



Structural and Piezoelectric Properties of $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ Ceramics, Near Morphotropic Phase Boundary ($0.140 \leq x \leq 0.160$)

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Ceramic pellet samples of $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($x = 0.140-0.160$, $y = 0.9$), were prepared using the conventional solid-state reaction method followed by double sintering. Structural and piezoelectric measurements of the prepared compositions were carried out at room temperature. For the compositions with $x \leq 0.150$, the converse piezoelectric constant (d_{33}^*), strain (%), coercive field (E_c) and remnant polarization (P_r), were found increasing with x , which were found anomalously to decrease with further increase in x above 0.150. Among the prepared compositions, maximum value of d_{33}^* was found 342 pm/V, for the samples with $x = 0.150$. The measured maximum values of strain (%), piezoelectric constant (d_{33}^*) and break in XRD peak shifting patterns of the prepared samples indicate composition dependent piezoelectric properties, showing morphotropic-like phase boundary (MPB), near $x = 0.150$ composition. The prepared compositions of lead-free BCZT ceramics will extend the possibilities to use this compound in the field of piezoelectric sensors.

Keywords: Ferroelectrics; solid state reaction; piezoelectric constant; X-ray diffraction

1 Introduction

ABO₃ type barium–calcium zirconate–titanate (BCZT) ferroelectric ceramics are interesting due to their wide electrical properties and non-toxic nature¹⁻³. Though the large piezoelectric constant lead-based perovskite ferroelectric compounds, e.g., lead zirconate titanate (PZT) and $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$, ($\text{B}' = \text{Zn, Mg, In and Sc}$ and $\text{B}'' = \text{Nb, Mo, Ta, and W}$),⁴⁻⁵ are available, but due to their toxic nature, they are less preferred to utilize, and the search for high piezoelectric constant lead-free compounds has attracted the attention recently^{1,6-10}.

Significant piezoelectric constant has been found in $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$, ($x, y = 0$ to 1) ceramics, near the morphotropic phase boundary^{11,12}. The structural and electrical properties of BCZT system have been investigated by Hennings¹³ & Yu *et al.*¹⁴. Tian *et al.*¹⁵ studied the composition variation of piezoelectric and structural properties by varying the Ba/Ca ratio in $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$, for the compositions with $x = 0$ to 0.20, and reported the existence of a typical MPB, near $x = 0.150$. The mechanism of the enhanced piezoelectricity around the MPB is of considerable significance. The polarization extension and rotation, presence of intermediate phases, and

elastic softening of lattice are the contributing factors to large piezoelectricity in $(\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ ceramics, at morphotropic phase boundary¹⁵. Thereby, great efforts have been devoted to studying the high level of piezoelectricity and the origin of this large piezoelectricity. The $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ ceramic systems receive significant attention because of the development of several possible polarization directions, at MPB, which may contribute to a large extremal remanent polarization and electromechanical coupling factor (k_s)⁵. Mondal *et al.*¹⁶ observed enhanced electrical properties in BCZT ceramics due to the cell deformation, near MPB region. An anomalous break in the peak shifting pattern has been reportedly observed, at MPB¹⁷. Hanani *et al.*¹⁸ found technologically potential piezoelectric properties of $(\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ compositions, near $x = 0.150$. Wang *et al.*¹⁹ observed significant piezoelectric properties of $(\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ lead-free ceramics with $x = 0.150$. Wu *et al.*^{20,21} observed the effect of sintering dwell time on piezoelectric properties of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ compounds, near $x = 0.150$, the morphotropic phase boundary. The enhanced electrical properties of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ compounds, near morphotropic phase boundary (MPB), may be attributed to the separation of two ferroelectric phases with different crystallographic

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parameters²²⁻²⁴. Therefore, ABO_3 type compounds are attracting considerable attention due to the significant hike in their piezoelectric properties, near the MPB.

