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# Synthesis and electrical properties of lead-free piezo electrics for magnetoelectric applications

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**Abstract.** The Lead-free piezoelectric polycrystalline materials, BaTiO<sub>3</sub> (BTO) and Ba<sub>0.85</sub>Ca<sub>0.15</sub>Zr<sub>0.1</sub>Ti<sub>0.9</sub>O<sub>3</sub> (BCZT) ceramic are prepared by sol-gel synthesis method. The synthesis dynamics and the effect of sintering temperature on the purity and the formation of morphotropic phase boundaries in these samples are investigated. X-ray Diffraction studies show the cubic phase for the BTO at low temperature, whereas it transforms into the tetragonal for high-temperature synthesis. The BCZT exists in the mixed phases of tetragonal and orthorhombic structures. Formation of MPBs in BCZT are observed for the sintering temperature above 1350 °C. Polarization (*P*) versus electric field (*E*) measurement shows enhanced polarization values for the BCZT in comparison to the BTO.

## 1. Introduction

Piezoelectric ceramics produce electricity upon the application of an external stress and vice versa. The amount of the piezoelectricity is characterized by the piezoelectric coefficient,  $d_{33}$  which measures the volume change when the piezoelectric material is subjected to the electric field. Such materials find many useful applications in the piezo generators, MEMS, sensors etc. [1-3]. Out of the available piezoelectrics, PbZr<sub>0.52</sub>Ti<sub>0.48</sub>O<sub>3</sub> (PZT) has attracted much attention and studied due to its high piezoelectricity ~ 500-600 pC/cm<sup>2</sup> [1]. Though PZT is very much a promising candidate for the industrial applications, its usage is limited by the toxicity of the material as the lead is harmful to human beings and also to the environment. Therefore, lead-free piezoelectric materials with high piezoelectric coefficient is much desirable. Much research is focused in this direction in search of new materials with high  $d_{33}$  and also to enhance the piezoelectricity of the existing materials. Barium titanate is another ferroelectric material paid much attention due to its good ferroelectricity and  $d_{33}$  ~ 191 pC/cm<sup>2</sup> value in its tetragonal structure [5]. Yan Wang *et al.* reported a  $d_{33}$  value of ~ 78 pC/cm<sup>2</sup> in Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> (NBT) ceramics [6]. However, these materials are still lacking in properties

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compared to the PZT and do not form an alternative to the PZT. However, it is found that the co-doping of Ca and Zr in Ba and Ti sites, respectively is very effective in improving the piezoelectricity [7]. Liu *et al.* [1] reported a very high piezoelectric coefficient,  $d_{33} \sim 620$  pC/N for the  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$  (BCZT) compound. In BCZT, the substitution of Ca and Zr lead to the lattice distortion and shrinkage of lattice volume due to the dissimilarity of the ionic radius of parent and doped ion. Moreover, the formation of morphotropic phase boundary (MPB) near to room temperature is observed in this system [1-4]. These MPBs are responsible for enhanced  $d_{33}$  value in comparison to BTO. Thus, BCZT has become a real substitute for PZT and it is environmental friendly.

There are several reports on the synthesis of BTO and BCZT using different techniques and characterized for the ferroelectricity [1-5]. However, these piezo electrics forms a composite with any suitable magnetostrictive compounds, for example,  $\text{NiFe}_2\text{O}_4$ ,  $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$  etc. These composites are called magnetoelectric (ME) composites, which have very promising applications in the field of spintronics, memory devices, sensors and biomedical applications. In order to achieve ME composites with magnetoelectric coupling, a proper piezoelectric material with small grain size, homogeneity, free from impurities is very much desirable. Thus, in this work we focus on the synthesis of the piezoelectric BTO, BCZT using the sol-gel synthesis and it is very effective to get small grain size, high homogeneity and can be prepared at much lesser temperatures compared to solid state reaction [8]. In this study, we synthesize BTO and BCZT ceramics using the sol-gel method and report the structural, electrical properties.

