



# Article Complex Dielectric and Impedance Spectroscopic Studies in a Multiferroic Composite of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>-BiFeO<sub>3</sub>

## Panda Alaka and Ramanujan Govindaraj \*

Materials Science Group, HBNI, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, Tamil Nadu, India; Ikpanda@igcar.gov.in

\* Correspondence: govind@igcar.gov.in

Received: 4 November 2018; Accepted: 28 November 2018; Published: 2 December 2018



**Abstract:** Complex dielectric and impedance spectroscopic studies have been carried out in a detailed manner on the system comprising of  $Bi_2Fe_4O_9$ -BiFeO<sub>3</sub> composite particles dispersed in a  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> matrix as prepared using ball milling and controlled annealing treatments. This multiferroic composite is observed to exhibit a giant dielectric constant associated with a low tangent loss. A non-Debye type of relaxation has been deduced based on complex modulus analysis. Based on these studies, the important role played by bismuth ferrite nanoshell in the core-shell composite of  $Bi_2Fe_4O_9$ -BiFeO<sub>3</sub> is elucidated for the observed complex impedance spectroscopic properties of the system. Electron hopping across Fe<sup>2+</sup>/Fe<sup>3+</sup> and oxygen vacancies are deduced to be playing an important role in conduction mechanisms based on activation energy analysis of the complex impedance spectroscopy results.

Keywords: Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>; dielectric; multiferroic; composite

## 1. Introduction

Coexistence of ferroelectric (paraelectric), ferromagnetic (antiferromagnetic), and ferroelastic properties in certain materials result in wide applications, such as sensors, actuators, and multistate memory and spintronic devices [1,2]. Yet, very few single-phase materials, such as BiFeO<sub>3</sub>, show this property at or near room temperature [3]. A thin film of BiFeO<sub>3</sub> has been demonstrated to show very large polarization [1], but it is deduced that the grain boundaries in a polycrystalline film and defect structures could result in degradation of ferroelectric polarization effects and leakage characteristics. Thus, the need for studies of multiphase or composite oxides based on bismuth iron oxides exhibiting multiferroic properties is very important [4–7]. To be considered as important, the composite material concerned should exhibit strong coupling effects, for example, between ferroelectric and antiferromagnetic properties [8,9]. Systems consisting of oxides, such as BiMnO<sub>3</sub>, BiFeO<sub>3</sub> and Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> [10] are reported to exhibit strong coupling of ferroelectric response of materials, such as BiFeO<sub>3</sub>, by composite oxides based on the former, which exhibit multiferroic properties at room temperature, is very important with respect to developing multifunctional devices.

This paper reports the results of detailed complex impedance spectroscopic studies on  $Bi_2Fe_4O_9$ -BiFeO<sub>3</sub> composite and explores its suitability for making charge storage devices based on high frequency applications. BiFeO<sub>3</sub> exhibits antiferromagnetic ordering ( $T_N = 643$  K) and is also ferroelectric ( $T_C \sim 1103$  K) at room temperature. On the other hand, another bismuth iron oxide based  $Bi_2Fe_4O_9$  is also multiferroic ( $T_C \sim 260$  K,  $T_N \sim 250$  K). With respect to dielectric studies, single phased  $Bi_2Fe_4O_9$  is observed to possess a low value of dielectric constant (~30–40) whereas BiFeO<sub>3</sub> single

This paper reports the bulk structural characterization of  $BiFeO_3-Bi_2Fe_4O_9$  composite as prepared by ball milling and local structural and magnetic properties using Mossbauer spectroscopy. Electrical properties of the  $BiFeO_3-Bi_2Fe_4O_9$  composite system have been studied in a detailed manner using complex impedance spectroscopic techniques to understand different relaxations, and are discussed.

## 2. Results and Discussion

#### 2.1. Structural Analysis

X-ray diffraction pattern obtained in the ball milled and annealed sample shows mainly the presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> (Cf. Figure 1). This can be deduced based on the stick patterns provided corresponding to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>. XRD pattern corresponding to the case of ball milled and annealed (BMA) sample confirms the formation of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and BiFeO<sub>3</sub> phases as expected along with Fe<sub>2</sub>O<sub>3</sub>. This implies a significant interaction of Bi<sub>2</sub>O<sub>3</sub> along with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, resulting in the formation of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> as well as BiFeO<sub>3</sub> phases. A significant presence of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> has been observed in the ball milled and annealed sample, hence Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> has been prepared through solid state reaction and the resulting XRD pattern (Figure 1c) shows that the sample contains a single phase of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>.



