MICROSTRUCTURAL AND ELECTRICAL STUDY OF

$(Ba_{0.6}Sr_{0.4})$ $(Zr_{1-X}Ti_X)O_3$ CERAMICS

C M Tawade[1], Shivanand Madolappa[2], Nagbasavanna Sharanappa[3], and R. L Raibagkar[4]

[1]*Department of Electronics & Communication Engineering, Bheemanna Khandre Institute of Technology, Bhalki-585328, Karnataka State, India*
[2]*Materials Research Center, Indian Institute of Science Bangalore, Karnataka State, India*
[3]*Department of Post Graduate Studies and Research in Materials Science, Gulbarga University, Gulbarga-585106, Karnataka State, India*
[4]*Department of Post Graduate Studies and Research in Materials Science, Gulbarga University, Gulbarga-585106, Karnataka State, India*
[4]*Author for correspondence: **rlraibagkar@rediffmail.com***
Contact details: Tel. +91-8472-263295; Fax: +91-8472-263206

Abstract

Ceramics of $(Ba_{0.6}Sr_{0.4})(Zr_{1-x}Ti_x)O_3$ (x=0.40,0.50) samples were prepared by solid state reaction method. Micro structural study was performed by scanning electron microscope revealed the particle sizes are in the range of 0.8 µm. The structures are irregular in shape. Dc resistivity property was studied with respect to temperature from room temperature to 673 K. temperature of maximum resistivity (T_{max}) are around 443 K and 378 K. dc dielectric constant, ac dielectric constant and dielectric loss were studied with respect to temperature from room temperature to 673 K at 100 Hz frequency. At higher temperature the dielectric constant of BSZT40 and BSZT50 is high. In the low frequency range dissipation factor is determined by the influence of ion conductivity.

Index Terms: Ceramics, Barium Zirconate, Microstructure, DC Resistivity, Dielectric Constant and Dielectric loss

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1. INTRODUCTION

Since the discovery of ferroelectric properties in $BaTiO_3$, a large number of ferroelectrics with the perovskite structure having a general formula ABO_3 perovskite has extensively been studied in search for new materials for device applications[1-2]. The growing interest in search of suitable materials for device has led to the development of large number of complex ferroelectric ceramics with a wide variety of composition and stable structure. $BaTiO_3$ –based solid solutions are environment friendly dielectrics with similar performances by as many Pb-based electro ceramics. Their properties can be tuned by composition and controlling their micro structural characteristics (porosity level, grain size, secondary phases, core-shell structures, etc.).

It is well known that $SrTiO_3$ forms solid state solution with $BaTiO_3$ without much decrease in dielectric permittivity [2] The Sr ion may take 12 co-ordination sites with eight near neighbors and four more distant ones. This modification assumes opposite displacement of Sr ion out of dodecahedron centre and is able to induce a dipolar moment whose occurrence leads to modification of Tc. $BaSrTiO_3$ have currently become very attractive for applications in decoupling capacitors, storage capacitors, and dielectric field tunable elements for high-frequency devices [3,4]. The high dielectric constant and low loss makes one of the promising candidates for dynamic random-access memory (DRAM) and tunable microwave device applications [5].

Barium zirconate titanate $BaZr_xTi_{1-x}$ O_3 [6-7] as an important member of the $BaTiO_3$ - based ferroelectric materials family , has been chosen as an alternative to $(Ba_{1-x}Sr)TiO_3$ solid state solution for tunable microwave applications. $BaZr_xTi_{1-x}O_3$ ceramics present high voltage resistance characteristics because Zr^{4+} is chemically more stable than Ti^{4+}. Furthermore $BaZr_xTi_{1-x}O_3$ ferroelectric in the paraelectric state reveals relatively more outstanding temperature stability compared with $(Ba_{1-x}Sr)TiO_3$ [7,8]. $BaZr_xTi_{1-x}O_3$ (BZT) system is one of the most attractive materials due to its phase formation mechanism [9, 10] local polar characteristics [11] and dielectric/tunable properties for microwave applications [12, 13]. $BaTiO_3$(BT) is known to form complete solid state solution with $BaZrO_3$ (BZ).It has been reported [14] that at 15 atoms Zr substitution the three transition temperatures of $BaTiO_3$, rhombohedra to orthorhombic ,orthorhombic to tetragonal and tetragonal to cubic, merge near room temperature and the doped material exhibits enhanced dielectric constant. Due to their novel properties of Sr doped $BaTiO_3$ and $BaZrTiO_3$, inspired us to work on micro structural, electrical and dielectric properties of $(Ba_{0.6}Sr_{0.4})(Zr_{1-x}Ti_x)O_3$ ceramics.

