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Structural and electrical properties of lead-free $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ ceramic

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Abstract. Lead-free $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) ceramic has been prepared by sol-gel synthesis method. The effect of sintering temperature on the structure of BCZT ceramic was investigated. X-ray Diffraction studies show the suppression of secondary phase TiO_2 with an increase in sintering temperature. The formation oftetragonal-orthorhombic morphotropic phase boundary is observed at the sintering temperature of 1350 °C. Polarization (*P*) versus electric field (*E*) measurementshows a remnant polarization of 1.32 μC/cm^{2}and coercive field of 4.33 kV/cm.

1. Introduction

Piezoelectrics are an important class of materials, which can produce electric signals in response to an applied mechanical stress. These materials have widespread interest due to their usefulness in the development of piezo-generators, sensors, piezo actuators, transducers etc. [1-4]. Among the available piezoelectrics, $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) is vastly studied material and very popular due to its excellent piezoelectric properties [1-3]. In spite of its advantages in terms of properties, the material is restricted for the usage in devices due to its toxicity. Thus, there is a growing demand for lead-free ceramics with high piezoelectric properties. Therefore, much research is dedicated to develop the new materials and to improve the piezoelectricity of the existed lead-free materials such as $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), $BaTiO_3$ (BTO) etc. The d_{33} value of these materials is comparatively lower than PZT (~ 600 pC/N). Hence, to enhance the piezoelectric properties, doping at A-site, and B-sites with suitable ions is adopted in the literature in these ABO_3 type perovskites. For example, BTO ceramics with Calcium and Zirconium dopingare extensively studied and show promising piezoelectric properties [5-8]. $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) is one such material, which shows high piezoelectric coefficient, d_{33} ~ 620 pC/N [1, 2] and good ferroelectric properties [6, 7, 9, 10]. In BCZT, Ca substitution in Ba site induces lattice distortion and shrinkage due to its smaller ionic radius. At the same time, Zr substitution brings the morphotropic phase boundary (MPB) near to room temperature [2]. The existence of MPBs helps in achieving high d_{33} value, making this material a real substitute for PZT [1, 2]. Moreover, BCZT along with the suitable magnetostrictive compound (such as $CoFe_2O_4$, $NiFe_2O_4$ etc.) can form a magnetoelectric composite and exhibit high magnetoelectric coupling due to its huge d_{33} value [3]. However, the synthesis of pure BCZT and the formation of MPBs is a challenging task as TiO_2 is prone to form during the synthesis and very high sintering temperatures are essential for MPBs. In this study, we synthesize BCZT using sol-gel

IOP Conf. Series: Materials Science and Engineering **577** (2019) 012066 doi:10.1088/1757-899X/577/1/012066

method and the effect of sintering temperature on the structure, formation of MPBs is discussed. Also, the electrical polarization studies are reported.

2. Experimental Details

Lead-free $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) ceramic was prepared by sol-gel synthesis technique. BCZT ceramic was synthesized using analytical reagent (AR) grade chemicals. The precursors used were Barium nitrate, Calcium nitrate, Zirconium oxynitrate and Titanium isopropoxide. Barium nitrate, Calcium nitrate, and Zirconium oxynitrate were taken and separately dissolved in deionized water. To dissolve Zirconium oxynitrate completely in deionized water, few drops of concentrated HNO_3 was also added. Titanium isopropoxide was taken in ethylene glycol, to prevent the formation of TiO_2. These solutions were mixed together with citric acid as a chelating agent and kept overnight for stirring. The latter solution was heated to form a gel and then dried to get ash. Synthesized powder was calcined at 900 ºC and sintered at two different temperatures 1350 ºC and 1550 ºC.

3. Results and discussion

3.1. Structural analysis

The effect of sintering temperature on the phase formation of BCZT is analyzed using X-ray Diffraction (XRD). The room temperature XRD pattern of BCZT samples sintered at 900 ºC, 1350 ºC, and 1550 ºC is shown in figure 1. It is observed that the BCZT phase formation started from the 900 °C and as the temperature increases, the crystallinity of the compound increases. Along with the BCZT phase, the peaks corresponding to the secondary phase, TiO_2 are observed around ~27° with relatively small intensities. As the sintering temperature increases to 1350 °C, the percentage of the TiO_2 phase have been suppressed and also favors the formation of tetragonal-orthorhombic morphotropic phase boundary (MPB). Therefore, the pure BCZT samples with MPBs can be achieved at high sintering temperature ≥ 1350 °C and this is essential to have good piezoelectric properties, which will be discussed in the later sections.

