



Sol-Gel Derived Barium Strontium Zirconate Titanate (Ba_{0.8}Sr_{0.2})(Zr_{0.2}Ti_{0.8})O₃ Powder and Ceramics

Manisha Chawla

Department of Physics, Zakir Husain Delhi College, University of Delhi, New Delhi

Monika Rawat

Department of Physics, Zakir Husain Delhi College, University of Delhi, New Delhi

Seema Rawat

Department of Physics, Zakir Husain Delhi College, University of Delhi, New Delhi

M. Fahim

*Corresponding author, Department of Physics, Zakir Husain Delhi College, University of Delhi, New Delhi

ABSTRACT

Barium strontium zirconate titanate (Ba_{0.8}Sr_{0.2})(Zr_{0.2}Ti_{0.8})O₃ [(Ba+Sr):(Zr+Ti) = 1:1] powder and ceramics were prepared using a sol-gel chemical route. BSZT ceramics prepared from the sol-gel derived powder were characterized for their structural, morphological, dielectric and ferroelectric properties. Temperature and frequency dependent dielectric properties were measured for these ceramics in the temperature range 30 to 200°C and at different frequencies of 100 Hz, 120 Hz, 1 kHz, 10 kHz, 20 kHz and 100 kHz. It was observed that ferroelectric to paraelectric transition temperature (T_c) reduced from ~120°C for pure Barium titanate (BaTiO₃) to around 20-30°C with the addition of strontium. Furthermore the addition of zirconium helped in increasing the dielectric constant at all frequencies. A well defined ferroelectric loop was observed for the ceramic. Remanent polarization (P_r) value of 0.5121 μC/m² was obtained for the sample at room temperature.

KEYWORDS : Barium strontium zirconate titanate, dielectric and ferroelectric properties, XRD, SEM

1.0 Introduction

Barium strontium titanate (Ba_{1-x}Sr_xTiO₃) (hereafter called BST) is one of the most important perovskite ferroelectrics that has been widely studied because of its moderate to high dielectric constant and adjustable ferroelectric to paraelectric phase transition temperature (depending on the value of x) that are a pre-requisite for application of ferroelectric material as capacitors [1–3]. The dielectric behavior of BST can be modified not only by controlling the Ba/Sr ratio but also through partial substitution of isovalent or aliovalent cations for A-sites and/ or B-sites in ABO₃ type perovskite system [4]. These partial substitutions and their influence on the structural and dielectric properties of BST ceramics have been extensively researched in the recent years. For instance, Huang et.al. [5] reported that Dy₂O₃-doped BST capacitor ceramics showed high permittivity (ε = 5245), low dielectric loss (tan δ = 0.0026) and high DC breakdown voltage (E_b = 5.5 MV/m) as compared to undoped BST. According to Zhao et al [6], comprehensive properties (ε = 3658, tan δ = 0.0093, Δε/ε = 14.1%) were obtained in Y₂O₃ and Dy₂O₃-doped BST ceramics. Li et al [7] reported that there was an alternation of substitution preference of Y³⁺ ions for the host cations in perovskite lattice. When the doping concentration is increased up to 0.5% (mole fraction) then Y³⁺ ions tend to occupy the B-sites, causing a drop in the dielectric constant. In the case of La₂O₃ addition, it has been reported that La³⁺ ions dissolved in the A-sites and effectively suppressed the grain growth of BST ceramics [8]. In the case of La₂O₃- and Sb₂O₃ co-doped BST ceramics, it has been reported that the ceramics exhibit typical perovskite structure and the average grain size decreases dramatically with increase in the content of Sb₂O₃ [9]. Both La³⁺ ions and Sb³⁺ ions occupy the A-sites in perovskite lattice. The tetragonal to cubic phase transition of La₂O₃ modified BST ceramics was of second order and the Curie temperature shifted to a lower value with increase in the La₂O₃ doping content. The phase transition of (La,Sb) co-doped BST ceramics was diffused and the deviation from Curie-Weiss law became more obvious with the increase in Sb₂O₃ concentration. The temperature corresponding to the dielectric constant maximum of (La,Sb)-co-doped BST ceramics decreased with increasing Sb₂O₃ content, which was attributed to the replacement of host ions by the Sb³⁺ ions. Chiou et al [10] reported that the lattice constant ratio c/a and Curie

