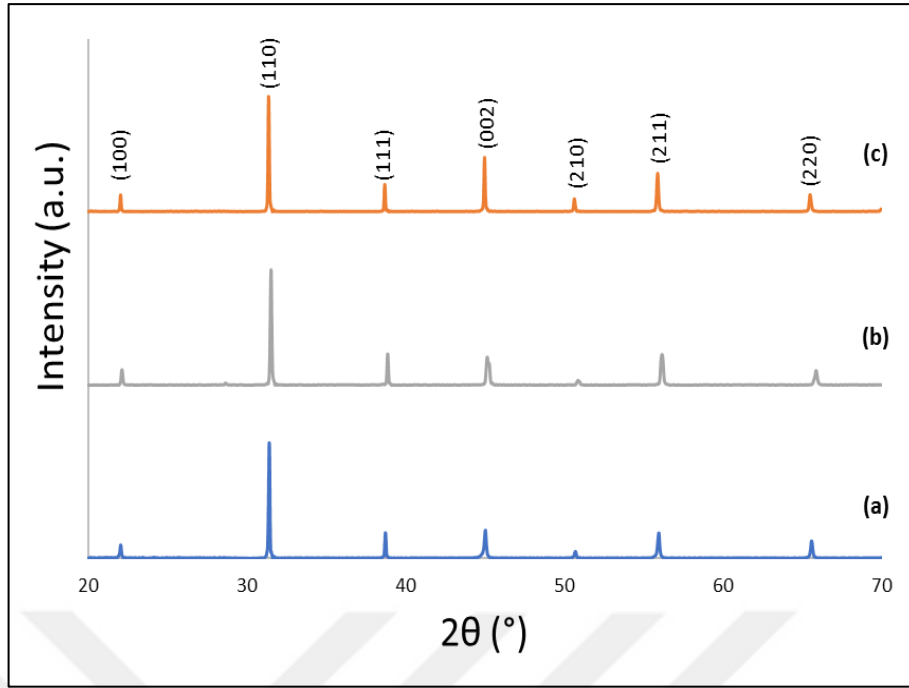


Figure 4.23: The XRD patterns of (a) 0.32 BCZT, (b) 0.50 BCZT, (c) 0.20 BCZT ceramics.

In Figure 4.24, SEM analysis results taken from the polished and thermally etched surfaces and cross-sections are given in order to investigate the microstructure of the samples. SEM images show all samples have relatively dense morphology with clear visible grain boundaries. According to Archimedes' method, density was calculated as 97% for the 0.32 and 0.20 BCZT samples and calculated as 93% for the 0.50 BCZT sample.