**Figure 1.** XRD patterns corresponding to (**a**) ball milled, (**b**) ball milled and annealed ball milled and annealed (BMA) sample with broadened peaks indicative of composite structure as compared to (**c**)  $Bi_2Fe_4O_9$  prepared through solid state reaction. Also shown are the stick patterns corresponding to  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

## 2.2. TEM Studies

Transmission electron microscopy studies reveal that there are core-shell structured particles occurring in the ball milled and subsequently annealed sample (Cf. Figure 2). Based on the analysis of the selected area electron diffraction (SAED) pattern corresponding to the core, it is deduced that the core is basically composed of  $Bi_2Fe_4O_9$ . Based on the FFT analysis, it is deduced that the shells

are amorphous in nature, thus these particles are deduced as having  $Bi_2Fe_4O_9$  as the core and a shell of amorphous bismuth ferrite and alpha- $Fe_2O_3$ . The presence of  $BiFeO_3$  and  $alpha-Fe_2O_3$  have been deduced based on the results of XRD and Mössbauer studies.



Figure 2. Transmission electron micrograph showing the presence of core-shell particles.

## 2.3. Mössbauer Studies

Mössbauer studies have been carried out in transmission geometry in order to mainly understand the local structure and magnetic properties of the phases existing in the samples. Resultant Mossbauer spectra (Cf. Figure 3) and analyzed hyperfine parameters (Cf. Table 1) are shown. In the ball milled sample, it is observed that almost all Fe atoms are associated with only  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, implying that most  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles exist as a single phase. Only about 4% of Fe atoms are observed to be associated with BiFeO<sub>3</sub>. While in the Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> sample prepared through the solid state route, it is observed that Mössbauer spectrum could be de convoluted into two doublets characteristic of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, with Fe atoms occupying octahedral and tetrahedral sites. It is observed that in addition to the doublet corresponding to Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, there occurs broad modified sextets related to BiFeO<sub>3</sub> evolved in the studied BMA sample, and the corresponding hyperfine parameters are presented in Table 1.



**Figure 3.** Mössbauer spectra corresponding to (**a**) ball milled mixture of Bi<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, (**b**) BMA, and (**c**) Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> sample.

Sample Details	i	Γ <sub>i</sub> mm/sec	δ <sub>i</sub> mm/sec	Δ <sub>i</sub> mm/sec	B <sub>hf</sub> Tesla	f <sub>i</sub>
BM-α-Fe <sub>2</sub> O <sub>3</sub> -Bi <sub>2</sub> O <sub>3</sub>	1 <sub>a</sub>	0.48	0.38	-0.21	51.8	0.75
	$1_b$	0.45	0.36	-0.15	50.3	0.18
	$1_{c}$	0.18	0.33	-0.14	53.4	0.04
	2 <sub>a</sub>	0.22	0.30	0.38	40.4	0.03
BMA	1 <sub>a</sub>	0.22	0.34	-0.18	51	0.34
	$1_b$	0.26	0.33	-0.15	52	0.12
	$2_d$	0.28	0.48	0.24	47.3	0.06
	2 <sub>b</sub>	0.26	0.44	1.09	46	0.05
	$2_{\rm c}$	0.24	0.50	0.23	35.5	0.07
	3 <sub>a</sub>	0.25	0.24	0.82	0	0.14
	3 <sub>b</sub>	0.3	0.38	0.53	0	0.22
Bi <sub>2</sub> Fe <sub>4</sub> O <sub>9</sub> (SSR)	3 <sub>a</sub>	0.32	0.29	0.86	0	0.51
	3 <sub>b</sub>	0.32	0.39	0.33	0	0.49

**Table 1.** Hyperfine parameters obtained through Mössbauer spectroscopy of samples subjected to different annealing treatments.

Mössbauer results presented in Table 1 show the presence of phases, such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, BiFeO<sub>3-x</sub>, and Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, indicated as 1, 2, and 3, respectively. Here, 1<sub>a</sub>,1<sub>b</sub>,1<sub>c</sub> corresponds to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, while 2 and 3 are due to Fe atoms associated with phases, such as BiFeO<sub>3</sub> and Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, respectively.

Hyperfine parameters deduced in the ball milled sample show mostly alpha-Fe<sub>2</sub>O<sub>3</sub> commensurate with XRD results. Mössbauer studies carried out in  $Bi_2Fe_4O_9$  prepared through the solid state route (Cf. Figure 3 and Table 1) show Fe atoms occupying tetrahedral and octahedral sites. In the case of BMA, it could be deduced that about 46% of Fe atoms are associated with alpha-Fe<sub>2</sub>O<sub>3</sub>, and the remaining fractions associated with magnetic interactions are due to BiFeO<sub>3</sub>.

Importantly, it is seen from the hyperfine components corresponding to BiFeO<sub>3</sub> that the presence of oxygen vacancies in this phase could be deduced as indicated by higher values of isomer shift compared to 0.3 mm/s corresponding to Fe<sup>3+</sup>. Hence, based on the XRD and Mössbauer results, it can be deduced that the system of the present study BMA is characterized to be a composite of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, BiFeO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

In the following section, we will mainly discuss the results of complex impedance spectroscopic studies in this composite.

#### 2.4. Complex Modulous Spectroscopic Studies

Complex modulous spectroscopy is an important tool for determination, analysis, and interpretation of dynamical aspects of electrical transport properties in materials, such as carrier/ion hopping rate and conductivity relaxation. Modulous spectroscopy results are mainly useful for distinguishing spectral components of materials having similar values of resistances, but different capacitances. These results are mainly used for suppressing electrode effects and to get the intrinsic effects corresponding to the sample.