temperature of BaTiO₃ ceramics also decreased with increasing the Sb concentration. Chan [11] prepared a series of (Ba^xSr_{1-x})(Zr_{0.1}Ti_{0.9})O₃ (x = 0, 0.05, 0.15, 0.25, 0.35, 0.45) ceramics by a conventional solid state reaction method. Thin films of the same composition were also deposited on different substrates. It was reported that with the increase in Sr content, the Curie temperature decreased linearly. However, the grain size also decreased with the increase in Sr content. Remanent polarization also decreased with the increase in Sr content. Badapanda et.al [12] have reported the optical and dielectric relaxor behaviour of Ba(Zr_{0.25}Ti_{0.75})O₃ prepared by solid-state reaction. The temperature dependent dielectric measurement in the frequency range from 1 kHz to 1 MHz indicated a diffused phase transition. The broadening of the dielectric permittivity in the frequency range as well as its shifting at higher temperatures indicated a relaxor-like behaviour for this material. In a similar work, dielectric properties of La/Zr co-doped Ba_{0.67}Sr_{0.33}TiO₃ ceramics prepared from citrate-nitrate combustion derived powders have been reported by Xu et.al. [13], who claimed that the dielectric constant as well as loss decreased with increasing Zr content. However, the additions strongly suppressed the grain growth of BST ceramics. It was also found that the temperature-permittivity characteristics for co-doped BST ceramic could be controlled using various dopant content. Recently new techniques have been reported for the synthesis of BSZT ceramics using chemical route. In the first paper, slip-casting technique for sol-gel synthesised BSZT ceramics have been reported by Chen et.al [14]. Initially sol-gel method was used to synthesise two different Ba_{0.75}Sr_{0.25}Zr_xTi_{0.95}O₃ powders one of high purity and the other of low purity. These two powders were subjected to slip casting followed by a pressureless sintering. Authors observed that there was a large difference in the sintered density and grain size for the pressureless sintered disks. In another paper, zirconium doped Barium strontium titanate Ba_{0.8}Sr_{0.2}Zr_xTi_{1-x}O₃ (x = 0.05, 0.1, 0.15 and 0.2) nanosized powders were prepared by a solvothermal method [15]. Authors claimed that using this method, the average particle size reduced with increasing Zr content and the average particle size was in the range 37-50 nm. Furthermore, Curie peaks in temperature-permittivity graph became broader and shifted towards lower temperature. Dielectric loss also decreased with increasing Zr content. Most of the research works cited above have used solid state

reaction method for preparing BSZT ceramics. Very few papers have reported on the dielectric and ferroelectric properties of BSZT ceramics fabricated using sol-gel derived powders. In the present work, BSZT ceramics were fabricated using sol-gel derived powder prepared using both A-site as well as B-site substitution. Temperature and frequency dependent dielectric properties are being reported in this paper.

2.0 Materials and methods

1.1 Raw material and synthesis of powder and ceramic Sol-gel synthesis of $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ powder and ceramics

The precursors for barium, strontium, titanium and zirconium were respectively barium acetate, strontium acetate, titanium tetrabutoxide and zirconium isopropoxide. All these chemicals were procured from Sigma-Aldrich. Glacial acetic acid [$\text{CH}_3\text{COOH} \geq 99.7\%$] and butyl alcohol [$\text{C}_4\text{H}_9\text{OH} > 99.5\%$] were used as solvents. Barium acetate and strontium acetate were mixed in glacial acetic acid and refluxed for 30 min using a sand bath. Titanium tetrabutoxide and Zirconium isopropoxide were mixed in butyl alcohol. After cooling down to room temperature, the Ba-Sr solution was mixed with Ti-Zr solution using a magnetic blender for 30 min. A small amount of acetylacetone [$\text{CH}_3\text{COCH}_2\text{COCH}_3$] was added as a stabilizer. The sol thus obtained was hydrolysed by adding 10-15 mL of distilled water. The sol was relatively clear and stable. The sol was covered with aluminium foil and kept in a desiccator to avoid air contamination and left overnight for gelation. The sol was still transparent and clear. However, it transformed into an opaque gel upon heating. The gel was then fired in air to obtain amorphous powder. The dry gel was calcined at 850°C for 2h in a muffle furnace to obtain a poly-crystalline powder. The BSZT powder so obtained was milled and die-pressed into thick pellets under a pressure of 300 MPa. These pellets were sintered at 1400°C for 2.5 hrs and 3hrs in a muffle furnace to obtain dense ceramics. The powder and ceramics BSZT were prepared using a procedure given in the flow chart (Fig.2.1).