## 2. Experimental Details

### 2.1. Synthesis of Barium Titanate ( $\text{BaTiO}_3$ )

For the preparation of BTO powder, precursors used are Barium Nitrate  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{H}_2\text{O}$  and Titanium Isopropoxide (TIP)  $(\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4)$ . These precursors are measured using appropriate stoichiometric ratio. Barium Nitrate is dissolved in deionized water with constant stirring. On the other hand, Titanium Isopropoxide is also dissolved in Ethylene Glycol and heated around  $50^\circ\text{C}$  with stirring. These two solutions are mixed together after they become transparent. An appropriate amount of citric acid is added to the mixed solution which acts as a chelating agent. This mixture is heated at  $90^\circ\text{C}$  until a transparent yellow colored solution is obtained. The above solution is heated at  $250^\circ\text{C}$  in the air until the brown residue is obtained. The brown residue is then heated at  $400^\circ\text{C}$  until a black solid mass is obtained. This mass is ground thoroughly and calcinated at  $1150^\circ\text{C}$  in a furnace for 10 hr and it forms the tetragonal phase of Barium Titanate powder.

### 2.2. Synthesis of Barium Calcium Zirconium Titanate ( $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ ):

Precursors used for the synthesis of BCZT are Barium Nitrate  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{H}_2\text{O}$ , Calcium Nitrate Tetrahydrate  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , Zirconium oxynitrate hydrate  $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and Titanium Isopropoxide (TIP). Precursors are measured using appropriate stoichiometric ratio. All these precursors except TIP are dissolved separately in de-ionized water and stirred well. Titanium Isopropoxide is dissolved in Ethylene Glycol under  $\text{N}_2$  atmosphere to avoid  $\text{TiO}_2$  formation during the mixing and heated at  $50^\circ\text{C}$  to obtain a clear solution. All these solutions are mixed together after they become transparent. An appropriate amount of citric acid is added to the mixture. A small amount of Oleic acid is also added to the mixture which acts as a surfactant. It is observed that in the first stage of the synthesis, a clear solution is obtained as shown in figure 1(a). However, after few hours of stirring at  $250^\circ\text{C}$ , a white precipitate of Zr is observed at the bottom of the beaker as shown in figure 1(b). This precipitate is dissolved and the solution becomes clear after adding few drops of con.  $\text{HNO}_3$  and stirring for 30 min (figure 1(c)). The solution is heated at  $250^\circ\text{C}$  until a black solid mass is obtained. Then this mass is ground finely and calcinated at  $1000^\circ\text{C}$  in a furnace for 10 hr to form BCZT powder.

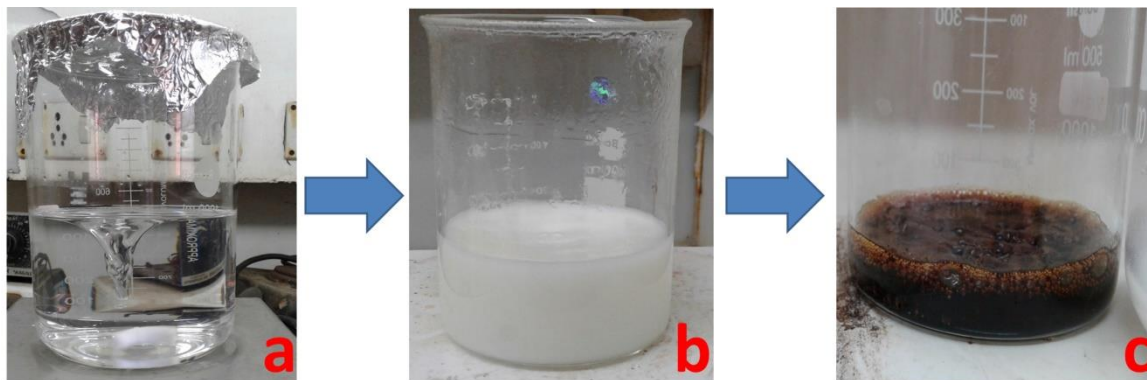


Figure 1. The sol-gel process of BCZT, (a). The clear solution of the precursors, (b). The precipitated solution in the intermediate state and (c). The clear and thick sol in the final stage.

2.3. Characterization techniques:

The crystalline structure and phase formation of the ceramics are investigated using X-Ray Powder Diffraction (XRD) ( $\text{Cu } K_{\alpha} = 1.5406 \text{ \AA}$ ). The room temperature ferroelectric measurements are done using Radiant Premier Ferroelectric Tester.

