Research Paper

Volume : 4 | Issue : 3 | March 2015 • ISSN No 2277 - 8179

Dielectric Behavior of Perovskite Barium Titanate and Barium Strontium Titanate Ceramics

Chemistry

KEYWORDS : BST ceramics, sol-gel technique, dielectric behaviour

Narendra Singh Rawat	Department of Physics, Zakir Husain Delhi College, University of Delhi, New Delhi
Manisha Chawla	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

Stoichiometric compositions [(Ba+Sr):Ti =1:1] of barium strontium titanate (Ba1-xSrxTiO3) (where molar concentration x = 0, 0.2, 0.3, 0.4, 0.5 and 1.0) powders were prepared using a sol- gel technique via acetate method. The as-fired amorphous powders were annealed at 850oC to form nanocrystalline powders. These powders were then cold-pressed to make pellets which were then sintered at 1300oC to form dense ceramics. These ceramic pellets were electroded using conductive silver paste and characterized for their frequency and temperature dependent dielectric behavior in order to investigate the effect of strontium concentration on the dielectric constant of barium titanate (BaTiO3). It was observed that with increasing strontium concentration the ferroelectric to paraelectric phase-transition temperature (Tc) shifted to lower temperatures and dielectric constant increased substantially. With a very small addition of Sr (Ba0.8Sr0.2TiO3), a high dielectric constant and a low dielectric loss (<0.1) were obtained at room temperature (25o C). The dielectric constant of BST ceramics measured at room temperature as a function of frequency did not change much with frequency and their magnitude was almost same at higher frequencies (1 kHz to 100 kHz).

1. Introduction

The choice of capacitors for memory applications depends on high thermal stability, high fatigue resistance, high dielectric constant, low dielectric loss, high charge storage capacity, and low leakage current density of the dielectric material. Barium titanate (BaTiO3) possesses all these characteristics and hence it is regarded as one of the promising material to replace SiO2 as dielectric material for such applications [1,2]. Demand for lead free dielectric and ferroelectric materials have further increased the significance of barium titanate based thin films and ceramics. Ferroelectric oxides crystallizing in perovskite structure possess relatively simple crystal structure that has the ABO3 stoichiometry. Typically A site cation is large and is coordinated by 12 anions in the lattice. The B-site cation is smaller- frequently it is a transition metal being six coordinated forming BO6 octahedral. The distortions of this octahedral leads to deviations from perfect cubic symmetry [3,4]. Barium Strontium Titanate (BST) Ba1-xSrxTiO3 which is known to adopt the ABO3-type structure is a continuous solid solution of BaTiO3 and SrTiO3 over the whole concentration range. In this case Ba and Sr are coordinated by 12 oxygen atoms and Sr is octahedrally coordinated with 6 oxygen atoms [5,6]. The properties of Ba1– xSrxTiO3 depend on the composition x. Partial substitution of Ba ions in pure BaTiO3strongly affects the ferroelectric-paraelectric phase transition temperature. SrTiO3 is usually added as a shifter in order to move the Curie point Tc to lower temperatures. It is well established that Tc of barium titanate decreases linearly with the amount of Sr2+ in place of Ba2+. For bulk Ba1–xSrxTiO3 ceramics, the Curie point varies from 120°C to –240 °C, whereas the relative electric permittivity (measured at room temperature and electric field of frequency ν = 1kHz) decreases from ε'~2000 to ε' ~300 for x from x = 0.0 to x = 1.0. As a result, the transition temperature, and hence the electrical and optical properties of Ba 1–x SrxTiO3, can be tailored over a broad range to meet the requirements of various electronic applications. Among the various methods used to prepare the BST powders, sol-gel processes are commonly applied in the preparation of BST fine powders and thin films due to the precise control of composition, ease of homogenous distribution of elements, cost effectiveness, relatively low temperatures and simple process requirements [7]. For a single phase cubic perovskite structure of Ba0.5Sr0.5TiO3 achieved at a calcination temperature of 800oC an optimum dielectric constant of 1164, dielectric loss of 0.063 and the lowest leakage current density of 49.4 pA/cm2 at 5V at room temperature have been reported [8].In this work, the frequency and temperature dependent dielectric behavior of BST ceramics (Ba1-xSrxTiO3 where molar concentration x = 0, 0.2, 0.3, 0.4, 0.5 and 1.0) prepared using sol-gel derived powders is being reported. These ceramics were characterized for their structural, morphological, dielectric and electrical properties. The main objective was to study the effect of A-site Sr substitution on the dielectric properties of BT.

