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Multifaceted Characterization of BFO-BST ferovskites: A Study of Dielectric Properties

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Abstract

Extensive research into the shared features of MF-ME materials has been conducted because to their potential utility in numerous modern technologies and their significant contributions to elementary physics. Among the several MF-ME materials that have been created or manufactured throughout the years, Bismuth Ferrite (BFO), also known as BiFeO3 or Bismuth Ferrite, is an innovative ferro-magnetoelectric material. This material exhibits a rhombohedral perovskite structure with crystal symmetry R3c or C6 3V, and it is stated to have remarkable thermal conductivity at temperatures of 830oC and 400oC. To add to the ongoing endeavor to enhance and alter the fundamental characteristics of Bismuth ferrite (BiFeO3), a multiferroic substance that has been recognized for its efficacy at room temperature, we set out to construct a BFO-BST prototype. Subsequently, we have investigated the BFO-BST system doped with La, Nd, and Sm extensively with regard to its dielectric, structural, ferroelectric, and microstructural characteristics.

Keywords: *conductivity, dielectric, ferroelectric, prototype, crystal.*

Introduction

The dielectric characteristics of BFO have been studied for over 40 years. Extensive research has been conducted on the dielectric phenomena of BFO single crystals, thin films, and ceramics, focusing on their temperature and frequency dependence. The tests were conducted using a conventional frequency response analyzer. Measurements of the temperature-dependent dielectric constant at microwave frequencies, ranging from 273K to 1150K. They observed a linear increase in the dielectric constant from ε=45 to 150, but the dielectric loss remained constant with a loss tangent of tanδ=0.09. The FE transition temperature was determined to be 1120K, however the measurement was imprecise. Bismuth ferrite (BFO) undergoes decomposition into Bi2Fe4O9 and F2O3 at elevated temperatures that are significantly lower than its melting point. The measurements of dielectric permittivity, AC and DC conductivity of BFO single crystals. The temperature dependence of dielectric permittivity was measured at 100 kHz and 1 MHz, as indicated by the inset in the upper frame. The lower frame inset displays the frequency dependence of the alternating current (AC) conductivity at a temperature of 100 K. The yellow stars symbolize outcomes obtained under microwave conditions, whereas the solid and hollow diamonds reflect different experimental conditions.

Materials and methods

The raw materials used to manufacture all of our samples were AR grade, 99.99% pure oxides (Bi2O3, La2O3, Sm2O3, Nd2O3, Fe2O3, TiO2) and carbonates (BaCO3, SrCO3).

Conductivity Study

The movement of charges that are weakly bound in a substance exhibit organized motion when influenced by an external electric field. This is the cause of transport phenomena or conductivity in dielectric materials, which is referred to as volume conductivity. The movement of charges in the presence of an alternating electromagnetic field (EMF) results in the generation of a conduction current, denoted as I. This current is determined by the equation I = jωεCoV, and it leads to the polarization of the dielectric material. The contribution of conductivity to dielectric loss is mathematically described by the following equation:

$$\sigma dc = \sigma' + j\sigma'' = [s'' + j(s' - s\infty)]$$

If a material has relative permittivity εr and dielectric loss tanδ at a frequency λ, then its AC conductivity is calculated by using the equation:

$$\sigma ac = sosrmtan\eth$$

Frequency dependent ac conductivity obeys the Jonscher's universal power law:

$$\sigma ac(m) = \sigma o + Amn$$

The symbol ζo represents the direct current conductivity, also known as ζdc. The angular frequency ω is equal to 2πf, where f is the frequency. A is a constant and n is a parameter that depends on frequency and can have values ranging from 0 to 1. The fluctuation in the value of n is caused by the discontinuous movement of charge carriers between randomly placed localized sites. The conduction caused by charge carriers is affected by two mechanisms: Quantum Mechanical Tunneling (QMT), which involves the passage of charge carriers through a barrier that separates localized sites, and Correlated Barrier Hopping (CBH), which involves the movement of charge carriers across the same barrier. These mechanisms often account for the presence of the Aωn term.