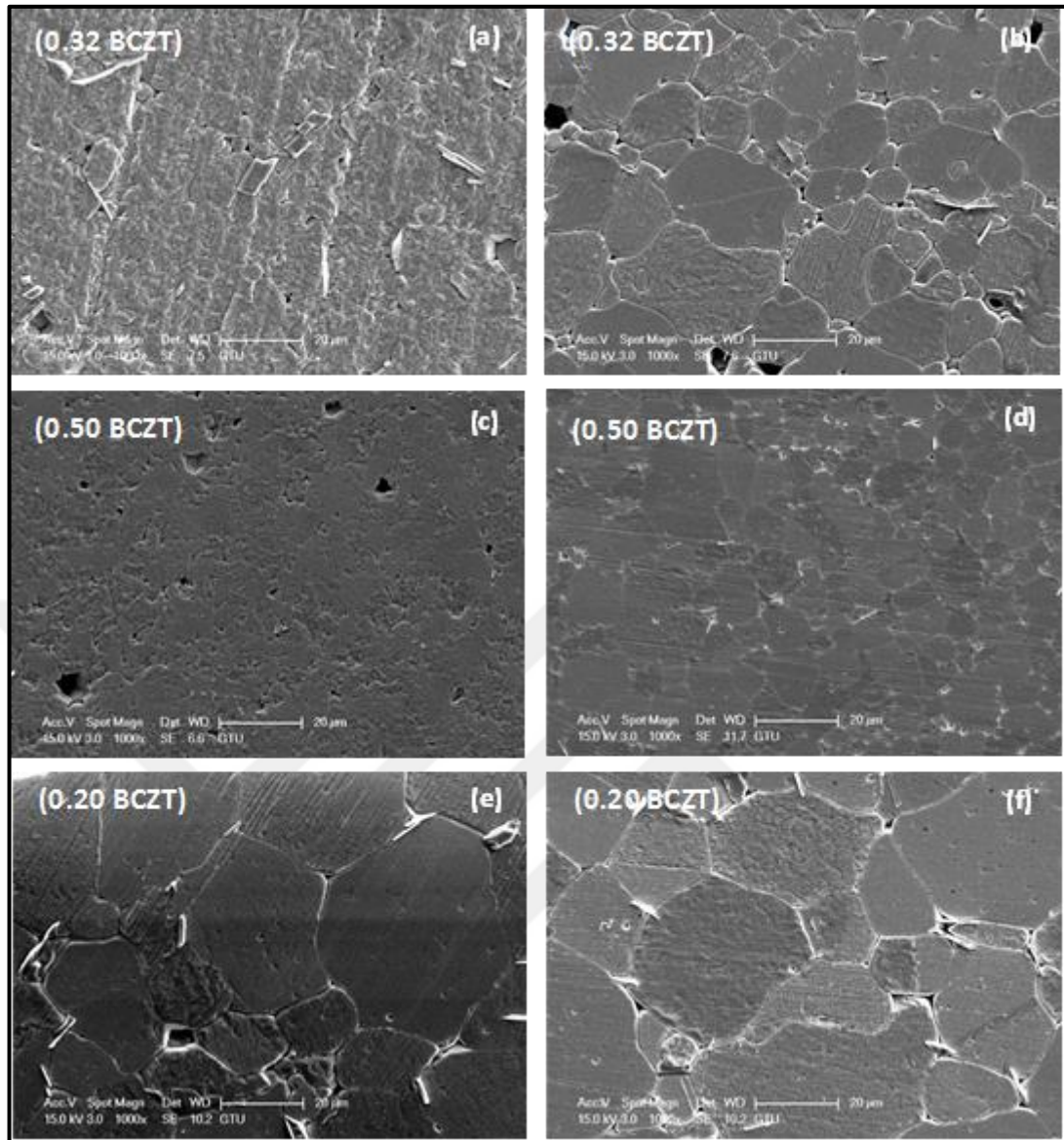


Figure 4.24: SEM images of (a), (c) and (e) cross-sectional and (b), (d) and (f) surfaces of the ceramics.

### 4.2.3. Electrical Characterization of BCZT Ceramics

#### 4.2.3.1. Dielectric Measurements of Temperature-Dependent

The dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) measurements of BCZT (0.32 & 0.50 & 0.20) ceramics taken at different frequencies depending on the temperature in the range of 1-100 kHz are given in Figure 4.25.