#### 2.4.1. Dielectric and Impedance Studies

Dielectric response of a system represents the variation of resistive and capacitive behavior with frequency and temperature as well distinguishing any anomaly around the transition temperature giving information about the possible magnetodielctric, magnetocapacitive, or magnetoelectric coupling.

Dielectric properties of the BMA sample are measured and compared in terms of frequency dependence of real part of the dielectric constant ( $\varepsilon_1$ ) at different temperatures of the samples (Cf. Figure 4). As shown in Figure 4a, a sharp decrease in the dielectric constant with an increase in frequency is indicative of a Maxwell-Wagner type relaxation due to space charge release, creating a

high impedance barrier at the sample electrode interface and thus a high value of the dielectric constant. With an increase in the frequency of the applied electric field, the dipoles are unable to follow the applied field and thus the dielectric constant ( $\varepsilon$ ) decreases and becomes independent of temperature in a high frequency region. A significantly large value of the dielectric constant has been observed in the sample. The step like dielectric relaxation is observed at low frequencies for low measurement temperatures. While the trend according to Koop theory is followed in both the cases, there is a plateau region in the low frequency region as seen in the  $\varepsilon_1$  vs. f plot, and correspondingly there occurs a peak in the tangent loss shown as the inset in the case of the ball milled and annealed sample (BMA). This plateau region is further observed to shift to a high frequency region with increasing temperature. This can be attributed to a new relaxation phenomena appearing in the case of the BMA sample due to

The frequency value at which the step like behavior occurs is observed to increase with an increasing temperature of the sample. The step like dielectric relaxation as observed at low temperatures in the case of BMA is understood to be due to polaron relaxation, which results from the carrier hopping process between  $Fe^{2+}$  and  $Fe^{3+}$ . Such a polaron hopping includes a dielectric relaxation process roughly explained by Debye theory. At low temperatures, electric dipoles freeze due to the relaxation process. The relaxation process is mainly dictated by the rate at which the polarization occurs and the frequency of the applied electric field.

the presence of off stoichiometric  $BiFeO_3$  as deduced from the Mössbauer results.

The dielectric relaxation is, in general, represented as:

$$\varepsilon(\omega) = \varepsilon_{\infty} + (\varepsilon_{0} - \varepsilon_{\omega})/(1 - i\omega\tau) = \varepsilon_{1}(\omega) + i \cdot \varepsilon_{2}(\omega)$$

where  $\omega$  is the angular frequency, and  $\varepsilon_0$  and  $\varepsilon_\infty$  are the static dielectric constant ( $\omega \to 0$ ) and permanent dielectric constant ( $\omega \to \infty$ ). Where  $\tau$  is the relaxation time and  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$  are the real and imaginary parts of the dielectric response, respectively. The loss factor is given as  $\tan \delta = \varepsilon_2(\omega)/\varepsilon_1(\omega)$ , while  $\delta$  is the phase difference between the applied electric field and induced current. While  $\varepsilon_2(\omega)$  can be obtained from the above equation as  $\varepsilon_2(\omega) = \omega \cdot \tau/1 + (\omega \cdot \tau)^2$  and the maximum of  $\varepsilon_2(\omega)$  lies around  $\omega \cdot \tau \approx 1$ .

A close observation of the plots (cf inset 4(a) show that a dielectric peak corresponding to a dielectric loss peak (cf Figure 4a(i),(ii)) is observed, which shifts to a high frequency with an increase in temperature. The presence of such a peak is indicative of conductive losses due to relaxing dipoles in the sample [12]. This occurs in a transition temperature range of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> (~300 K) and shifts towards the magnetic transition temperature of BiFeO<sub>3</sub> (~500 K). Being a sum property,  $\varepsilon_{eff}$ ' is expected to include  $\varepsilon$  values from the phases in the composite that is from Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, BiFeO<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> as well. An observation of a similar anomaly in the dielectric constant has been previously observed and discussed for BiFeO<sub>3</sub> [13]. The shifting of the loss peak implies that it is a thermally activated process [13].

The dielectric relaxation time,  $\tau$ , is given as  $\tau^{-1} = \tau_0^{-1} \exp(-E_a/k_BT)$ , with  $E_a$  as the activation energy required for relaxation and  $k_BT$  as the thermal energy. As the maximum of  $\varepsilon_2(\omega)$  lies around  $\omega \cdot \tau \approx 1$ , from the tangent loss curve corresponding to different temperatures, the values of the dielectric relaxation time have been obtained. Plotted in Figure 4c is the variation of the natural logarithm of dielectric relaxation time with inverse temperature. From the slope of the linear graph, the value of the activation energy for relaxation could be obtained as around 0.6 eV, matching well with the thermally activated mechanism of charge carrier transport across the interface of the grain/grain boundary. The loss peak could be fitted with the Arrhenius equation and fitted with a straight line [14]. The activation energy obtained is 0.6 eV (cf Figure 4c), which is close to that of the energy corresponding to Fe<sup>2+</sup>/Fe<sup>3+</sup> electron hopping due to the oxygen vacancies present in the constituting phases [15]. The insets in Figure 4a show the discontinuity around the transition temperature region of both the phases.



