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INVESTIGATIONS ON DIELECTRIC PROPERTIES OF LEAD FREE $(Ba_{0.95}Ca_{0.05})(Zr_{0.075}Ti_{0.925})O_3$ COMPOSITION

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Abstract –
The paper reports Synthesis, Structural analysis, Microstructural analysis, Elemental analysis and Dielectric properties of $(Ba_{0.95}Ca_{0.05})(Zr_{0.075}Ti_{0.925})O_3$ composition. The $(Ba_{0.95}Ca_{0.05})(Zr_{0.075}Ti_{0.925})O_3$ composition 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 $(Ba_{0.95}Ca_{0.05})(Zr_{0.075}Ti_{0.925})O_3$ confirms the existence of diffuse phase transition characteristics. The present observations suggest that $(Ba_{0.95}Ca_{0.05})(Zr_{0.075}Ti_{0.925})O_3$ composition could be useful lead free ferroelectric.

KEY WORDS: *Solid State Reaction, Dielectric properties, Tetragonal, diffuse phase.*

1.INTRODUCTION

Ferroelectric materials with perovskite structures are useful for microelectronic devices. The most widely used ferroelectric material is $BaTiO_3$ (BT). The structure of unit cell is temperature dependent. There are three phase transitions in order of decreasing temperature (120°C, 5°C, -90°C) [1]. The substitution of Sr, Pb ,Ca and Zr into BT shows interesting ferroelectric properties. Zhuang et al. reported that addition of even a small quantity of Ca ions at Ti-sites leads to a diffused phase transition curve and lowers the phase transition temperatures [2]. Tiwari et al. reported that calcium doping increases the phase transition temperatures of BCT ceramics and Ba^{2+} substitution by Ca^{2+} leads to diffused transition curve. Earlier it was believed that Ca substitution decreases the Curie temperature [3]. Recently, it has been reported that Ca doping can also increase the Curie temperature depending on the powder preparation method & the site occupancy of calcium [4]. Apart from BT, BZT and BCT, $(Ba,Ca)(Zr,Ti)O_3$ (BCZT) is a good candidate for a variety of applications.

There are number of reports available on the study of $(Ba_{1-x}Ca_x)(Zr_yTi_{1-y})O_3$ ceramics. 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 [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].

The paper reports synthesis, structural analysis, Microstructural analysis, elemental analysis and dielectric properties of $(Ba_{0.95}Ca_{0.05})(Zr_{0.075}Ti_{0.925})O_3$ (BCZT2) composition.

2. EXPERIMENTAL

The BCZT2 solid composition 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°C 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°C for 24 h. The Bruker D8 advance X-ray diffractometer was used for the determination of XRD pattern. The microstructure

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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 tanδ .

3. RESULT AND DISCUSSION

3.1 Structural Analysis

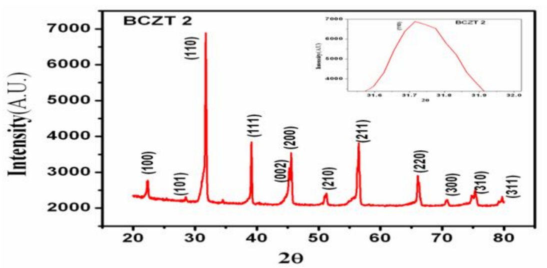

Fig.1: XRD pattern of BCZT2 composition.

Fig.1 show XRD pattern of $(Ba_{0.95}Ca_{0.05})(Zr_{0.075}Ti_{0.925})O_3$ (BCZT2) 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 composition 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 also determined using Scherer's formula with Gaussian fitting data. It is observed that the particle size is found out to be 55.40 nm, lattice parameters a is 3.789 A^0 , c is 4.001 A^0 and degree of tetragonality c/a is 1.055. The values of degree of tetragonality (c/a) for of BCZT2 ceramic are found to be around 1, same as reported for $BaTiO_3$ based ceramics.

