American Journal of Engineering Research (AJER) 2020
American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN: 2320-0936
Volume-9, Issue-1, pp-378-383
www.ajer.org
Research Paper
Open Access

Effect of Sr^{2+}doping on the structural and dielectric properties of$BaTiO_3$ lead free piezoelectric ceramics

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Abstract: *In order to investigate effect of Sr ions on the structural and dielectric properties of$BaTiO_3$, a series of $(Ba_{1-x}Sr_x)TiO_3$(x=0.0, 0.05, 0.1, 0.2 and 0.4mol%)were prepared by Sol gel method. The calcination and sintering temperatures were carried out at 1000^oC and 1200^oC respectively for 2h. To evaluate the functional groups of the BST calcined powders, FT-IR has been used. The structure and phase identification were identified by X ray diffraction (XRD), and all the peaks were indexed by BT (tetragonal structure P4/mm space group) perovskite structure and no second phases can be observed. In addition to, all the peaks were shifted to the higher degree by increasing Sr amount indicate decreasing the lattice parameters Morphology and the microstructures of the ceramic compositions were observed by scanning electron microscope (SEM).Dielectricproperties and impedance analysis as a function of temperature and frequency for the BST ceramics wereinvestigated.*

I. INTRODUCTION

Ferroelectric materials or ferroelectrics refer to the group of dielectrics having the property of spontaneous polarization(i.e.,they retain a dipole even after an applied voltage has been removed).The key characteristics of aferroelectric crystal are that the direction of the polarization can be reversed by application of an electric field and that ahysteresis loop results .Ferroelectrics mainly have two characteristics ,asymmetry and high dielectric constant or high permittivity [1,2].Barium Titanate(BaTiO3) was the first discovered piezoelectric transducer ceramic that sufficied the need of ahigh dielectric constant material for capacitor application during world war II in mind 1940s [3].Addition ions in BaTio3 structure at the A or B site reduce change in electric properties .based on the transducer application ,Sr2+ is used to reduce Tc but Ca2+ have negligible change in curie temperature[4,5].

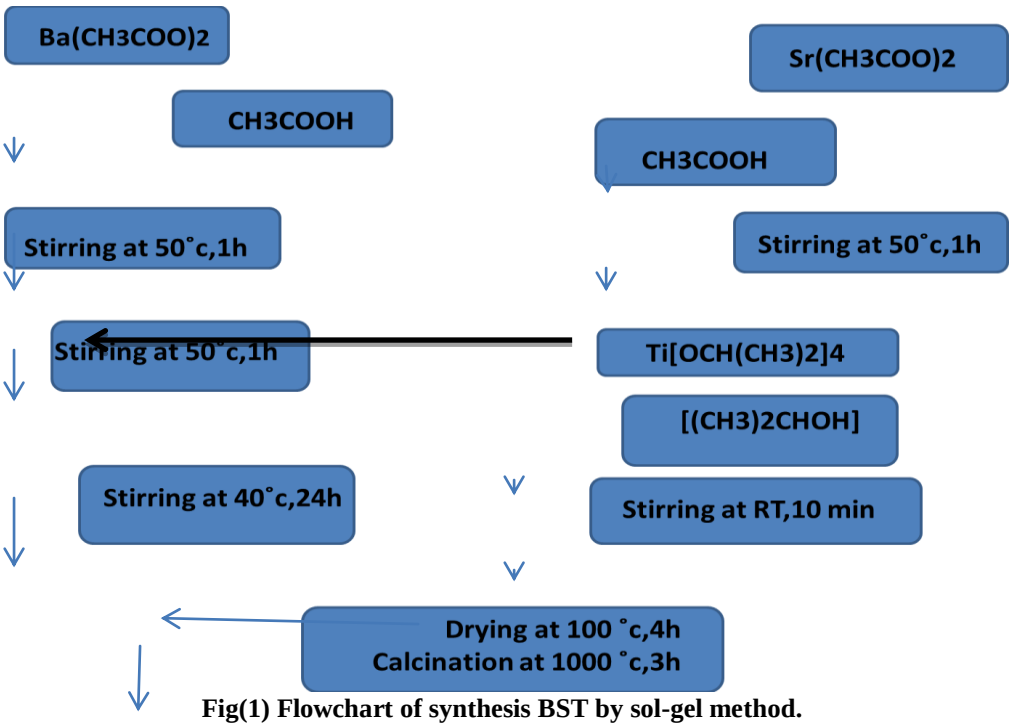
Synthesis method played asignificant role in determining the microstructure ,electrical and optical properties of ferroelectric ceramics [6,7].electrical properties are strongly dependent on the grain size and the crystalline structure [8].Howaver ,chemistry co-precipitation[9],organic acid precursor[10,11],microemulsion [12,13], etc. This paper focused on developing and understantanding the synthesis behavior of nanosized barium strontium powders by Sol-gel process.