The quantity of DC conductivity, which is triggered by thermal energy, follows the Arrhenius relation.

$$\sigma dc = \sigma oexp\ (-Ea)/kBT$$

The symbol σo represents the pre-exponential term, Ea stands for the activation energy, kB denotes the Boltzmann constant, and T represents the absolute temperature. The electrical conductivity in a material changes from being independent of frequency (dc conductivity) to being dependent on frequency (ac conductivity) as the frequency increases. This transition occurs at a certain frequency called the hopping frequency (ωp), which may be analytically determined.

$$(m) = [1 + (m\diagup mp)]$$

Results and discussion

Transport or Conductivity Studies

The electrical conductivity of dielectric/ferroelectric materials is investigated because to the significant influence of electric signals on many physical properties such as mechanical, dielectric, and optical characteristics. A material that is classed as an ionic or electronic conductor is associated with the category of charge carriers (electrons/holes or cations/anions) that dominate the conduction events. The higher values of direct current (dc) conductivity observed in actuality are attributed to the presence of free charge carriers that are absent in dielectric materials.

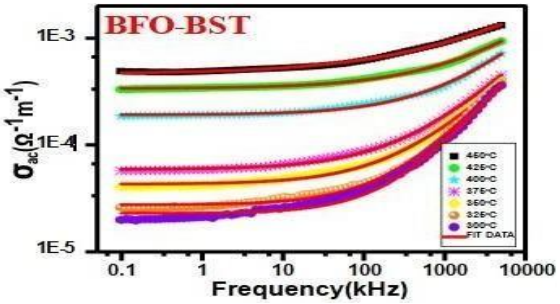

Figure 1. Frequency dependent variation of AC conductivity plot of BFO-BST [BiFeO3] 0.5 [(BaSr)0.5TiO3] 0.5

The conductivity at low frequencies and high temperatures is mostly caused by the grain boundary effect, namely through the dominance of the Maxwell-Wagner mechanism. This has been confirmed through investigations on the dielectric properties that vary with frequency. The frequency-dependent AC conductivity can be described by a power law equation,

$$\zeta ac\ (\omega) = \zeta o + A\omega n.$$

In this equation, ζo represents the DC conductivity, ω is the angular frequency (equal to 2πf), A is a constant, and n is a parameter that depends on temperature. For charge carriers that undergo hopping-type motion, n has values between 0 and 1. For translational motion, n is greater than 1. The graph of AC conductivity has a low frequency plateau region, which is commonly referred to as DC conductivity (ζdc), and a frequency-dependent component, ζac. The graph is theoretically fitted using a power law equation, and the fitting parameters include the values of ζdc, A, and n. At elevated temperatures, a frequency-dependent plateau of low strength emerges, which may be closely linked to direct current conductivity (ζdc or ζo). The foregoing investigation indicates that a hopping conduction mechanism, specifically the Universal Dielectric Response (UDR), is responsible for governing the high temperature range in all doped samples of Series-I. The observed rise in ac conductivity as temperature increases in all the materials investigated can be attributed to the Negative Temperature Coefficient of Resistance (NTCR) feature, which is influenced by the presence of thermally activated charge carriers.