2. MATERIALS AND METHOD:

Ceramic powders of $(Ba_{0.6}Sr_{0.4})(Zr_{1-x}Ti_x)O_3$ (x=0.40, and 0.50) were prepared by conventional solid state reaction method from weighed amounts of Barium carbonate ($BaCO_3$; M/s. s. d. fine-chem. Ltd, Mumbai, India, purity 99.99%), Strontium carbonate ($SrCO_3$), Zirconium oxide (ZrO_2) and Titanium oxide (TiO_2) (all HiMedia, India, purity 99.99%). The starting materials were ground for 4 hrs and calcined at 1273 K for 12 Hrs. They were further ground for 2 hrs and subjected for pre-sintering at 1273 K. This product obtained was again ground for 2hrs and pressed into circular shaped disc pellets (diameter 10 mm and thickness 2-3 mm) using 5% PVA as a binding agent. Pellets were sintered at 1273 K for 8 hrs. The morphology of the sintered pellets was investigated by scanning electron microscope (SEM) using JSM/8048/SM, JEOL, Japan. Behavior was studied using Wayne Kerr 4300 LCR meter with variation of temperature range from room temperature to 800 K at 100 Hz frequency range.

3. RESULTS AND DISCUSSION:

A) Microstructure Study:

Structural details of the samples are discussed elsewhere [15]. Figure 1 displays the scanning electron micrographs of the synthesized samples. The average grain size was calculated by line intercept method and is given in Table I.

Grain Size=1.56 C/M*N
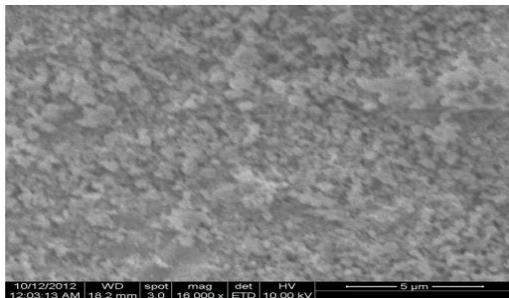
a) BSZT 40
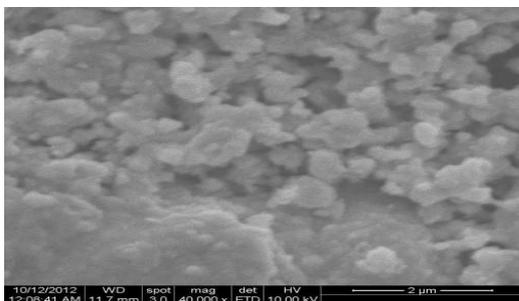
b) BSZT 50

Fig1. SEM micrographs of a) BSZT40 and b) BSZT50 Ceramic samples.

Table 1: Grain size, electrical and dielectical data of $(Ba_{0.6}Sr_{0.4})(Zr_{1-x}Ti_x)O_3$ ceramics

Composition (X)	Grain size in μm	Dc resistivity In Ω cm⁻¹			Dc dielectric		AC dielectric constant at 100 Hz		
		ρ_{RT}	ρ_{Tc}	T_c in K	ε_{RT}	ε_{max}	ε_{RT}	ε_{max} x10^4	T_c
0.40	0.81	7.55	1295	443	215	266	3108	5.536	743
0.50	0.80	7.55	1712	378	211	238	3108	2.757	713