2.2 Material Characterization

X-ray diffraction

Structural characterization of $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramic sintered for 3 h was done using X-ray diffraction. Figure 2.2 shows a comparison of the X-ray diffractograms of BT, BST and BSZT. The peaks show polycrystalline nature and confirm the formation of BSZT structure.

Scanning Electron Microscopy (SEM)

Morphological properties of $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramic were studied using scanning electron microscope (SEM). The photomicrograph showing the formation of grains is shown in Fig. 2.3.

FT-IR spectroscopy

FT-IR spectrogram of BSZT powder is shown in Fig. 2.4. The peak $\sim 593\text{cm}^{-1}$ is due to TiO_6 octahedral.

Dielectric characterization

AC frequency dependent values of parallel capacitance (C_p) and loss tangent or dissipation factor ($\tan \delta$ or D) of the ceramics pellets were measured using Agilent 423B precision LCR meter. The actual thickness of samples was measured using a micrometer before electroding by application of conductive silver plate using a paint brush. Electroded samples were placed in a sample cell between two electrodes and voltage was applied. The parallel capacitance (C_p) was measured on the LCR meter. Dielectric constant was calculated using the formula:

$$(\epsilon) = C/C_0$$

where, $C_0 (= \epsilon_0 A/d)$ is the capacitance with vacuum between parallel plates and $\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$ is the permittivity of free space, A is the area of electrode sample, and d is the thickness of the sample. Dissipation factor (D or $\tan \delta$) was directly measured on the LCR meter. To calculate ac conductivity, parallel capacitance (C_p) and dissipation factor (D or $\tan \delta$) from 100 Hz up to 100 KHz was measured. $\sigma_{ac}(\omega)$ was calculated by using following expression:

$$\sigma_{ac}(\omega) = 2f\epsilon_0\epsilon'' = 2f\epsilon_0\epsilon'' \tan \delta$$

where $\tan \delta$ is the dissipation factor, $\omega = 2\pi f$ is the angular frequency ϵ' is the dielectric constant ($\epsilon''/\epsilon' = \tan \delta$), and ϵ'' is the dielectric loss.

Ferroelectric characterization

The ferroelectric loop of the sample was obtained using a Sawyer-Tower circuit. The loop was observed on a cathode ray oscilloscope. Figure 2.5a and b respectively show the photographs of ferroelectric loop obtained on BT and BSZT ceramic. Using these loops remanent polarization (P_r) as well as saturation polarization (P_s) were calculated for both BT and BSZT. For BT the P_r and P_s values were $0.0843 \mu\text{Cm}^{-2}$ and $0.1665 \mu\text{Cm}^{-2}$ respectively. In the case of BSZT, P_r and P_s values were $0.5121 \mu\text{C}/\text{m}^2$ and $1.0241 \mu\text{C}/\text{m}^2$ respectively.

3.1 Results and discussion

Temperature and frequency dependent dielectric behavior of $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics sintered for 2.5hrs and 3hrs at 1400°C are shown in Fig. 3.1. Figure 3.1a shows the temperature dependent dielectric constant of $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics sintered at 1400°C for 2.5 hours. It is clear from the figure that the value of dielectric constant does not differ much at room temperature at all frequencies. However, as the temperature is increased, the difference in the values of dielectric constant becomes more prominent at lower frequencies, particularly at Tc. At Tc, at 1 kHz, a high value of around 3400 was obtained for this ceramic. For other higher frequencies the values decreased considerably. Figure 3.1b shows the temperature dependent dielectric loss of the same ceramics. Dielectric loss was found to be below 0.1 at all frequencies close to room temperature. However, at Tc the dielectric loss was also the maximum.

