3. Result and Discussion

3.1 Structural Analysis

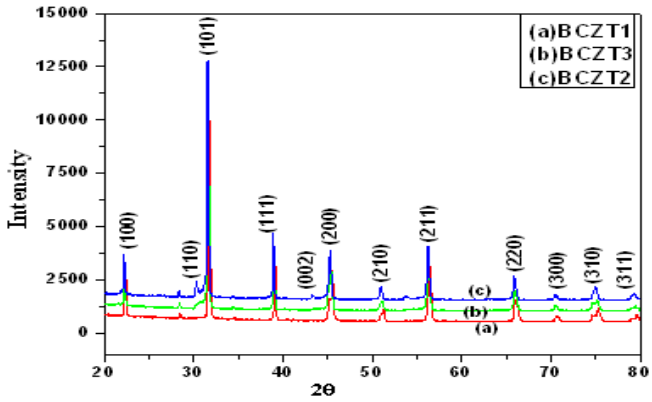

Figure 1: XRDs of BCZT Compositions.

Fig.1 show X-ray diffractograms of $(Ba_{0.95}Ca_{0.05})(Ti_{0.90}Zr_{0.10})O_3$(BCZT1), $(Ba_{0.95}Ca_{0.05})(Ti_{0.925}Zr_{0.075})O_3$(BCZT2) and $(Ba_{0.925}Ca_{0.075})(Ti_{0.925}Zr_{0.075})O_3$(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 (A°)	c(A°)	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

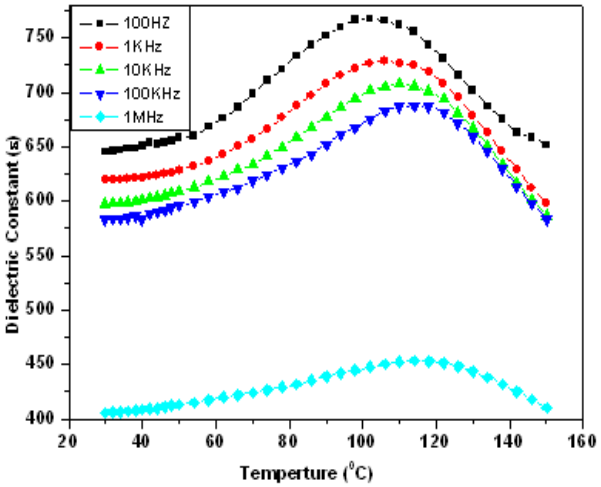

Figure 2: Variation of ε Vs T for BCZT1

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 Tc and then decreases smoothly, where Tc 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 Tanδ at room temperature ($Tan\delta_{RT}$), maximum value of ε(ε_{max}), loss tangent Tanδ at Tc ($Tan\delta_{Tc}$) and Tc 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]

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

Here γ is diffusivity and δ is diffusion parameter.
The diffusivity γ gives information on the character of the phase transition; for γ=1, a normal Curie Weiss law is obtained, for γ=2, it describes a complete diffuse phase transition. From the observed log $(1/\varepsilon - 1/\varepsilon_{max})$ verses log (T-Tc), 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 Tc 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.

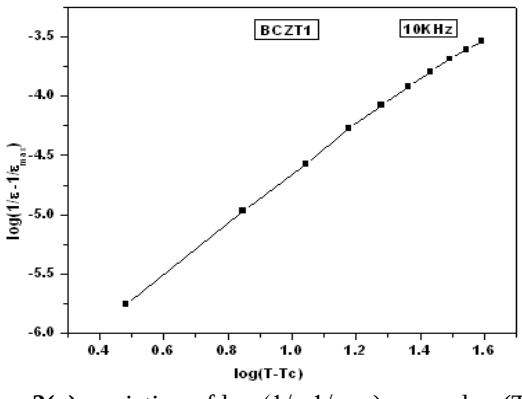

Figure 3(a): variation of log $(1/\varepsilon - 1/\varepsilon_{max})$ verses log (T-Tc) for BCZT1