2.0 Materials and Methods

Table 1 shows the properties and source of the various chemicals used in the present synthesis. The starting materials were Barium acetate [Ba(CH3COO)2 ≥99%], Strontium acetate [Sr(CH3COO)2] and Titanium tetrabutoxide (97%). Glacial acetic acid [CH3COOH ≥99.7%] and butyl alcohol [C4H9OH>99.5%] were used as solvents. Calculated amounts of Barium acetate and strontium acetate were weighed to synthesize stoichiometric compositions of (Ba1-xSrxTiO3) (where molar concentration x = 0, 0.2, 0.3, 0.4, 0.5 and 1.0)[(Ba+Sr):Ti = 1:1] powders. The weighed amount of these compounds were mixed together in glacial acetic acid and refluxed at 100 °C for 0.5h using a sand bath. The Ba-Sr solution was cooled down to the room temperature and then the calculated amount of Titanium Tetrabutoxide mixed with butyl alcohol was added and the resulting solution was stirred again using a magnetic blender for 0.5h at room temperature. After stirring, the sol was hydrolysed using 10-15 ml of distilled water. Small amount of acetylacetone [CH3COCH2COCH3] was added as stabilizer. The sol was relatively clear and stable. It was covered with aluminium foil and kept in a dessicator to avoid air contamination. It was left in open for gelation and it gelated in 3 days. The obtained gel was fired at 350 °C in air for 3-4 hrs. The as-fired powder obtained was amorphous in nature. This powder was calcined at 850°C for 3h in a muffle furnace to obtain a poly-crystalline powder. The BST powder so obtained was milled and die-pressed into thick pellets under a pressure of 300 MPa. The samples were finally sintered at 1300oC for 3h at a heating rate of 10oC/min. The powder and ceramics were prepared using a procedure given in the

flowchart (Fig. 1). The sample designation and compositions are listed in Table 2.

2.1 Material Characterization Structural characterization of barium titanate and barium strontium titanate (BST 73) powder calcined at 850oC was done using X-Ray Diffractometer. Diffractograms of BT powder, BST powder and BST ceramic are shown in Fig.2.The peaks show a polycrystalline nature and confirm the formation of tetragonal structure of BT and BST.

2.1.1 Dielectric studies

AC frequency dependent values of parallel capacitance (Cp) and loss tangent or dissipation factor (tanδ or D) of the ceramic pellets were measured by using Agilent 4263B precision LCR meter. The actual thickness of samples was measured using a micrometre before electroding. Electroding was done using conductive silver paste using a paint brush. Electroded samples were placed in a sample cell between two electrodes and voltage was applied. The parallel capacitance (Cp) was measured on the LCR meter. Dielectric constant (ε′) was calculated using the formula:

$\varepsilon' = C/C0$ .....(1)

where, Co (=ϵ 0A/d) is the capacitance with vacuum between parallel plates, and ϵ 0(=8.85 x 10-12 F/m) is the permittivity of free space, A is the area of electrodes, and d is the thickness of the sample. Dissipation factor (D or tanδ) was directly measured on the LCR meter.To calculate ac conductivity, parallel capacitance (Cp) and dissipation factor (D or tanδ) from 100 Hz up to 100 kHz was measured. σac(ω) was calculated by using the following expression:

$\sigma ac(\omega) = 2\pi f\epsilon\ 0\varepsilon'' = 2\pi f\epsilon\ 0\varepsilon' \tan\delta$ ..... (2)

where, tanδ is the dissipation factor, ω=2πf is the angular frequency, ϵ 0 is the permittivity of free space (=8.865×10-12 F/m), ε′ is the dielectric constant (ε″ /ε′ = tanδ), and ε″ is the dielectric loss.

Temperature dependent and frequency dependent dielectric parameters were measured from room temperature (30oC) to 200oC at 100Hz, 120 Hz, 1 kHz, 10 kHz and 100 kHz.

