

Ferroelectric Relaxation Behavior of Lead free BCZT Ceramics

S. D. Chavan¹, D. J. Salunkhe²

¹Department of Physics, D.B.F. Dayanand College of Arts and Science Solapur , 413002, India.

²Nano-composite laboratory, Karmaveer Bhaurao Patil Mahavidyalaya, Pandharpur, Solapur, 413304, India

Abstract - The paper reports the synthesis of $(\text{Ba}_{(1-x)}\text{Ca}_{(x)})(\text{Zr}_{(y)}\text{Ti}_{(1-y)})\text{O}_3$ (BCZT) compositions by solid state reaction route with $x = 0.05, 0.075$ and $y = 0.075, 0.10$. The temperature dependent dielectric properties indicate a diffuse phase transition. A broad dielectric maximum, which shifts to higher temperature with increasing frequency, signifies the relaxor behavior of these compositions and maximum dielectric constant (ϵ_{max}) was found at the Curie temperature (T_c). The value of the relaxation parameter γ ranges from 2.09 to 1.66 for frequency 100Hz to 1MHz estimated from the linear fit of the modified Curie – Weiss law, indicates the relaxor nature of BCZT compositions. The dielectric relaxation rate follows the Vogel – Fulcher relation to supports relaxor nature. The slim P–E hysteresis loop with nonzero remnant polarization indicates the relaxor nature of BCZT compositions.

Key words: Solid State Reaction, dielectric properties, relaxor nature

1. Introduction

Ferroelectric materials with perovskite structures are useful for microelectronic devices. Lead-based piezoelectric ceramics have been an industry standard for many decades and are widely used in actuators, sensors, and transducers because of their excellent electrical properties [1]. The lead based ceramics are facing global restrictions due to their toxicity [2]. The most widely used ferroelectric material is BaTiO_3 (BT), which belongs to the family of ABO₃ perovskite structure. However, the structure of unit cell is temperature dependent. There are three phase transition in order of decreasing temperature (120 °C, 5 °C, -90°C) [3]. The substitution of Sr, Pb, Ca and Zr into BT shows interesting ferroelectric properties. Zhuang et al. reported that addition of even a small quantity of Ca ions at Ti-sites leads to a diffused phase transition curve and lowers the phase transition temperatures [4]. Tiwari et al. reported that calcium doping increases the phase transition temperatures of BCT ceramics and Ba^{2+} substitution by Ca^{2+} leads to diffused transition curve. Earlier it was believed that Ca substitution decreases the Curie temperature [5]. But recently, it has been reported that Ca doping can also increase the Curie temperature depending on the powder preparation method & the site occupancy of calcium [6]. Ca-doped BaTiO_3 has been used as a ceramic capacitor. It is a promising photorefractive material [7]. The another important ferroelectric material is $\text{BaZr}_{(x)}\text{Ti}_{(1-x)}\text{O}_3$ (BZT),

which is lead free ferroelectric material with high value of dielectric constant [8,9]. In the BaTiO_3 – BaZrO_3 system, it has been reported that at ~15 atom % Zr substitution the three transition temperatures of BaTiO_3 , rhombohedral to orthorhombic, orthorhombic to tetragonal and tetragonal to cubic, merge near room temperature and the doped material exhibits enhanced dielectric constant [10]. With further increase in Zr contents beyond 15 atomic %, a diffuse dielectric anomaly in ceramic has been observed with the decrease in the transition temperature and the material showed typical relaxor behavior in the range 25-42 atomic %

Zr substitution [11,12]. Liu et al. reported that the composition $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ lies close to the tricritical point of rhombohedral, tetragonal and cubic phases. They had investigated the composition-piezoelectric constant relationship and they found that $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ showed a large piezoelectric constant d₃₃~620 pC/N. They showed that this composition was very close to morphotropic phase boundary (MPB) [13]. Relaxor behavior has been found in many lead-free materials, such as KNbO_3 – BaTiO_3 [14], KNbO_3 – BaTiO_3 – CaTiO_3 [15] and BaTiO_3 – BaZrO_3 – BaLiF_3 [16]. We reported a typical relaxor behavior of a new composition having a general formula $(\text{Ba}_{(1-x)}\text{Ca}_{(x)})(\text{Zr}_{(y)}\text{Ti}_{(1-y)})\text{O}_3$ (BCZT), for $x = 0.05$ and 0.075 & $y = 0.075$ and 0.1 .

