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FERROELECTRIC AND IMPEDANCE STUDY OF $(Ba_{0.95}Ca_{0.05})(Ti_{0.90}Zr_{0.10})O_3$ CERAMIC

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ABSTRACT

Extremely small amounts of Ca and Zr doping on the A and B site of $BaTiO_3$ resulting in a solid solution of $(Ba_{(1-x)}Ca_{(x)})(Zr_{(y)}Ti_{(1-y)})O_3$ (BCZT) with x = 0.05 and y = 0.10. The BCZT composition is synthesized via ceramic route of synthesis. The XRD pattern reveals the presence of tetragonal phase. 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 BCZT composition possesses useful values of maximum polarization (P_{max}) and remnant polarization (Pr). The investigations on impedance analysis observed that BCZT is single phase ferroelectric compound. The present observations suggest that BCTZ composition could be useful lead free ferroelectric ceramic.

KEYWORDS : Ceramic, Polarisation, Ferroelectric, Hysteresis.

1.INTRODUCTION

Apart from BT, BZT and BCT, $(Ba,Ca)(Zr,Ti)O_3$ (BCZT) is a good candidate for a variety of applications. The applications such as multilayer ceramic capacitors, piezoelectric actuators and positive temperature coefficient resistors (PTCR). The BCZT possesses excellent dielectric, ferroelectric and piezoelectric properties. The properties of BCZT can be controlled by varying the composition of Ba/Ca and Zr/Ti. However, BCZT requires a high sintering temperature >1450^{0}C, which not agree with the requirements of industry. In order to decrease the sintering temperature, it is necessary to produce powders of BCZT with fine particle sizes and homogeneous distribution. The co-doping by Ca^{+2} and Zr^{+4} ions plays a critical role in maintaining the electrical properties of $BaTiO_3$ ceramics. There are number of reports available on the study of $(Ba_{1-x}Ca_x)(Zr_yTi_{1-y})O_3$ ceramics. In 2009, Liu and Ren reported one of the most promising lead-free ferroelectric systems, Ca^{+2} and Zr^{+4} doped $BaTiO_3$ (BCZT) which exhibits excellent piezoelectric behavior (d33 ~ 620pC/N) [1]. He pointed out that doping amount of Ca^{+2} and Zr^{+4} will influence the piezoelectric behavior of BCZT. Mahajan et al. also pointed out that, it will increase the ferroelectric properties by doping Ca^{+2} and Zr^{+4} in $BaTiO_3$ based materials [2]. The BCTZ are commonly used as key materials for high capacitance multilayer ceramic capacitors (MLCCs) with a temperature specification of Y5V and Ca^{+2} and Zr^{+4} are employed for broadening and shifting the dielectric maximum at the curie point to room temperature [3]. Thus 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 [4]. Min Shi et al. reported effect of annealing processes on the structural and electrical properties of the lead-free thin films of $(Ba_{0.9}Ca_{0.1})(Ti_{0.9}Zr_{0.1})O_3$ [5]. S.K.Ye et al. reported the structure and electrical properties of 001 textured $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$ lead-free piezoelectric ceramics [6]. Jiafeng et al. reported that BCZT is a novel material with higher value of dielectric constant and piezoelectric properties [7]. Chavan et al reported that BCZT possesses ferroelectric relaxor behavior [8].

For present paper $(Ba_{0.95}Ca_{0.05})(Ti_{0.90}Zr_{0.10})O_3$ is selected to be a ferroelectric phase for investigations on ferroelectric and impedance study. $(Ba_{0.95}Ca_{0.05})(Ti_{0.90}Zr_{0.10})O_3$ abbreviated as BCZT 1 is a promising lead free ferroelectric material.

2. EXPERIMENTAL

The BCZT1 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

Fig.1 show XRD pattern of $(Ba_{0.95}Ca_{0.05})(Ti_{0.90}Zr_{0.10})O_3$ (BCZT1) ceramic. The presence of sharp and well defined diffraction peaks indicate that this composition 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 compositions under investigations 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 also determined using Scherer's formula with Gaussian fitting data. It is observed that the particle size is found out to be 46.47 nm, lattice parameters a is 3.972 A^0 , c is 4.018 A^0 and degree of tetragonality c/a is 1.011. The values of degree of tetragonality (c/a) for of BCZT1 ceramic are found to be around 1, same as reported for $BaTiO_3$ based ceramics.