3.0 Results and discussion

Temperature dependent dielectric constant and dielectric loss of all the ceramics measured at 1 kHz are shown in Fig 3a and Fig 3b respectively. From Fig, 3a it is clear that the Tc of BaTiO3 (~120oC) has shifted to the lower temperatures (<30oC) for BST samples with addition of Sr content. Furthermore, values of dielectric constant decrease sharply with increase in temperature in paraelectric phase. These values are in accordance with the reported literature according to which the dielectric constant can be varied by changing the Ba/Sr ratio [9]. 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 [10]. BST composition (Ba0.8Sr0.2TiO3) exhibits the highest dielectric constant and a Tc ~30oC which is closer to the room temperature. SrTiO3 shows lowest dielectric constants at all temperatures. Figure 3b shows that the dielectric loss is very small (<1) for all the samples minimum being that for BaTiO3 and Ba0.5Sr0.5TiO3.Figure 4a and 4b show the frequency dispersion of dielectric constant (ε') and dielectric loss (ε") respectively of all the samples measured at room temperature (25oC). From Fig. 4a it can be seen that at higher frequencies (>1 kHz) a very slight change is observed in the values of dielectric constant. (Ba0.8Sr0.2TiO3) shows highest values of dielectric constant at all frequencies. Similarly, there is no or little variation of dielectric loss at higher frequencies (>1 kHz) for all the samples except SrTiO3 and Ba0.6Sr0.4TiO3. Figure 5 shows the temperature dependent dielectric constant of barium titanate ceramics at different frequencies. It is observed that Tc for BaTiO3 is almost constant at 120oC at all frequencies. Below Tc (ferroelectric phase), dielectric constant is distinguishable at different frequencies. However near and above Tc (paraelectric phase) the magnitude of dielectric constant remains same and independent of frequency. Figure 6 shows the variation of dielectric constant as a function of mole fraction of Sr. With small addition of Sr content (x = 0.2) a very high value of dielectric constant and a lower Tc are obtained at room temperature.

4.0 Conclusions

Bulk ceramics of Barium strontium titanate (Ba1-xSrxTiO3) prepared using fine powders derived from sol-gel method showed that with increasing strontium concentration the ferroelectric-paraelectric phase transition temperature (Tc) shifts to lower temperatures. With a very small addition of Sr (Ba0.8Sr0.2TiO3), a very high dielectric constant (emax>2000) and a low dielectric loss (<0.1) is obtained at room temperature (25oC). The dielectric constant of BST ceramics shows no frequency dispersion at higher frequencies (1 kHz to 100 kHz).

Acknowledgements

Authors wish to express gratitude to University Grants Commission (UGC) for the funding of this project. (NSR) and (MC) are grateful to UGC for a project fellowship.

S.No	CHEMICAL NAME	MOLECULAR FORMULA	MOLECULAR WEIGHT(g/mol)	CAS No.	PURITY/ ASSAY (%)
1.	Barium acetate	$Ba(CH_3COO)_2$	255.42	543-80-6	≥99
2.	Strontium acetate	$Sr(CH_3COO)_2$	205.71	543-94-2	-
3.	Acetic acid	CH_3COOH	60.05	64-19-7	≥99.7
4.	Titanium tetrabutoxide	$Ti(OC_4H_9)_4$	340.32	5593-70-4	97
5.	Butanol	C_4H_9OH	-	71-36-3	>99.5
6.	Acetylacetone	$CH_3COCH_2COCH_3$	100.12	123-54-6	≥99

Table 2 :Sample designation and composition(BaxSr1-xTiO3)

Sample designation	Sample name	Ba(1-x)	Sr(x)
BT	$BaTiO_3$	1.0	0.0
BST82	$Ba_{0.8}Sr_{0.2}TiO_3$	0.8	0.2
BST73	$Ba_{0.7}Sr_{0.3}TiO_3$	0.7	0.3
BST64	Ba0.6Sr0.4TiO3	0.6	0.4
BST55	Ba0.5Sr0.5TiO3	0.5	0.5
ST	$SrTiO_3$	0.0	1.0