2. Experimental

The BCZT solid solutions have been synthesized using ceramic route of synthesis using the precursors BaCO_3 , SrCO_3 , ZrO_2 and TiO_2 of AR grade. The stoichiometric amounts of the precursors were well mixed together and ground for 2 hours in an agate mortar with pestle. Considering the earlier reports, the calcination was carried out at 1150 °C. The calcined powder was mixed with a polyvinyl acetate (PVA) binder solution and compacted into disk shaped samples with a diameter of 1.0 cm and a thickness of nearly 1.0 mm. The final sintering process was carried out at 1200 °C for 24 h in two steps. The silver paint was used for electroding the samples. The Bruker D8 advance X-ray diffractometer was used for the determination of X-ray diffractograms. The HP4284A LCR-Q meter was used for the measurements of dielectric constant ϵ , loss tangent $\tan\delta$ and P-E hysteresis loops were determined using P-E loop tracer, Marine India Pvt. Limited.

3. Result and Discussion

3.1 Structural Analysis

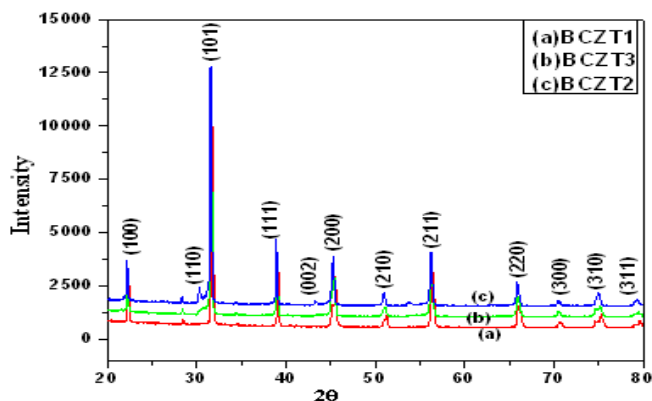


Figure 1: XRDs of BCZT Compositions.

Fig.1 show X-ray diffractograms of $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ti}_{0.90}\text{Zr}_{0.10})\text{O}_3$ (BCZT1), $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ti}_{0.925}\text{Zr}_{0.075})\text{O}_3$ (BCZT2) and $(\text{Ba}_{0.925}\text{Ca}_{0.075})(\text{Ti}_{0.925}\text{Zr}_{0.075})\text{O}_3$ (BCZT3) respectively. it could be seen from that the compositions under investigations are polycrystalline in nature and all the peaks in the spectra could be accurately indexed using standard JCPDS data. Further, no peak corresponding to any impurity phase is observed in the X ray diffractograms. The lattice parameter ‘a’ and ‘c’ corresponding to tetragonal crystal structure are determined from X ray diffractograms. The parameter a, c and c/a for BCZT1, BCZT2 and BCZT3 are shown in Table1. The crystallite size is also determined using Scherer’s formula and is shown in Table1.

Table 1: Particle size D, lattice parameters a, c and c/a for various BCZT composition

Composition	D nm	a (Å)	c (Å)	c/a
BCZT1	33.49	3.972	4.0186	1.0117
BCZT2	42.13	3.7893	4.001	1.0558
BCZT3	38.03	3.966	4.4267	1.1161

From the table, it is observed that the crystallite size increases with an increase with Ca concentration.