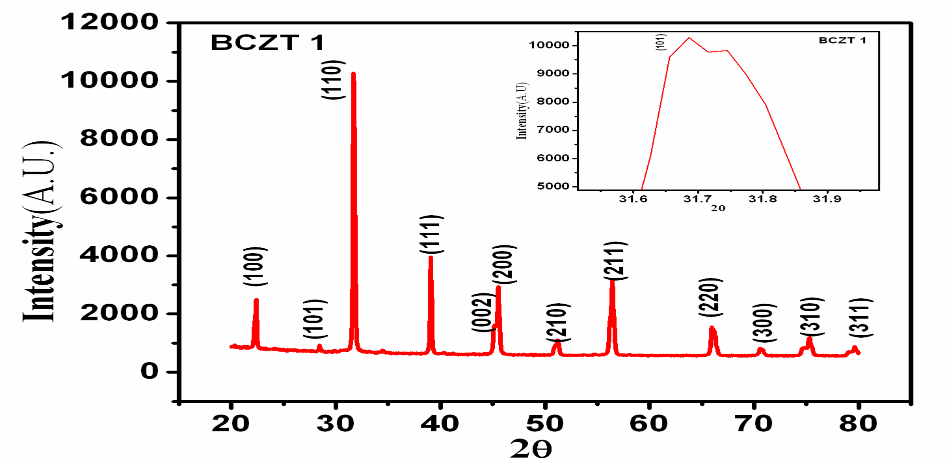

Figure 1: XRD pattern of BCZT1 ceramic.

3.2 Microstructural Analysis

Figure 2 show SEM image of BCZT1 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 BCZT1 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 BCZT1 composition is observed to be 0.8630 µm. This result shows that Ca^{2+} ion and Zr^{4+} ion substitution in BT modifies the grain size and morphology.

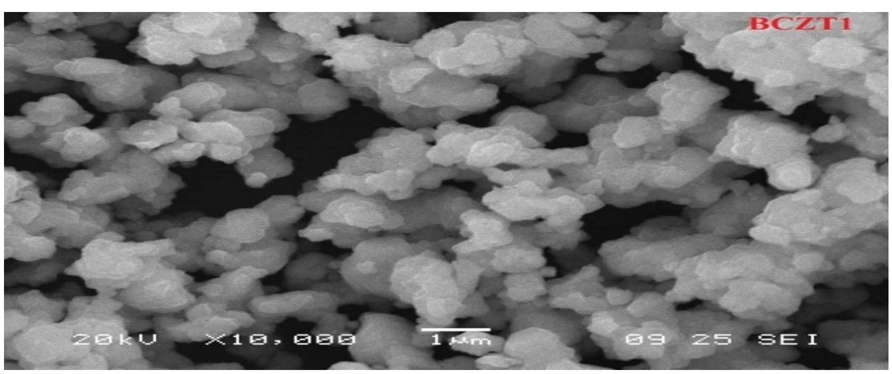

Figure 2: SEM images of BCZT1 ceramic.

3.3 Ferroelectric Properties

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 ($> 10^9\ \Omega$.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 BCZT1 composition are obtained by using P-E loop tracer. The measurements are carried out at different applied field. The thickness of BCZT1 sample was 1.22 mm. Room temperature P-E loop recorded at a frequency of 50 Hz for BCZT1 composition is shown in figure 3, Table 1 shows the values of maximum polarization (P_{max}), remnant polarization (Pr) and a coercive field (E_C) for BCZT1 composition at different applied electric field.

Table 1 for BCZT1 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 40KV applied electric field, the value of remnant polarization (Pr) is observed to be 0.255 $\mu c/cm^2$ indicates that BCZT1 composition possesses higher internal polarizability, electromechanical coupling, electro optic activity and strain. The value of coercive field (E_C) is observed to be 2.218 kV/cm indicates that BCZT1 composition possesses smaller grain size and it also indicates soft behavior.

A remnant polarization (Pr) is 0.1437 $\mu c/cm^2$, maximum polarization (P_{max}) is 1.7928 $\mu c/cm^2$ and a coercive field (E_C) is 1.2894 kV/cm were obtained under a maximum applied electric field of 18 kV/cm for BCZT1 ceramic.

P-E loops for BCZT1 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 BCZT1 composition is slim hysteresis loops, which is one of the characteristic of relaxor ferroelectric. A low coercive field implies that the studied BCZT 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 [9].

