International Journal of Electronics and Communication Engineering (IJECE)
ISSN(P): 2278-9901; ISSN(E): 2278-991X
Vol. 4, Issue 5, Aug - Sep 2015, 1-8

International Academy of Science, Engineering and Technology
Connecting Researchers; Nurturing Innovations

DIELECTRIC STUDY OF $BaZr_{0.5}Ti_{0.5}O_3$ FERROELECTRIC RELAXOR CERAMIC

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ABSTRACT

The nanoparticle of barium zirconate titanate (BZT) ceramic was synthesized by solid state reaction method at 1200°C. Single perovskite phase having cubic symmetry is confirmed by X-Ray Diffraction. There are two transition temperatures present around 200K and 330K. The dielectric properties reveal that BZT is a relaxor ferroelectric confirmed by diffusion of two phases (tetragonal and cubic phase). The dielectric constant of BZT ceramics exhibited broad peaks curve near the Tm. This behavior may be caused by the inhomogeneous distribution of Zr^{4+} ions into the Ti sites and/or by the mechanical stresses on the grains. The broadness indicates the diffuse phase transition from ferroelectric to paraelectric phase. That is to say, there is diffuse transition behavior in $BaZr_{0.5}Ti_{0.5}O_3$ ceramics.

KEYWORDS: XRD, Dielectric Constant, Ferroelectric, Relaxor

INTRODUCTION

Relaxor ferroelectric materials have the considerable attention due to the wide applications in the electromechanical transducers, acoustic sensors and multilayer capacitors and medical ultrasonic etc. [1, 2]. The piezoelectric property of these materials facilitate in the field of sensing and actuating elastic changes. Barium titanate ($BaTiO_3$) is the most common ferroelectric oxide in the perovskite ABO_3 structure, which is used as a capacitor because of its high dielectric constant [3, 4, 5]. In order to reduce the dielectric loss at low frequencies, ZrO_2 was doped into $BaTiO_3$ to form barium zirconate titanate ($BaZr_xTi_{1-x}O_3$) [6]. BZT has attracted great attention for its potential applications for the microwave technology [9, 10], due to its high dielectric constant, low dielectric loss and large tunability [11]. In recent years, many studies are focused on preparation, microstructure and dielectric properties of BZT materials [7, 8 and 12]. The conventional preparation of BZT ceramics is solid state reaction between oxides and carbonates at high temperature. The method requires repeated cycles of mixing respective oxides and calcinations at high temperature to achieve complete phase formation. Moreover, the powders are easily agglomerated and often contaminated by impurities incorporated from grinding media or incomplete reactions, and the grain size of the ceramics is inhomogeneous. When Zr content increases up to $x \sim 0.20$ is observed the limit between ferroelectric/relaxor behavior [13, 14]. Ravez and Simon [15] reported a typical relaxor like behavior in BZT ceramics with Zr content up to $x \geq 0.25$. Tang et al. [16] showed that the BZT ceramics with a high Zr content ($x = 0.30$ and 0.35) present a ‘‘slim’’ hysteresis loop, which is a typical relaxor ferroelectric behavior due to the existence of micro polar regions. BZT presents good dielectric properties due to its low dielectric loss and reasonable dielectric constant [17-19]. The microwave dielectric properties of this material are interesting for the development of capacitive and nonvolatile memory cells (DRAM’s and FeRAM’s) [20–22].