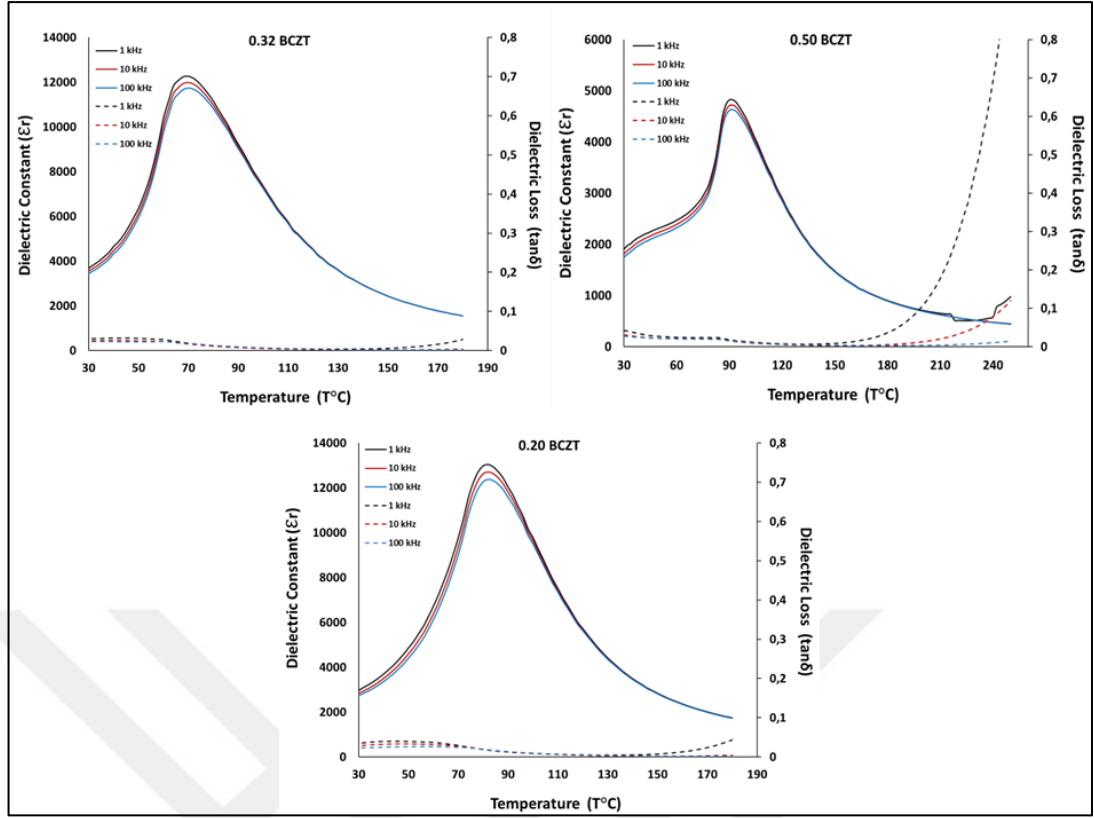


Figure 4.25: Temperature dependence of dielectric loss and dielectric constant of 0.32 BCZT, 0.50 BCZT, and 0.20 BCZT.

For ceramics with compositions  $x=0.32$ ,  $x=0.50$ , and  $x=0.20$ , measurements were taken from room temperature to 180-250°C with a ramp rate of 2°C/min.  $T_c$ ,  $\epsilon_r$ , and  $\tan\delta$  values of 0.32 BCZT, 0.50 BCZT, and 0.20 BCZT ceramics at 1 kHz frequency are given in Table 4.5.

The compositions  $x=0.32$ ,  $x=0.50$ , and  $x=0.20$  are located in multiphase regions and strong dielectric behavior is obtained in these regions. The proximity of the multiphase region temperatures and the phase transition temperature, the  $T_c$ , to the room temperature at which the dielectric results are obtained affects the dielectric behavior [61]. Therefore, the  $T_c$  and the temperature at which the triple point is located, the composition  $x=0.32$ , which is closest to room temperature, give the highest dielectric response. Then the composition  $x=0.20$  and  $x=0.50$ , respectively, show strong dielectric behavior.

Table 4.5:  $T_c$ , dielectric coefficient and dielectric loss value of ceramics at room temperature.

| Sample    | $T_c$ ( $^{\circ}\text{C}$ ) | $\epsilon_r$<br>[RT, @1 kHz] | $\tan\delta$<br>[RT, @1 kHz] |
|-----------|------------------------------|------------------------------|------------------------------|
| 0.32 BCZT | 70                           | 3697                         | 0.029                        |
| 0.50 BCZT | 92                           | 1909                         | 0.042                        |
| 0.20 BCZT | 82                           | 2969                         | 0.034                        |

#### 4.2.3.2. Ferroelectric Measurements

In Figure 4.26, polarization-electric field (P-E) hysteresis loops of ceramics were measured in an electric field between 10-50 kV/cm, at room temperature and at 1 Hz period.