Presently, $(Ba_{1-x}Ca_xZr_{1-y}Ti_y)O_3$ ($x = 0.140-0.160$, $y = 0.9$), samples of BCZT ceramics have been prepared by solid-state reaction method following double sintering, at $1300\text{ }^\circ\text{C}$, for 4 hrs, each cycle. The structural behavior and piezoelectric properties of the prepared $(Ba_{1-x}Ca_xZr_{1-y}Ti_y)O_3$ compositions were observed. The composition dependence of structure, converse piezoelectric constant (d_{33}^*), strain (%), coercive field, polarization current, and remnant polarization of the BCZT samples were measured, for the compositions near MPB, $x = 0.150$.

2 Experimental procedure

The samples of $(Ba_{1-x}Ca_xZr_{1-y}Ti_y)O_3$ ($x = 0.140-0.160$, $y = 0.9$) ceramics were prepared using solid-state reaction technique with double sintering. For this purpose, raw powders of $BaCO_3$, $CaCO_3$, TiO_2 and ZrO_2 were selected. All the selected raw powders have purity greater than 99.5% (from MERCK, Germany). Initially, the powders were dried separately to remove the absorbed moisture, at $200\text{ }^\circ\text{C}$ for 2 hours. Furthermore, they were weighed in the stoichiometric ratio to prepare the compositions of $(Ba_{1-x}Ca_xZr_{1-y}Ti_y)O_3$ ceramics. The compositions were manually ground for 2 hrs in acetone, and then dry for 4 hrs. To remove carbonate, the compositions were calcined at $1100\text{ }^\circ\text{C}$ for 4 hrs. The calcined mixture was ground for 1 hour. Furthermore, the compositions were pressed into pellets with $\sim 2\text{ mm}$ thick and 8 mm diameter, at 0.2 GPa pressure. The prepared pellets of $(Ba_{1-x}Ca_xZr_{1-y}Ti_y)O_3$ ($x = 0.140-0.160$, $y = 0.9$) were sintered for 4 hours, at $1300\text{ }^\circ\text{C}$ temperature. Furthermore, the sintered samples were crushed and taken for another cycle of sintering process²⁵. The sintered compositions were electroded, with conducting paste of silver, in metal-insulator-metal (MIM) configuration. For piezoelectric and polarization measurements of the prepared compositions, piezometer (AixACCT Systems, GmbH) and PE loop tracer are used, respectively. For structural analysis, X-ray diffractometer (PANalytical, X'PERT PRO, with $CuK\alpha_1$ radiation of wavelength 1.5406 \AA) is used to measure the XRD patterns of $(Ba_{1-x}Ca_xZr_{1-y}Ti_y)O_3$ ($x = 0.140-0.160$, $y = 0.9$). The X-ray machine collect the data at a scanning rate of $6^\circ/\text{min}$.

3 Results and discussion

The X-ray diffraction (XRD) patterns of the prepared BCZT compositions, observed at room

temperature, were shown in Fig. 1. The X-ray diffraction patterns of BCZT pellet samples were found matched with "Inorganic Crystal Structure Database" (ICSD), data code 01-075-1608²⁶. The prepared compositions of BCZT ceramics show pure orthorhombic structure with (111), (102), (022), and (220), etc. peaks.

In the prepared composition range, the prominent peaks were, generally, found shifting to smaller angle with rising x , except for the samples with $x = 0.150$. For the composition with $x = 0.150$, a break in the peaks shifting pattern was observed, the peaks shift to higher angle, representing an abnormal structural nature for this sample. Fig. 2 exhibits the peak (111) shifting pattern. The observed break in the peak shifting patterns may be attributed to the lattice change. Workers observed similar incident for the pellet samples of $(Na, K)NbO_3$ ceramics, near MPB^{17,27}.

The lattice parameters of BCZT ceramics were evaluated from the measured X-ray diffraction data, Table 1. In a/b ratio vs. composition (x) plot, an anomalous dip was observed for the samples with $x = 0.150$, showing an abrupt sample dependent structural change at this x , Fig. 3. Shirane *et al.* observed similar variations of a/b ratio with sample (x), in BCZT ceramics²⁶. The lattice parameters were measured manually. The selected space group is 'Amm2' type.