Figure 3.1c shows the temperature dependent dielectric constant of $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics sintered at 1400°C for 3 hours. At Tc, at 1 kHz, a high value of around 3630 was obtained for this ceramic. Thus, a slight increase in sintering time improved the dielectric constant of BSZT ceramic. Figure 3.1d shows the temperature dependent dielectric loss of the same ceramics. Dielectric loss was found to be below 0.1 at all frequencies close to room temperature. However, at Tc the dielectric loss was also the maximum. Temperature dependent dielectric constant and dielectric loss of all the three ceramics measured at 1 kHz are shown in Fig 3.2a and Fig 3.2b respectively. From Fig. 3.2a it is clear that the Tc of BaTiO_3 ($\sim 120^\circ\text{C}$) has shifted to the lower temperatures ($< 30^\circ\text{C}$) for BST samples with addition of Sr content. Furthermore, values of dielectric constant decreased sharply with increase in temperature in paraelectric phase. These trends are in accordance with the reported literature according to which the dielectric constant can be varied by changing the Ba/Sr ratio [16]. It has been reported that dielectric constant increases with decrease in Sr content. Highest dielectric constant is obtained at room temperature when (Ba+Sr)/Ti ratio is 1:1 [17]. BST composition $(\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3)$ exhibits the highest dielectric constant ~ 2000 and Tc $\sim 30^\circ\text{C}$ which is closer to the room temperature. However, when Zr was substituted, dielectric constant reached up to 3600 but Tc remained around room temperature.

Figure 3.3 show the frequency dispersion of dielectric constant (ϵ') of all the three samples measured at room temperature (28°C). It is evident from the figure that $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ shows highest values of dielectric constant at all frequencies.

3.2 Conclusions

Bulk ceramics of Barium strontium Zirconium titanate $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ prepared using fine powders derived from sol-gel method showed that with strontium substitution the ferroelectric-paraelectric phase transition temperature (Tc) shifts to lower temperatures. With a very small addition of Sr ($\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$), a very high dielectric constant ($\epsilon'_{\text{max}} > 2000$) and a low dielectric loss (< 0.1) is obtained at room temperature (25°C). The dielectric constant of BST ceramics shows no frequency dispersion at higher frequencies (1 kHz to 100 kHz). With further substitution of Ti by Zr at B-site, a still higher dielectric constant was obtained.

Acknowledgement

Authors acknowledge the University Grants Commission (UGC), India funding for this work under the Major Project scheme. One of the authors (MC) is grateful to UGC for a Project Fellowship.

Fig. 2.1: Flow chart for the preparation of BSZT powder and ceramic

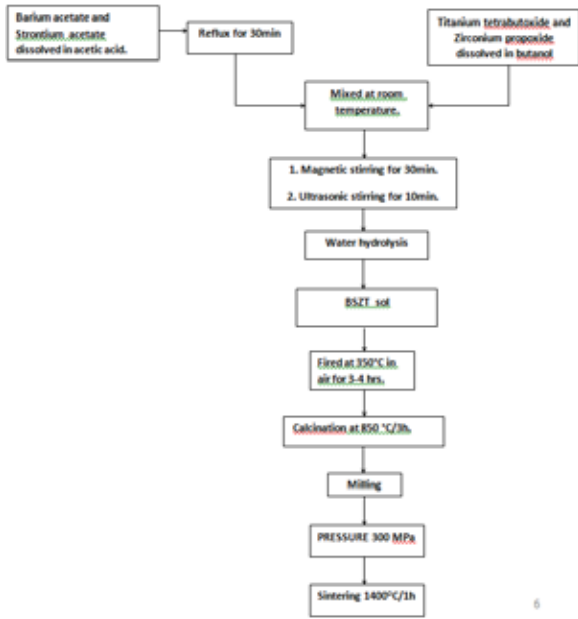


Fig. 2.2 XRD diffractograms of Barium titanate, Barium Strontium titanate and barium strontium zirconium titanate

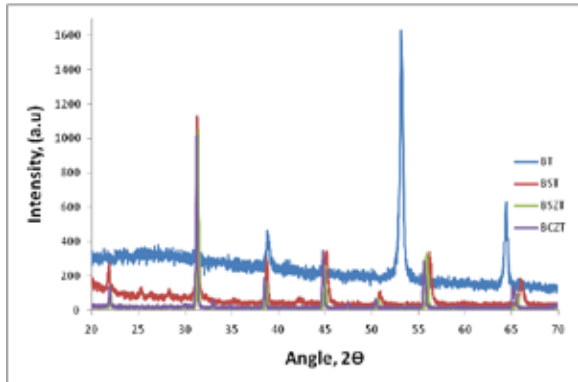


Fig. 2.3: Scanning electron micrographs at two different magnifications showing the grain formation in BSZT ceramics sintered at 1400°C for 1 hr

