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TEMPERATURE DEPENDENT DIELECTRIC PROPERTIES OF LEAD FREE $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ FERROELECTRIC CERAMIC

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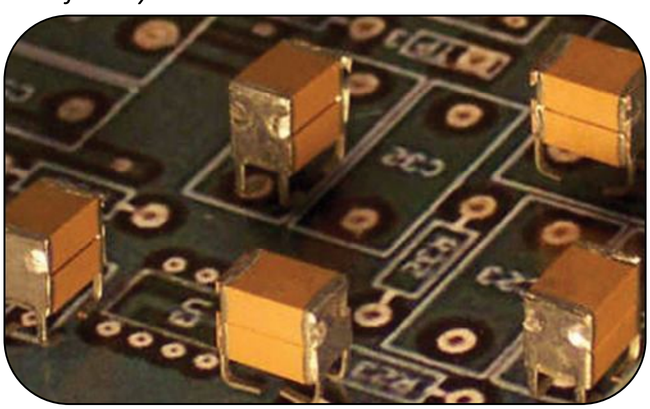
ABSTRACT :
The paper reports synthesis, structural analysis, microstructural analysis, elemental analysis and temperature dependent dielectric properties of $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ ceramic. The $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ ceramic is synthesized via ceramic route of synthesis. The studies on crystal structure show tetragonal crystal structure. 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 dielectric properties show diffuse phase transition and exhibit satisfactory dielectric constant with low tanδ. The value of the relaxation parameter γ ranges between 1 and 2 shows relaxor nature. The nonlinear behavior for $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ confirms the existence of diffuse phase transition characteristics. 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.



KEY WORDS: *Ceramic, Dielectric, Ferroelectric, Diffuse.*

1.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 analysis, microstructural analysis, elemental analysis and temperature dependent dielectric properties of $(Ba_{0.925}Ca_{0.075})(Zr_{0.075}Ti_{0.925})O_3$ (BCZT3) ferroelectric ceramic.

2. EXPERIMENTAL

The BCZT3 solid ceramic 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 h 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) and loss tangent $\tan\delta$.

3. RESULT AND DISCUSSION

3.1 Structural Analysis

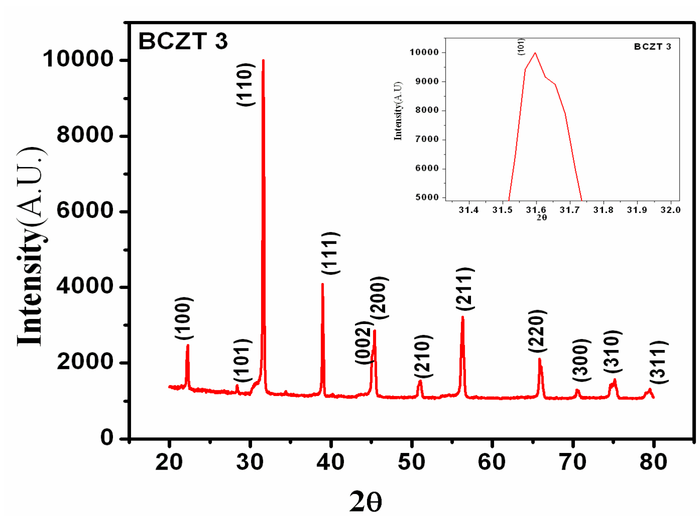


Figure.1: XRD pattern of BCZT3 ceramic.

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

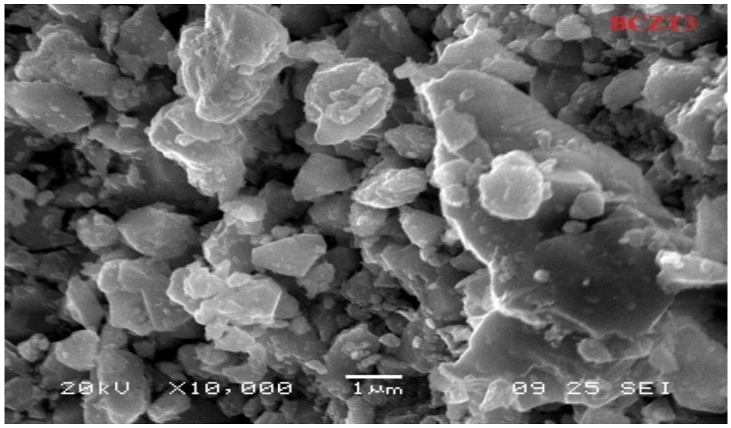


Figure 2 : SEM image of BCZT3 ceramic.

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 BCZT2 sample is stoichiometric. The observed atomic percentage from EDAX is presented in the table 1.