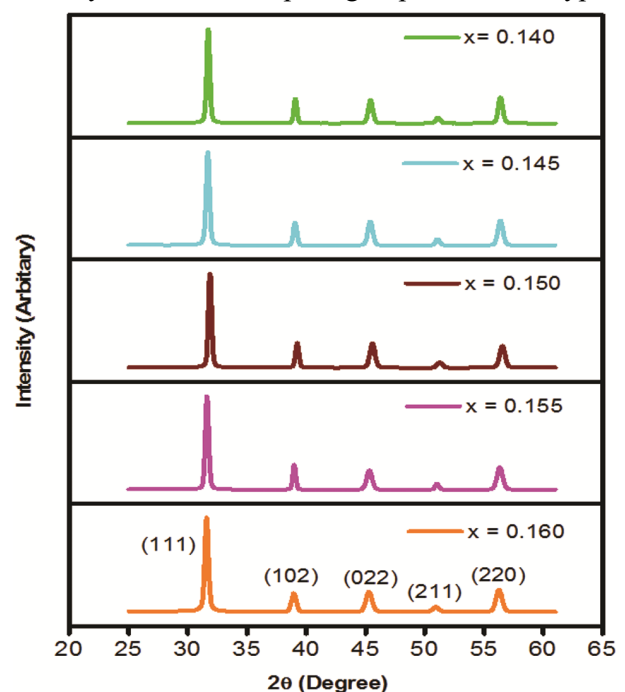


Fig. 1 — X-ray diffraction patterns of $(Ba_{1-x}Ca_xZr_{1-y}Ti_y)O_3$ ($x = 0.140-0.160$, $y = 0.9$) ceramics.

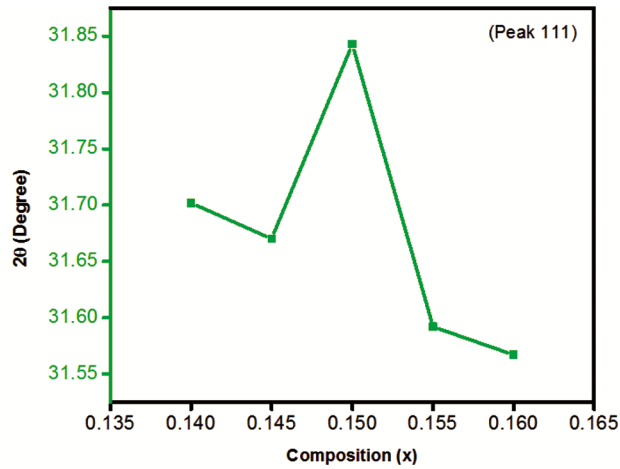


Fig. 2 — Peak (111) shifting tendency with sample (x), in $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($x = 0.140-0.160$, $y = 0.9$) ceramics.

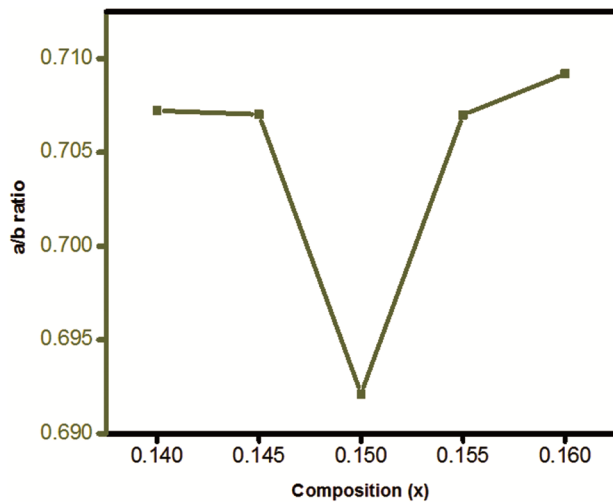


Fig. 3 — Variation of a/b ratio with sample (x), in $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($x = 0.140-0.160$, $y = 0.9$) ceramics.

Table 1 — Lattice parameters of $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($x = 0.140-0.160$, $y = 0.9$) ceramics.