Experimental

The nanoparticle of barium zirconate titanate was prepared by solid state reaction method. The mixture of barium carbonate ($BaCO_3$), zirconium dioxide (ZrO_2) and titanium dioxide (TiO_2) were mixed together in 1:0.5:0.5 molar ratio and

ground for 7 hrs with a mortar and pestle to prepare barium zirconate titanate. Wet mixing was done with ethanol to obtain a homogeneous powder mixture. This was followed by pre-sintering in a furnace for 5 hrs at 600 °C and then reground before final sintering at 1200 °C for 5 hrs. The dry mixtures were granulated by adding 4 wt % polyvinyl alcohol(PVA) binder, and pressed into pellets having thickness of 1-2 mm and the diameter of 10 mm by applying a pressure of 10 MPa. The pellets were dried at 100 °C for overnight and finally sintered in closed double crucibles at optimized temperature of 1100 °C for 4 h with a heating rate of 5°C/min and natural cooling rate. The X-ray diffraction (XRD) pattern was recorded using D8-Discover system of M/s Brucker (Germany), equipped with Cu-K_α radiation (λ=0.154 nm) with scan step of 0.002^0 and a counting time of 0.5s/step in the range of 2θ=20-80^0. The dielectric properties of the samples were measured with an Agilent 4285A precision LCR meter in the frequency range 20 kHz to 2MHz.

RESULTS AND DISCUSSIONS

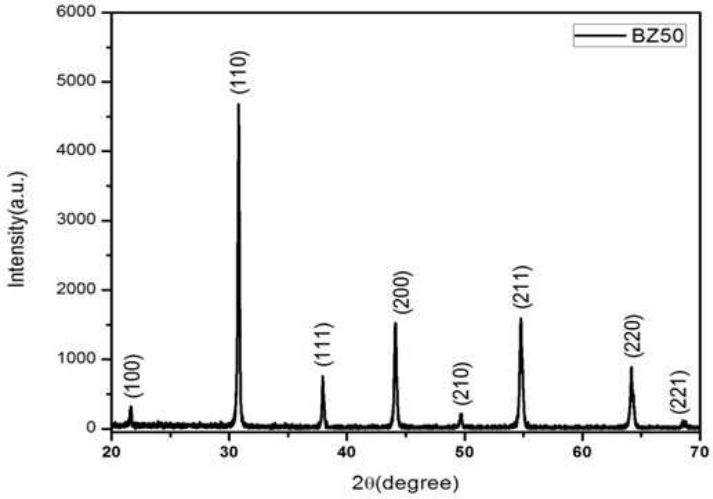

Figure 1: XRD Pattern of Bazr$_{0.5}$Ti$_{0.5}$O$_3$ Ceramic

X-Ray Diffraction Analysis

The XRD patterns of the $BaZr_{0.5}Ti_{0.5}O_3$ nanoparticles after final sintering at 1200 °C are shown in the figure 1. It shows the pure phase formation of the BZT nanoparticles.

The composition $Ba(Ti_{0.5}Zr_{0.5})O_3$, was indexed in cubic system (space group Pm-3m) and the pattern was very similar to the standard PDF-2 card No. 36-0019 (for Cubic $Ba(Ti_{0.75}Zr_{0.25})O_3$). It has been suggested that the solid solution Ba $(Ti_{1-x}Zr_x)O_3$ does not exist for x>0.42 [26]. However, in the present investigation the solid solution $Ba(Ti_{0.5}Zr_{0.5})O_3$ was found to exist as a single phase perovskite.

The crystallite size was determined by using the Scherrer formula [13] form the most instance peak (311)

$$D = \frac{0.9\,\lambda}{B\cos\theta} \tag{1}$$

Where λ is the wavelength of X-ray used, θ is the Bragg's angle, β is the full width at half maximum (FWHM) in radian. The lattice parameter for this cubic system was estimated by using the relation:

$$\frac{2sin\theta}{\lambda} = \frac{1}{a}\sqrt{(h^2 + k^2 + l^2)} \tag{2}$$

Specific surface area (surface area per unit mass) can be calculated by the following relation

$$S = \frac{6000}{D\rho_x} \tag{3}$$

Where D is the crystallite size, is the X-ray density.

The X-ray density was calculated by using the formula

$$\rho_x = \frac{ZM}{NV} \tag{4}$$

Where M is the molecular weight of the samples, N is the Avogadro number, a is the lattice constant and 5 stands for the number of formula units in a unit cell.