Where C is the length of the scale, M is magnification of the micrograph and N is number of intercepts of grains. As a result of co-doping, abnormal grains were observed in ceramic samples. The grain size of BSZT40 and BSZT50 is almost same. The concentration of Ti increases there is no change in the grain size as shown in the figure. This is due to Zr^{4+} rich and stronger than Ti^{4+} ions and may be the low sintering effect. The structures are irregular in shape. The formation of large grains with irregular shapes could be a result of the variations on the kinetics of movement from boundary to boundary, since the grain-boundary energy is dependent on the grain-boundary orientation and grain-boundary mobility [16]. An average grain size observed from the SEM images is bigger than the one calculated from the Scherrers' equation.

B) Electrical Study

The dc resistivity of the sample as a function of temperature for SBZT40 to SBZT50 samples is plotted in figure 2. Resistivity parameters estimated from plot are summarized in Table 1. The temperature of maximum resistivity (T_{max}) for the SBZT40 and SBZT50 to ceramics was around 443 K and 378 K above 513 K. Resistivity increases with increase in temperature up to 443 K and 378 K a then the linear decrease in resistivity as a function of temperature is due to the oxygen vacancies, which act as mobile charge species, creating free electrons. The low resistivity at high temperature is due to desorption of chemisorbed oxygen atoms at the grain boundaries upon heating, resulting in a decrease of potential barrier height.

It is considered that the microstructure variation by doping can affect the electrical resistivity [17]. Lowly doping can reduce the electrical resistivity by charge compensation and carrier generation; where as highly doping (excess doping) can cause to raise the resistivity by grain boundary pinning and grain refinement as well as increase and overlapping of potential barrier at grain boundaries.
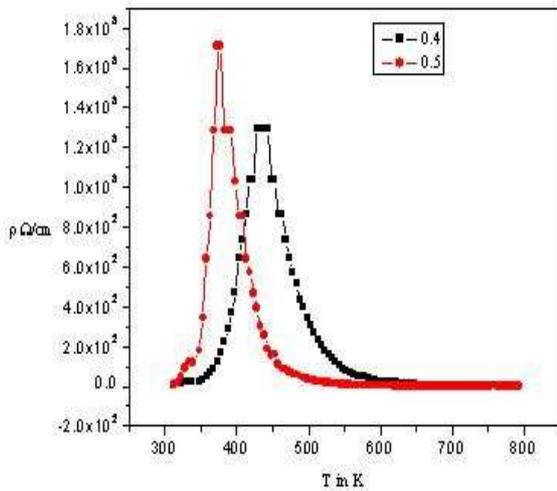
Fig2. DC resistivity as a function of temperature

Figure 3 represents the temperature dependence of dielectric constant was measured from room temperature to 673 K in the dc field. Dielectric parameters estimated from plot are summarized in Table 1. As the temperature increases dielectric constant is also increases. At higher temperature the dielectric constant of BSZT40 and BSZT50 is high. The concentration of Ti increases there is decrease the value of dielectric constant. This is may be due to the irregular grain size of the samples as shown in SEM micrographs. Since the charge hopping is thermally activated process, dielectric polarization increases with increase in temperature resulting in increase of ε_r.