FIG. 1 - FLOWCHART FOR THE PREPARATION OF BARIUM

Volume : 4 | Issue : 3 | March 2015 • ISSN No 2277 - 8179

STRONTIUM TITANATE USING SOL-GEL METHOD

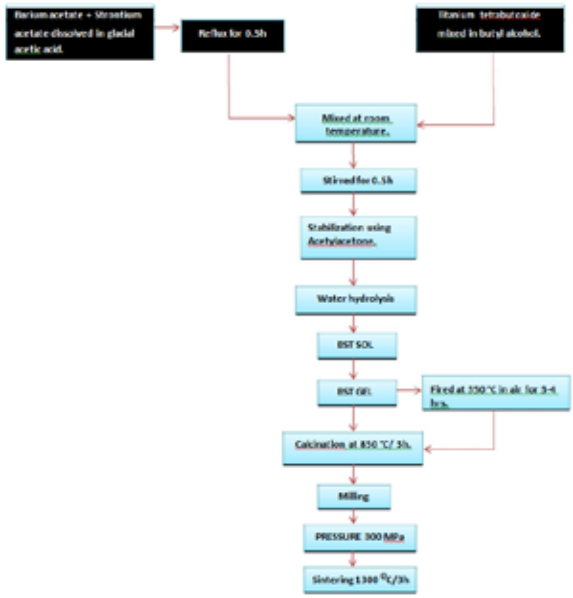


Fig. 2 XRD diffractograms of Barium titanate and Barium Strontium titanate

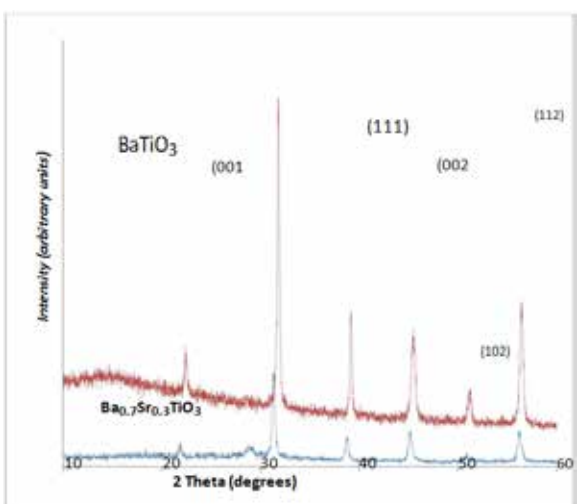


Fig 3a: Influence of Sr++ substitution on temperature dependent dielectric constant (measured at 1 kHz) of Barium titanate ceramics sintered at 1300oC

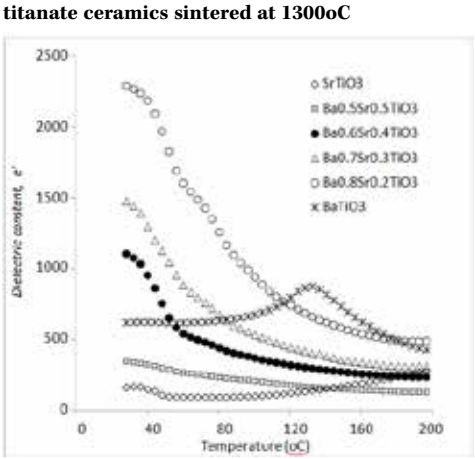


Fig 4a: Influence of Sr++ substitution on room temperature (30oC) dielectric constant (measured at different frequencies) of Barium titanate ceramics sintered at 1300oC

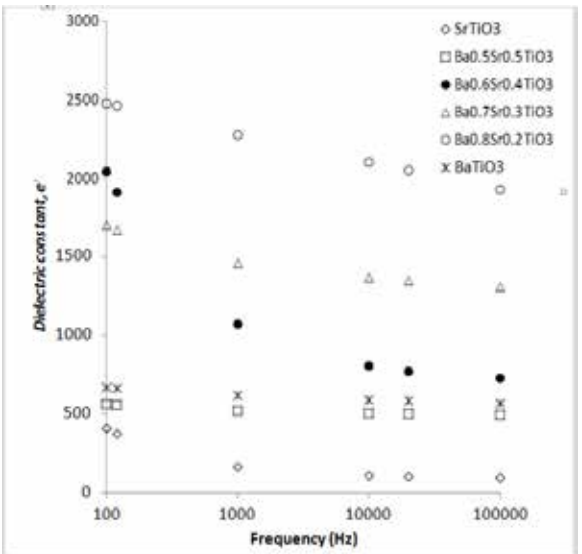


Fig 4b: Influence of Sr++ substitution on room temperature (30oC) dielectric loss (measured at different frequencies) of Barium titanate ceramics sintered at 1300oC

