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# Effect of Frequency and Temperature on The Electrical & Dielectric Properties of $Ba_{0\cdot6}Sr_{0\cdot4}Fe_xTi_{(1-x)}\ O_{3-\delta\ (x=0.1)}$ [BSFT]

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***Abstract* – *The ac impedance and dielectric properties of $Ba_{0\cdot6}Sr_{0\cdot4}Fe_xTi_{(1-x)}\ O_{3-\delta\ (x=0.1)}$ ceramics in a wide frequency range at different temperatures have been studied. The compound was prepared by a high-temperature solid-state reaction technique. Dielectric and electrical impedance properties of the system in the range of frequency (42Hz -2 MHz) at different temperatures showed that the properties of this material are highly depended on temperature and frequency. The nature of frequency dependence of ac conductivity confirms the Jonscher's power law & the temperature dependence of dc conductivity obeys the Arrhenius behavior.***

***Keywords: Dielectrics, Impedence spectroscopy, Jonscher's power law ,Arrhenius behavior, BSFT ($Ba_{0\cdot6}Sr_{0\cdot4}Fe_xTi_{(1-x)}\ O_{3-\delta\ (x=0.1)}$).***

## I. INTRODUCTION

Dielectric and electrical characteristics of ceramic materials has gained importance as the field of solid state physics continues to expand. The recent global need to reduce environmental contamination by lead-based materials has urged to synthesis lead-free ceramic materials [1].

Ferroelectric oxides got acceptance in research for variety of applications due to their unique ferroelectric, piezoelectric, and pyro electric properties. (Ba Sr)TiO3 (barium strontium titanate), in ceramic form, has got a major role due to its high dielectric response and easy tunability near the ferroelectric phase transition temperature *Tc* [5].

## II. MODELLING

Impedance spectroscopy is used as a powerful technique for the study of the dielectric behavior of crystalline and polycrystalline ceramic materials, especially ionic conductors, ferroelectrics and ferromagnetics [6-9]. The main applications for ceramic dielectrics are as capacitive elements in electronic circuits and as electronic insulation [10]. The properties can be improved by adding dopants to the parent sample. The new materials synthesised can be used in dielectric ceramics capacitors, multilayer capacitors etc due to its high dielectric constant and low dielectric loss. The values of the dielectric constant depend on the synthesis route, which means purity, density, temperature, frequency and concentration of dopants [11].

## III. PREVIOUS WORK

A wide literature survey on this area exhibit that such work has been reported rarely. Attempt has been made to study the the frequency dependence of electrical (dielectric constant/loss and impedance/conductivity) parameters[2-4]. Out of the many compositions Barium Titanate possesses a very high degree of structural stability and compositional flexibility due to its ability to accommodate a wide variety of cations on both A and B sites[9]. In this paper we report our extensive studies on electrical (impedance and conductivity) properties of Fe doped Barium Strontium Titanate, BSFT ($Ba_{0\cdot6}Sr_{0\cdot4}Fe_xTi_{(1-x)}\ O_{3-\delta\ (x=0.1)}$) [9].

## IV. PROPOSED METHODOLOGY

Ceramics with the chemical formula $Ba_{0\cdot6}Sr_{0\cdot4}Fe_xTi_{(1-x)}\ O_{3-\delta\ (x=0.1)}$ [BSFT] was prepared by the solid state reaction technique according to their molecular formula via a high-energy ball milling process through mechanically assisted synthesis. For preparing sample, the reagent grade chemicals of high purity Barium Carbonate, Strontium Carbonate, Ferric Oxide and Titanium dioxide were used [5]. The concentrations of Sr and Fe were varied according to the formula to obtain the desired sample of homogeneity and purity. Presence of Fe in the new sample will contribute for the enhanced electrical &dielectric properties.