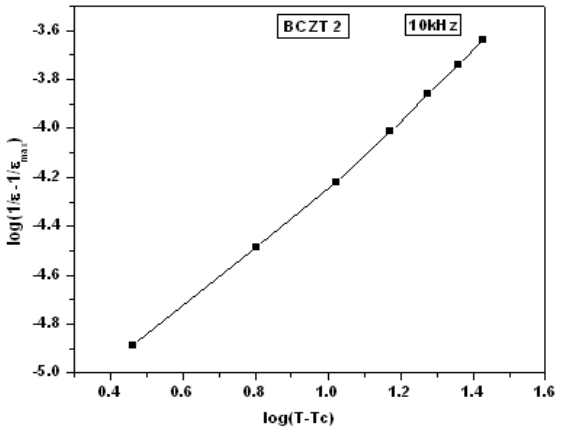

Figure 3(b): variation of log ($1/\varepsilon-1/\varepsilon_{max}$) verses log (T-Tc) for BCZT2

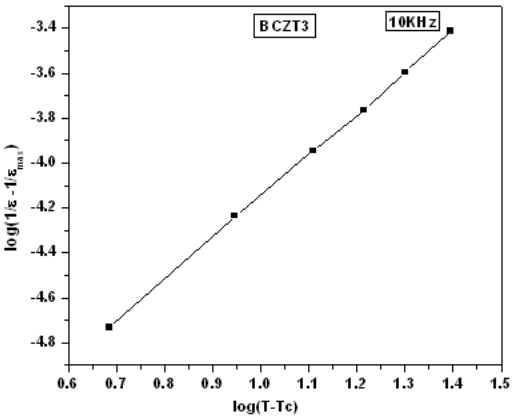

Figure 3(c): variation of log ($1/\varepsilon-1/\varepsilon_{max}$) verses log (T-Tc) for BCZT3

The variation of log ($1/\varepsilon-1/\varepsilon_{max}$) verses log (T-Tc) for BCZT2 and BCZT3 also shows a behavior similar to BCZT1. Fig.3 (a), (b), (c). shows variation of log ($1/\varepsilon-1/\varepsilon_{max}$) verses log (T-Tc) for BCZT1,BCZT2 and BCZT3. Table 3 and 4 shows variation of ε , ε_{RT} ,Tan δ_{RT}, TanδTc ,ε_{max}, Tc ,γ and б 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 Tc with frequency is fitted to Vogel – Fulcher relation as given in Eqn.2.