3. Results and discussion

3.1. Structural analysis

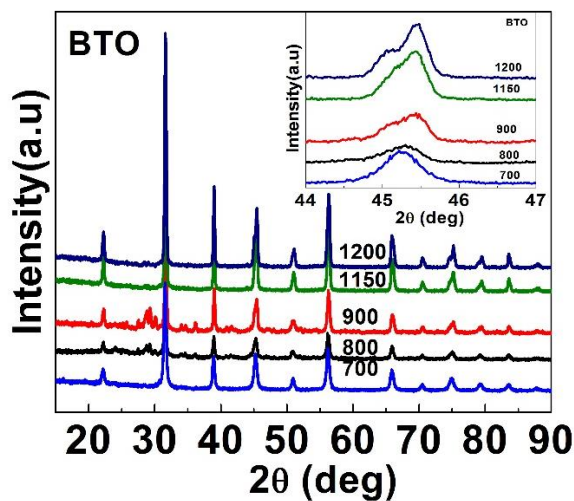


Figure 2. X-ray diffraction of BTO. The inset shows the zoomed portion of the same around 45°.

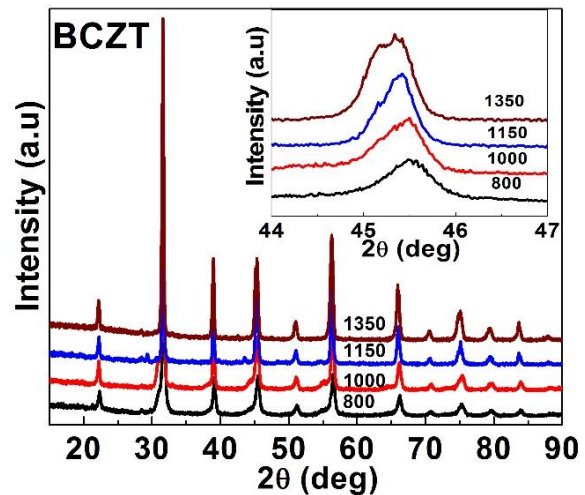


Figure 3. X-ray diffraction of BCZT. The inset shows the zoomed portion of the same around 45°.

The BTO and BCZT samples prepared using the sol-gel are heated at different temperatures and analyzed the phase formation. It is very common that the high-temperature sintering leads to the grain growth due to the diffusion. To have good magnetoelectric interaction, the piezoelectric phase with the high surface area is preferable. Hence, the required phase at small grain size is needed. This can be achieved by careful monitoring of the evolution of structural phase with sintering temperature. Figure 2 shows the XRD pattern of BTO and BCZT samples heated at different temperatures, starting from 700 °C to 1350 °C. The observed diffraction pattern for BTO and BCZT at high temperatures clearly indicates that all the diffraction peaks are matching with the standard data, ICSD collection # 67519

and # 187673 respectively. Along with the BTO and BCZT phases, the peaks corresponding to the secondary phase,  $\text{TiO}_2$  are observed around  $\sim 27^\circ$  with relatively small intensities. As the sintering temperature increases, the percentage of the  $\text{TiO}_2$  phase have been suppressed. From the XRD pattern, it is observed that there is no splitting of the peaks characterizing the (2 0 0)/(0 0 2) planes around  $45^\circ$  for the lowest sintering temperatures (700 °C to 1000 °C), which indicates the cubic phase of BTO and BCZT. In the cubic phase, they are noncentrosymmetric and have no net polarization. To get the ferroelectric properties, the systems need to have tetragonal phase. Therefore, the temperature is further increased to  $\geq 1150$  °C. As the temperature increases, the splitting in the peaks around  $45^\circ$  appears, which corresponds to the tetragonal phase. The space group of barium titanate under the study is found to be  $P4/mmm$ . In the tetragonal phase, the unit cell shows the noncentro symmetry thereby inducing the net polarization in these systems.

The mixed phase is highly necessary for BCZT to get the high piezoresponse. At elevated temperatures, i. e.  $> 1150$  °C, the formation of tetragonal-orthorhombic morphotropic phase boundary (MPB) has been observed. This is confirmed from the splitting at  $45^\circ$  which is corresponding to tetragonal and the peak around  $66^\circ$  which belongs to the orthorhombic phase. Therefore, the pure phase of tetragonal BTO and mixed phase BCZT sample with MPB can be achieved at sintering temperature for  $\geq 1150$  °C. These observations are very much supported by the Rietveld refinement performed by considering the tetragonal phase for BTO and a mixed phase of tetragonal with  $P4mm$  and orthorhombic phase with  $Amm2$  space group for BCZT.