The dielectric studies for the sample BSFT ($Ba_{0\cdot6}Sr_{0\cdot4}Fe_xTi_{(1-x)}\ O_{3-\delta\ (x=0.1)}$) was carried out using HIOKI-3532-50 LCR Hi TESTER from 42Hz - 2MHz frequency, in the temperature range 300C-6000C. The pre-sintered mixture was ground and pressed into pellets. All the pellets sintered, were plated using air-drying silver paste to ensure good contacting. The electrical measurements were carried out by inserting the sample between two parallel plate conductors forming cell capacitor. The whole arrangement was placed in non - inductive furnace for heating at different temperatures [30C-600 °C] [1].

## V. SIMULATION/EXPERIMENTAL RESULTS

The dielectric constant with frequency variation for different temperatures is plotted.

BSFT

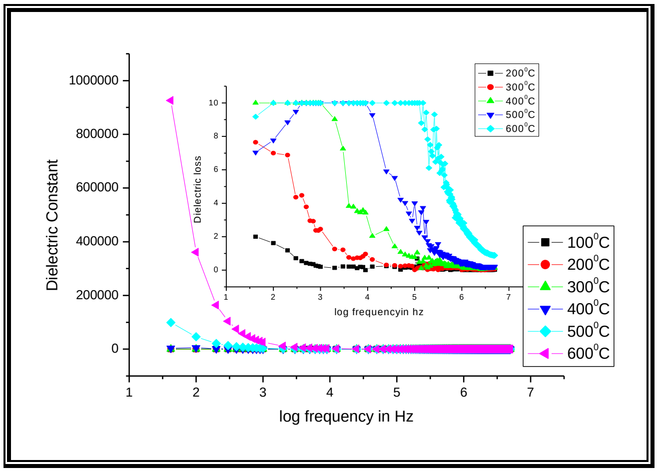


Fig.1.ε’-withlogf

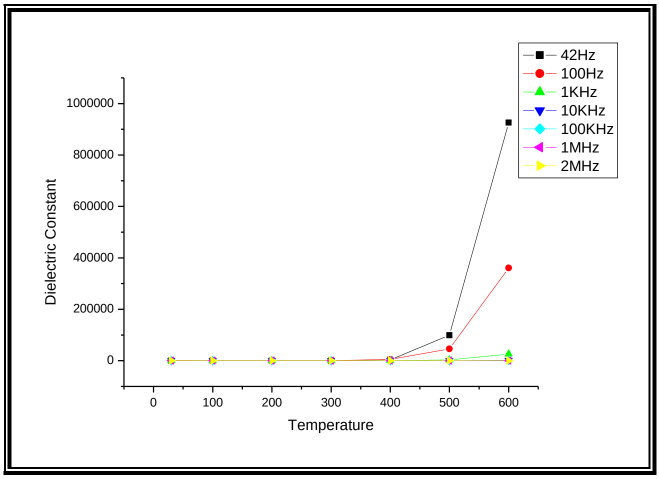


Fig.2 ε’-with T

Fig.1 shows the frequency dependence of dielectric constant (ε´) & dielectric loss (tan δ) (in inset) of BSFT at different temperatures while fig.2 shows the dielectric constant (ε’) with temperature for different frequencies .

It is well observed that ε´ gradually decreases with increasing frequency in a given temperature range. On increasing temperature, ε´ increases apparently, which becomes even more significant at low frequency. The decrease in ε´ at higher frequencies is due to the space charges, which leads to the high dielectric constant and significant frequency dispersion [13-14]. This indicates the thermally activated nature of the dielectric relaxation of the system [6]. In Fig.1, the loss tangent peak is found above temperature 3000C, and showed a continuous trend of shifting towards high frequencies[15]. For the sample BSFT ( $Ba_{0\cdot6}Sr_{0\cdot4}Fe_xTi_{(1-x)}O_{3-\delta}$ $_{(x=0.1)}$) the dielectric constant value at low temperatures has a higher value than in BSFTO(BaSr0.6Fe0.4TiO3) due to the higher concentration of Fe [1]as shown in Fig.3 [1].