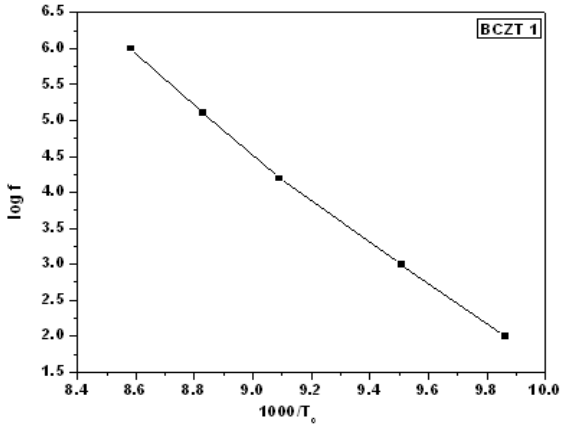

Figure 4(a): variation of log f verses 1000/Tc for BCZT1

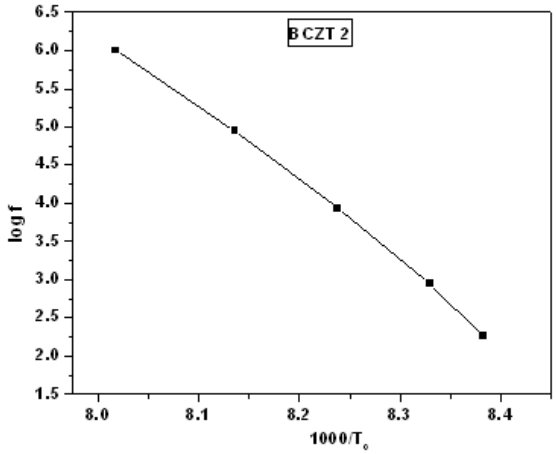

Figure 4(b): variation of log f verses 1000/Tc for BCZT2

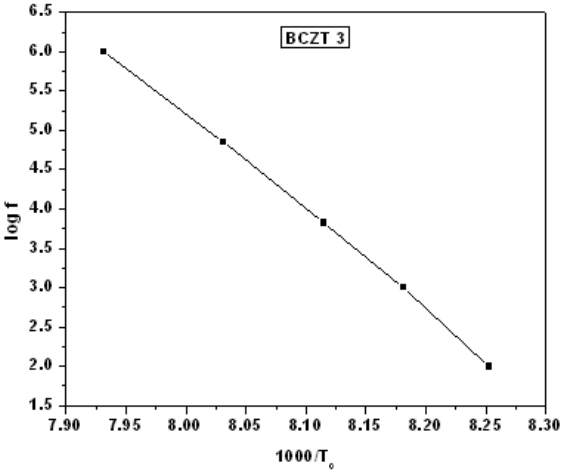

Figure 4(c): variation of log f verses 1000/Tc for BCZT3

Fig. 4 (a), (b), (c) shows the variation of log f verses 1000/Tc 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.

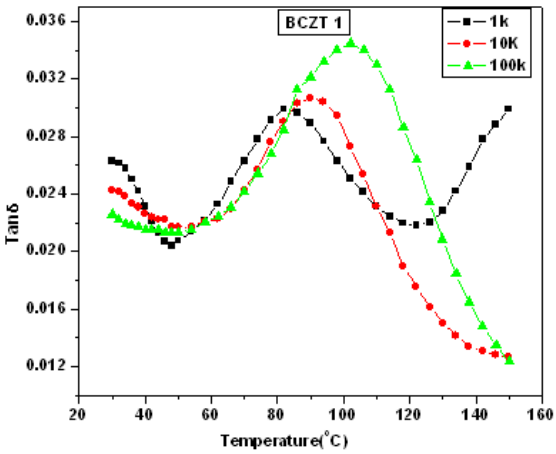

Figure 5: variation of Tan δ as a function of T at frequencies 1 kHz, 10 kHz and 100k Hz for BCZT1 composition

Fig. 5 shows variation of Tan δ as a function of T at frequencies 1 kHz, 10 kHz and 100k Hz for BCZT1

composition. It is observed that the Tan δ verse T possesses a peak at a temperature in the vicinity of Tc. Further, it is also observe that the temperature of peak in Tanδ 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 Tanδ 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 δ 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 Tanδ verses 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

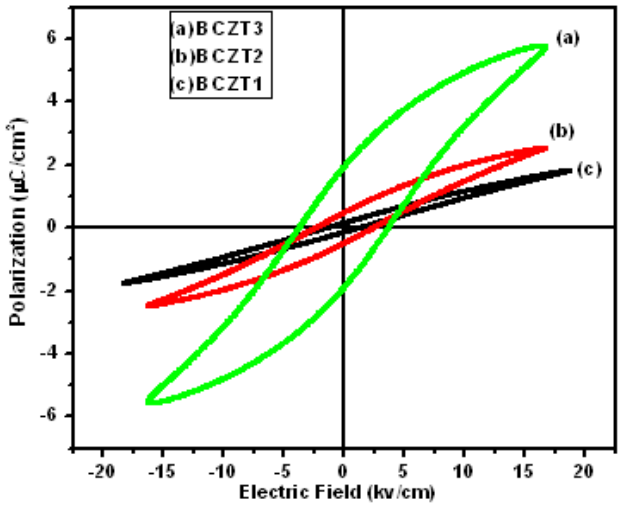

Figure 6: P-E Hysteresis loops of BCZT Compositions

Fig.6 shows P–E hysteresis loop for BCZT1, BCZT2 and BCZT3 compositions. It is observe 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 Pr/p max is still very small. Thus all the BCZT compositions being studied possesses 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 Pmax, Pr, Ec and Pr/Pmax for BCZT1, BCZT2 and BCZT3 composition.

