Effect of Poling on Ferroelectric Properties and Leakage Current Behavior of $0.7Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.3(Ba_{0.7}Ca_{0.3})TiO_3$Lead Free Ceramics

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Abstract: Lead-free ferroelectric $0.7Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.3(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-BCT) ceramics have been prepared by sol-gel auto combustion technique. XRD pattern reveals the realization of single phase material. Rietveld refinement of the XRD patterns confirms the rhombohedral structure having space group *R3m*. FESEM micrograph shows a highly dense microstructure. The effect of electrical poling on ferroelectric properties and leakage current behavior discussed in detail. The variation of leakage current with the electric field is in consistent with the space charge conduction mechanism.

INTRODUCTION

Ferroelectric materials with perovskite structure have a wide range of applications in electronic devices, multilayer ceramic capacitors, infrared detector, actuators, transducers and tunable microwave devices [1]. Generally, lead-based ferroelectric systems are mainly used for various device applications due to theirsuperior dielectric and ferroelectric properties. However, due to the toxicity of lead-based materials and the environmental concern, tremendous efforts have been made to develop lead-free ferroelectric systems for such applications. Among the different lead-free ferroelectric materials such as $BaTiO_3$, $KNbO_3$, $NaNbO_3$, $Na_{0.5}Bi_{0.5}TiO_3$, $K_{0.5}Na_{0.5}NbO_3$, $BaTiO_3$is an important optionas it doesn't contain any poisonous volatile element [2]. Substitution with appropriate dopants at A-site and/ or B-site can control the ferroelectric transition temperature (Tc) and electrical properties of $BaTiO_3$ to the great extent[3]. The substitution of Ca increases the stability of the tetragonal phase and also helps in excluding the formation of the unwanted hexagonal phase of $BaTiO_3$ (BT) [4]. However, an addition of Ca doesn't affect the Curie temperature of BT rather it lowers the polymorphic phase transition (PPT). On the otherhand, the addition of Zr at the Ti-site increases the chemical stability of the material [3]. Recently, a BT based solid solution, $(1\text{-}x)BaZr_{0.2}Ti_{0.8}O_3$-$x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-BCT), has attracted great attention due to its high piezoelectric properties as reported by Liu and Ren group [5]. In order to improve the dielectric, piezoelectric and ferroelectric properties of BT, many research work have been performed by varying the Ba/Ca and Zr/Ti ratio. In the present case, we are interested in studying the structural, ferroelectric and leakage current behavior of $0.7Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.3(Ba_{0.7}Ca_{0.3})TiO_3$. Synthesis of BZT-BCT requires very high calcination temperature to get a phase pure material using a conventional solid-state reaction route. Due to high-temperature synthesis conditions, getting high quality materials is sometimes difficult. To improve the physical properties from application point of

DAE Solid State Physics Symposium 2018
AIP Conf. Proc. 2115, 030019-1–030019-4; https://doi.org/10.1063/1.5112858
Published by AIP Publishing. 978-0-7354-1851-6/$30.00

view, synthesis of high-quality stoichiometric ceramics powder at lower temperature synthesis conditions and improved microstructure is needed. Next, to get the desired piezo and ferroelectric properties for a polycrystalline material, electrical poling (E-poling) is one of the essential requirement. It is a technique which used to orient the random ferroelectric domain along the direction of the applied field. The conditions for poling such as time, temperature and voltagehave to be optimized first to enhance ferroelectric and piezoelectric properties. Most of the research works are mainly focused on the structural and electrical properties of BZT-BCT. However, very little literature are available on the effect of poling on ferroelectric properties and leakage current behavior in detail. In view of this, we have synthesized $0.7Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.3(Ba_{0.7}Ca_{0.3})TiO_3$ (0.7BZT-0.3BCT) by sol gel auto combustion technique. The effects of poling on ferroelectric and leakage current behavior werestudied and possible conduction mechanism discussed.

EXPERIMENTAL WORK

Ceramics of $0.7Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.3(Ba_{0.7}Ca_{0.3})TiO_3$ were synthesized by sol-gel auto combustion technique. Precursors materials, Titanium Isopropoxide, $Ba(NO_3)_2$, $ZrO(NO_3)_2.XH_2O$, $Ca(NO_3)_2.4H_2O$, were used as oxidizer (O) and urea as fuel (F) by maintaining F/O ratio to be 1. Stoichiometry amount of this oxidizer and fuel were dissolved in distilled water. Then nitric acid and acetic acid were added to the solution and continuously stirred and heated so that a gel was formed. The gel then kept to a furnace which is preheated at 450°C for combustion. Then the desired residue formed and it was grinded followed by calcination at 900°C. The calcined powders were then mixed with PVA and pressed into cylindrical pellets with the aid of a uniaxial hydraulic press. The pellets were then sintered at 1450°C for 4 hours. X-ray diffraction (XRD) experiments were performed using Rigaku-JAPAN Ultima IV with Cu Kα radiation for the confirmation of phase formation. The morphological study of the material was investigated using Field emission scanning electron microscope (FESEM) NOVA Nano SEM 450. The room temperature hysteresis loop (P-E) and I-V measurements were carried out using ferroelectric loop tracer (Radiant Ferroelectric Tester) for the poled and unpoled sample at a frequency of 10 Hz.

