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INVESTIGATIONS ON FERROELECTRIC AND IMPEDANCE PROPERTIES OF Ca AND Zr MODIFIED $BaTiO_3$ CERAMIC

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ABSTRACT:
Extremely small amount of Ca and Zr doping on A and B site of $BaTiO_3$ resulting in a solid solution of $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$.The $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ ceramic is synthesized via ceramic route of synthesis. The XRD pattern reveals the presence of tetragonal phase. The SEM image clearly shows that the sintered sample has dense structure. The EDAX spectrum indicates that the sample is consistent with their elemental signals and stoichiometry. The investigations on the P-E hysteresis loop reveal that $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ ceramic possesses useful values of maximum polarization (P_{max}) and remnant polarization (Pr). The investigations on impedance analysis observed that $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ is single phase ferroelectric compound. The present observations suggest that $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ ceramic could be useful lead free ferroelectric ceramic.

KEYWORDS: *Ceramic, Hysteresis, Impedance, Ferroelectric.*

INTRODUCTION

Ferroelectric materials with perovskite structures have received much attention due to their excellent functional properties, such as piezoelectricity, pyroelectricity and electrooptic effects, 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]. However, there is growing environmental concern about the use of lead in such products and the European Union has already introduced legislation to restrict the use of a range of hazardous substances which is directly relevant to the piezoelectrics [2]. The newly discovered lead-free (Ba,Ca)(Ti, Zr)O3,BCTZ, ceramics [3-4] have attracted great attention due to the excellent piezoelectric properties (with *d*33 =500–600 pC/N). Depending on the chemical composition, various ferroelectric/ antiferroelectric or paraelectric phases with slightly different dielectric properties and crystal structures of different type are formed. conductivity of the material [5].

BCTZ has higher dielectric constant and more stable temperature coefficient of capacitance than that of $BaTiO_3$. Huajun Sun et al. reported effects of cobalt and sintering temperature on electrical properties of $Ba_{0.98}Ca_{0.02}Zr_{0.02}Ti_{0.98}O_3$ lead-free ceramics [6]. Min Shi et al. reported effect of annealing processes on the structural and electrical properties of the lead-free thin films of $(Ba_{0.9}Ca_{0.1})(Ti_{0.9}Zr_{0.1})O_3$ [7]. Jiafeng et al. reported that BCZT is a novel material with higher value of dielectric constant and piezoelectric properties [8]. Chavan et al reported that BCZT possesses ferroelectric relaxor behavior [9].

The paper reports synthesis, structural, microstructural and elemental analysis of $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ (BCZT3) for the investigation on ferroelectric and impedance properties.

2. EXPERIMENTAL

The BCZT3 solid solutions have been synthesized via ceramic route of synthesis using the precursors $BaCO_3$, CaO, 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. The calcination was carried out at 1150^0C for 12 h. The calcined powder was mixed with a polyvinyl acetate (PVA) binder solution and compacted into disk shaped samples. The final sintering process was carried out at 1200^0C for 24 h. The Bruker D8 advance X-ray diffractometer was used for the determination of XRD pattern. The microstructure of sintered pellets was studied by using JEOL JSM -6360A Analytical Scanning Electron Microscope. The HP4284A LCR-Q meter was used for the measurements of dielectric constant (ε), loss tangent tanδ for determination of impedance. P-E hysteresis loops were determined using P-E loop tracer, Marine India Pvt. Limited.