3.2 Dielectric Properties

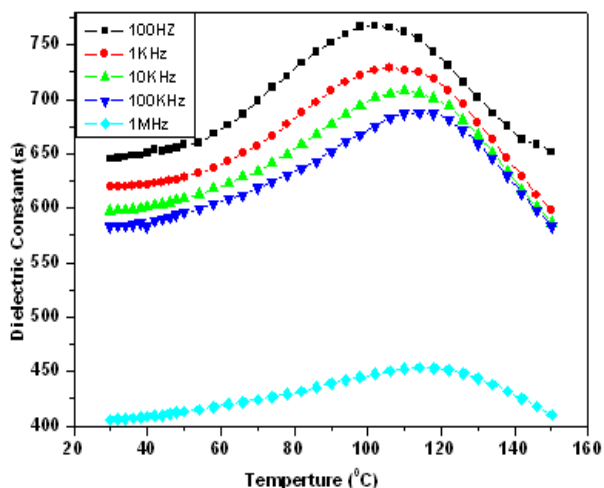


Figure 2: Variation of ε Vs T for BCZT1

Fig. 2 shows variation of dielectric constant (ϵ) as a function of temperature (T) at frequencies 100Hz, 1kHz, 10kHz, 100kHz and 1MHz for BCZT1 composition. Here ϵ is measured relative to the dielectric constant of free space i.e. ϵ_0 . From fig. 2, it is seen that the value of ϵ increases gradually to a maximum value ϵ_{max} with increases in temperature up to the transition temperature T_c and then decreases smoothly, where T_c shifts to higher temperature side as the frequency increases. This behavior is a typical of a relaxor ferroelectric.

Table 2 shows the magnitude of ϵ at room temperature (ϵ_{RT}), loss tangent $\text{Tan}\delta$ at room temperature ($\text{Tan}\delta_{RT}$), maximum value of ϵ (ϵ_{max}), loss tangent $\text{Tan}\delta$ at T_c ($\text{Tan}\delta_{Tc}$) and T_c for various frequencies of measurement for the BCZT1 composition. In case of BCZT1 composition Ca is substituted at A site, while Zr is substituted at B site of ABO_3 type ferroelectric system, more than one cation at A and B site may lead to various local region of different relaxation time. These polar micro domains are responsible for the observed relaxor behavior. To parameterize this observe variation of ϵ versus T behavior, the ϵ in the paraelectric region is fitted to an equation [18][19]

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_{max}} + \frac{(T - T_c)^\gamma}{2\epsilon_{max}\delta^2} \quad (1)$$

Here γ is diffusivity and δ is diffusion parameter.

The diffusivity γ gives information on the character of the phase transition; for $\gamma=1$, a normal Curie Weiss law is obtained, for $\gamma=2$, it describes a complete diffuse phase transition. From the observed $\log(1/\epsilon - 1/\epsilon_{max})$ versus $\log(T - T_c)$, values of γ and δ are determined and are also shown in Table 2. It is seen that γ is nearly equal to 2 at lower frequencies (100Hz & 1 KHz), while it decreases as frequency of measurement increases. This observation suggests that the BCZT1 composition possesses a diffuse phase transition characteristics of a relaxor material [20]. To confirm the existence of relaxor contribution, variation of T_c as a function of frequency has been fitted to an equation [21][22].

$$f = f_0 \exp \left[\frac{-Ea}{k_B(T_m - T_f)} \right] \quad (2)$$

Where f_0 is the attempt frequency, Ea is the measure of average activation energy, k_B is the Boltzmann constant and T_f is the freezing temperature.

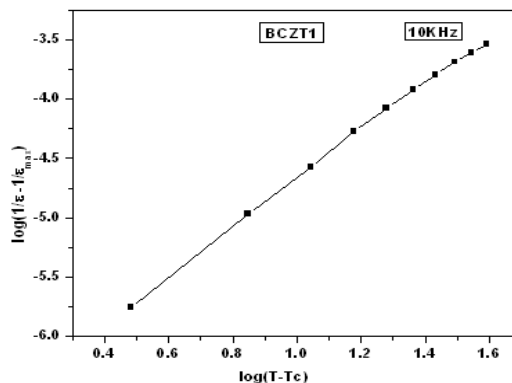


Figure 3(a): variation of $\log(1/\epsilon - 1/\epsilon_{max})$ verses $\log(T - T_c)$ for BCZT1

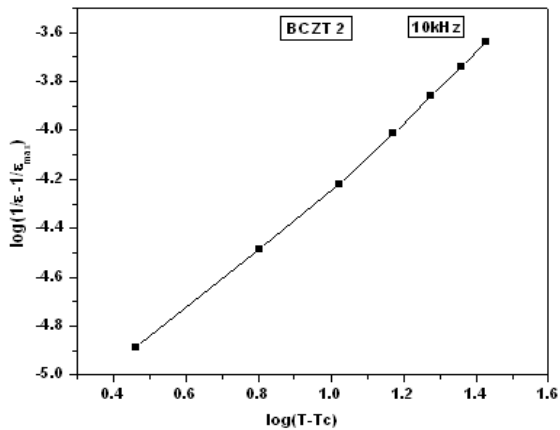


Figure 3(b): variation of $\log(1/\epsilon - 1/\epsilon_{max})$ versus $\log(T-T_c)$ for BCZT2