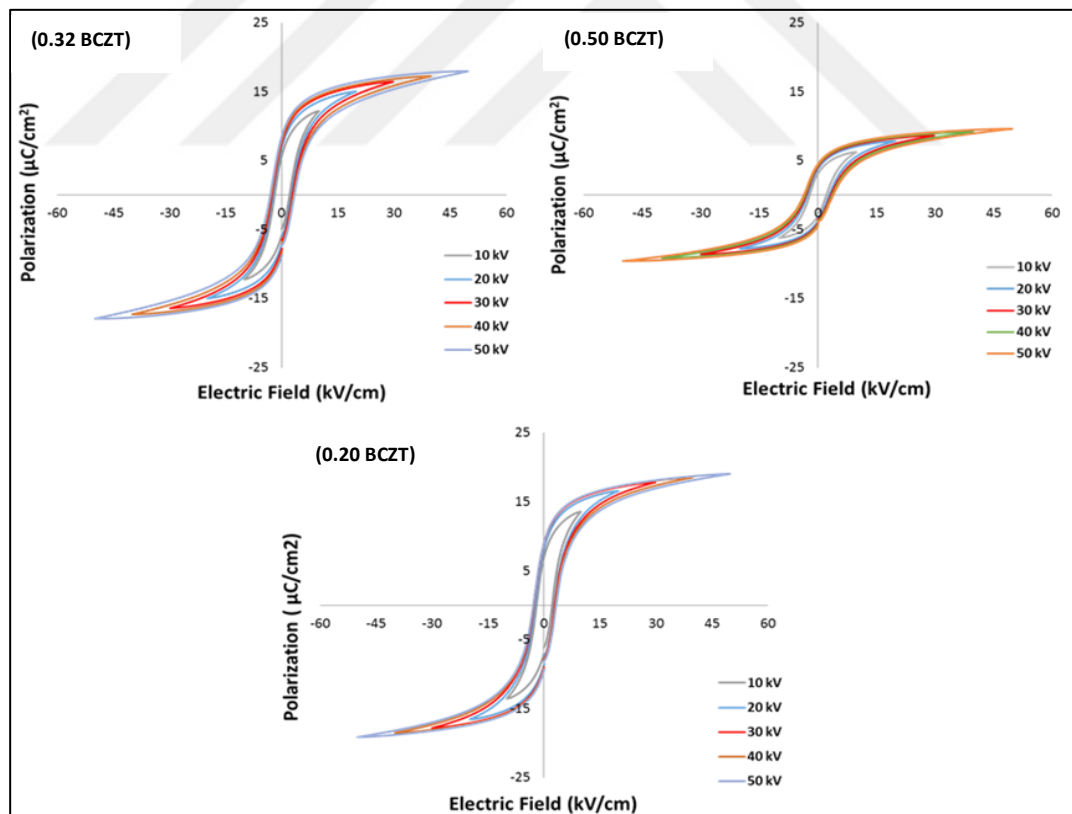


Figure 4.26: The P – E hysteresis loops of BCZT ceramics.

The remnant polarization ( $P_r$ ), maximum polarization ( $P_{max}$ ), and coercive electric field ( $E_c$ ) values of the ceramics are given in Table 4.6.

Table 4.6:  $P_r$ ,  $P_{max}$  and  $E_c$  values of the ceramics.

| Sample    | $P_{max}$<br>( $\mu\text{C}/\text{cm}^2$ ) | $P_r$<br>( $\mu\text{C}/\text{cm}^2$ ) | $E_c$<br>( $\text{kV}/\text{cm}$ ) |
|-----------|--------------------------------------------|----------------------------------------|------------------------------------|
| 0.32 BCZT | 17.95                                      | 8.80                                   | 3.30                               |
| 0.50 BCZT | 9.57                                       | 4.60                                   | 4.10                               |
| 0.20 BCZT | 19.08                                      | 9.30                                   | 3.30                               |

In Figure 4.27, polarization-electric field hysteresis loops of ceramics under 50 kV/cm electric field are given comparatively.

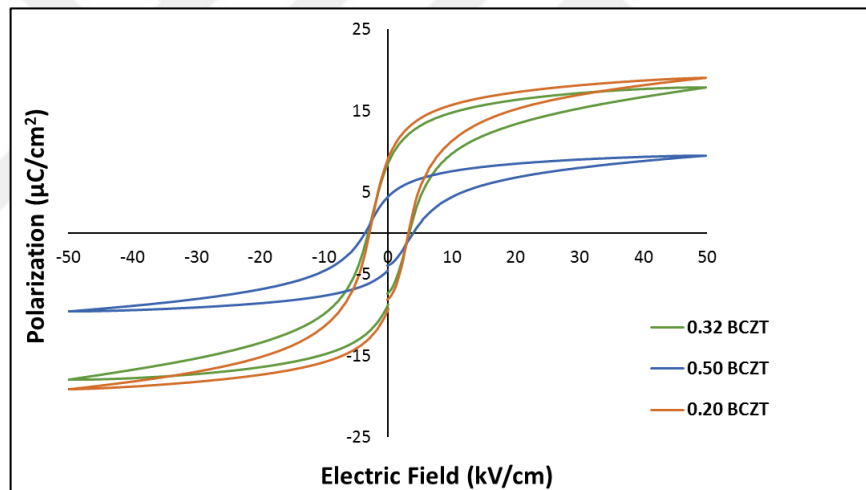


Figure 4.27: Comparative hysteresis loops of 0.32 BCZT, 0.50 BCZT, and 0.20 BCZT ceramics.

The figures show that all samples exhibit relatively thin and low-loss saturated hysteresis loops. The  $x=0.50$  composition contains the micron-sized domains and nanodomains miniaturized on the domains at room temperature in MPB. Miniaturized nanodomains provide relaxor ferroelectric properties to the structure. The ordering of relaxor nano regions in the structure of relaxor ferroelectrics is more difficult than long-range polar ordering found in normal ferroelectrics [60].