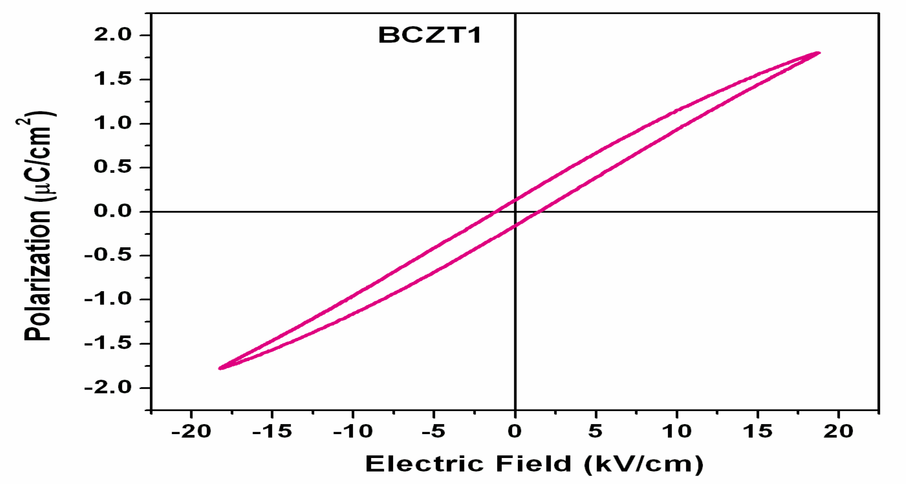

Figure 3: Ferroelectric hysteresis Loop of BCZT1 composition

Table 1: Values of P_{max}, P_r and E_C for BCZT1 composition at different applied electric field.

	Electric Field kv/cm	P_{max} μc/cm^2	P_r μc/cm^2	E_c kv/cm
BCZT1	15	1.652	0.116	1.057
	18	1.792	0.143	1.289
	23	2.187	0.175	1.372
	25	2.390	0.191	1.585
	30	2.573	0.205	1.601
	33	2.957	0.223	2.059
	35	3.130	0.233	2.114
	40	3.344	0.255	2.219
	42	3.610	0.307	2.643

3.4 Impedance Analysis

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 [10]. 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 BCZT1 composition. Figures 4 show the Z''imaginary part) verses Z'(real part) for BCZT1 composition. 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.

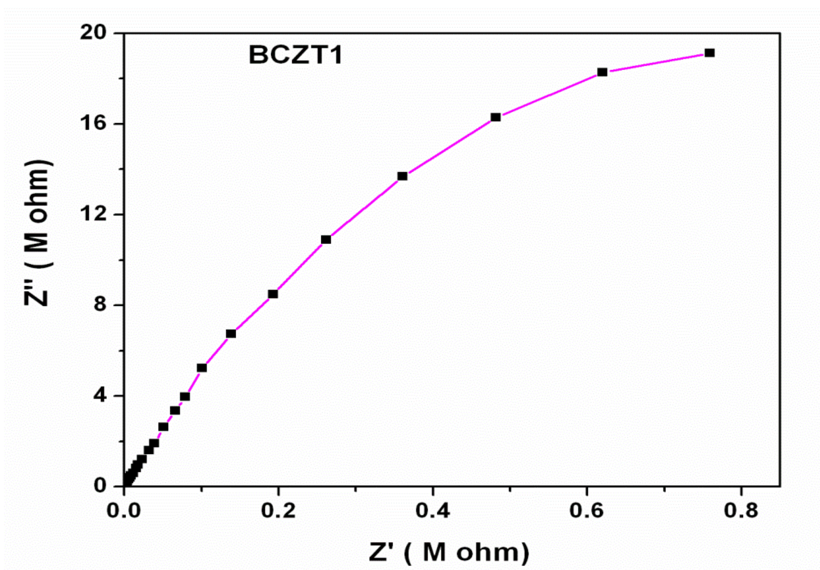

Figure 4: Z'' Vs. Z' for BCZT1 composition.

4. CONCLUSION

The ferroelectric composition $(Ba_{0.95}Ca_{0.05})(Ti_{0.90}Zr_{0.10})O_3$ is synthesized using ceramic route of synthesis. The room temperature XRD pattern suggests that the composition 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 BCZT composition possesses useful values of maximum polarization (P_{max}) and remnant polarization (Pr). The investigations on impedance analysis observed that BCZT 1 is single phase ferroelectric compound. The present observations suggest that BCTZ 1 composition could be useful lead free ferroelectric ceramic.

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