Strontium-doped barium titanate (BST) has been widely used for various applications .such as fields of electronics and telecommunications .because of its high dielectric constant , large electric field tunabilities,relatively low dielectric losses[14,15].

II. EXPERIMENTAL

The perovskite (Ba1-xSrx)TiO3 lead free nano-ceramics (x=0.0, 0.05,0.1,0.2 and 0.4mol% of Sr) were synthesized by using Sol-gel technique. Both of barium acetate Ba(CH3COO)2, strontium acetate Sr(CH3COO)2 and titanium isopropoxideTi[OCH(CH3)2]4 were used as the precursor for obtaining barium , strontium and titanium. glacial acetic acid (CH3COOH) was used as a solvent for barium acetate and calcium acetate, and 2-propanol [(CH3)2CHOH] was used as a solvent for titanium isopropoxide. Fig.1. shows the flowchart of the sol gel procedures. In the beginning, Stoichiometric weight of barium acetatewas dissolved in 20ml of acetic acid by using magnetic stirrer at 60oC, for 1hour, after that Stoichiometricproportion of Strantium acetate was dissolved in 5ml of acetic acid by magnetic stirrer at 60oC for half an hour. The two separated solution were mixed and refluxed at 60oC with vigorous stirring for 1h to obtain a transparent solution. At the same time of refluxing, 10ml of 2-propanol was added to the Stoichiometric weight of titanium

isopropoxide and kept in magnetic stirrer for half an hour at room temperature. The titanium isopropoxide solution was added to the Ba-Sr solutions, and the all mix was left for 24h at 40oC until to form a thick of white gel of BCT containing organic materials. Finally, the gel was kept in the hot plate and dried at 100oC, for 4h dwell time to obtain amorphous powder of BST. The amorphous powder was calcined at 900oC, for 3h in a covered platinum crucible to avoid any possibility of contamination during the thermal treatment. The calcined powder was grind in a mortar pestle and sieved through 38µm grid to obtain fine single phase powder. Hydraulic pressure was used to form a cylinder pellets with 10mm in diameter and 1.5mm in thickness inside the steel die. The pellets were sintered at 1300oC, 4h and (10oC/min) as heating/cooling rate in the covered platinum crucible in an air. X-ray diffractometre(PANalyticalx'Pert PRO diffractometre) (XRD) with CuKα radiation was used to record the diffraction pattern for both of BCT calcined powder and sintered ceramics at room temperature. The morphology and microstructure of BST calcined powder and ceramics were examined using Scanning electron microscope equipped with an energy-dispersive X-ray (EDS) analyzer (SEM-EDS) (JEOL, JEM-2100 – Japan). Small amount of calcined powder was mixed with (potassium bromide, KBr) and a (Jasco Model 4100 –Japan). was used to identify the IR-active functional group of the present compositions in the wide range of wave number (4000-400cm-1). A layer of gold was deposited into the top and bottom surface of the sintered pellets for carried out the dielectric measurements. The dielectric properties for all the sintered ceramics dependant of frequency (100Hz-8MHz) were studied by using **(HIOKI 3532-50 LCR HITESTER).**P-E loop measured at room temperature by (**RADIANT Precision premium II Multiferroic Ferroelectric Test System10 kV HVI-SC-Model609B**)



Fig(1) Flowchart of synthesis BST by sol-gel method.