**Figure 4.** Temperature dependence of (**a**) dielectric permittivity. Corresponding variations marked inside rectangular panels are magnified and shown in insets as (i) and (ii), respectively. (**b**) shows the core-shell structured particle having dielectric constants,  $\varepsilon_C$  and  $\varepsilon_s$ , for the core and shell, respectively. While (**c**) shows the variation of  $\ln(\tau \cdot \tan \delta)$  with 1000/T.

The high dielectric response is mainly contributed by the shell and interfacial polarization i.e., Maxwell–Wagner polarization. In a core-shell structure, which is present in a medium with a dielectric constant,  $\varepsilon$ , with the core having a dielectric constant,  $\varepsilon_C$ , and thickness, L, while if these values corresponding to the shell are  $\varepsilon_S$  and d, the effective dielectric constant at low frequencies is given,  $\omega$ , as:

$$\varepsilon^* \approx (\varepsilon_C/\varepsilon) + (\varepsilon_S/(\varepsilon \,\delta \,[1 + i\omega\tau])) \approx L\varepsilon_S/d$$

where in the above equation  $\delta$  is given as d/L. In the present case, taking the value of the dielectric constant (of  $\varepsilon_5$ ) of BiFeO<sub>3-x</sub> as around 50 and d as typically of the order of a few nm ( $\approx$ 1 nm) and L as a few micron, we could get the value of  $\varepsilon^*$  typically of the order of  $0.5 \times 10^5$ , typically matching with the results around low frequencies obtained in this study, and thus elucidating the giant dielectric response of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and bismuth iron oxide in a core-shell structure. Further, the presence of insulating  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the outer shell significantly enhances the effect of polarization of charges at the bismuth ferrite interface. In the present case, it is important to note that both the basic value of the intrinsic dielectric constant ( $\varepsilon_5$ ) and the interface effect in terms of the thickness of the shell and interface effects contribute for the enhanced value of the giant dielectric relaxation.

Thus, the strong polarization effects are understood to be due to between electron trapped oxygen vacancies of BiFeO<sub>3</sub> and that in any other cation (Bi<sup>3+</sup>), thus inducing space charges between the insulating core (Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>) and inner surface of the shell of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. High values of permittivity associated with a strong maximum in the dielectric losses have been reported in bismuth iron oxide based thin films and core-shell structures.

Variation of the real part of impedance with frequency at different temperatures are shown in Figure 5. The Z' value decreases with increase in T and merges at a higher frequency and becomes constant. This implies space charge release in the material [16]. The zoomed in region in Figure 5a shown as arrow depicting the constancy of the modulus value at the low frequency region, which decreases with frequency and becomes zero. A corresponding peak is observed in the Z" vs. f plot (Cf Figure 5b), which shows broad and asymmetric peaks shifting towards a high frequency and indicative of the non-Debye type due to the distribution of relaxation as the width of the peak varies for different temperatures [17]. The Arrhenius fitting of the peak frequency versus the inverse of temperature (Figure 5c) could be fitted with a straight line with a high value of activation energy possibly due to the inhomogeneous grain boundary effects due to the occurrence of multiple multiferroic phases.





Figure 5. Cont.



(c)

1000/T (K<sup>-1</sup>)

0 -2

-8 -10 -12

-4 -6 μ

**Figure 5.** (a) and (b) show the frequency dependence of the real (top) and imaginary (bottom) part of the impedance, respectively. Shown in the insets are magnification of rectangular panels showing the variation of Z' and Z'' with frequency. While (c) shows Arrhenius fitting of the peak frequency of the variation of Z''.

The imaginary and real part of impedance values plotted (Cf Figure 6) showing semicircles known as a Cole-Cole plot is effective in separating out the spectral component contribution of resistance from the grain, grain boundary, and electrodes. The shifting of the intercept on abscissa corresponds to the total resistance contribution and is observed to shift with an increase in temperature indicative of the resistive property that is the bulk resistance,  $R_b$  [18]. This implies that, with increasing temperatures, the conductivity of the sample increases as more electrons are free to contribute to conduction due to available thermal energy. The observation of a semicircle may indicate that the constituent phases must be existing in a compact manner, like the core-shell type of particles, due to which the overall contribution is coming as a single semicircle even though three phases are present. As the grain and grain boundary are distinctively different in their order of magnitude, it is difficult to get two semicircles corresponding to the grain and grain boundary on one scale [19]. Thus, modulus analysis is an effective plot to observe this effect prominently as, instead of resistance, it is characterized by capacitive effects in the sample, which comes close for the grain and grain boundary. This is discussed in detail subsequently.