The lattice parameters for the BZT ceramic were a = b = c = 4.1005 A that confirms the cubic structure. The crystallite size of the calcinated powder is calculate by Scherrer formula and found to be 55.31±0.01 nm. The strain found 1.2×10^{-3} and the X-ray density is 6.56 gm/cm^3.

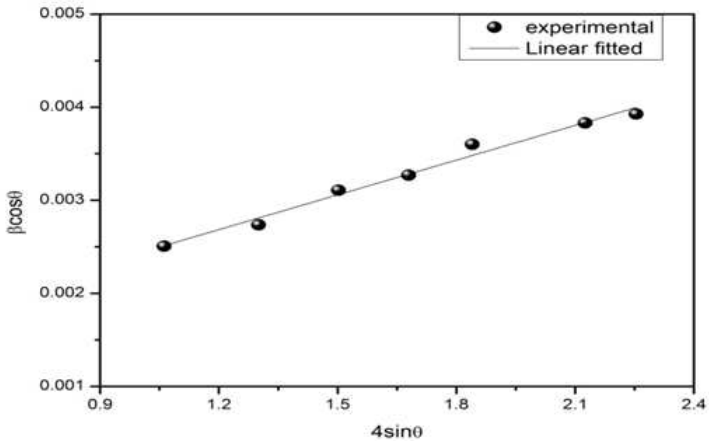

Figure 2: W-H Plot of $BaZr_{0.5}Ti_{0.5}O_3$ Ceramic

The ceramic compositions were synthesized in the present study through successive calcinations and long time sintering etc. These processing may be responsible for the formation of a single phase solid solution of the same.

Dielectric Analysis

Figure 3 shows the temperature dependences of dielectric constant of the BZT ceramic in the frequency range 20Hz to 2 MHz. Firstly, it can be found that the Curie temperature (T_C), corresponding to the maximum relative permittivity(ε_{max}), of the BZT ceramic is 300K. . There is low temperature transition is also visualized near around 160 K having a broad peak. The dielectric constant increases with increasing temperature and decreases as we go to higher frequency range.

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \tag{5}$$

Figure 3 shows that the value of ε' increases gradually to a maximum value (T_m) with increase in temperature up to the transition temperature and then decreases smoothly, indicating a phase transition. The maximum of dielectric permittivity, ε'_{max} and the corresponding temperature maximum T_m, depend upon the measurement frequency. The magnitude of dielectric constant decreases with increase in frequency and the maximum is shifting to higher temperature.

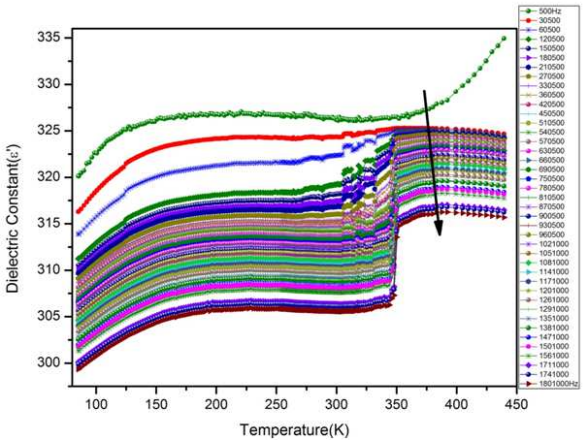

Figure 3: Dielectric Constant Behaviour of Samples in the Temperature Range 80K To 450K at Different Frequencies

Dielectric tangent loss (tanδ) was calculated using the relation

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (6)$$

As shown in Figure 4, the dielectric loss values of the ferroelectric phase were reduced substantially at room temperature in the paraelectric phase (above T_m). The imaginary part of the spectrum shows that there is an increase in dielectric loss peak temperature with increase in frequency. This indicates that the dielectric polarization is of relaxation type in nature such as dipolar glasses. In analogy with spin glasses, such a behavior of the dynamic susceptibility in disordered ferroelectric is supposed to be concerned with the existence of the broad spectrum of relaxation times. It is generally considered that the Debye model is based on the assumption of a single relaxation time. The model fails because of the existence of a distribution of relaxation times. Such a distribution of relaxation time implies that the local environment seen by individual dipoles differs from site to site. This is a reasonable assumption in amorphous materials. As a rule [23], this relaxation occurs in disorder ionic structures, particular, in solid solutions.