Lattice Parameters (Calculated)			
Composition (x)	a (Å)	b (Å)	c (Å)
0.140	3.9976	5.6525	5.6424
0.145	3.9975	5.6539	5.6469
0.150	3.9661	5.7304	5.5363
0.155	4.0013	5.6594	5.6617
0.160	4.0048	5.6470	5.6627

The polarization vs. electric field (P- E) hysteresis loops of the prepared BCZT samples were measured at room temperature, at 1 Hz frequency (triangular wave), with an applied peak electric field of 8.28 kV/cm. The observed P- E hysteresis loops for the prepared compositions have been shown in Fig. 4. The hysteresis loops show a good ferroelectric nature of the prepared ceramics. Fig. 5 shows the observed

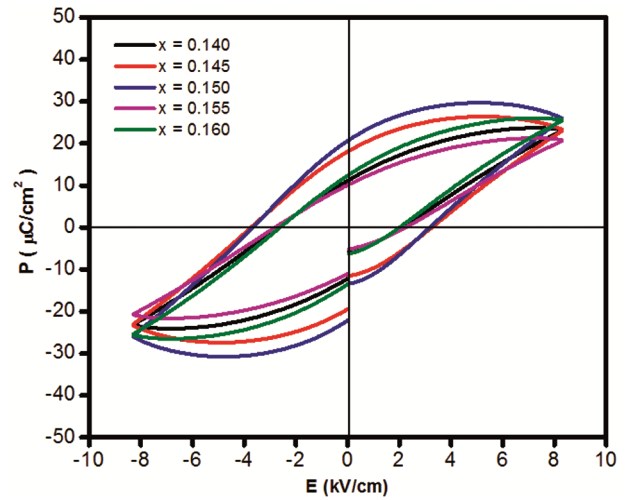


Fig. 4 — Polarization vs. electric field (P- E) hysteresis loops of $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($x = 0.140-0.160$, $y = 0.9$) ceramics.

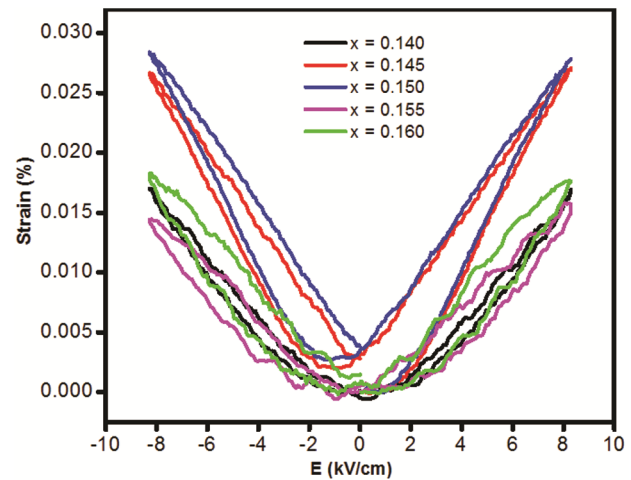


Fig. 5 — Plot of strain (%) with electric field, in $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($x = 0.140-0.160$, $y = 0.9$)

strain (%) vs. electric field characteristics of the prepared BCZT samples. The observed butterfly loops show the hard domain reorientation characteristic of the prepared samples²⁸.

Generally, electroceramics have two main categories. They are called dielectric and conductive ceramics. The electroceramics may show mechanical strain upon applying an applied electric field and vice versa. The observed electric field- induced strain experience two types of contribution. The intrinsic contributions are responsible to exhibit electrostriction and piezoelectric effects, while the extrinsic contributions may show domain wall movement in materials having ferroelectric domain structures. The converse piezoelectric effect exhibits a

mechanical strain upon applying an electric field. The converse effect consists of a linear dependence of the strain upon the applied electric field, which can be elongation or contraction depending on the relative direction of the applied electric field and the material's polarity²⁸. The ferroelectric domain may change when an electric field was applied on the prepared ceramics. The domain walls simultaneously contribute to the changes in polarization and strain. The observed strain is firmly negative exhibiting that the compositions experiences elongation along the electric field direction. Furthermore, strain response, piezoelectric effect and electrostriction, incorporates the contribution of domain wall movement, which contributes increase to a complex nonlinear and hysteretic nature, with a typical strain- electric field loop similar to a butterfly- like shape²⁸.