Figure 6. Cole-Cole plot of the composite (inset zoomed in region shown in box).

### 2.4.2. Modulus Analysis

Modulus analysis is an impressive technique to rule out completely or suppress the electrode effect and deal with the electrical conduction mechanisms (hopping) occurring in the sample in terms

M" vs. f

Bi2Fe4O9 SSR

of the grain and grain boundary only. This helps in separating the region with similar resistances and different capacitances, and thus suppress the electrode effect to understand the relaxation properties of ionic conductors and polycrystalline materials [20]. The Argand plot of modulus can get rid of the ambiguity that comes from the grain and grain boundary effect and is shown in Figure 6.

The modulus represents the relaxation of the electric field in the material when electric displacement remains constant so that the electric modulus represents the real dielectric relaxation process [21]. For all the temperature ranges, to start with the M' value is small, which implies the negligible/zero electrode effect [22]. M' measures the ability of the material to store energy and M" is effective to understand the ionic conduction mechanism [23]. The plot of M' and M" (Cf. Figure 7) shows continuous dispersion with frequency, implying short range mobility of the charge carriers. The observation of a plateau in the mid frequency region shifts, which implies the existence of frequency relaxation in the material [24]. The increase in M' with frequency shows that the relaxation distribution is spreading over the range of frequency and is accompanied by a peak in M" plots. The broad and asymmetric peak in M" is again indicative of the non-Debye type relaxation with a distribution of relaxation time. The ions that interact in its surrounding will introduce a perturbed potential and affect the motion of neighboring ions. Thus, this cooperative motion will give rise to a distribution of the relaxation time [25]. In general, the region to the left of the M"peak implies a range in which charge carriers are mobile over long distances, and that to the right is the range in which the carriers are confined to potential wells over a short range [13,26]. Shown in Figure 8 is also the Arrhenius fitting of M" peaks in terms of the variation of  $\ln (M(\tau))$  with 1000/T. The variation shows the occurrence of two distinct slopes. Similar observation on  $ZrTiO_4$  is discussed by Victor et al. [19], wherein they got two peaks with an activation energy 0.52 eV for the high frequency and 1.32 eV for the low frequency. The low frequency peak with higher activation energy is attributed to the grain boundary barrier formation against electron conduction where the ionic motion is more easily compared to the tightly packed grains. The low frequency grain with lower activation energy is understood as if the electron is trapped in shallow potential wells or oxygen vacancies. In this case, the observation of two peaks in M" can be understood as governed by the inhomogenities due to the presence of different phases of the composite system. Shifting of the M" peak toward the high frequency with an increase in temperature is similar to that of ionic conductors and semiconductor [19]. The activation energy and relaxation time corresponding to the two peaks of the M" plot are given in Table 2. The presence of two activation energies is indicative of the two conductive mechanisms viz., conduction through the grain and grain boundary that is occurring in the sample, which could be deduced from modulus plots more clearly.

The Argand plot M" vs. M' (Cf. Figure 8) shows two semicircles corresponding to the grain boundary and grain, respectively, with no sign of a third semicircle (due to electrode effect). The intercept of the first semicircle is the inverse of the grain boundary capacitance and that of the second is the inverse of the total capacitance in series [19].

solid state route (SSR) corresponding to one peak.						
Plot	Sample	E <sub>a</sub> (eV)	$ au_0$ (s)	Possible Mechanism Involved		
Tan δ vs. f	BM 3 step	0.6	$2.853 imes10^{-13}$	Fe <sup>2+</sup> /Fe <sup>3+</sup> electron hopping		
Z" vs. f	BM 3 step	1.5	$1.28 imes10^{-16}$	Grain boundary barrier		
M" vs. f	BM 3 step low f peak	1.13	$2.97  imes 10^{-15}$	Grain boundary barrier		
M" vs. f	BM 3 step high f peak	1.01	$8.77  imes 10^{-15}$	Oxygen vacancies		

0.6

 $7.02 \times 10^{-14}$ 

Fe<sup>2+</sup>/Fe<sup>3+</sup> electron hopping

**Table 2.** Arrhenius fitting of tangent loss and impedance for the ball milled and annealed (BMA) sample with two peaks corresponding to two peaks in M<sup>"</sup> (upper inset) for Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> prepared through solid state route (SSR) corresponding to one peak.



**Figure 7.** Variation of real and imaginary part of the electric modulus (top left and right) with frequency at different temperatures.



**Figure 8.** (a) shows the variation of  $\ln(\tau(M''))$  with 1000/T argand plot of M'' vs. M' is shown in (b).

The relaxation time is the time required for the recombination of charges till the capacitor is fully discharged during which the field is no longer applied. As can be seen from Table 2, the activation energy and correspondingly the time required for dielectric relaxation is higher for oxygen vacancy defects and thus the hopping from  $Fe^{2+}/Fe^{3+}$ . While the dielectric relaxation time for the composite is 10 times higher as compared to single phase  $Bi_2Fe_4O_9$ , implying that the composite shows better capacitive effect and hence charge storage effects [27].