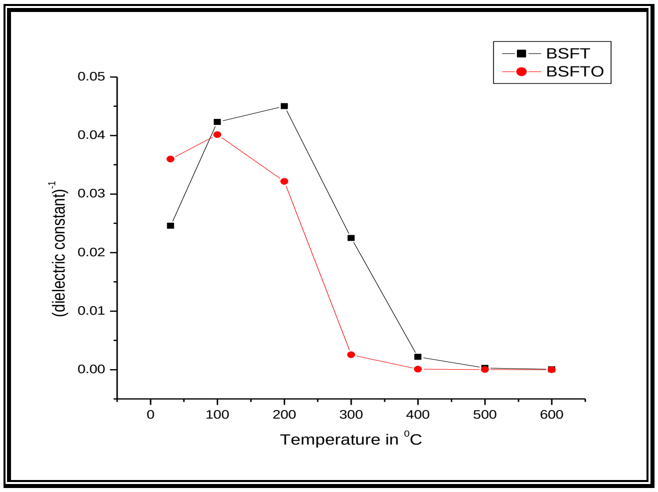


Fig.3 (ε’)-1 with T for BSFT &BSFTO

Dielectric loss or loss tangent, tan δ, representing the wastage of energy decreases first with increase in frequency. But remains constant after a certain value. The frequency dependence of loss tangent is the result of the conductive mechanisms. [9].

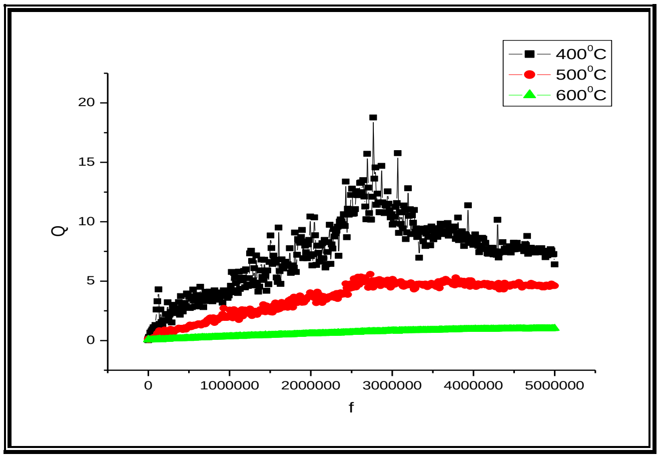


Fig.4 Qvalues of BSFT with frequency.

The rapid rise of tan δ in the high-temperature region is due to the free charge carriers. Since the concentration of free charge carriers is temperature dependent, the rate of loss also rises in the higher temperature region. But the loss factor is inversely proportional to frequency, space charges disappear at higher values of frequencies. The Q value of the sample is inversely proportional to the dielectric loss factor as in Fig .4.

## 2.2 IMPEDANCE STUDIES

The electrical properties of the material BSFT ($Ba_{0\cdot6}Sr_{0\cdot4}Fe_xTi_{(1-x)}$ $O_{3-\delta}$ $_{(x=0.1)}$) was studied over range of frequency(42-2Mhz) with temperature increase using a complex impedance spectroscopy (CIS) technique. This method helps to separate the real and imaginary components of the complex impedance and related parameters, and hence provides information of the structure-property relationship of the material. The polycrystalline materials show grain and grain boundary properties. The contributions can be well displayed in a complex plane[17].

If (Z', M', ε', Y') and (Z ", M", ε", Y") are the real and imaginary components of the complex impedance, electrical modulus, permittivity and admittance then, Complex impedence $Z(\omega)$ $(= Z' - jZ'')$. The complex electric modulus $M(\omega)$ $(= 1/\varepsilon(\omega) = M' + jM'')$. Dielectric loss, $\tan\delta = \varepsilon''/\varepsilon' = M'/M'' = -Z'/Z'' = Y''/Y'$. The complex electric modulus (M) reflects the dynamic properties of the sample alone[1].