Therefore, relaxor ferroelectrics usually have inferior  $P_{\max}$ ,  $P_r$ ,  $E_c$ , and hysteresis loss values. The compositions  $x = 0.32$  and  $x=0.20$ , operate at a triple invariant point where the MPB and the paraelectric phase intersect. Therefore, the structures of these ceramics are closer to normal ferroelectricity which have larger  $P_{\max}$ ,  $P_r$ ,  $E_c$ , and hysteresis loss values. Crystallite size values also support the relaxor properties ranking of ceramics. The average crystallite size is 82.3 nm for the 0.32 BCZT, 68.8 nm for the 0.50 BCZT, and 102 nm for the 0.20 BCZT.

#### 4.2.3.3. Temperature-Dependent Hysteresis Measurement and Electrocaloric Analysis

Temperature-dependent polarization measurements of BCZT (0.32 & 0.50 & 0.20) ceramics shown in Figure 4.28, Figure 4.29, and Figure 4.30 were made under 40 - 50 kV/cm electric field from 90°C to 0°C in 1 Hz periods.

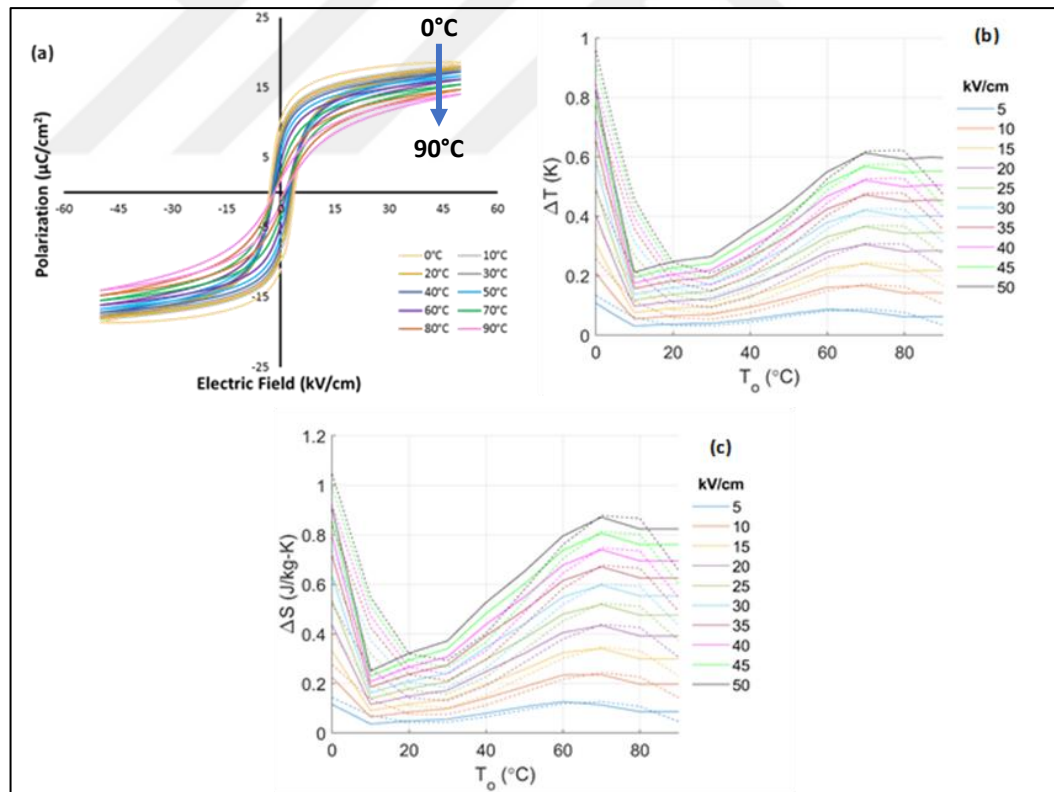


Figure 4.28: For 0.32 BCZT ceramics (a) P-E curve at different temperatures, (b)  $\Delta T$ - $T_0$  plot, and (c)  $\Delta S$ - $T_0$  plots at different electric fields.