The normalized plot of M" as well as Z" is shown in Figure 9, which shows a non-coincident of frequency of occurrence of maxima, which implies two different phenomena contributing for the relaxation in the modulus and impedance, respectively. This indicates the non-Debye type behavior of the system in the temperature range of 423 K–623 K [28].



**Figure 9.** Variations of Z" and M" normalized with respect to their maximum values with the frequency at different temperatures are shown.

## 2.4.3. Conductivity Analysis

Conductivity of ferroelectric material is an important phenomenon to understand for its piezo and pyroelectric behavior as well as the conductivity which in turn depends upon the dielectric behavior of the sample. Further, there is a strong coupling between the temperature and frequency dependent behavior of the conductivity. The ac conductivity ( $\sigma_{ac}$ ) study signifies the presence of single or multiple relaxation in the material. In this case, the ac conductivity plot with respect to frequency at different temperatures (cf Figure 10) can be divided into a low frequency plateau governed by random hopping of electrons contributing to dc conductivity and a high frequency dispersive region dependent upon  $\omega^n$  (where  $\omega$  is the angular frequency and n is a constant dependent upon frequency and temperature) and defines the type of conductivity [28] related to the hopping of electrons between trap levels situated in the bandgap [25].



**Figure 10.** Conductivity fitted plots (inset shows the variation of *n* with respect to 1000/T (K<sup>-1</sup>).

*n viz.*: (i) Quantum mechanical tunneling (QMT) through barriers separately localized sites and (ii) Correlated Barrier Hopping (CBH) over the same barrier [30]. *n* has two different trends with respect to frequency and time. If *n* is *T* independent and decreases with  $\omega$  then  $\sigma_{ac}$  originates from QMT while n decreases with increasing *T* for CBH. Funke et al. reported for  $n \leq 1$  that hopping involves translational motion and for n > 1 there occurs localized hopping of charges without the charges leaving the neighborhood [31]. Hopping conduction is consistent with the fact that high density of states (DOS) in the material having a bandgap similar to that of a semiconductor, which can be understood as an increase in temperature of the delocalization of charge carrier support polaron formation and hopping occurs between neighboring sites [32].

The *n* values throughout the *T* range from 373 K onwards is observed to be < 1, implying that our results are correlating with the CBH model in the mentioned *T* range and the hopping involves translational motion with sudden jumps. The variation is shown in the plot. The significance of the plot further confirms the sum property of the conductive behavior due to which there are two slopes corresponding to the constituent phases of the composite. From the fitted parameter in the given temperature range, the height of the potential well can be calculated using the formula,  $n = 1 - 6k_BT/W_m$ , where k<sub>B</sub> and *T* are the Boltzmann constant and absolute temperature respectively, and  $W_m$  is the depth of the potential well [33].

The non-dispersive dc conductivity with respect to 1000/T is plotted as shown in Figure 10 and could be fitted with a straight line of an Arrhenius type with two slopes very close by. The dc conductivity increases with *T*, which in turn implies the decrease in Rb, and thus the material exhibits a negative temperature coefficient of resistance (NTCR) similar to a semiconductor [34,35].

The presence of two multiferroic phases in this case is understood to be contributing to the total dielectric properties. In addition, the resistance of the composite particles is observed to be much higher than the typical value of resistance corresponding to individual multiferroic phases, which implies that the dielectric properties of the combined phases is enhanced. Two different mechanisms are understood to be involved in the relaxation of dielectric and impedance behavior of BiFeO<sub>3</sub>-Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite particles (Cf. Table 2).

#### 3. Materials and Methods

Laboratory grade starting oxides,  $Bi_2O_3$  and  $Fe_2O_3$ , in the ratio of 1:3 are taken towards the formation of required composite in the  $Fe_2O_3$  matrix. The oxides are taken for high energy ball milling using stainless steel balls of different sizes in isopropanol medium for efficient milling for 4 h with 30 min heating and subsequent cooling process. Prior to ball milling, only  $Fe_2O_3$  was milled for 3 h to reduce its grain size as well as to improve the surface for reaction to form the required composite. The obtained milled powder was converted into pellets of 10 mm diameter and ~2 mm thickness using hydraulic press and sintered for 12 h at 1073 K and 10 h at 1123 K with intermittent grindings and further sintered at 1073 K for 24 h and will be henceforth referred to as ball milled and annealed (BMA) sample. The resulting mixture was powdered and characterized by means of XRD (Inel 2000 X-Ray Diffractometer with Cu k<sub>a</sub> source in Bragg-Brentano geometry) for phase analysis.

<sup>57</sup>Fe Mössbauer spectroscopy studies have been done in constant acceleration mode and in transmission geometry of the spectrometer (Wissel make) using <sup>57</sup>Co dispersed in the Rh matrix for phase and magnetic analysis. Mossbauer studies have also been carried out in pure Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> in order to delineate the defect components associated with composite of BiFeO<sub>3</sub> and Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>. Dielectric studies have been carried out in a detailed manner on the composite sample using a high resolution Alpha Analyzer (Novocontrol GmbH make). Since the main component of the composite of the present study is Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> (which is the most stable oxide of bismuth and iron based oxides), structural and Mossbauer results on Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> prepared by the solid state reaction route are also discussed.