### 3.2 Ferroelectric properties

Figure 3. shows the Polarization ( $P$ ) versus Electric field ( $E$ ) loop for the BTO and BCZT sample. The polarization is measured by applying the voltage at room temperature. The voltage values are converted to the field values by considering the sample dimensions and represented in the  $x$ -axis of figure 3. The  $P$ - $E$  loop of both the samples shows the nonlinear field response, which indicates the ferroelectric behavior. It is also found that the loops are not saturated within the breakdown field. From the figure, a remnant polarization ( $P_r$ ) of  $1.23 \mu\text{C}/\text{cm}^2$ , high field polarization ( $P_{\text{max}}$ ) of  $5.76 \mu\text{C}/\text{cm}^2$  and coercive field ( $E_c$ ) of  $3.82 \text{ kV}/\text{cm}$  is observed for BCZT, whereas these values are increased in the case of BTO, exhibiting  $P_r \sim 2.77 \mu\text{C}/\text{cm}^2$ ,  $P_{\text{max}} \sim 9.21 \mu\text{C}/\text{cm}^2$ , and  $E_c \sim 2.18 \text{ kV}/\text{cm}$ .

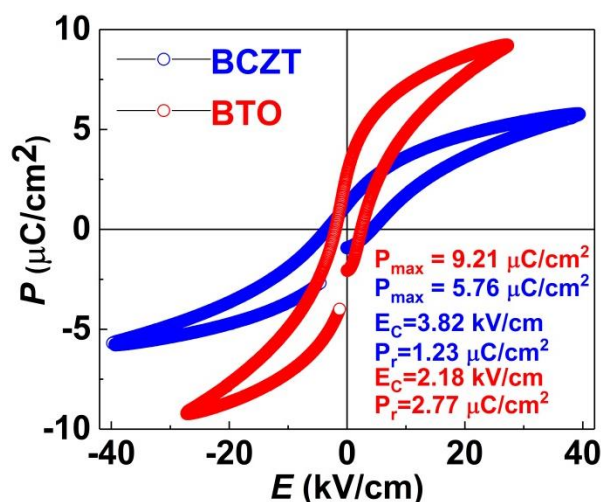


Figure 3.  $P$ - $E$  loops of BTO and BCZT ceramics at room temperature.

The ferroelectricity in the BTO comes due to the asymmetry in the arrangement of Ti-O ions along  $c$ -axis of the tetragonal unit cell. BCZT also has the similar origin of piezoelectricity, accompanied by the extra contribution from the MPBs caused by the tetragonal – Orthorhombic structural transition at

room temperature. Though the polarization in BCZT is expected to be high, in the present study, the lowest values of the polarization compared to BTO may be due to the presence of oxygen vacancies in the BCZT or less density of the compound.

#### 4. Conclusion

Lead-free BaTiO<sub>3</sub> and Ba<sub>0.85</sub>Ca<sub>0.15</sub>Zr<sub>0.1</sub>Ti<sub>0.9</sub>O<sub>3</sub> were synthesized successfully by sol-gel technique. XRD results confirm the BTO in tetragonal phase while BCZT exists in the mixed phase of tetragonal and orthorhombic. The desired ferroelectric phase of these compounds is achieved only at the high temperatures,  $\geq 1150$  °C. Rietveld refinement confirms the presence of MPBs due to the mixed phase of tetragonal-orthorhombic for BCZT ceramics sintered at high temperatures,  $\sim 1350$  °C. *P-E* loop measurement shows the clear ferroelectric nature for both BTO and BCZT samples. In the present study, the polarization values of BTO are greater than BCZT may be due to the presence of oxygen vacancies in the BCZT. The values of  $P_r$  reduced from  $2.77 \mu\text{C}/\text{cm}^2$  for BTO to  $1.23 \mu\text{C}/\text{cm}^2$  for BCZT. Thus, BTO and BCZT are found to be a good substitute for PZT and these lead-free piezoelectrics can be used to form the magnetoelectric composite with a suitable magnetostrictive compound to attain the high ME coupling for the spintronics and memory applications.

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