The dependence of Z, M, Z’, M’, Z” and M” with frequencies can be clearly analyzed from the following figures

Fig.5(a)

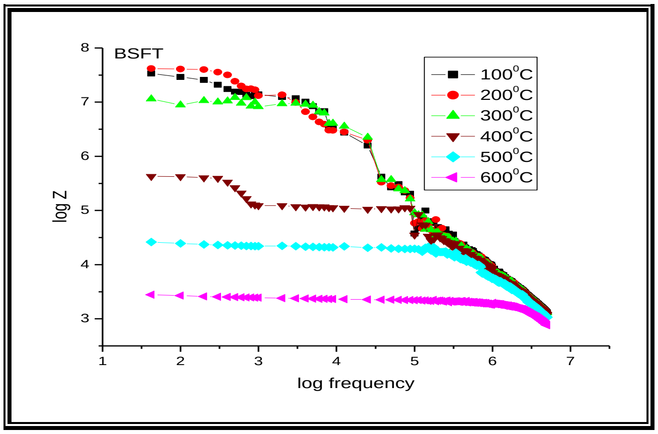


Fig.5(b)

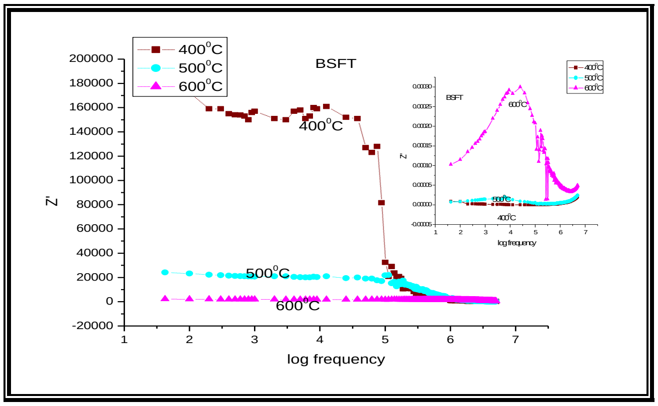
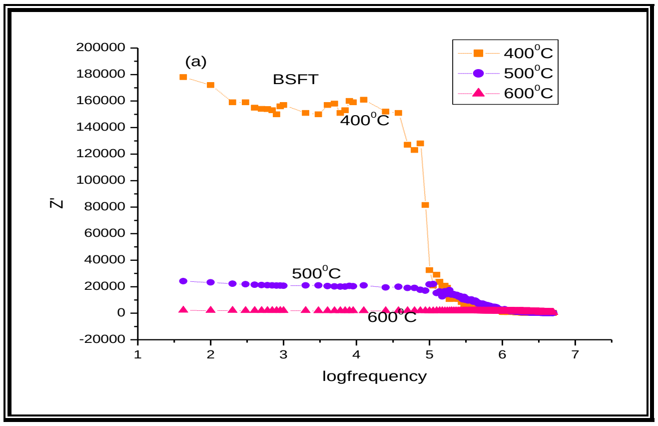


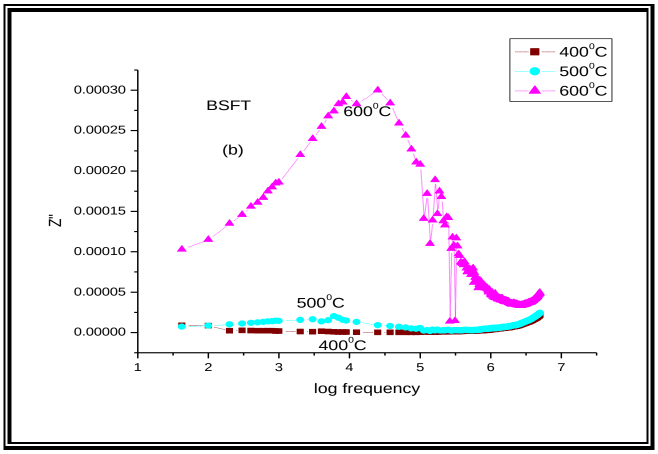
Fig.5(a) showing log Z with log frequency for BSFT while Fig.5(b) shows the variation of Z’& Z” with log frequency.