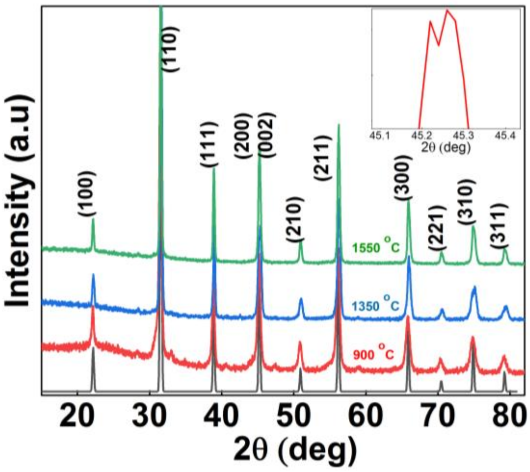

Figure 1. X-ray diffraction of BCZT. The inset shows the zoomed portion of the same around 45°.

At room temperature, the BCZT ceramic possesses tetragonal phase, which is characterized by splitting of the (2 0 0)/(0 0 2) peaks around 2θ ~ 45º (see the inset of figure 1). The BCZT ceramics also shows orthorhombic phase, featured with a single peak at around 2θ ~ 66º [2]. In the present study, both these peaks are observed which confirms the existence of two phases which leads to the formation of MPBs. Further, Rietveld refinement is performed on the XRD data using the FullProf suite.The diffraction pattern of the BCZT sample sintered at 1350 ºC is well refined with tetragonal structure with *P4mm* space group and orthorhombic structure with *Amm2* space group. The best fitting is confirmed by the *R*-

IOP Conf. Series: Materials Science and Engineering **577** (2019) 012066 doi:10.1088/1757-899X/577/1/012066

factors. The refined XRD data along with the fitting parameters is depicted in figure 2. The schematic of the unit cell, representing the arrangement of atoms of both the phases are shown in the inset.

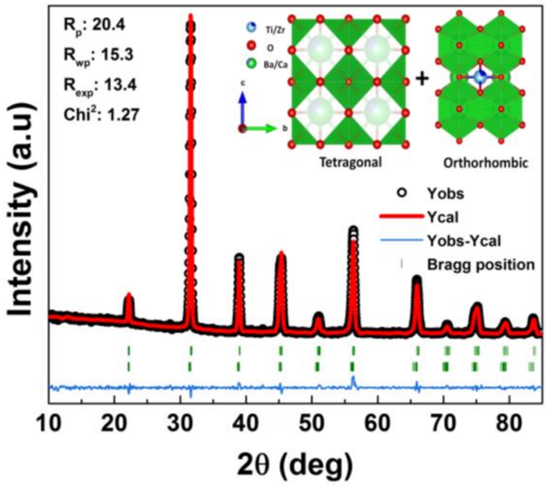

Figure 2. Rietveld refinement plot for $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$. The inset shows the schematic diagram of the unit cells of orthorhombic and tetragonal phases.

The resulting structural information with lattice parameters, unit cell volumeis summarized in table1.

Table 1. Refined structural parameters for $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ sample.

Phase	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
Tetragonal	3.9932	3.9932	4.0159	64.04
Orthorhombic	4.0043	5.6717	5.7077	129.63

In order to find out the contribution of microstrain, Williamson Hall analysis is carried out. The plot of $\beta \cos\theta$ versus 4 $\sin\theta$ for the sample understudy is shown in figure 3. From this, the microstrain is found to be ~ 0.0017. Using Debye Scherrer formula crystallite size is calculated, which is approximately ~ 35 nm.