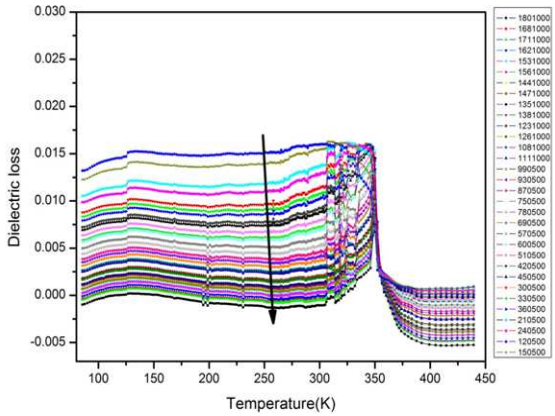

Figure 4: Dielectric Loss Tangent (tanδ) Behaviour of the Samples in the Temperature Range 80K to 450K

The result indicates that there is diffuse phase transition in the BZT ceramics. Diffuse phase transition is generally characterized by broadening of the dielectric constant maximum at the transition temperature, a large separation between the maxima of dielectric constant and dielectric loss and a deviation from the Curie-Weiss law in the vicinity of T_C [24]. It is known that the dielectric permittivity of a normal ferroelectric above the Curie temperature follows the Curie-Weiss law described by

$$1/\varepsilon = (T - T_0)/C \quad (T > T_C) \tag{7}$$

Where T_0 is the Curie-Weiss temperature and C is the Curie-Weiss constant.

The change of inverse dielectric constant with respect to temperature is shown in Figure 5. It can be seen that the dielectric behavior doesn't completely follow Curie-Weiss law at temperatures above the critical point (T_C). According to Curie-Weiss law, the Curie-Weiss temperature can be obtained from linear extrapolation of inverse dielectric constants in the high-temperature region.

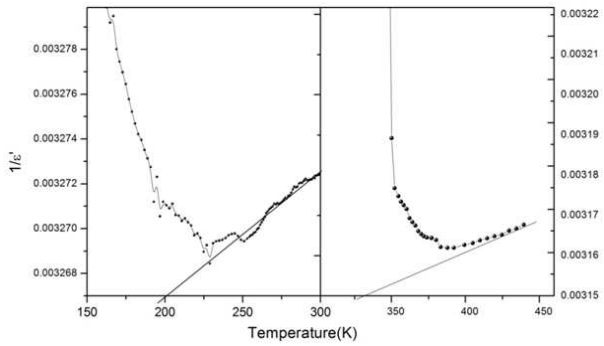

Figure 5: Temperature Dependence of the Inverse Permittivity of the BZT Ceramic Prepared by Solid State Reaction Method

A modified Curie-Weiss law was proposed by Uchino et al. to describe the diffuseness of the ferroelectric phase transition as [25]:

$$1/\varepsilon - 1/\varepsilon_m = (T - T_m)^{\gamma} / C' \tag{8}$$

Where γ and C' are assumed to be constant, ε_m and Tm represent dielectric constant maximum and the

corresponding temperature, γ is diffuseness constant. The parameter γ gives information on the character of relaxor ferroelectric material: for γ = 1, a normal Curie-Weiss law is followed i.e. a normal ferroelectrics, whereas γ = 2 describe a complete diffuse phase transition i.e. typical relaxor ferroelectrics. The plots of $\ln(1/\varepsilon-1/\varepsilon_m)$ as a function of $\ln(T-T_m)$ for the BZT ceramics prepared by two methods are shown in Figure 5. A linear relationship is observed. The slope of the fitting curves by Eq. (8) is used to determine the γ value.