Above graphs with frequency clearly shows that the impedence of the material [BSFT] falls as frequency is increased. Both the real and complex impedence components shows a steep decrease as the frequency and temperature increases. But (M’&M”) the electrical modulus components rises as the temperature takes higher values.The values are even close to zero at low frequencies.

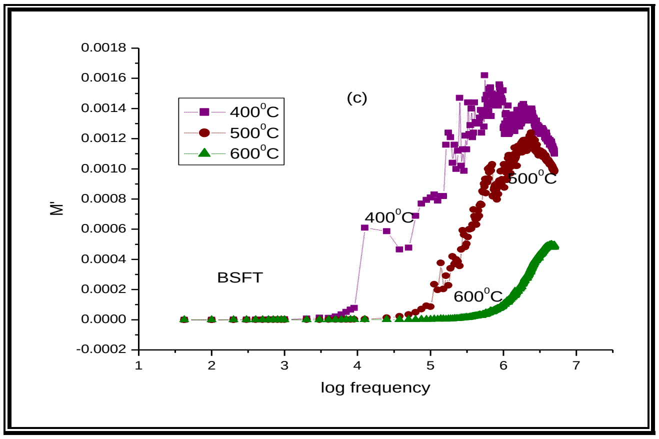
6(a)



6(b)



The rapid rise of tan δ in the high-temperature region is due to the free charge carriers. Since the concentration of free charge carriers is temperature dependent, the rate of loss also rises in the higher temperature region. But the loss factor is inversely proportional to frequency, space charges disappear at higher values of frequencies. The Q value of the sample is inversely proportional to the dielectric loss factor as in Fig .4.



6(c)

6(d)

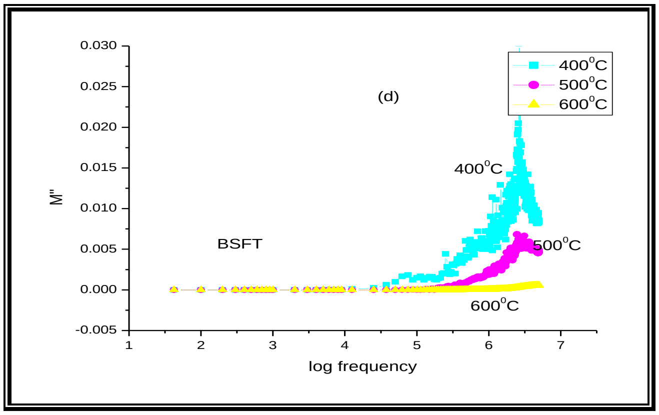


Fig.6(a-d)shows the dependence of Z', Z", M' &M" with frequency

The distinct behavior becomes prominent after temperature 400◦ C. This throws light that the phase formation attained has made the sample to be conductive. With increase in frequencies Z' (or M') gets a maximum value (Z' 'max/M' max) known as relaxation frequency (f r). This is due to the presence of immobile charges at lower temperatures, or due to the interface states which cannot pass ac signal at high frequencies. [15]. The peak height in Z' with frequency plot is proportional to the resistance, while the peak height in M' plot is inversely proportional to the capacitance of the sample [12].