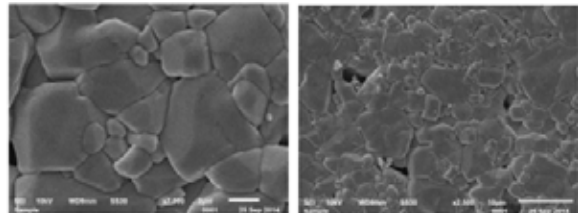


Fig. 2.4: FT-IR spectrogram of BSZT crystalline powder

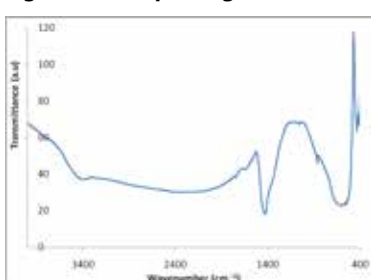


Figure 2.5a and b respectively show the photographs of ferroelectric loop obtained on BT (left) and BSZT (right) ceramics

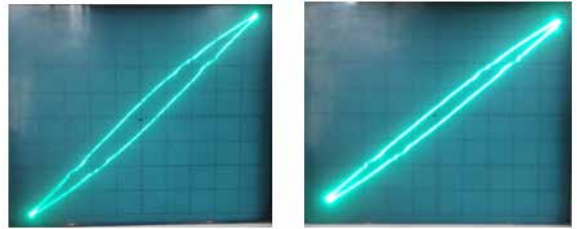


Fig.3.1a Plot of dielectric constant vs temperature for $(Ba_{0.8}Sr_{0.2})(Zr_{0.2}Ti_{0.8})O_3$ ceramics sintered at 1400 °C for 2.5 hrs.

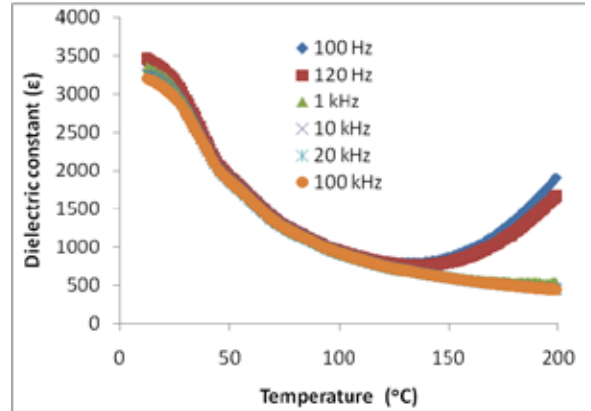


Fig. 3.1b Plot of dielectric loss vs temperature for $(Ba_{0.8}Sr_{0.2})(Zr_{0.05}Ti_{0.95})O_3$ ceramics sintered at 1400 °C for 2.5 hrs.

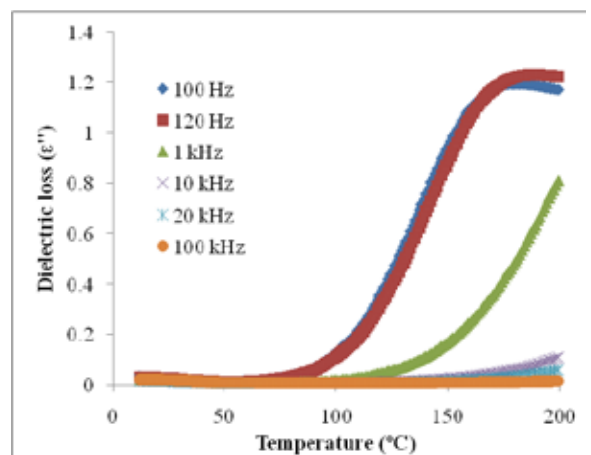


Fig.3.1c Plot of dielectric constant vs temperature for BSZT sintered at 1400 °C for 3hrs.