3. RESULT AND DISCUSSION

3.1 Structural Analysis

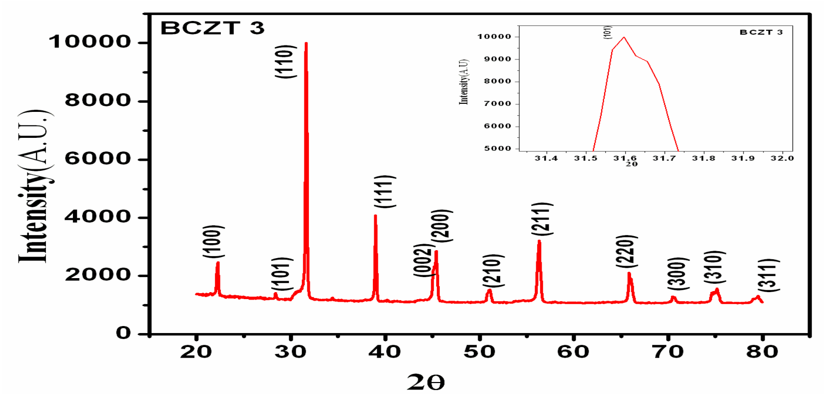

Figure 1 show XRD pattern of $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ (BCZT3) ceramic. The presence of sharp and well defined diffraction peaks indicate that this ceramic has a degree of crystallinity at a long range. The result suggest that Ca^{2+} and Zr^{4+} have been successfully incorporated into $BaTiO_3$ lattice to form inhomogeneous solid solution, It is seen that the ceramic under investigation are polycrystalline in nature and all the peaks in the XRD pattern could be accurately indexed using standard JCPDS data (JCPDS card no. 740646). Further, no peak corresponding to any impurity phase is observed in the XRD pattern. The particle size (t) is determined using Scherer's formula with Gaussian fitting data. It is observed that the particle size is found out to be 55.33 nm, lattice parameters a is 3.966 A^0 , c is 4.426 A^0 and degree of tetragonality c/a is 1.115. The values of degree of tetragonality (c/a) for of BCZT3 ceramic are found to be around 1, same as reported for $BaTiO_3$ based ceramics.

3.2 Microstructure Analysis

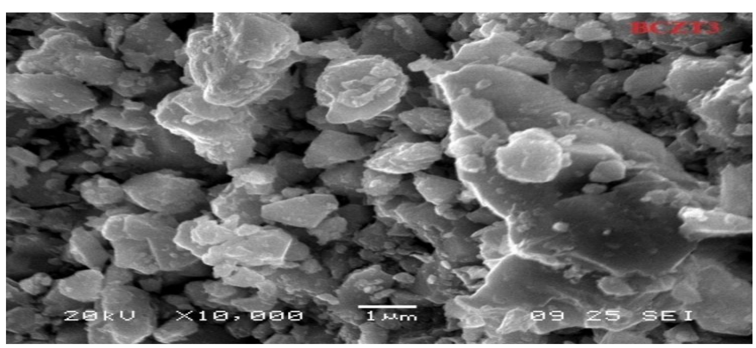

Figure 2 : SEM image of BCZT3 ceramic.

Figure 2 show SEM image of BCZT3 ceramic. The SEM image clearly shows that the sintered sample has dense structure with non-uniform grain size distribution and it is seen to be spongy. The SEM image of the sintered sample depends on the method of preparation as well as Ca and Zr content. The SEM image of BCZT3 ceramic was obtained in reflection mode. The measurement of grain size is carried out by measuring the length of grain boundaries, compared with the scale of SEM measurement and then calculated the grain size. Repeating the same procedure for different grains and an average grain size is calculated. The average grain size of BCZT3 composition is observed to be 1.984 µm. This result shows that Ca^{2+} ion and Zr^{4+} ion substitution in BT modifies the grain size and morphology. Such evolution in grain size and morphology may be explained by the change of interface atomic structure or grain boundary structure caused by Ca and Zr substitution, which significantly affects the microstructure evolution during sintering [10].

3.3 Elemental Analysis

The EDAX spectrum is used for quantitative elemental analysis and composition of the BCZT3 composition. Figure 3 shows EDAX spectrum of BCZT3 ceramic prepared by ceramic route of synthesis. The spectrum indicates that the sample is consistent with their elemental signals and stoichiometry as expected. The corresponding peaks are due to the Ba, Ca, Ti , Zr and O elements, whereas not any additional impurity peak is observed and it implies that the prepared sample is pure in nature. The detailed analysis of sample shows the atomic weight ratio of (Ba, Ca):(Ti, Zr) ≈ 1.0 and suggests the obtained BCZT3 sample is stoichiometric. The observed atomic percentage from EDAX is presented in the table 1.

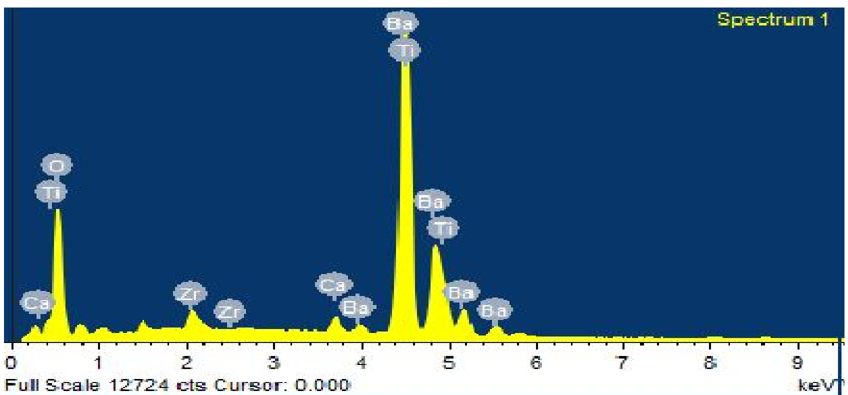

Figure 3: EDAX spectrum of BCZT3 ceramic.