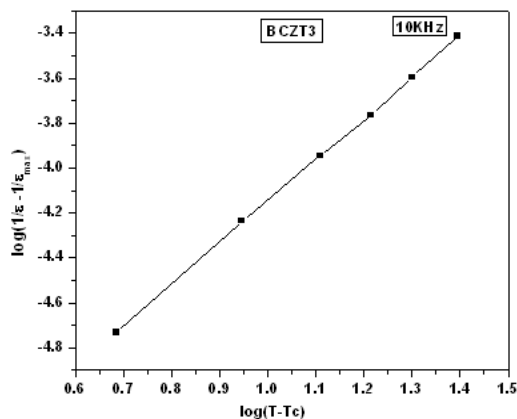


Figure 3(c): variation of $\log(1/\epsilon - 1/\epsilon_{max})$ versus $\log(T-T_c)$ for BCZT3

The variation of $\log(1/\epsilon - 1/\epsilon_{max})$ versus $\log(T-T_c)$ for BCZT2 and BCZT3 also shows a behavior similar to BCZT1. Fig.3 (a), (b), (c). shows variation of $\log(1/\epsilon - 1/\epsilon_{max})$ versus $\log(T-T_c)$ for BCZT1, BCZT2 and BCZT3. Table 3 and 4 shows variation of ϵ , ϵ_{RT} , $\tan \delta_{RT}$, $\tan \delta_{Tc}$, ϵ_{max} , T_c , γ and δ at various frequencies for BCZT2 and BCZT3 respectively. From Table 3 and 4, it is seen that in case of BCZT2 and BCZT3 that the γ lies in between 1 and 2 indicating a partial relaxor behavior. In this case also γ is higher at lower frequency (100Hz) and decreases as frequency increases to 1 MHz. To confirm the existence of relaxor contribution, variation of T_c with frequency is fitted to Vogel – Fulcher relation as given in Eqn.2.