RESULT AND DISCUSSION

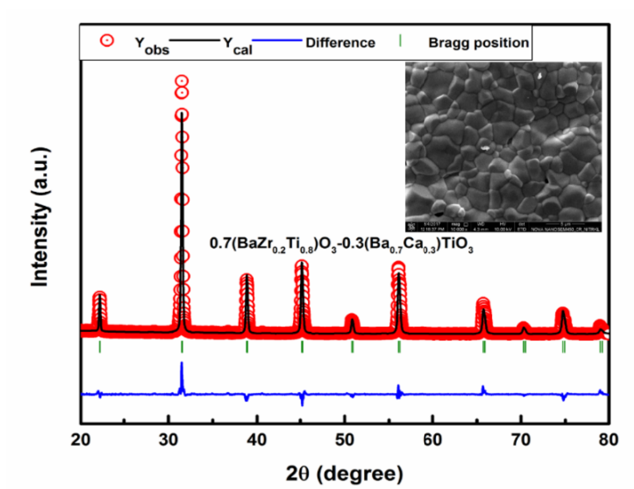

FIGURE 1. Rietveld refined XRD pattern of 0.7BZT-0.3BCT. Inset shows the SEM microstructure of 0.7BZT-0.3BCT

The room temperature Rietveld refined XRD pattern of 0.7BZT-0.3BCT ceramics is shown in Fig. 1. The XRD pattern shows the formation of a single phase perovskite structure without any other impurity phase. The sharp and well-defined peaks confirm that the material is poly-crystalline in nature. The Rietveld refinement of the XRD pattern was performed using the Full Proof Software package to find out the structural parameter such as lattice parameters, Rp, Rwp, χ^2. Rietveld refinement was carried out using the rhombohedral structure with space group *R3m* [6]. A close match between the experimental and simulated data(as shown in Fig. 1)with the goodness of fit χ^2= 3.89suggests the synthesis of high-quality materials. The obtained cell parameters are a=b=5.6770(3) Å, c=6.9509(6) Å with a unit cell volume of 194.005 Å^3. The inset of Fig. 1 shows the FESEM micrograph of the pellet sintered at 1450 $^\circ$C. The micrograph shows a highly dense microstructure with an inhomogeneous distribution of grain size. The average grain size of the material was found to be around 1.5-2 μm which was calculated using the line intercept method.

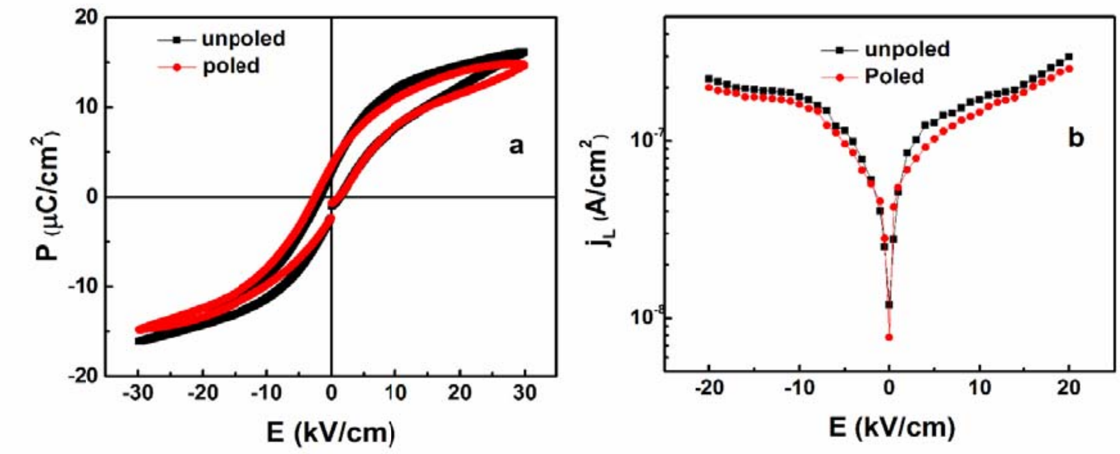

FIGURE 2. (a) Room temperature hysteresis loop (b) Leakage current as a function of electric field of 0.7BZT-0.3BCT