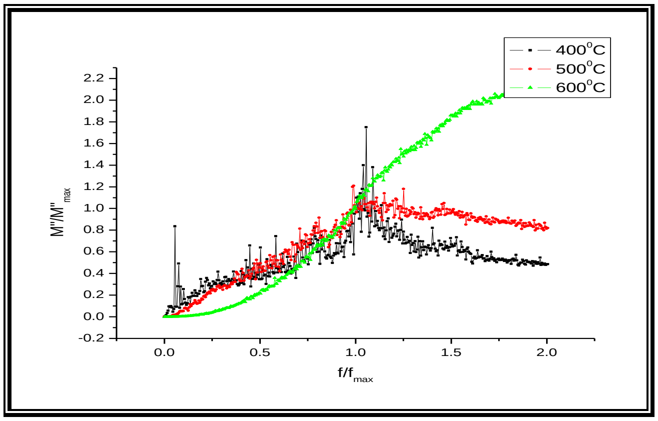


Fig.7

Fig.7 shows the modulus master curve of the sample BSFT $(Ba_{0.6}Sr_{0.4}Fe_xTi_{(1-x)}\ O_{3-\delta}\ {}_{(x=0.1)})$ at higher temperatures. The modulus peak maximum shifts to higher frequencies as temperature is raised. The overlap of the curves indicates that the dynamical processes are temperature independent [17]. Also the *M"/M" max* curves are not symmetric but wider than the Debye peaks showing a non-exponential & non-Debye behavior of the relaxation.

## 2.3.STEINHART–HART EQUATION:

The temperature coefficient is a basic concept in thermistor calculation [17] .Steinhart–Hart equation is given as

$$1/T = A + B\ln R + C\,(\ln R)\,3 \;---\; - \;Eqn.(1)$$

where T is measured in Kelvins. A, B and C are the curve fitting coefficients and ln R is the natural logarithm of resistance in ohms. Solving this equation set we obtain following values for fitting coefficients of Steinhart–Hart equation: A=1.4825E-3, B =1.66E-4&C= 2.614E-7.

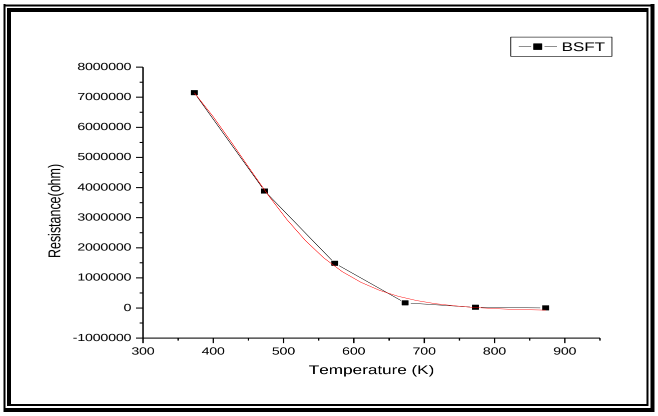


Fig.8-R-T graph of BSFT

The A, B and C values obtained from the fitting are well within standard acceptable value of thermistor.

| T(K) | R(Ω) |
|---|---|
| 373 | 7.15E6 |
| 473 | 3.88E6 |
| 573 | 7.48E6 |
| 673 | 1.72E5 |
| 773 | 2.32E4 |
| 873 | 2.11E3 |

## 2.4.SENSITIVITY INDEX OF A THERMISTOR [β]

The sensitivity index of thermistor gives an important specification of thermistor materials &its components. The sensitivity index of a thermistor [β] can be expressed as

$$\beta = [T\,TN/(TN - T)][\ln RT/RN] \; - - - - \; Eqn(2)$$

where RT is the resistance at temperature T; RN is the resistance at temperature TN. Figure below shows

sensitivity index in the temperature range of 100–600 K. β is a material characteristic which shows the resistance change percentage per degree centigrade[17].

Barium titanate materials being ferroelectric has temperature dependent dielectric constant values. Below the Curie point temperature, the high dielectric constant prevents the formation of potential barriers between the crystal grains, leading to a low value of resistance [18] .In this region the sample exhibits a small negative temperature coefficient. At the Curie point temperature, the dielectric constant falls & allows the formation of potential barriers at the grain boundaries and the resistance increases sharply with temperature showing an apparent PTC behavior in BSFT($Ba_{0\cdot6}Sr_{0\cdot4}Fe_xTi_{(1-x)}\,O_{3-\delta\,(x=0.1)}$).

$$\alpha = (1/R)[d(R)/dT] = -\beta / T\,2) \; - - - - \; Eqn(3)$$

Because the resistance of a thermistor is temperature dependent, the α value of the particular thermistor material is also nonlinear across the temperature range.