The value of diffuseness constant γ is 1.74 which confirms the relaxor nature of BZT ceramic.

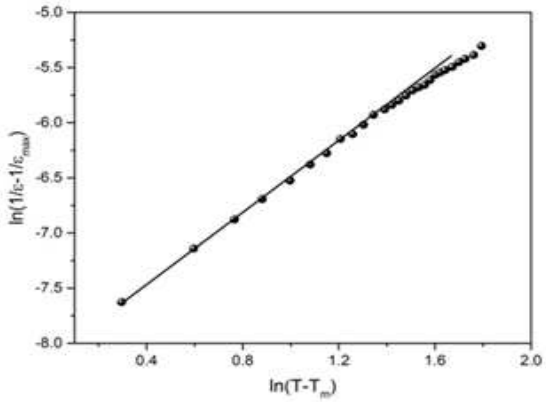

Figure 6: Dependence of ln $(1/\varepsilon-1/\varepsilon_m)$ on ln$(T-T_m)$ at 1.5MHz

The broadened dielectric maximum (in **ε**' vs temperature curve) and its deviation from Curie–Weiss law are the main characteristics of a diffuse phase transition of the material. The diffuse phase transition and deviation from Curie-Weiss type law may be assumed to be due to disordering.

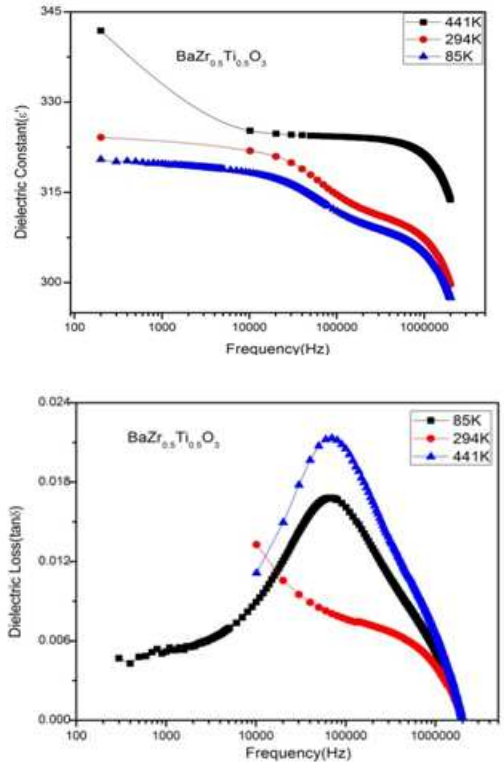

Figure 7: Dielectric Constant and Dielectric Loss Tangent (Tanδ) Behaviour of the BZT Ceramic in the Frequency Range 75 Khz To 2mhz for Different Temperature (85, 294 And 441K)

Figure 7 shows the frequency dependency of dielectric constant and dielectric loss of $BaZr_{0.5}Ti_{0.5}O_3$ ceramic. The dielectric constant decreases with increasing frequency. The dielectric constants for all the temperature were very stable in the frequency range 1 kHz to about 1 MHz. In general, dielectric constant decreases due to the decrease in polarizability of the atoms in the structure. At high frequency, a dielectric loss peak is observed. As mentioned earlier, several possible causes exist for such dispersion including the hypothesis of the influence of the contact resistance between the probe and electrode, and resonance due to high dielectric constant. Similar frequency dispersion behavior was also reported for other ferroelectric materials [27,28]. This behavior is verified by changing the electrode area.

CONCLUSIONS

The BZT ceramic was prepared by solid state reaction method at 1200 °C. The prepared BZT ceramic have single perovskite phase with cubic symmetry. There are two transitions found in the dielectric behavior of BZT ceramic one is near 200K and other is 330 K. The diffuseness constant is greater than 1 which indicates the relaxor ferroelectric behaviour. Moreover, the dielectric properties and ferroelectric phase transition temperature (T_m) of BZT ceramics are strongly dependent of Zr content in the lattice.

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