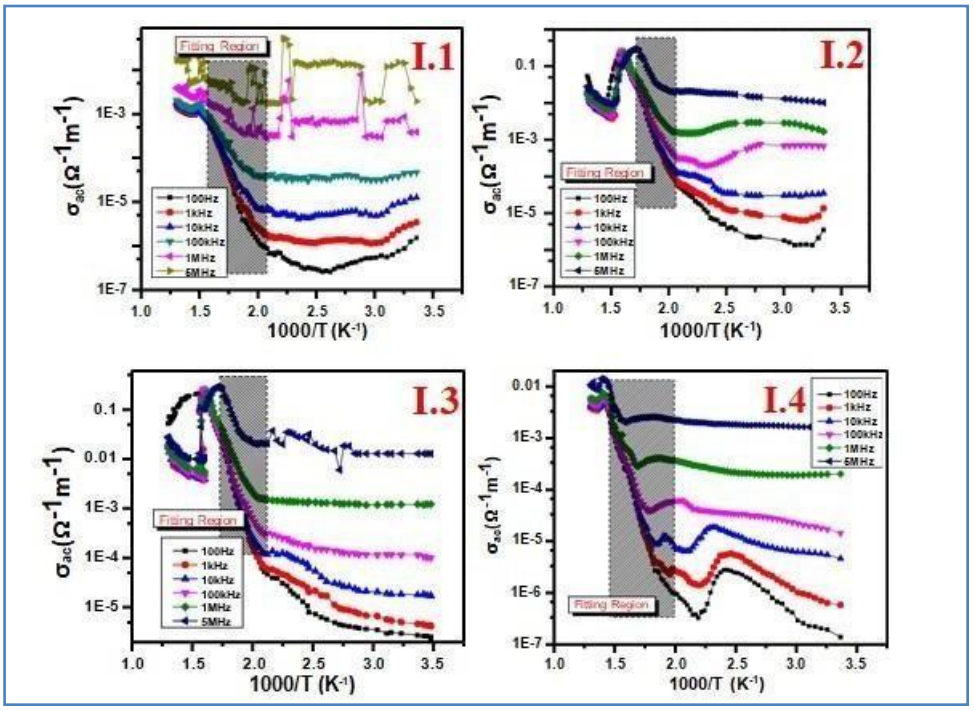

Figure 2. Temperature dependent variation of AC conductivity or Arrhenius plots of [BixLa(1-x)(BaSr)0.5]0.5[FeTi]0.5O3 (I.1).x=0, (I.2).x=0.25, (I.3).x=0.5 and (I.4).x=0.75.

The study of conductivity is focused on the control exerted by charge carriers. The decrease in activation energy is attributed to the decrease in frequency. However, at higher frequency, the hopping is limited to the nearest neighboring defect sites due to the shorter response time available to respond to external factors. The activation energies (Ea) were determined for all samples by performing linear regression on the experimental data points in the high temperature range. The values of Ea for different frequencies and temperatures are presented in Table 1. The movement of electric charges between specific locations is facilitated by an increasing external force, which decreases the energy required for activation as the frequency increases. The low activation energies reported are attributed to the electron hopping that occurs between ions with different vacancies.

Table 1. Activation energies (Ea) of BFO-BST & Series-I samples recorded for different frequencies in the high temperature zone.

Frequency	ActivationEnergy(E_a)ofBFO-BST&Series-Isamples(ineV)				
	BFO-BST	**LA1(x=0)**	**LA2(x=0.25)**	**LA3(x=0.5)**	**LA4(x=0.75)**
100Hz	-	0.133	0.541	0.72	1.30
1kHz	-	0.12	0.50	0.697	1.18
10kHz	0.078	0.08	0.46	0.54	1.16
100kHz	0.067	0.066	0.393	0.47	1.07
1MHz	0.043	0.05	0.31	0.41	0.97
5MHz	0.023	0.043	0.215	0.39	0.88

Conclusion

The BFO-BST and Series-I (or La doped) samples demonstrate adherence to Jonscher's universal power law in terms of their conductivity. However, for the Nd and Sm doped BFO-BST samples, namely the Series-II and Series-III samples, the conductivity spectrum follows the modified or double power law. The presence of varying slopes in the plot suggests the presence of distinct conduction processes. The AC conductivity graphs for all samples, according to Arrhenius, indicate that the conduction mechanism in the samples is frequency-dependent and is caused by hopping processes. These mechanisms result in greater activation energy values at high temperatures.

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