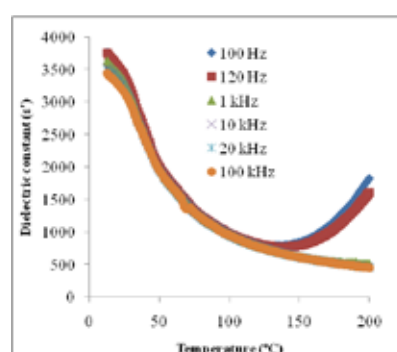
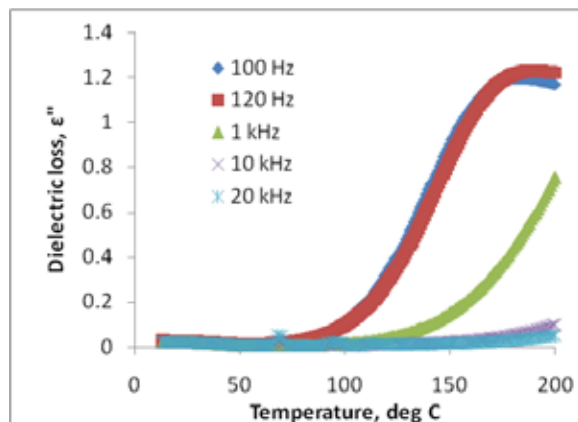
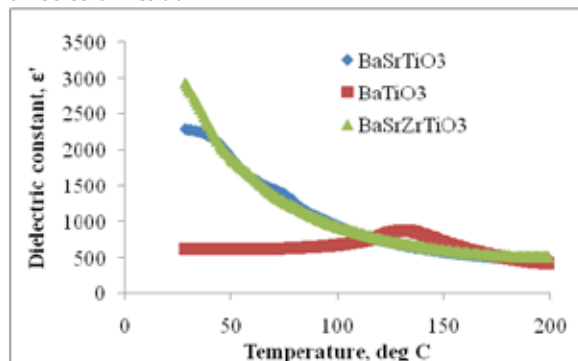
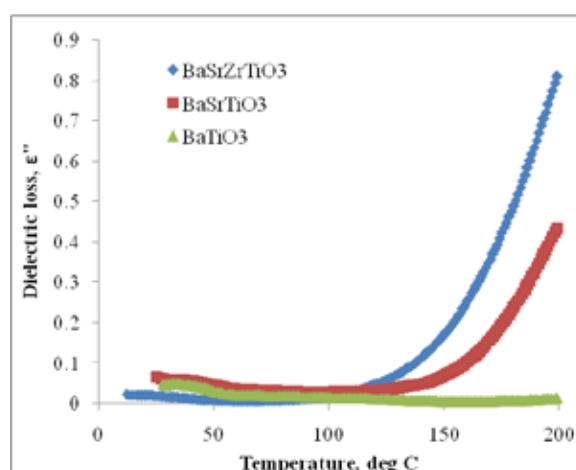
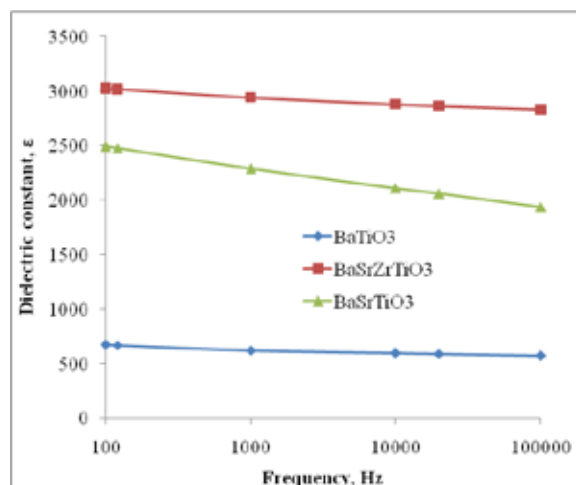


Fig.3.1d Plot of dielectric loss vs temperature for BSZT sintered at 1400 °C for 3hrs**Fig. 3.2a** Temperature dependent dielectric constant of three ceramics at 1 kHz**Fig. 3.2b** Temperature dependent dielectric loss of three ceramics at 1 kHz**Fig.3.3:** Influence of Zr on room temperature (28°C) dielectric constant (measured at different frequencies) of Barium titanate.**REFERENCES**