III. RESULTS AND DISCUSSION

3.1. Characterization of BCT calcined powder:

Fig(2) shows the X-Ray powder diffraction of the powder of B1-xSxTiO3 where x=(0.0,0.05,0.1,0.2 and 0.4)mol %of Sr Sample calcined at 1000oC for 4 h .All samples crystallize in the pure perovskite phase ,All the diffraction peaks can be matched with the standard data of (pdf No.0.1-0.75-0.473) and (P4/mm space group)according to the JCPDS database .In addition we note that when the strontium doping rate was increased ,the diffraction peaks slightly shift toward higher angles

[16]

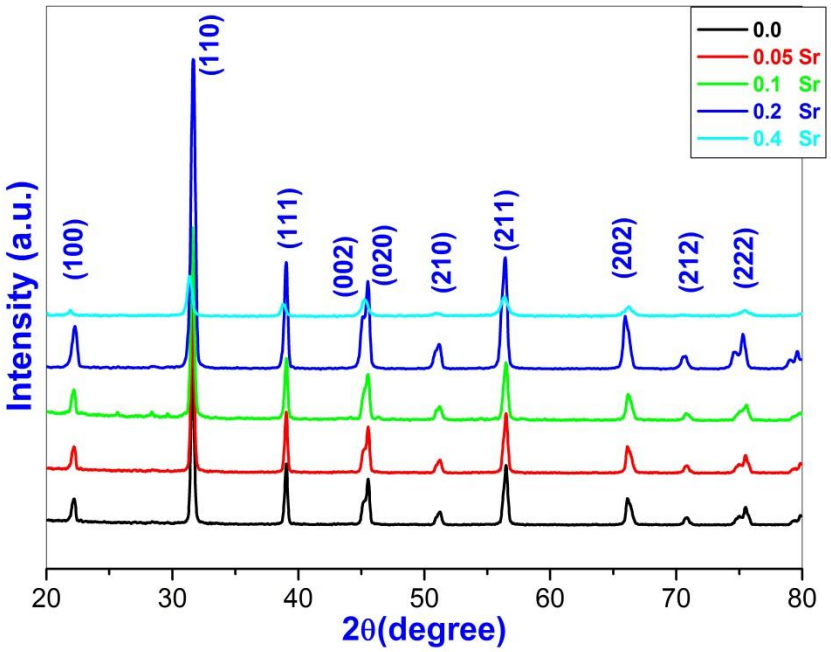
The particle size of the BST calcined powder was calculated by scherrerEq(1)

$d=0.94\lambda/\beta\cos\theta$

where d, λ, β and θ represent the particle size,wavelength of the CuKα radiation (λ=1.5418˚A),full width at half maximum of peak

Sr doping gives rise to aslight transformation from quadratic (pure BT) to pseudo cubic phase (BSTx,x>0.2) as revealed by the peak (200) in the range 44˚<2θ<47˚ ,These two peaks tend to merge as observed for the three other compositions**[17].**

In addition we note that when strontium content increases,the tetragonality of the structure decreases and that for x>0.2 in sr ,the structure stabilizes in the pseudo cubic one ,due to electrostatic repulsions between 3d electrons of Ti^{4+} ions and 2p electrons of O^{2-}ion**[18].**



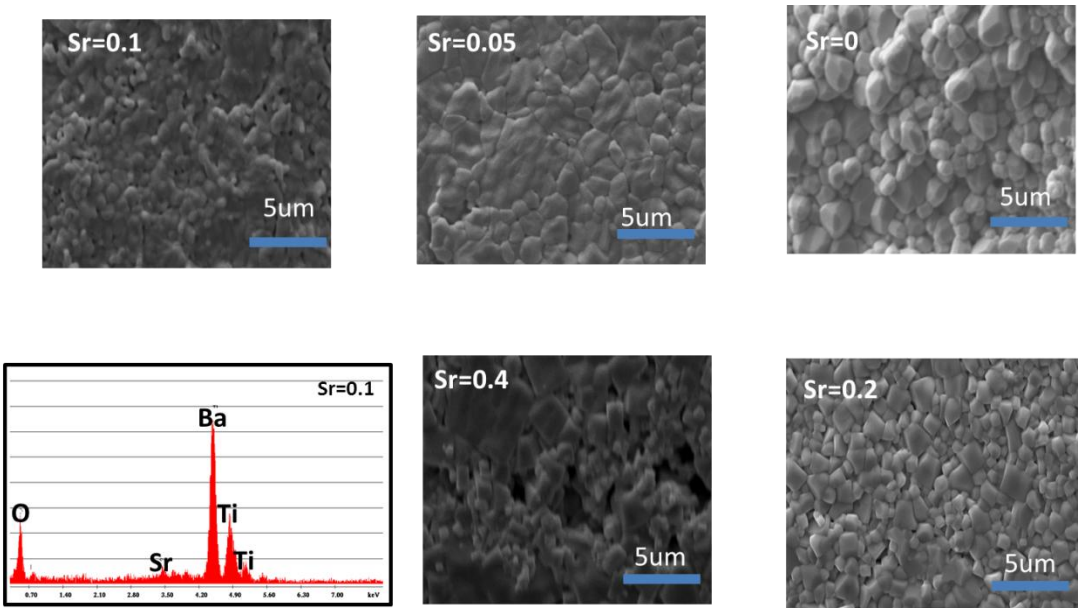
Fig(2).XRD patterns of the B1-xSxTiO3 where (0<x≤0.4)calcined powder 1000˚ C/3h.