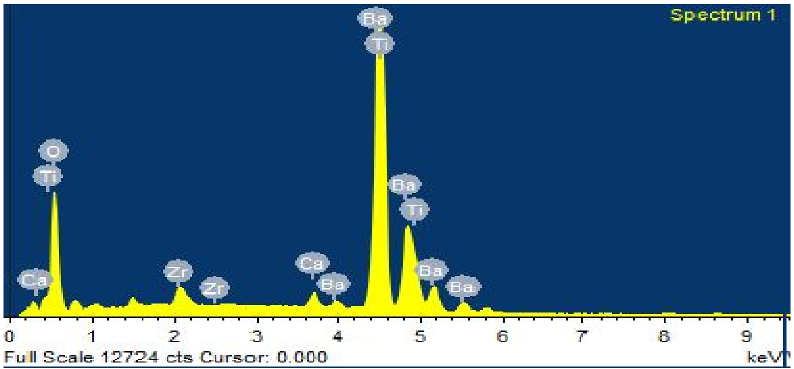


Figure 3: EDAX spectrum of BCZT3 ceramic.

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

3.4 Temperature Dependent Dielectric Properties

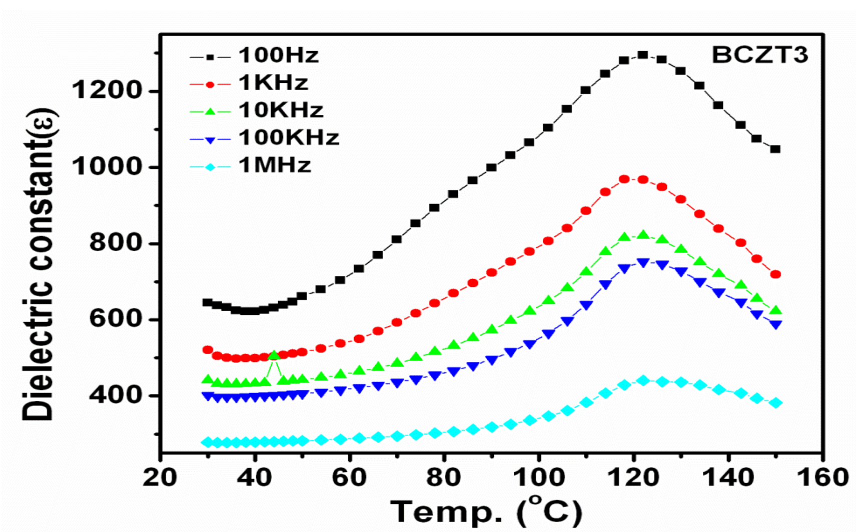


Figure 4: Dielectric constant (ε) verses Temp. for BCZT3 at different frequencies.

Figure 4 show variation of dielectric constant (ε) as a function of temperature (T) at different frequencies for BCZT3 ceramic. 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 with the increases of frequency. This is a typical behavior of a relaxor ferroelectric. Table 2 shows the maximum value of ε(ε_{max}), loss tangent Tanδ at T_c ($Tan\delta_{Tc}$) and T_c for various frequencies for the BCZT3 composition. To parameterize this observe variation of ε versus T behavior, the ε in the paraelectric region is fitted to an equation 1 [11].

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon max} + \frac{(T-Tc)^{\gamma}}{2\,\varepsilon max\,\delta^2} \qquad 1 \le \gamma \le 2 \qquad (1)$$

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. The plot of log ($1/\varepsilon - 1/\varepsilon_{max}$) verses log ($T-T_c$) shows linear relationship for BCZT3 ceramic. By fitting Equation (1) to the data, the values of γ and б are determined and are also shown in table 3. It is seen that 1≤ γ ≤ 2. These observations suggest that BCZT3 ceramic possess a diffuse phase transition characteristics. The nonlinear behavior for BCZT3 ceramic confirms the existence of diffuse phase transition characteristics. [12-13].

Table 2 –Tc,, ε_{max},,$Tan\delta_{Tc}$, γ and б for BCZT3 ceramic.

	Frequency Hz	Tc (°C)	ε_{RT}	$Tan\delta_{RT}$	ε_{max}	$Tan\delta_{Tc}$
BCZT3	100	119.80	662.36	0.218	1293.52	0.344
	1K	120.05	520.77	0.147	972.11	0.172
	10K	121.17	440.97	0.095	820.72	0.097
	100K	122.79	401.73	0.057	752.23	0.067
	1M	124.72	278.11	0.179	438.64	0.255

Table 3: γ and D for BCZT3 ceramic.

	Frequency Hz	γ	D × 10^{-4}
BCZT3	100	1.952	0.056
	1K	1.806	1.081
	10K	1.720	0.069
	100K	1.702	0.916
	1M	1.690	2.302

4. CONCLUSION

The ferroelectric ceramic BCZT3 are synthesized using ceramic route of synthesis. The room temperature XRD study suggests that ceramic is polycrystalline in nature. The studies on crystal structure show tetragonal crystal structure. 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 temperature dependent dielectric properties show a diffuse phase transition and also exhibit a satisfactory dielectric constant and low dielectric loss tan δ. The value of the relaxation parameter γ ranges between 1 and 2 indicate the relaxor nature. The nonlinear behavior for BCZT3 confirms the existence of diffuse phase transition characteristics .Thus BCTZ3 ceramic could be useful lead free ferroelectric ceramic.

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