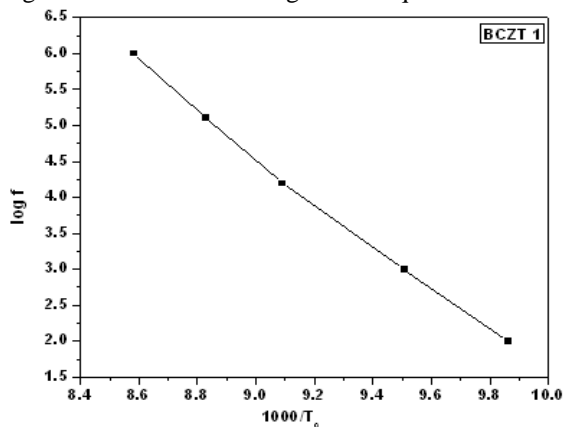


Figure 4(a): variation of $\log f$ versus $1000/T_c$ for BCZT1

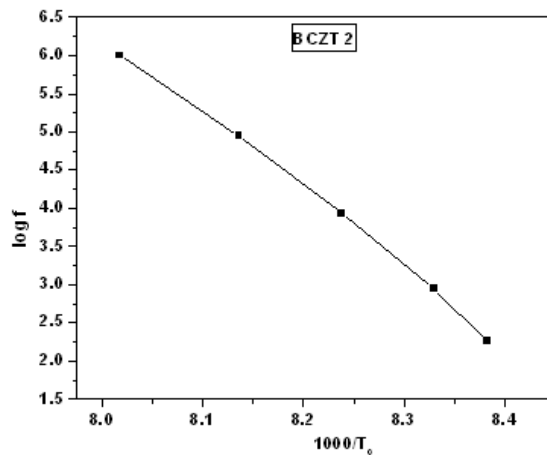


Figure 4(b): variation of $\log f$ versus $1000/T_c$ for BCZT2

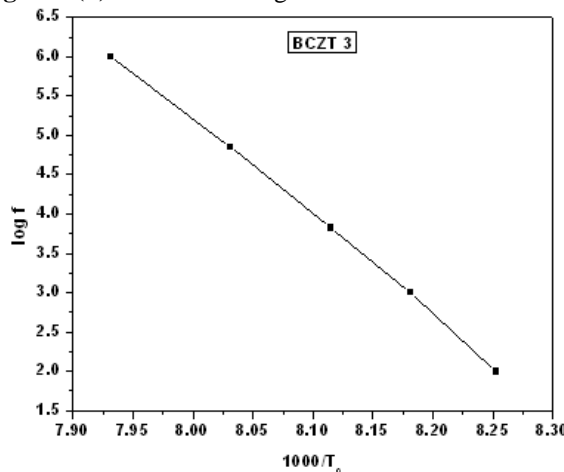


Figure 4(c): variation of $\log f$ versus $1000/T_c$ for BCZT3

Fig. 4 (a), (b), (c) shows the variation of $\log f$ versus $1000/T_c$ for BCZT1, BCZT2 and BCZT3. The nonlinear behavior for BCZT1, BCZT2 and BCZT3 confirms the existence of relaxor contribution. Here it could be seen that relaxor contribution increases with increasing Zr content, which occupy B site. This qualitative relationship is expected as the shift of ion from the center of charge symmetry causes polarization in case of ABO₃ ferroelectric.

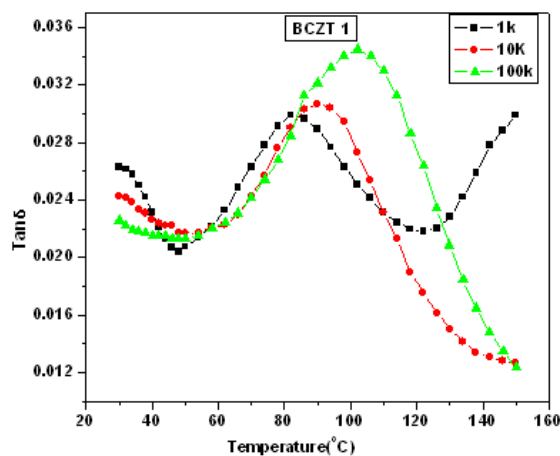


Figure 5: variation of $\tan \delta$ as a function of T at frequencies 1 kHz, 10 kHz and 100k Hz for BCZT1 composition

Fig. 5 shows variation of $\tan \delta$ as a function of T at frequencies 1 kHz, 10 kHz and 100k Hz for BCZT1

composition. It is observed that the $\tan \delta$ versus T possesses a peak at a temperature in the vicinity of T_c . Further, it is also observed that the temperature of peak in $\tan \delta$ also shifts towards higher temperature as frequency of measurement increases. This behavior may occur because of presence of grain-grain boundary interface, reported for certain titanate systems. It is also reported that the $\tan \delta$ become maximum, where the time require for foreign electron to cross the of grain-grain boundary interface become equal to the reciprocal of the frequency of the measurement. Additionally the nature of peak in the $\tan \delta$ behavior is similar to a diffuse phase transition, which may occur because relaxor nature of BCZT1. Thus BCZT1 appear to be a relaxor ferroelectric having separate grain-grain boundary regions possessing different dielectric relaxation frequency.

In case of BCZT2 and BCZT3 the variation of $\tan \delta$ versus T is also similar to the variation for BCZT1. Thus BCZT2 and BCZT3 are also relaxor material having grain-grain boundary regions possessing different dielectric relaxation frequency.