The room temperature hysteresis loop of 0.7BZT-0.3BCT is shown in Fig. 2(a). A well-defined slim hysteresis loop was observed for both poled and unpoled sample. From the hysteresis loop, the remnant polarization 2Pr = Pr^{+0} - Pr^{-0} and coercive field Ec= (Ec^{+0} - Ec^{-0})/2 are calculated for both the poled and unpoled sample. At lower electric field the polarization value is small because it required a sufficient high field to align all dipoles along the direction of applied field. When a sufficient amount of high field is applied the polarization value increases. After E-poling to the sample a well saturated hysteresis loop is observed. This is due to the reduction of vacancy by free charge carriers which make the octahedra more stable results in the enhancement of net dipole moment along the applied field. The E-poling weakens the pinning of domain wall and defect which may be an important factor to get a saturated loop [7]. The 2Pr and Ec values are found to be around 5.78μC/cm^2, 1.66kV/cm and 5.38μC/cm^2, 1.59kV/cm for unpoled and poled sample respectively which is close to previously reported value [3].This low value of the coercive field indicates that the material is a soft ceramic.

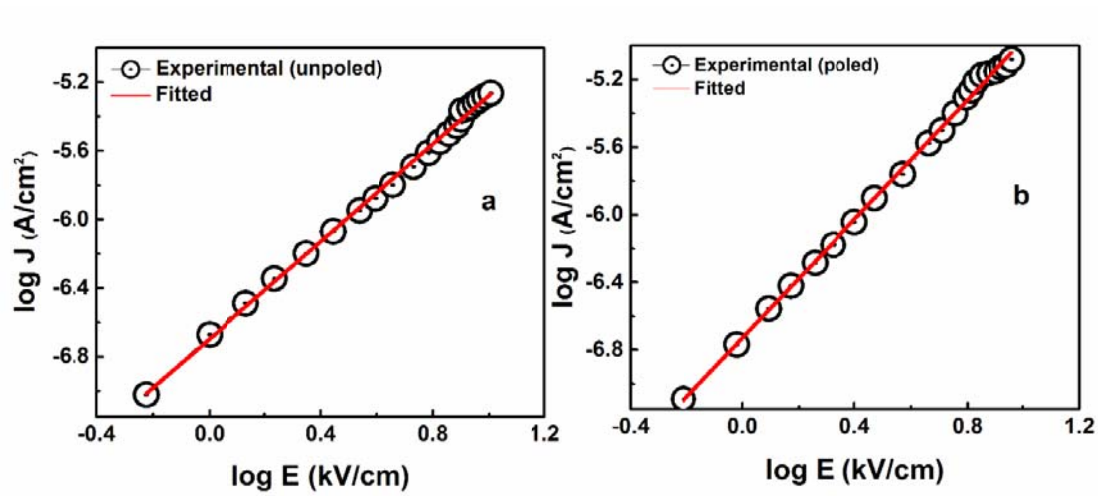

FIGURE 3. Fitting of SCLC mechanism of (a) Unpoled (b) Poled sample of 0.7BZT-0.3BCT

The room temperature leakage current behavior as a function of applied electric field (E) is shown in Fig. 2(b). The leakage current is nearly symmetrical for both side of the applied field for both poled and unpoled sample.At lower field the leakage current increases sharply while its value is nearly constant above 10kV/cm. After poling the sample, the leakage current decreases. This indicates that the electrical poling reduces the oxygen vacancy by free charge carriers and the defects are trapped in grain and grain boundaries.To further investigate the current conduction mechanism, three mechanisms have been taken into account i. e. Poole-Frenkel (PF),Schottky emission (SE), and space charge limited current conduction mechanism (SCLC) [7]. We have fitted the experimental data for the above three conduction mechanism, in which the best fit has been observed for the SCLC mechanism. To validate the SCLC mechanism, the experimental data were fitted by using eq. (1) as shown in Fig. 3(a) and (b)

$$J_{SCLC} = \frac{9}{8d}\mu_p \varepsilon_r \theta E^2 \qquad (1)$$

Where E= electric field, ε_r= dielectric constant of the material, ε_0= dielectric constant in free space, μ_p= mobility of the charge carriers and θ=ratio between the total induced free charge carriers to the trapped charge carriers. The experimental data must be in complete agreement with the straight line fits based on the differenttransport phenomena, and theoretically, the slope of the curve shows the optical dielectric constant of the materials.The slope of the curve for the unpoled sample is found to be around 1.5 while for poled sample its value is around 2. These value of slope favors the SCLC mechanism and the current conduction mechanism is due to the discrete charge carriers.

CONCLUSION

The sol-gel auto combustion technique was successfully utilized for the preparation of ferroelectric 0.7BZT-0.3BCT. Structural studies and Rietveld refinement confirmed the formation of single phase perovskite structure without any impurity phases. The microstructural studies demonstrates the inhomogeneous distribution of grain size with highly dense microstructure. The electrical poling reduces the leakage current, and improved the ferroelectric properties.

ACKNOWLEDGMENTS

Smaranika Dash acknowledges Ministry of Human Resource Development, India for the research fellowship.

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