## 4. Conclusions

This work discusses in a detailed manner the results of complex impedance spectroscopic studies carried out in a composite of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>-BiFeO<sub>3</sub> particles as separated by Fe<sub>2</sub>O<sub>3</sub>. Impedance spectroscopic results showing the occurrence of a single semicircle corresponding to that of the composite system consisting of  $Bi_2Fe_4O_9$ -BiFeO<sub>3</sub> might be occurring in core-shell configurations, which is consistent with TEM results. The dielectric properties of the composite system are understood in a detailed manner. Temperature dependence of dielectric properties of the composite has been observed to be superior as compared to a single system of either  $Bi_2Fe_4O_9$  or  $BiFeO_3$ . The composite material exhibits a transition temperature around room temperature ( $\approx$  300 to 500 K), which is much higher than the ferroelectric transition temperature of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and lower as compared to that of BiFeO<sub>3</sub>. This result provides the scope for its enhanced and superior applications in the electronic industry as compared to individual phases by discarding the issues related to cryogenic or the need of high temperatures for exhibiting multiferroicity behavior. Further, a much higher value of the dielectric constant with a low loss factor of the composite as compared to pure BiFeO<sub>3</sub>. In addition, this value of the giant dielectric constant is stable over a wide temperature and frequency ranges. This establishes that the composite could be extensively used as a high temperature capacitor (in the interval  $\approx$  300 to 500 K, wireless communications, and microwave and RF applications in electrical systems [36–38]. Electron hopping across  $Fe^{2+}/Fe^{3+}$  and oxygen vacancies are deduced to be playing an important role in conduction mechanisms based on activation energy analysis of the complex impedance spectroscopy results.

Author Contributions: Conceptualization—R.G.; Methodology, Validation, Formal Analysis, Investigation, Writing-Original Draft Preparation, Writing-Review & Editing—R.G. and A.P.

Funding: This research received no external funding.

**Acknowledgments:** Authors are thankful to G. Amarendra, Director, MSG for his support and encouragement. Alaka acknowledges DAE for support of her fellowship. Also we thank P. Magudapathy for XRD measurements and broadband dielectric spectrometer central facility in IITB for dielectric measurements.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

- Wang, J.; Neaton, J.; Zheng, H.; Nagarajan, V.; Ogale, S.; Liu, B.; Viehland, D.; Vaithyanathan, V.; Schlom, D.; Waghmare, U. Epitaxial BiFeO<sub>3</sub> mutliferroic thinfim heterostructures. *Science* 2003, 299, 1719–1722. [CrossRef] [PubMed]
- Erenstein, W.; Mathur, N.; Scott, J. Multiferroic and magnetoelectric materials. *Nature* 2006, 442, 759–765. [CrossRef] [PubMed]
- 3. Hill, N.A. Why are there so few magnetic ferroelectrics? J. Phys. Chem. B 2000, 104, 6694–6709. [CrossRef]
- 4. Singh, K.; Negi, N.S.; Kotnala, R.K.; Singh, M. Dielectric and magnetic properties of (BiFeO<sub>3</sub>)1-x(PbTiO<sub>3</sub>)x ferromagnetoelectric system. *Solid State Commun.* **2008**, *148*, 18–21. [CrossRef]
- 5. Uniyal, P.; Yadav, K.L. Synthesis and study of multiferroic properties of ZnFe<sub>2</sub>O<sub>4</sub>-BiFeO<sub>3</sub> nanocomposites. *J. Alloy. Compd.* **2010**, *492*, 406–410. [CrossRef]
- 6. Sahu, T.; Behera, B. Investigation on structural, dielectric and ferroelectric properties of samarium-substituted BiFeo<sub>3</sub>-PbTiO<sub>3</sub> composites. *Adv. Dielectr.* **2017**, *1*, 1750001–1750006. [CrossRef]
- Bajpai, O.P.; Kamdi, J.B.; Selvakumar, M.; Ram, S.; Khastgir, D.; Chattopadhyay, S. Effect of surface modification of BiFeO<sub>3</sub> on the dielectric, ferroelectric, magneto-dielectric properties of polyvinylacetate/BiFeO<sub>3</sub> nanocomposites. *Express Polym. Lett.* **2014**, *8*, 669–681. [CrossRef]
- Adhlakha, N.; Yadav, K.L. Structural, magnetic, and optical properties of Ni0.75Zn0.25Fe<sub>2</sub>O<sub>4</sub>-BiFeO<sub>3</sub> composites. *J. Mater. Sci.* 2014, 49, 4423–4438. [CrossRef]
- 9. Ryu, J.; Priya, S.; Uchino, K.; Kim, H. Magnetoeelctric effect in composites of magnetostrictive and piezoelectric materials. *J. Electroceram.* **2002**, *8*, 107–119. [CrossRef]
- 10. Rao, C.N.R.; Sundaresan, A.; Saha, R. Multiferroic and magnetoelectric oxides. *J. Phys. Chem. Lett.* **2012**, *3*, 2237–2246. [CrossRef]