4.2.SEM characterization

The morphology of powders has been investigated by figure (3)show the morphologies , observed by SEM of of (Ba1-xSrx)TiO3 (x = 0.0, 0.05, 0.1, 0.2 and 0.4 mol%) at 1200˚c for 4 h obtained by sol-gel method.The morphology shows all the compositions exhibit fully dense microstructures with absence completely the porosity exist in the grain boundary ,which means the sintering conditions were enough to obtain afully dense microstructure.Forall samples ,the morphology exhibits a homogeneous microstructure and uniformly distributed of the grain size .The grain size for all the ceramics are smaller than the grain size for same compositions that are prepared by the solid state reaction technique**[19]**and this could be the main reason for decreasing the sintering temperature from 1400˚c to 1200˚c,Also , the grain size was observed tend to decrease with increasing the Sr^{2+}concentration ,and these results confirmed the XRD results.This result may be associated with the substitution of the larger Ba^{2+} ion by the smaller Sr^{2+}ionand the angle of diffraction are respectively.

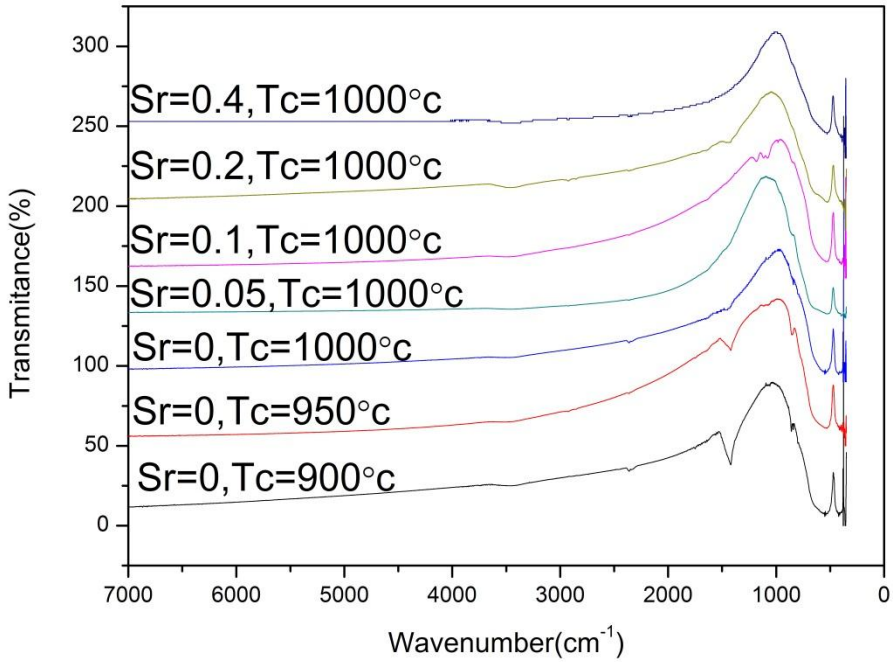
On the other hand , the elementary cell volume is reduced with Sr doping as seen in fig ( ),propably due to the smaller ionic radius of Sr^{2+}=1.32˚A compared to that of Ba^{2+}=1.49˚A.

EDX analysis for BST ceramic Sr=0.05 show absence of contamination.



Fig(3).SEM micrographs of the $B_{1-x}S_xTiO3$ ceramics sintered at 1200ºc and EDS of Sr=0.05.