Fig 9(a)& (b)below shows both the sensitivity behaviour changes& the variation of α parameter of BSFT.

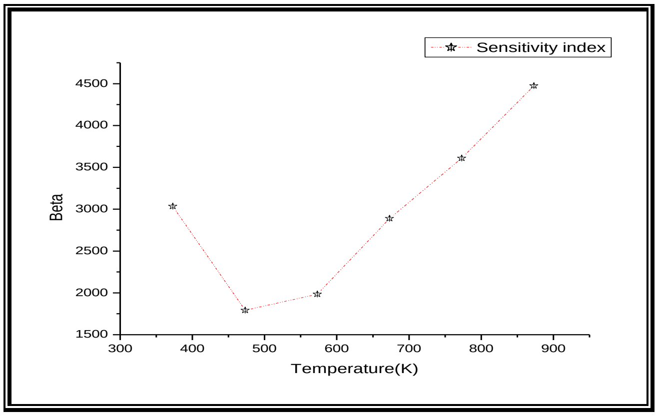


Fig9(a)

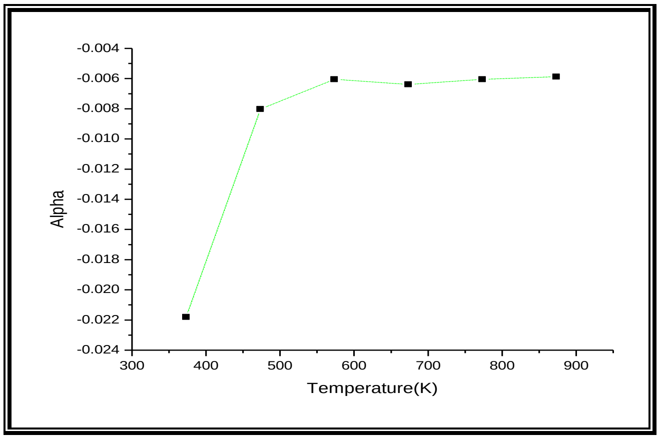


Fig 9(b)

## 2.5 CONDUCTIVITY MEASUREMENTS

a)ac Conductivity, σac

Ac electrical conductivity studies provides a good quality check on the electrical transport properties of the material. Using Jonscher's power law, $\sigma ac(\omega) = \sigma dc + A\omega n \; - - - Eqn(4),$ where σdc,(frequency independent plateau in the low frequency region), A is the temperature dependent pre-exponential factor and n the frequency exponent which takes values between 0&1is frequency independent but temperature and material dependent. The experimental σac values proves Jonscher's power law as given in Fig .10

The conductivity graphs clearly specifies three regions: (1) dispersion in the low frequency area, 2) an intermediate plateau & 3) conductivity dispersion at high frequency region. $\sigma_{ac}$ independent in the low frequency region is generally known as hopping frequency, but shifts towards higher-frequency side with increase of temperature as already reported [19]. The increasing value of $\sigma_{ac}$ with frequency rise is due to the disordering of cations between neighboring sites, and space charges. The dispersion gets lowered as frequency is increased. This conductivity rise with temperature points to a thermally activated process. $\sigma_{ac}$ depends inversely on dielectric loss as observed in Fig and its inset. This result owes to the literature where it is reported as due to the series resistance effect [20].

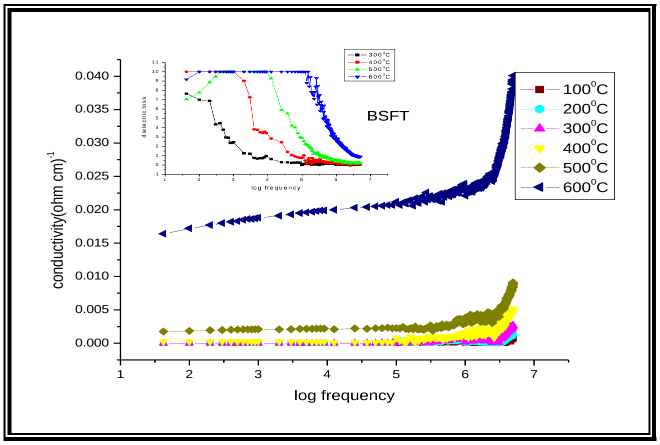


Fig .10 $\sigma_{ac}$ with log f graph.