Table 1: Elemental compositions of Ba, Ca, Ti , Zr and O atoms evaluated by using EDAX Technique.

Element	Weight %	Atomic %
O	39.29	78.66
Ca	0.90	0.72
Ti	14.71	9.84
Zr	2.24	0.79
Ba	42.86	10.00
Total	100	100

3.3 Ferroelectric study

The P –E hysteresis loop is the most important measurement on ferroelectric materials for characterizing its electrical behavior. A considerable amount of information can be obtained from P –E hysteresis loop.

1. High remnant polarization (Pr) is related to higher internal polarizability, electromechanical coupling, electro optic activity and strain.
2. The coercive field (Ec) indicates the grain size of the given material. Higher Ec means smaller grain size and lower Ec means higher grain size.
3. High degree of loop squareness indicates better homogeneity and uniform grain size.
4. An off centered loop at the zero voltage point indicates some degree of internal bias that may caused by an internal space charge.
5. The sharpness of loop tips indicates higher electrical resistivity (> 10^9 Ω.cm).
6. The slope of the hysteresis loop at any point is equal to large signal dielectric constant ε.
7. High induced polarization in relaxor material indicates high electrooptic coefficients and high electrostriction strain.
8. Sudden large change in polarization is a result of incipient dielectric breakdown.
9. Low coercive field Ec indicates the materials soft behavior.
10. Slim hysteresis loop indicates low losses in the material.

An ideal P-E loop is symmetrical in nature with positive and negative values of coercive field (Ec) and also positive and negative values of remnant polarization (Pr) are equal. The values of coercive field (Ec), remnant polarization (Pr) and the shape of P-E loop may be affected by many factors such as thickness of the sample, mechanical stress, preparation condition, thermal treatment and charged defects.

The ferroelectric hysteresis loops of BCZT3 composition are obtained by using P-E loop tracer. The measurements are carried out at different applied field. The thickness of BCZT3 sample was 1.34 mm. Room temperature P-E loop recorded at a frequency of 50 Hz for BCZT3 composition is shown in figure 4, Table 2 shows the values of maximum polarization (P_{max}), remnant polarization (Pr) and a coercive field (E_C) for BCZT3 composition at different applied electric field.

Table 2 for BCZT3 composition shows that as applied electric field increases, the values of maximum polarization (P_{max}), remnant polarization (Pr) and coercive field (E_C) also increases. At 15KV applied electric field, the value of remnant polarization (Pr) is observed to be 1.477μc/cm^2 indicates that BCZT3 composition possesses higher internal polarizability, electromechanical coupling, electro optic activity and strain. The value of coercive field (E_C) is observed to be 3.031kV/cm indicates that BCZT3 composition possesses smaller grain size and it also indicates soft behavior.

A remnant polarization (Pr) is 1.930 μc/cm^2, maximum polarization (P_{max}) is 5.515 μc/cm^2 and a coercive field (E_C) is 3.580 kV/cm were obtained under a maximum applied electric field of 20 kV/cm for BCZT3 ceramic.

P-E loop for BCZT3 composition are symmetrical in nature with positive and negative values of coercive field (Ec) and also positive and negative values of remnant polarization (Pr) are equal. P-E loops for BCZT3 composition is slim hysteresis loop, which is one of the characteristic of relaxor ferroelectric. A low coercive field implies that the studied BCZT3 ceramic is "soft" with respect to the electric field. In studied ceramic, it can be observed that all ceramic are typically soft, with a very low coercive field Ec and a relatively high remnant polarization Pr. These results are in good agreement with reported result [11-12]

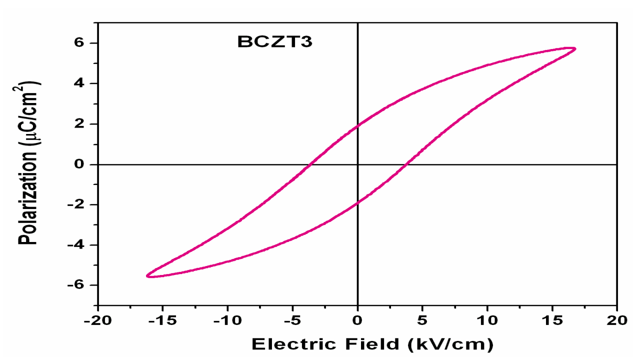

Figure 4: Ferroelectric hysteresis Loop of BCZT3 composition

Table 2: Values of P_{max}, P_r and E_C for BCZT3 composition at different applied electric field.