For the prepared compositions, highest value of strain (%) was observed for the composition with $x = 0.150$. The converse piezoelectric constant (d_{33}^*) is obtained as the ratio of the strain (maximum) to the electric field (maximum), *i.e.*, S_{\max}/E_{\max} ²⁹, and was calculated from the butterfly characteristics of the BCZT ceramics. For the prepared compositions, a plot of the piezoelectric constant (d_{33}^*) with composition (x), at RT, has been shown in Fig. 6. The value of (d_{33}^*) was found maximum to be 342 pm/V, for the compositions with $x = 0.150$, among the prepared compositions. Singh *et al.* observed similar piezoelectric characteristics for the pellet samples of (Na, K)NbO₃ ceramics, near MPB³⁰. The observed distinct change in converse piezoelectric properties, at

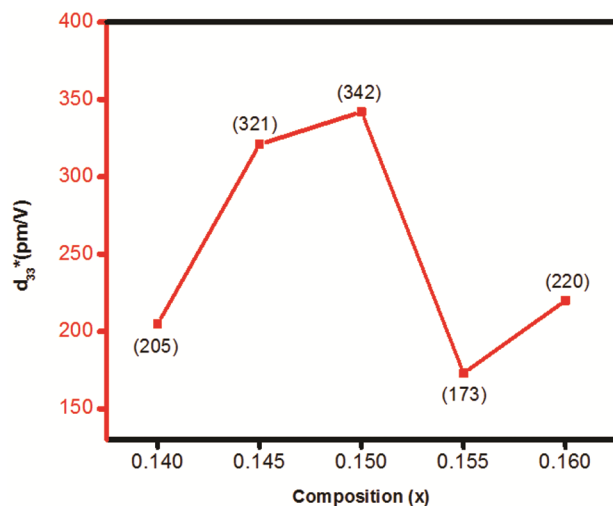


Fig. 6 — Plot of converse piezoelectric constant (d_{33}^*) with sample (x), in $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($x = 0.140- 0.160$, $y = 0.9$) ceramics.

$x = 0.150$, may be attributed to the lattice change, near the MPB.

For the prepared BCZT compositions, the observed variation of coercive field (E_c) and remnant polarization (P_r) with Ca content (x) have been shown in Fig. 7. In the prepared composition range, maximum value of remnant polarization (P_r) was found $20.82 \mu\text{C}/\text{cm}^2$; and maximum coercive field (E_c), $3.384 \text{ kV}/\text{cm}$, for the samples with $x = 0.150$. These observations may be attributed to the greater deformation in the lattice of the BCZT ceramics, near MPB, at $x = 0.150$ ^{15,31}. The variation of polarization current with the applied electric field was shown in Fig. 8. The highest magnitude ($3.48 \times 10^{-5} \text{ A}$) was observed for the compositions with $x = 0.150$, among the prepared samples.

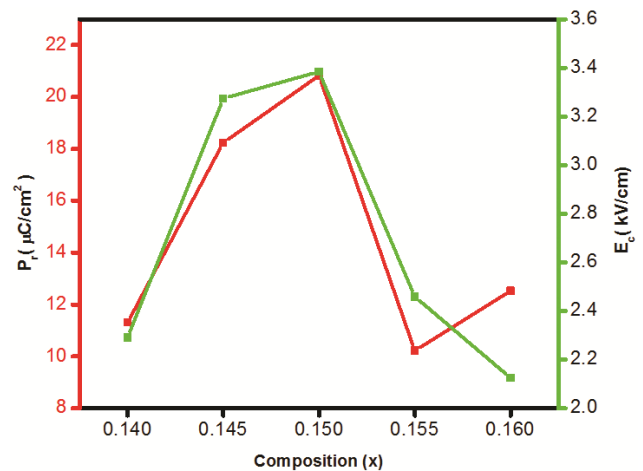


Fig. 7 — Variations of coercive field (E_c) and remnant polarization (P_r) with sample (x), in $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($x = 0.140- 0.160$, $y = 0.9$) ceramics.