Ferroelectric Properties

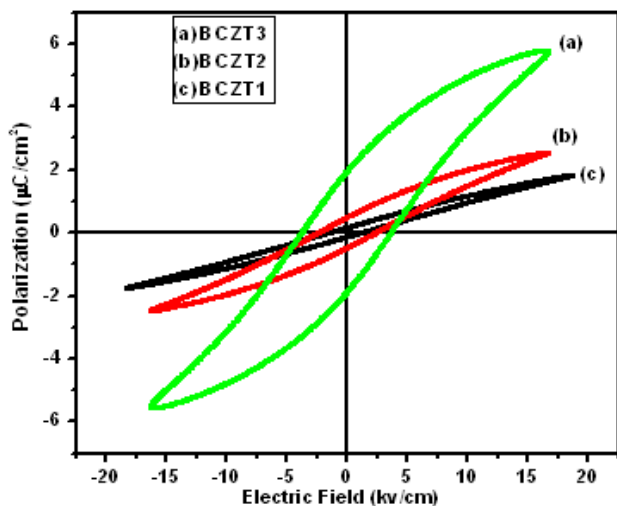


Figure 6: P-E Hysteresis loops of BCZT Compositions

Fig.6 shows P-E hysteresis loop for BCZT1, BCZT2 and BCZT3 compositions. It is observed that for BCZT1 & BCZT2, the P-E hysteresis loops are slim, which are characteristic of relaxor ferroelectric. In case of BCZT3, P-E loop shows a remarkable polarization. However the P_r/p_{max} is still very small. Thus all the BCZT compositions being studied possess a relaxor contribution, may be partial in case of BCZT2 and BCZT3. It is already reported that substitution of Zr leads to the reduction of hysteresis loss and lead to slim hysteresis loop [23] [24] [25]. Table 5 shows P_{max} , P_r , E_c and P_r/P_{max} for BCZT1, BCZT2 and BCZT3 composition.

4. Conclusion

The ferroelectric compositions $(Ba_{(1-x)}Ca_x)(Zr_yTi_{(1-y)})O_3$ for $x=0.05, 0.075$ and $y=0.075, 0.1$ are synthesized using ceramic route of synthesis. The room temperature XRD study

suggests that the compositions are polycrystalline in nature. The behavior of relaxor ferroelectric BCTZ compositions is studied in the temperature range from 30°C to 150°C in the frequency range from 100Hz to 1MHz. All compositions show a diffuse phase transition. The value of the relaxation parameter γ ranges from 2.09 to 1.66 indicates the relaxor nature of BCTZ compositions. The variation of Curie temperature T_c with frequency obeys Vogel-Fulcher relation, strongly suggest the relaxor nature of the BCTZ ceramics. The investigations on hysteresis loop with non zero remnant polarization (P_r) and slim hysteresis loops shows that all BCZT compositions are of relaxor ferroelectric.

5. Acknowledgement

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Authors Profile



S. D. Chavan received the B.Sc and M.Sc degree in Physics from Shivaji University, Kolhapur in 1987 & 1989. He is working as a Associate Professor in Department of Physics, D.B.F. Dayanand college of Arts and Science, Solapur, 413002, India



Dr. D. J. Salunkhe received the B.Sc and M.Sc degree in Physics from Shivaji University, Kolhapur in 1982 & 1984. He received Ph.D in Material science from Shivaji University, Kolhapur in 2007. He worked as a Controller of Examinations, Solapur University, Solapur. He is working as a Associate Professor in Department of Physics, Karmaveer Bhaurao Patil Mahavidyalaya, Pandharpur, Solapur, 413304, India.

Table 2: T_c , ϵ_{max} , $Tan\delta_{Tc}$, γ and $\bar{\sigma}$ for BCZT1 composition

Frequency HZ	T_c	ϵ_{max}	$Tan\delta_{Tc}$	γ	$\sigma * 10^{-4}$
100	101.38	767.75	0.04149	2.098	0.08029
1K	105.18	728.32	0.02325	1.9238	1.8449
10K	110.96	706.32	0.02314	1.8441	0.2729
100K	114.26	688.06	0.03125	1.7911	2.1660
1M	116.50	453.33	0.2057	1.6632	0.5299

Table 3: T_c , ϵ_{max} , $Tan\delta_{Tc}$, γ and $\bar{\sigma}$ for BCZT2 composition

Frequency HZ	T_c	ϵ_{max}	$Tan\delta_{Tc}$	γ	$\sigma * 10^{-4}$
100	121.17	1260.24	0.03278	1.9486	1.636
1K	122.23	1239.48	0.01763	1.9259	0.03811
10K	123.10	1211.98	0.01792	1.5952	0.7053
100K	123.35	1181.89	0.03194	1.5576	1.2827
1M	126.08	716.49	0.2369	1.4158	0.8652

Table 4: T_c , ϵ_{max} , $Tan\delta_{Tc}$, γ and $\bar{\sigma}$ for BCZT3 composition

Frequency HZ	T_c	ϵ_{max}	$Tan\delta_{Tc}$	γ	$\sigma * 10^{-4}$
100	119.80	1293.52	0.3448	1.9521	0.05675
1K	120.05	972.11	0.1727	1.8065	1.0818
10K	121.17	820.72	0.09708	1.7207	0.06956
100K	122.79	752.23	0.06711	1.7023	0.9169
1M	124.72	438.64	0.2557	1.6901	2.3029