	Electric Field kv/cm	P_{max} µc/cm^2	P_r µc/cm^2	E_c kv/cm
BCZT3	7	2.534	0.971	2.320
	9	3.078	1.050	2.487
	10	3.762	1.196	2.714
	12	4.433	1.451	2.978
	15	4.492	1.477	3.031
	16	5.118	1.632	3.335
	20	5.715	1.930	3.580

3.4 Impedance Study

The electrical behavior of the compound has been studied over a range of temperature and frequency using the complex impedance spectroscopy technique. This technique enables us to separate the real and imaginary components of the electrical parameters and hence provides a true picture of the material properties. Each representation can be used to highlight a particular aspect of the response of a sample. The electrical properties often presented in terms of immittance functions [impedance (Z), admittance (Y), permittivity (ε), and electrical modulus (M)]. The impedance measurement on a material gives us data having both resistive R (real part) and reactive X (imaginary part) components. It can be displayed conventionally in a complex plane plot (Nyquist or Cole–Cole diagram). Impedance spectroscopy has been proved to be a powerful method to estimate the contribution of the grain, grain boundaries and film/electrode effect on the charge transport phenomenon in peroveskite materials [13]. The complex impedance

$$Z^*(f) = Z'(f) + Z''(f)$$

Where Z' and Z'' represent the real and imaginary part of impedance respectively.

The semicircular pattern in the impedance spectrum is a representative of the electrical process taking place in the material.

The complex impedance could be measured accurately only for f = 20 Hz to f =1MHz for BCZT3 ceramic. Figures 5 show the Z''(imaginary part) verses Z'(real part) for BCZT3 ceramic. It is observed that with increase in Z', Z'' also increases and then decreases and the curve moves towards Z' indicating increase in the conductivity of sample. The Z'' verses Z' curve is observed to follow a single semicircle as expected for a single-phase ferroelectric compound [12].

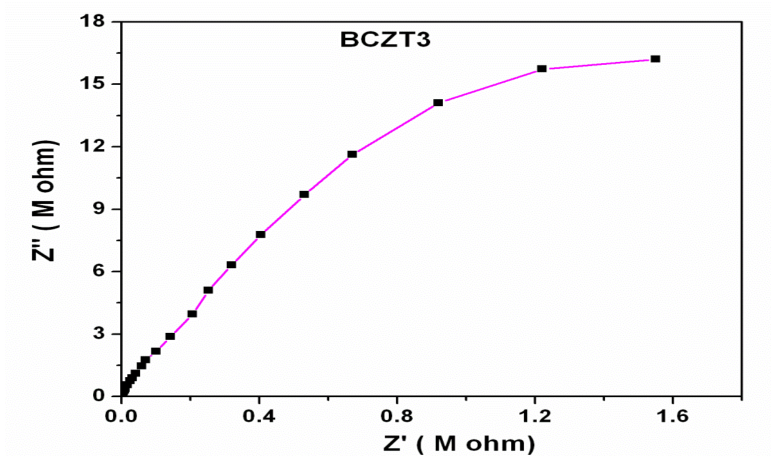

Figure 5: Z'' verses Z' for BCZT3 ceramic.

4. CONCLUSION

Ferroelectric ceramic $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ is synthesized using ceramic route of synthesis. The room temperature XRD pattern suggests that the ceramic is polycrystalline in nature. The SEM image clearly show that the sintered sample have dense structure with non-uniform grain size distribution. The investigations on the P-E hysteresis loop reveal that BCZT3 ceramic possesses useful values of maximum polarization (P_{max}) and remnant polarization (Pr). The investigations on impedance analysis observed that BCZT3 is single phase ferroelectric compound. The present observations suggest that BCTZ 3 ceramic could be useful lead free ferroelectric ceramic.

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