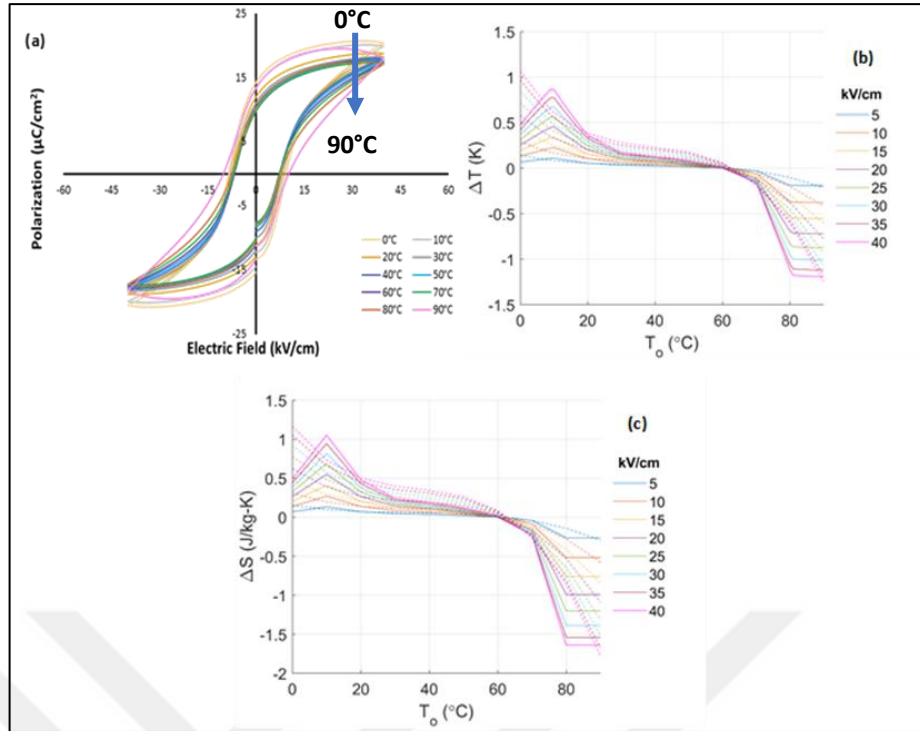


Figure 4.29: For 0.50 BCZT ceramics (a) P-E curve at different temperatures, (b)  $\Delta T$ - $T_0$  plot, and (c)  $\Delta S$ - $T_0$  plots at different electric fields.

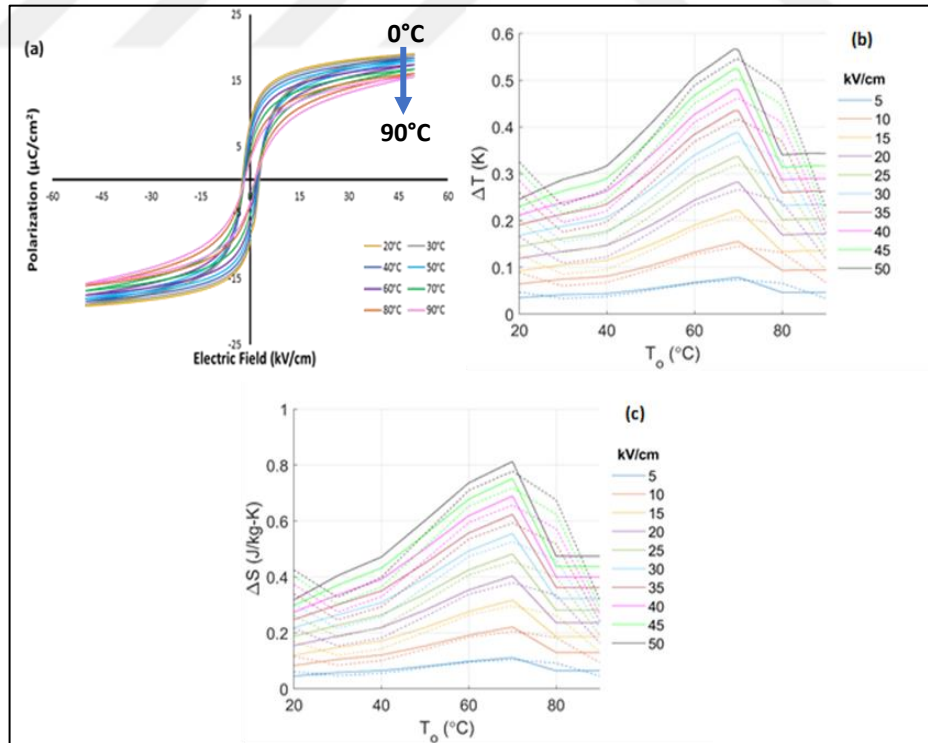


Figure 4.30: For 0.20 BCZT ceramics (a) P-E curve at different temperatures, (b)  $\Delta T$ - $T_0$  plot, and (c)  $\Delta S$ - $T_0$  plots at different electric fields.