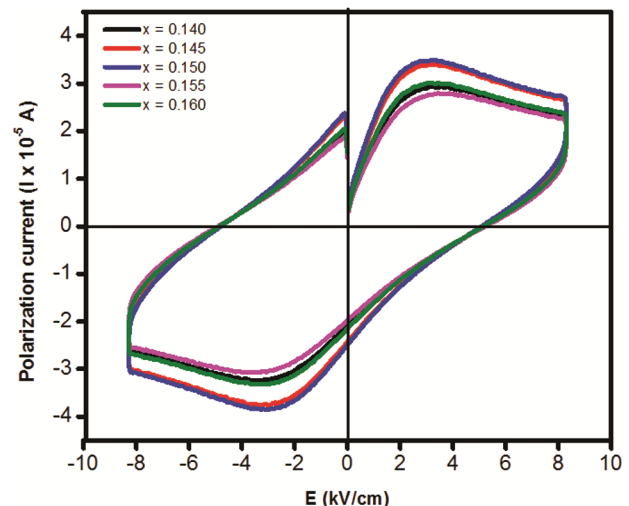


Fig. 8 — Variations of polarization current with electric field, in $(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($x = 0.140- 0.160$, $y = 0.9$) ceramics.

The internal stress, defects, and morphology of the ceramics considerably depend on the processing conditions³², and on the purity as well as on the grain size of the starting materials³³. The electrical properties considerably depend on the crystallographic information, grain size and density of the prepared samples^{34,35}. The low permittivity of the grain boundary contributes low polarization in the ferroelectrics. Also the available space charges at the grain boundary may help to exclude polarization charges on the grain surface, and may result polarization discontinuity. Therefore, a depolarization field appears and further the polarization reduces, in the smaller grain ceramics. With increasing Ca component (x), the density of the BCZT ceramics was reportedly found to increase, reaching maximum for $x = 0.150$, which decreases with further increase in x; whereas the grain size was found having opposite variation, *i.e.*, it decreased with increasing x, reaching minimum for $x = 0.150$, and increases with further increase in x³⁶. The increase or decrease in the number of grain boundaries depends on the grain size of the ceramics, while larger grains result less no. of grain boundaries and vice versa. The smaller grain size, for $x = 0.150$ composition, would have more number of grain boundaries, and result to reduced polarization, in the BCZT ceramics. But the observed remnant polarization (P_r) and coercive field (E_c) were found maximum for the sample with $x = 0.150$, which shows that these parameters are a composition dependent property rather than the density or the grain size of the BCZT ceramics. A similar observation on the dielectric properties of BCZT ceramics has been reported in a previous communication³⁶.

For the prepared composition range, these measurements indicate that the structure, strain (%), converse piezoelectric constant (d_{33}^*), remnant polarization and coercive field of the BCZT ceramics significantly depend on composition and show morphotropic- like boundary near $x = 0.150$ composition.

4 Conclusion

$(\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ ($x = 0.140- 0.160$, $y = 0.9$) samples were prepared using solid- state reaction method with double sintering. The piezoelectric and structural properties were observed for BCZT ceramic samples. For the prepared BCZT ceramics, a continuous XRD peaks shifting pattern was observed with varying x, with a break for the samples with

$x = 0.150$, which indicated a strong composition dependent structural anomaly. Among the prepared compositions, the piezoelectric constant (d_{33}^*), strain (%), remnant polarization, polarization current and coercive field were observed maximum, for the sample with $x = 0.150$. The structural anomaly, and extremal values of converse piezoelectric constant (d_{33}^*), strain (%), remnant polarization, and coercive field show a MPB- like composition, near $x = 0.150$, in the prepared BCZT ceramics.

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