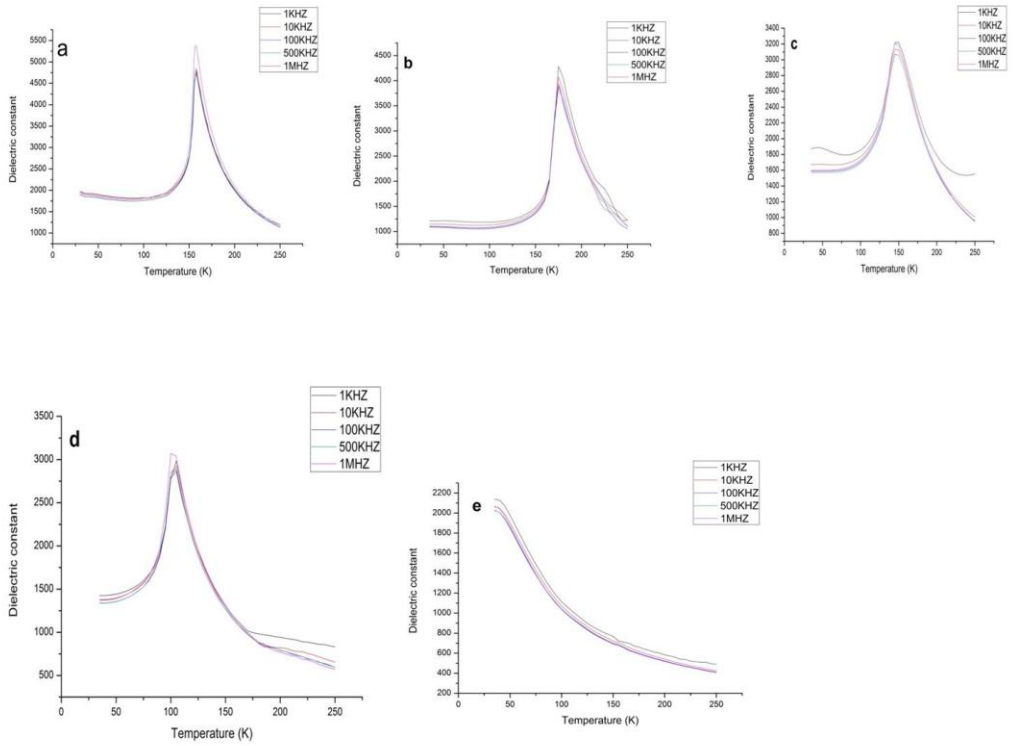
FTIR spectroscopic measurements were used to investigate binding in the prepared Sr doped BaTiO3 powders.FTIR spectra in the range of 0-7000cm^{-1}.Two intense bands at 1430 and 1556cm^{-1} are assigned to symmetrical and antisymmetric vibrations respectively (titanium-bound carboxylic groups(COO^-) or stretching of barium)[20,21].the two broad peaks between 1000 and 1200cm^{-1} can be attributed to isopropyl groups bound to the titanium atoms in amonodentate mode and traces of the carbonate in small amount .At frequency 900cm^{-1} to 1700cm^{-1} act the vibration band of the organic (carboxylic) groups decreased with the increase of the strontium doping rate (it disappeared)for x=0.4 , in conformity with XRD results, while the Ti-O absorption peaks become more prominent.



Fig(4).FTIR spectra of the $B_{1-x}S_xTiO3$ where (0<x≤0.4)calcined powder Sr(900-1000° C/3h).

4.3.DIELECTRIC PROPERTIES:

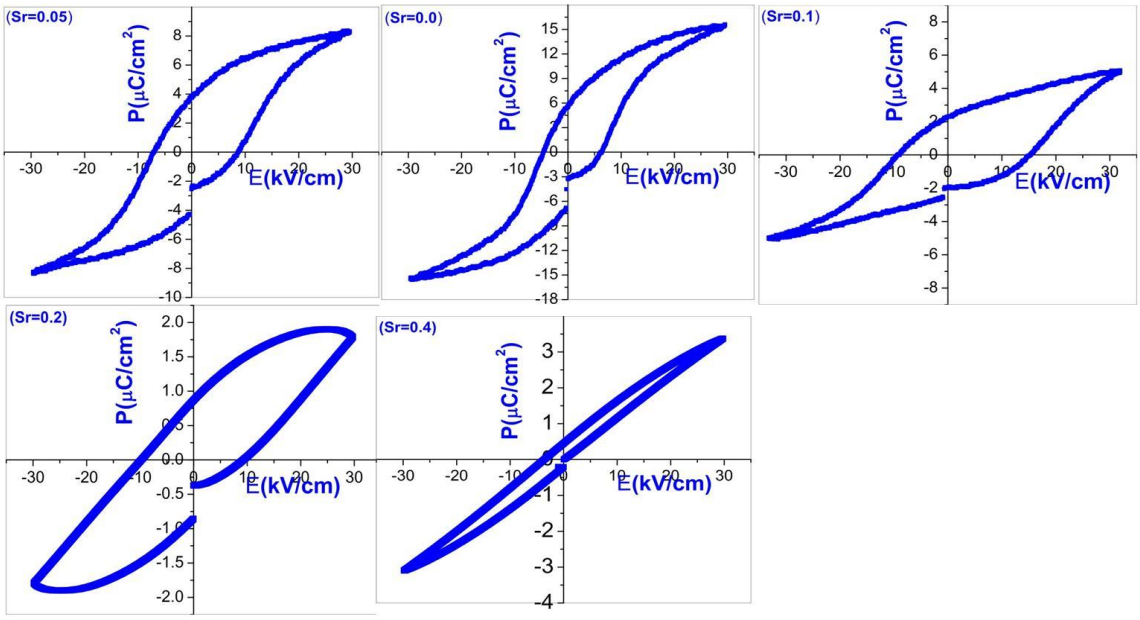
Temperature dependence of dielectric constant for $(Ba_{1-x}Sr_x)TiO_3$ ceramics(0,0.1,0.2 and 0.4) at four different frequenceies (1KHZ,10KHZ,100KHZ and 500KHZ) are shown in fig (5).the general behavior of permittivity temperature curve for all the compositions can be described as the value of permittivity increased with increasing temperature (curie temperature),then decreased with temperature(paraelectricpase).No clear dielectric dispersion was observed before and after T_c with changing frequency[22,23].The maximum value of dielectric constant decreases with increasing of Sr^{2+} constant ,Sr doping in BaTiO3 has been reported to reduce ashift in T_c from the standard value of 150^oc towards roomtemperature ,this is possibly due to the dominant role played by the smaller particle size and the adsorbed Oxygen at grainboundaries than the dopant ion in lowering the T_c .In the last case ,the maximum value of permittivity (ε_{max}) decreased with increasing the applied frequency ,this behavior as mentioned above can be interpreted according to the Maxwell-Wanger mechanism .The sample Sr=0.05 possess the maximum value of permittivity compared to the other compositions . This is because the grain size of the ceramics are decreased significantly with increasing Sr concentration due to the different ionic radius between Sr and Ba ions.



Fig(5).Variation of dielectric constant againt temperature for $B_{1-x}S_xTiO3$ where ($0<x\leq0.4$) ceramics ,at five frequencies

4.4.P-E hysteresis loops:

Fig(6) showed the measured P-E hysteresis loops of the $Ba_{1-x}Sr_xTiO3$ (x=0.0,0.05,0.1,0.2 and 0.4).All samples show the squared hysteresis loops; The spontaneous polarization was calculated to be 6,4,2,1 and 0.5 $\mu c/cm^2$ for x=0.0,0.05,0.1,0.2 and 0.4 mol% of Sr .The doping of acceptor dopants like Srcauses the creation of the positively charged oxygen vacancy thatneutralizes the introduced effective negative charge introduced**[24].** Defect dipole suture thus created. These dipoles at the same time behave as elastic dipoles due to the difference in ionic radius of Ba^{2+} and Sr^{2+}.When an electric field is applied , the onset of spontaneous polarization and strain will tend tonreorient defect dipoles along the polarization direction , so as to reduce their potential energy .polarization direction on each side of adomain wall was fixed by the presence of defects and the walls become more complex to be in motion **[25].**



Fig(6).P-E hysteresis loops of the $B_{1-x}S_xTiO3$ bipolar ceramics ($0<x\leq0.4$) at 1HZ at room temperature

IV. CONCLUSION

In this paper we have given the study of the influence of Sr doping on the dielectric properties of BaTiO3 .The samples were prepared by the recent Sol-gel route. The structural characterization of the various concentrations of BST by XRD reveals acomplete crystallization in the pureperovskite structure.Dielectric studies reveal that Sr doping lowers the temperature of the ferro to paraelectric.

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