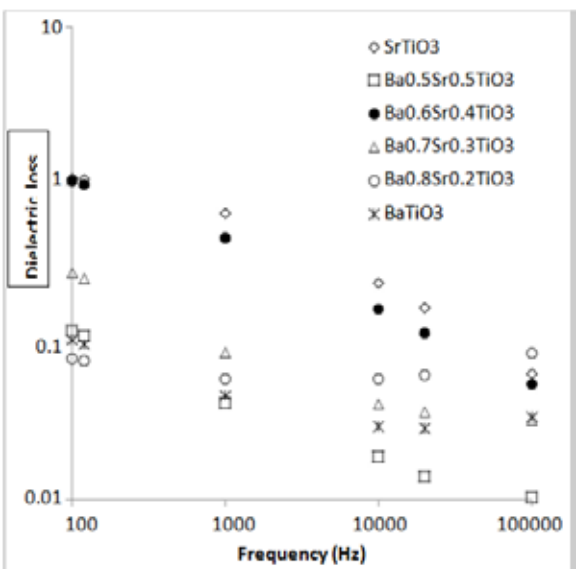


Fig 3b: Influence of Sr++ substitution on temperature dependent dielectric loss (measured at 1 kHz) of Barium titanate ceramics sintered at 1300oC

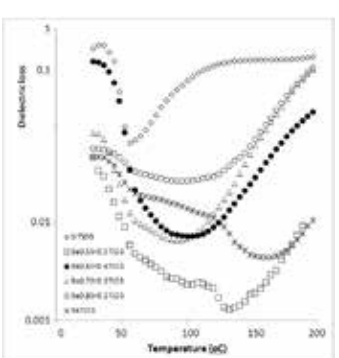


Fig 5: Temperature and frequency dependent dielectric con-

stant of Barium titanate ceramic sintered at 1300oC

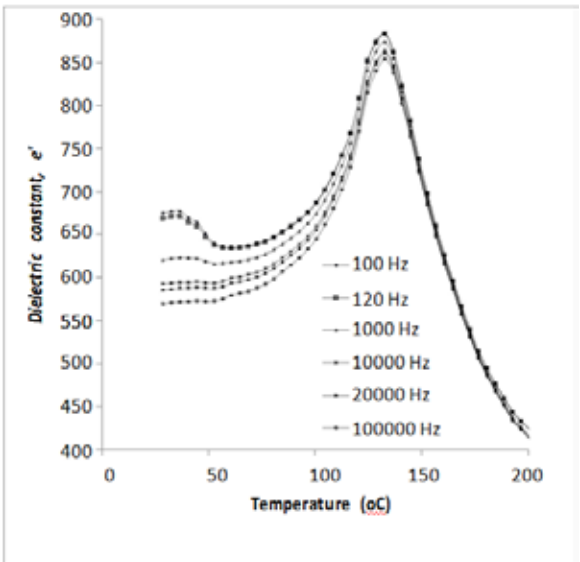
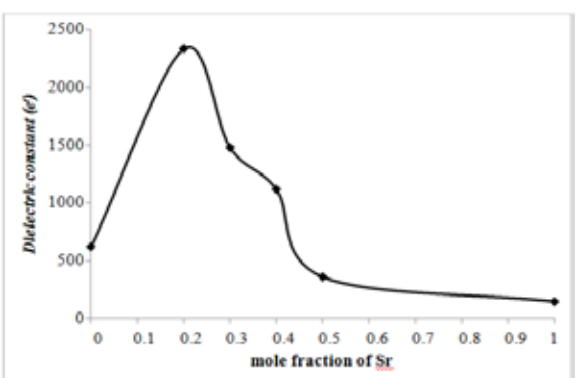


Fig. 6 : Variation of dielectric constant (measured at 1 kHz at room temperature 25oC) of barium titanate as a function of the mole fraction of strontium



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