4. Conclusion

The ferroelectric compositions $(Ba_{(1-x)}Ca_{(x)})(Zr_{(y)}Ti_{(1-y)})O_3$ 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 Tc 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 (Pr) and slim hysteresis loops shows that all BCZT compositions are of relaxor ferroelectric.

5. Acknowledgement

All Authors are thankful to DRDO-NRB, New Delhi for Financial Support.

References

[1] J. F. Tressler, S. Alkroy, R. E. Newnham, J. Electroceram. , 2 (1998) 257–272.
[2] S. H. Choy, W. K. Li, H. K. Li, K. H. Lam, and H. L. W. Chan, Study of BNKLBT-1. 5 composites vol. 102, no. 11, Article ID 114111, 2007.
[3] E. Wainer and A. N. Soloman, Titanium Alloy. Mfg. Co. Ele. Report 8, (1943).
[4] Z. Q. Zhuang, M. P. Harner, D. M. Smyth. , Mat. Res. Bull 22, 1329(1987).
[5] A. J. Moulson, J. M. Herbert, Electro-ceramic materials: Properties and Applications, Chapman and Hall, London, NY (1990).
[6] V. S. Tiwari, D. Pandey, P. Groves, J. Phys. D 22 837 (1989).
[7] Lin T F, Hu C T and Lin I N 1990 J. Appl. Phys. 67, 1042.
[8] J. Zhai, Dan Hu, Xi Yao, Zengkui Xu, and Hyden Chen, J. Eur. Cerm. Soc., 26, (2006), 1917.
[9] F. M. Pontes, M. T. Escote, C. C. Escudeiro, E. R. Leite, E. Longo, A. J. Chiquito, P. S. Pizini and J. A. Verala, Appl. Phys., 96, (2004), 4386.
[10] D. Henning, A. Schnell, G. Simon, J Am. Ceram Soc, 65 (1982) 539.
[11] Z. Yu, R. Guo, A. S. Bhalla, J. Appl. Phys, 88 (2000), 410.
[12] Z. Yu, R. Guo, A. S. Bhalla, Appl. Phys. Lett, 81(2002), 1285.
[13] W. F. Liu and X. B. Ren, Phys. Rev. Lett. 103, 257602 (2009)].
[14] F. Bahri, H. Khemakhem, M. Gargouri, et al. , Solid State Sci. 5 (2003) 1445.
[15] J. Ravez, A. Simon, Solid State Sci. 1 (1999), 25.
[16] A. Kerfah, K. Taibi, A. G. Laidoudi, A. Simon and J. Ravez, Materials Letters 42 (2000), 189- 193.
[17] P. Hansen, D. Henning and H. Schreinemacher, J. Am. Ceram. Soc. 81, 1369 (1998).
[18] G. A. Smolenskii and A. I Agranovskya, Sov. Phys. Tech. Phys. 3, 1380(1958).
[19] Z. Yu, C. Ang, R. Guo and A. Bhalla, J, Appl. Phys. 92, 2655 (2002)].

[20] I. Levin, rt al. J. Solid State Chem. 175 (2003), 170-181
[21] H. Vogel, Z. Phys. 22, 645(1921).
[22] G. Fulcher, J. Am. Ceram. Soc. 8, 339(1925).
[23] Sandeep Mahajan1, O P Thakur1, Chandra Prakash, and K Sreenivas. Bull. Mater. Sci., Vol. 34, No. 7, December 2011, pp. 1483–1489.
[24] A. Dixit, S. B. Mujumdar. R. S. Katiyar and A. S. Bhall, App. Phy. Lett. 82(16)(2003), 2679-2681.
[25] B. Beleckas, J. Gerigas and S. Stefanovich, Litovskii Fizicheskii Sboenik, 29(1989), 202.

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: Tc, ε_{max}, $Tan\delta_{Tc}$, γ and σ for BCZT1 composition

Frequency HZ	Tc	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: Tc, , ε_{max}, $Tan\delta_{Tc}$, γ and σ for BCZT2 composition

Frequency HZ	Tc	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: Tc, , ε_{max}, $Tan\delta_{Tc}$, γ and σ for BCZT3 composition

Frequency HZ	Tc	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