Figure 4 shows the variation of dielectric constant (ε_r) as a function of temperature for from room temperature to 800 K at frequency at 100 Hz forBSZT40 and BSZT50 ceramics. At higher temperature above 523 K, εr increases up to phase transition temperature and then decreases which is the normal behavior of most of perovskite materials. The initial value for ε' at the lower temperature range is responsible for the polarization caused by ionic conduction, while the behavior of εr at the higher temperature range is characteristic of dipolar relaxation. The frequency dependant dielectric behavior illustrates no dielectric dispersion, which may be due to the orientation polarization. The increase of εr is mainly because of the domain contribution. The high value of εr at higher temperature can be explained by the temperature dependent characteristic of domain wall motion and/or the increase in the drift mobility of electron [18]. At low temperature, domain movement is intricate so that the extrinsic role of domain walls to the dielectric response is small. At low temperature, domain movement is intricate so that the extrinsic role of domain walls to the dielectric response is small.
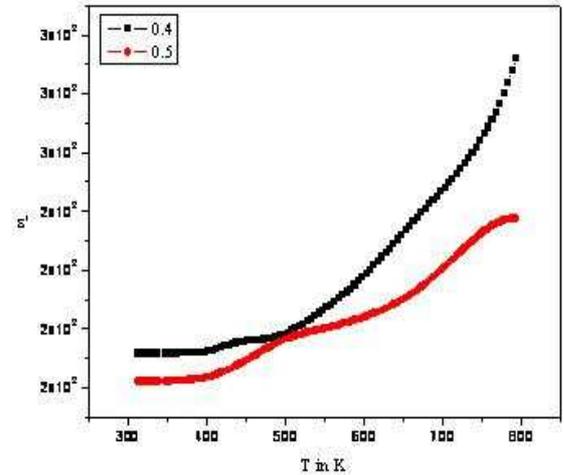
Fig3. DC dielectric constant as a function of temperature of BSZT40 and BSZT50
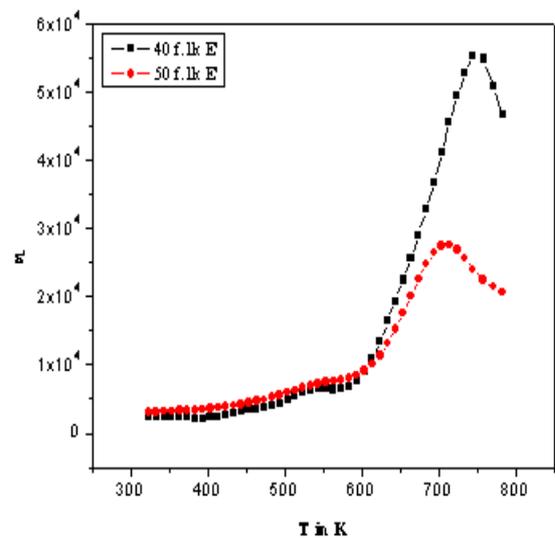
Fig4. AC dielectric constant as a function of temperature at 100 Hz frequency of BSZT40 and BSZT50 ceramic sample

Figure 5 shows the frequency dependence of the dissipation factor (tanδ) for all the studied samples. All the samples show the same behaviour where tanδ increases with increasing temperature maxima are observed in the studied temperature range. In the low frequency range tanδ is determined by the influence of ion conductivity.
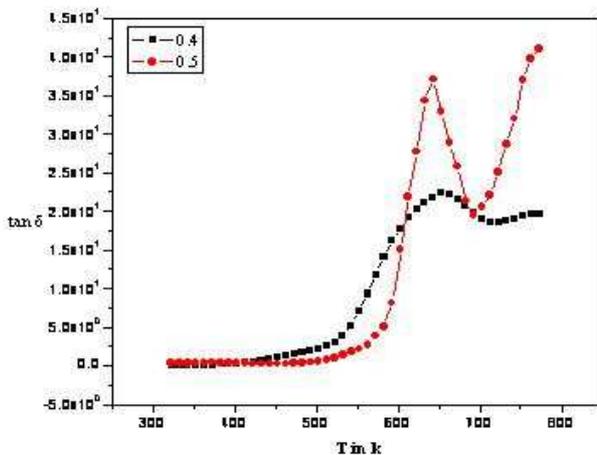
Fig5. Dissipation factors as a function of temperature at 100 Hz of BSZT40 and BSZT50 ceramic sample

CONCLUSIONS

The samples BSZT40, BSZT50 were synthesized by solid state reaction route. Microstructural study was performed by SEM which reveals the particle sizes are irregular in shape and are in the range of around 0.8 micrometer. Temperatures of maximum resistivity (T_{max}) are around 443 K and 378 K. The dielectric constant is very high these samples are used for storage capacitors. In the low frequency range dissipation factor is determined by the influence of ion conductivity.

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