- [1] Alexandru H V, Berbecaru C, Ioachim A, Nedelcu L, Dutu A. BST solid solutions, temperature evolution of the ferroelectric transitions, Appl Surf Sci, (2006), 253(1): 354–357. | [2] Ioachim A, Toacsan M I, Banciu M G, Nedelcu L, Dutu A, Antohe S, Berbecaru C, Georgescu L, Stoica G, Alexandru H V. Transitions of barium strontium titanate ferroelectric ceramics for different strontium content, Thin Solid Films, (2007), 515(16): 6289–6293. | [3] Ianculescu A, Berger D, Viviani M, Ciomaga C E, Mitoseriu L, Vasile E, Drăgan N, Crișan D. Investigation of Ba1-xSrxTiO3 ceramics prepared from powders synthesized by the modified Pechini route, J Eur Ceram Soc, (2007), 27(13–15): 3655–3658. | [4] Li Y, Qu Y. Dielectric properties and substitution mechanism of samarium-doped Ba0.68Sr0.32TiO3 ceramics, Mater Res Bull, (2009), 44(1): 82–85. | [5] Huang X Y, Gao C H, Chen X C, Zheng X L, Huang G J, Liu H P. Dielectric properties of Dy2O3-doped (Ba,Sr)TiO3 ceramics, J Rare Earths, (2004), 22(z3): 226–228. | [6] Zhao C, Huang X Y, Guan H, Gao C H. Effect of Y2O3 and Dy2O3 on dielectric properties of Ba0.7Sr0.3TiO3 series capacitor ceramics, J Rare Earths, (2007), 25(Sp.2): 197–200. | [7] Li Y, Qu Y. Substitution preference and dielectric properties of Y3+-doped Ba0.62Sr0.38TiO3 ceramics, Mater Chem Phys, (2008), 110(1): 155–159. | [8] Zhang J, Zhai J, Chou X, Yao X. Influence of rare-earth addition on microstructure and dielectric behavior of Ba0.6Sr0.4TiO3 ceramics, Mater Chem Phys, (2008), 111(2–3): 409–413. | [9] Zhang Chen, Qu Yuan-fang. Dielectric properties and phase transitions of La2O3- and Sb2O3-doped barium strontium titanate ceramics, Trans. Nonferrous Met. Soc. China 22(2012) 2742–2748 | [10] Chiou B S, Wang I H. Effect of MgO addition on the electrical transport properties of highly Sb-doped BaTiO3 ceramics, J Mater. Sci: Mater Electron, (1998), 9(2): 145–150. | [11] Chan, Ngai-yui, Thesis on "Study of barium strontium zirconate titanate thin films and their microwave device applications" Hong Kong Polytechnic University, <http://hdl.handle.net/10397/4260>, (2010) | [12] T Badapanda, S K Rout, L S Cavalcante, J C Sczacoski, S Panigrahi, E Longo and M Siu Li, Optical and dielectric relaxor behaviour of Ba(Zr0.25Ti0.75)O3 ceramic explained by means of distorted clusters, J. Phys. D: Appl. Phys. (2009), 42 (17), 175414 | [13] Zunping Xu, H. Qiang, Chunlin Song, Dielectric properties of La/Zr co-doped Ba0.67Sr0.33TiO3 ceramics prepared from Citrate-Nitrate combustion derived powders, Chongqing College of Humanities, China 3 (2014)-1966-3 | [14] Ching-Fong Chen, Quinn R. Maksteiner, Graham King, Slip casting of sol-gel synthesized barium strontium zirconium titanate ceramics, Los Alamos National Laboratory, USA (2013) 48, 5788-5800 | [15] Wenxing Zhang, Lixin Cao, Wenwen Wang, Ge Su, Synthesis, microstructure and dielectric properties of zirconium doped barium strontium titanate obtained by solvothermal method, Institute of Material Science and Engineering, Ocean University of China, (2012) – 1084-7 | [16] M.Yamamuka, T. Kawahara, T. Makita, A.Yuuki and K. Ono, Japanese Journal of applied Physics 35, (1996) 729 | [17] T. Kawahara, M. Yamamuka, T. Makita, J. Naka, A. Yuuki, N. Mikami and K.Ono, Japanese Journal of Applied Physics 33, (1996) 5129 |