3.2 Microstructure Analysis

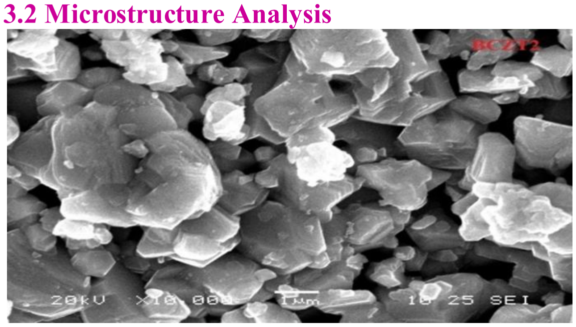

Figure 2 : SEM image of BCZT2 ceramic.

Figure 2 show SEM image of BCZT2 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 BCZT2 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 BCZT2 composition is observed to be 1.494 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 .

3.3 Elemental Analysis

The EDAX spectrum is used for quantitative elemental analysis and composition of the BCZT2 composition. Figure 3 shows EDAX spectrum of BCZT2 composition 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.

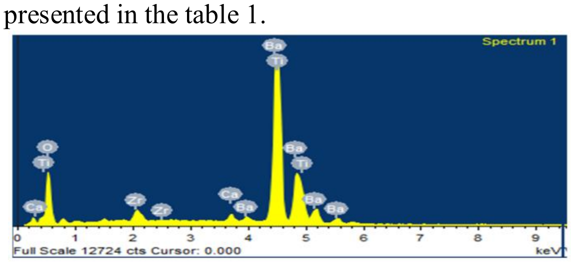

Figure 3: EDAX spectrum of BCZT2 composition.

Table 1: Elemental compositions of Ba, Ca, Ti , Zr and O atoms evaluated by using EDAX Technique (BCZT2 composition)..

Element	Weight %	Atomic %
O	34.63	75.12
Ca	0.81	0.70
Ti	16.29	11.81
Zr	1.39	0.53
Ba	46.88	11.85
Total	100	100

3.4 Dielectric Properties

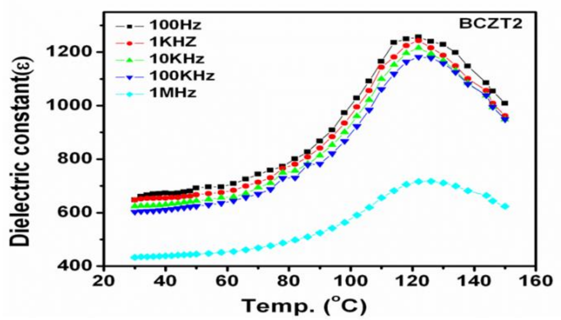

Figure 4: Dielectric constant (ε) verses Temp. for BCZT2 at different frequencies.

Figure 4 show variation of dielectric constant (ε) as a function of temperature (T) at different frequencies for BCZT2 composition. 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 (Tanδ_{Tc}) and T_c for various frequencies for the BCZT2 composition. To parameterize this observe variation of ε versus T behavior, the ε in the paraelectric region is fitted to an equation [10, 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/ε-1/ε_{max}) verses log (T-T_c) shows linear relationship for BCZT2 composition. 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. This observation suggests that BCZT2 composition possess a diffuse phase transition characteristics [12]. The nonlinear behavior for BCZT2 confirms the existence of diffuse phase transition characteristics.

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

	Frequency Hz	Tc (°C)	ε_{RT}	Tanδ_{RT}	ε_{max}	Tanδ_{Tc}
BCZT2	100	121.17	695.56	0.015	1260.24	0.032
	1K	122.23	656.71	0.025	1239.48	0.017
	10K	123.10	629.89	0.029	1211.98	0.017
	100K	123.35	610.09	0.023	1181.89	0.031
	1M	126.08	436.81	0.163	716.49	0.236

Table 3: γ and D for BCZT2 composition.

	Frequency Hz	γ	D ×10^{-4}
BCZT2	100	1.948	1.636
	1K	1.925	0.038
	10K	1.595	0.705
	100K	1.557	1.282
	1M	1.415	0.865

4.CONCLUSION

The ferroelectric composition BCZT2 are synthesized using ceramic route of synthesis.The room temperature XRD study suggests that composition 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 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 BCZT2 confirms the existence of diffuse phase transition characteristics Thus BCTZ2 composition could be useful lead free ferroelectric composition.

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