(b) dc Conductivity, σdc

Fig .11 shows the variation of $\sigma_{dc}$ as a function of inverse of the absolute temperature.

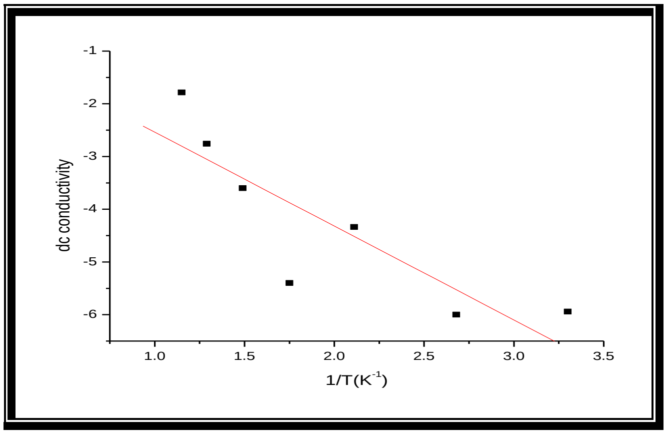


Fig.11 σdc as a function of inverse of absolute temperature

The graph shows a linear rise with temperature. The value of bulk conductivity of the sample at different temperatures is obtained from the $\sigma_{ac}$ plot of the sample by theoretical fitting using Joncher's power law. At higher temperature, the conductivity versus temperature response can be explained by a thermally activated transport of Arrhenius type.

The activation energy is obtained as1.78eV. The low activati4on energy values confirms the hopping mechanism in the material under study[15]. The conductivity of the sample BSFT is very less than the sample BSFTO ,already reported[1].

## VI. CONCLUSION

The frequency and temperature dependent dielectric dispersion analysis of the ferroelectric ceramic BSFT ($Ba_{0}{\cdot}_{6}Sr_{0}{\cdot}_{4}Fe_{x}Ti_{(1-x)}$ $O_{3-\delta}$ $_{(x=0.1)}$) has been well studied. The impedance studies indicate that the relaxations in the samples are due to the presence of polarizing species. Mobility of ions and imperfections in the material contributes to the space charge polarization at higher temperature. A better & detailed analysis of the electrical properties in terms of bulk and grain-boundary contribution have been discussed.

From the temperature sensitivity studies of the BSFT ($Ba_{0}{\cdot}_{6}Sr_{0}{\cdot}_{4}Fe_{x}Ti_{(1-x)}$ $O_{3-\delta}$ $_{(x=0.1)}$) it is clear that below the Curie point temperature, the sample exhibits a small negative temperature coefficient. At the Curie point temperature, the dielectric constant decreases, resistance increases sharply with temperature in BSFT ($Ba_{0}{\cdot}_{6}Sr_{0}{\cdot}_{4}Fe_{x}Ti_{(1-x)}$ $O_{3-\delta}$ $_{(x=0.1)}$) showing a positive temperature thermistor characteristics.

The $\sigma_{ac}$ conductivity plots well confirm the Jonscher's power law. The temperature dependence of dc conductivity through the Arrhenius law proves the hopping mechanism in the sample..

## VII. FUTURE SCOPES

Due to the PTCR properties, barium titanate ceramic materials is most often found used as thermistor /thermalswitches. Judicious and careful selection of dopants like Fe contributes for the reduction of dielectric properties giving high conductive potential for the material $Ba_{0}{\cdot}_{6}Sr_{0}{\cdot}_{4}Fe_{x}Ti_{(1-x)}$ $O_{3-\delta\ (x=0.1)}$.

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