Table 4.7: Electrocaloric results of BCZT compositions.

| Sample                                      | 0.32 BCZT    |      | 0.50 BCZT     |      | 0.20 BCZT    |      |
|---------------------------------------------|--------------|------|---------------|------|--------------|------|
| $\Delta E$ (kV/cm)                          | 50           |      | 40            |      | 50           |      |
| Temperature                                 | 0°C          | 90°C | 0°C           | 90°C | 20°C         | 90°C |
| $P_{\max}$<br>( $\mu\text{C}/\text{cm}^2$ ) | 18.6         | 14.0 | 20.4          | 17.9 | 19.0         | 15.7 |
| $P_r$<br>( $\mu\text{C}/\text{cm}^2$ )      | 10.3         | 1.8  | 14.2          | 13.3 | 8.6          | 2.9  |
| $E_c$<br>(kV/cm)                            | 3.7          | 1.2  | 9.2           | 10.5 | 2.8          | 1.4  |
| $T_c$                                       | ~70°C        |      | ~92°C         |      | ~82°C        |      |
| $\Delta T(\text{K})$                        | 0.60 K ~70°C |      | 0.80 K ~ 10°C |      | 0.56 K ~70°C |      |

In Table 4.7, the electrocaloric results of all BCZT ceramics were given. 0.32 BCZT and 0.20 BCZT have the highest value of  $\Delta T$  near the  $T_c$ . But the situation is different for 0.50 BCZT.

According to the phase diagram of BCZT (Figure 2.16), the composition  $x=0.50$  operates in MPB at room temperature. Since the combination of tetragonal-rhombohedral phases will occur around the MPB, the number of possible polarization directions is 14 in total. The rise of possible polarization directions number in which the dipoles can move allows the material to be easily polarized and the entropy increases. Therefore, the highest value of  $\Delta T$  is in the region close to room temperature.

The reason why  $E_c$  is lower at 0°C than at 90°C is that the domain boundaries move more easily at low temperatures. Other compounds (BZT and 0.32 & 0.20 BCZT) have the highest  $\Delta T$  values in regions near to the  $T_c$  because of the ferroelectric-paraelectric phase transition in the determined compositions.

Table 4.8: Comparison of EC properties of BCZT (x= 0.32 & 0.50 & 0.20).

| Material  | T <sub>c</sub><br>(°C) | $\Delta T$ [K] |             | $\Delta S$<br>[J/kg <sup>-1</sup> K <sup>-1</sup> ] |             | $\Delta T/\Delta E$<br>[10 <sup>-6</sup> KmV <sup>-1</sup> ] |             | $\Delta S/\Delta E$<br>[10 <sup>-6</sup> J/mkg <sup>-1</sup> K <sup>-1</sup> V] |             | T span | Average<br>Crystallite<br>Size<br>(nm) |
|-----------|------------------------|----------------|-------------|-----------------------------------------------------|-------------|--------------------------------------------------------------|-------------|---------------------------------------------------------------------------------|-------------|--------|----------------------------------------|
|           |                        | 40<br>kV/cm    | 50<br>kV/cm | 40<br>kV/cm                                         | 50<br>kV/cm | 40<br>kV/cm                                                  | 50<br>kV/cm | 40<br>kV/cm                                                                     | 50<br>kV/cm |        |                                        |
| 0.32 BCZT | 70                     | 0.50           | 0.60        | 0.70                                                | 0.90        | 0.13                                                         | 0.12        | 0.18                                                                            | 0.18        | 70     | 82.3                                   |
| 0.50 BCZT | 92                     | 0.80           | -           | 1.10                                                | -           | 0.20                                                         | -           | 0.28                                                                            | -           | 10     | 68.8                                   |
| 0.20 BCZT | 82                     | 0.47           | 0.56        | 0.65                                                | 0.80        | 0.12                                                         | 0.11        | 0.16                                                                            | 0.16        | 70     | 102.0                                  |

As shown in Table 4.8, with increasing the applied electric field, all compositions exhibit an increase in  $\Delta T$  and  $\Delta S$  values and a decrease in electrocaloric coefficients [ $\Delta T_c/\Delta E$ ,  $\Delta S/\Delta E$ ]. The reason why 0.32 BCZT and 0.20 BCZT give close each other electrocaloric results is that they both operate at triple points in their phase diagrams. In the BZT-XBCT system, 0.32 BCZT has Zr=0.20 and Ca=0.30 composition,  $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ , while 0.20 BCZT has Zr=0.15 and Ca=0.20 composition,  $(1-x)\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3-x(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$ . As it is known from the BZT part, the Zr=0.20 composition adds relaxor properties to the structure and this increases the electrocaloric properties. However, Ca=0.30 composition is structurally more homogeneous than Ca=0.20 composition. As is known from the literature, structural heterogeneities lead to polar nanodomains, which increase electrocaloric properties. In this case, the properties that Zr and Ca add to the structure balance each other. Thus, 0.32 BCZT results are close to 0.20 BCZT but larger than it.