3.2 Piezoelectric properties

Figure 4. shows the Polarization (P) versus Electric field (E) loop for the BCZT sample. Measurement is done by sweeping the field between -50 kV/cm and 50 kV/cm at room temperature. The P-E loop confirms the nonlinear ferroelectric behavior of the sample without saturation even at an applied field of 50 kV/cm. From the figure, a remnant polarization (P_r) of 1.32 μC/cm^2, high field polarization (P_{max}) of 6.2 μC/cm^{2}and coercive field (E_C) of 3.47 kV/cm is also observed. In piezoelectric materials, a change in polarization state is coupled with a piezoelectric strain. A plot of strain versus applied electric field was obtained by plotting square of measured polarization versus the applied electric field. Figure 5 shows the variation of strain with the field, which exhibits a butterfly loop as expected for a piezo/ferroelectric material.

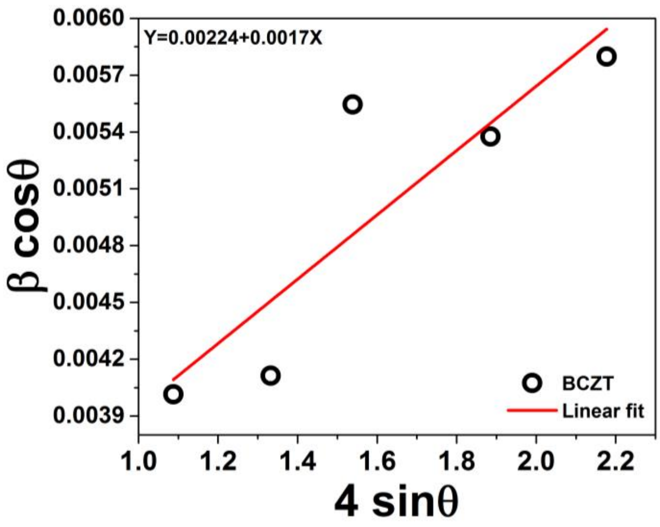

Figure 3. W-H plots of BCZT ceramics.

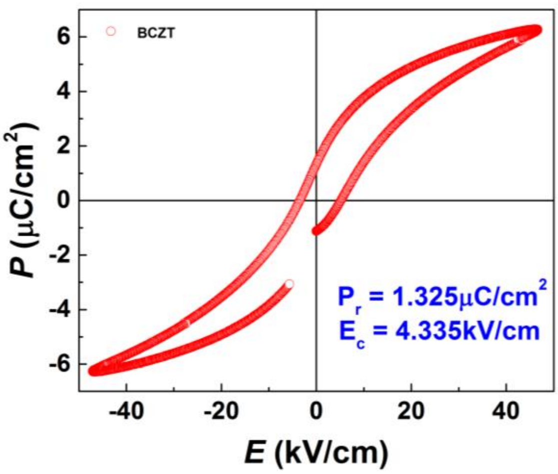

Figure 4. Polarization versus electric field loop for BCZT at room temperature.

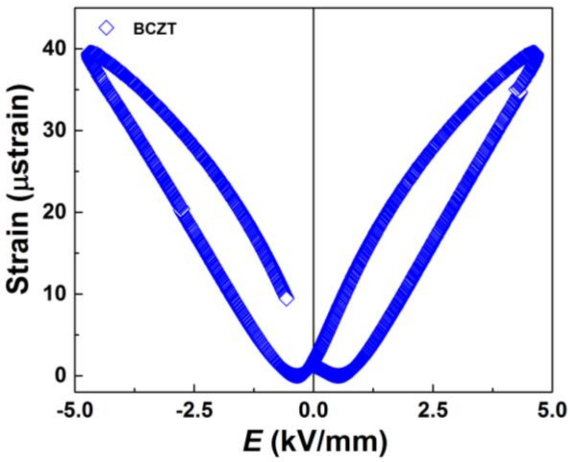

Figure 5. Strain versus electric field loop of BCZT.

4. Conclusion

Lead-free $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ was synthesized successfully by sol-gel technique. The crystallite size is estimated to be ~ 35 nm. XRD results and Rietveld refinement confirms the presence of tetragonal-orthorhombic morphotropic phase boundary at room temperature for BCZT ceramics sintered at 1350 ºC. Also, *P-E* measurement shows the ferroelectric nature of the BCZT sample with (P_r) of 1.32 μC/cm^2. Thus, BCZT is a good substitute for PZT and can be used as a piezoelectric medium for forming a magnetoelectric composite to attain the spintronic applications.

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IOP Conf. Series: Materials Science and Engineering **577** (2019) 012066 doi:10.1088/1757-899X/577/1/012066

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