0.50 BCZT has the greatest electrocaloric results. Because the x=0.50 composition operating in MPB near the tricritical point contains micron-sized domains and nanodomains miniaturized on the domains. Miniaturized nanodomains provide the structure with relaxor ferroelectric properties. X=0.50 composition containing Zr=0.20 rate as in 0.32 BCZT contributes extra to the increase of electrocaloric properties.

The average crystallite sizes of the ceramics (82.3 nm for 0.32 BCZT, 68.8 nm for 0.50 BCZT, and 102 nm for 0.20 BCZT) support the electrocaloric results. The reason why an inferior electric field is applied to 0.50 BCZT is that the ceramic has a

less dense structure than other compositions as seen in the SEM and Archimedes results.



## 5. CONCLUSION

In this thesis, BZT, BZ-BT, and BCZT ceramics with different compositions at critical phase points were produced from the powders prepared by the solid-state reaction method, and then structural and electrical characterizations of the samples were carried out.

BZT and BZ-BT (0.15 & 0.20) compositions were selected at critical points in the phase diagram.  $X=0.15$  compositions show normal ferroelectric properties and operate at the invariant critical point which paraelectric cubic, tetragonal, orthorhombic, and rhombohedral coexisted phases. At these critical points, the contribution of the increasing number of polarization directions to ECE has been reported.

$X=0.20$  compositions also show relaxor ferroelectric properties. At this critical point, the contribution of polar nano regions which provide additional degrees of freedom and this causes higher entropy change. Obtaining small crystallite size, thinner hysteresis loops (low  $P_r$  and  $P_{max}$  values), and the low coercive field, the frequency dependence of the dielectric properties, and the wide phase transition confirm the relaxor properties of the  $x=0.20$  composition. The fact that the Curie temperatures are low in both compositions (0.15 & 0.20) allows us to work close to room temperature. When the electrocaloric results are examined, for the  $\Delta T$  value, the effect of frequency is higher for  $x=0.15$  compositions and the effect of the electric field is higher for  $x=0.20$  compositions.  $X=0.20$  compositions, which are relaxor ferroelectric with nanodomains that require less energy to align the dipoles, the applied electric field is more effective on the ECE properties.

However, when all electrical results are examined, the electrical property values of BZ-BT are significantly lower than BZT. It is thought that BZ-BT composition shifts from critical points due to the production method of BZ and BT.

Because of a wide operating temperature with high electrocaloric results, 0.20 BZT is considered a good candidate for electrocaloric applications.

At BCZT ceramics, the compositions of  $x=0.32$  and  $x=0.20$  were studied at the triple phase point. In addition, in the BZT-XBCT system, 0.32 BCZT has  $Zr=0.20$  and

Ca=0.30 composition, while 0.20 BCZT has Zr=0.15 and Ca=0.20 composition. The Zr=0.20 composition adds relaxor properties to the structure, and the Ca=0.20 composition provides structural heterogeneity leading to polar nanodomains in the structure. Their presence at the critical phase point and the Ca/Zr ratios increase the number of polarization directions and thus the electrocaloric properties were increased.

0.50 BCZT was also studied at the MPB near the tricritical point. This composition includes micron-sized domains and nanodomains miniaturized on the domains. It also has the Zr=0.20 composition in the BZT-XBCT system. All these conditions provide the structure with relaxor ferroelectric properties and increase the electrocaloric properties extra.

The order of magnitude of the crystallite size values, electrical measurement results (low  $P_r$  and  $P_{max}$  values), and electrocaloric measurement results confirm that 0.50 BCZT exhibits the highest relaxor ferroelectric property.

In addition to the various advantages of all BCZT compositions, the  $x=0.50$  composition has a high  $\Delta T$  value in low electric fields and near room temperature, indicating that it is a good candidate for electrocaloric applications.

In the continuation of the study, the density and therefore the breakdown strength can be increased with different doping. In this way, efficiency can be raised by obtaining higher electrocaloric results.

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