- 11. Varshney, D.; Kumar, A.; Verma, K. Effect of A site and B site doping on structure, thermal and dielectric properties of BiFeO<sub>3</sub> ceramics. *J. Alloy. Compd.* **2011**, 509, 8421–8426. [CrossRef]
- 12. Pélaiz-Barranco, A.; Gutierrez-Amadon, M.P.; Huanosta, A.; Valenzuela, R. Phase transition in ferromagnetic and ferroelectric ceramics by ac measurement. *Appl. Phys. Lett.* **1998**, *73*, 2039–2041. [CrossRef]
- 13. ELmezayyen, A.S.; Reicha, F.M. Preparation of Chitosan Copper Complexes: Molecular Dynamic Studies of Chitosan Copper Complexes. *Open J. Appl. Sci.* **2015**, *5*, 415–421. [CrossRef]
- 14. Arrhenius, S. Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren. Z. Phys. Chem. 1889, 4, 226–248. [CrossRef]
- Gheorghiu, F.; Calugaru, M.; Ianculescu, A.; Mustcate, V.; Mitoseriu, L. Preparation and functional characterization of BiFeO<sub>3</sub> ceramics: A comparative study of the dielectric properties. *Solid State Sci.* 2013, 23, 79–87. [CrossRef]
- 16. PŁcharski, J.; Weiczorek, W. PEO based composite solid electrolyte containing nasicon. *Solid State Ion*. **1988**, 28–30, 979–982. [CrossRef]
- 17. Singh, H.; Kumar, A.; Yadav, K.L. Structural, dielectric, magnetic, magnetodielectric and impedance spectroscopic studies of BiFeO<sub>3</sub>-BaTiO<sub>3</sub> ceramics. *Mater. Sci. Eng. B* **2011**, *176*, 540–547. [CrossRef]
- 18. Satpathy, S.; Mohanty, N.; Behera, A.; Behera, B. Dielectric and electrical properties of 0.5(BiGd0.05Fe0.95O<sub>3</sub>)-0.5 (PbZrO<sub>3</sub>) composite. *Mater. Sci.* **2014**, *32*, 59–65. [CrossRef]
- 19. Victor, P.; Bhattacharrya, S.; Krupanidhi, S.B. Dielctric relaxation in laser ablated polycrystalline ZrTiO<sub>4</sub> thin films. *J. Appl. Phys.* **2003**, *94*, 5135–5142. [CrossRef]
- 20. Kolte, J.; Daryapurkar, A.S.; Gulwade, D.D.; Gopalan, P. Microwave sintered Bi0.90La0.10Fe0.95Mn0.05O<sub>3</sub> nanocrstal ceramics: Impedance and modulus spectroscopy. *Ceram Int.* **2016**, *42*, 12914–12921. [CrossRef]
- 21. Pradhan, D.K.; Choudhary, R.N.P.; Samantaray, B.K. Studies of structural, thermal and electrical behavior of polymer nanocomposite electrolytes. *Express Polym. Lett.* **2008**, *2*, 630–638. [CrossRef]
- 22. Yakuphanoglu, F.; Senkal, B.F. Electronic and thermoelectric properties of polyaniline organic semiconductor and electrical characterization of Al/PANI MIS diode. *J. Phys. Chem. C* 2007, *111*, 1840–1846. [CrossRef]
- 23. Angell, C.A. Dynamic processes in ionic glasses. *Chem. Rev.* **1990**, *90*, 523–542. [CrossRef]
- 24. Pribosic, I.; Makovec, D.; Drofenic, M. Electrical properties of donor and acceptor doped BaBi<sub>4</sub>Ti4O<sub>15</sub>. *Eur. Ceram. Soc.* **2001**, *21*, 1327–1331. [CrossRef]
- Anand, K.; Ramamurthy, B.; Veeraiah, V.; Vijaya Babu, K. Effect of Magnesium substitution on structural and dielectric properties of LiNiPO<sub>4</sub>. *Mater. Sci.* 2017, 35, 66–80. [CrossRef]
- 26. Dutta, A.; Sinha, T.P.; Jena, P.; Adak, S. AC conductivity and dielectric relaxation in ionically conducting sodalime-silicate glasses. *J. Non-Cryst. Solids* **2008**, *354*, 3952–3957. [CrossRef]
- 27. Baral, A.; Meher, K.R.S.P.; Varma, K.B.R. Dielectric behavior of Sr<sub>2</sub>SBMnO<sub>6</sub> ceramics fabricated from nanocrystalline powders prepared by molten salt synthesis. *Mater. Sci. Bull.* **2011**, *34*, 53–60. [CrossRef]
- Mohapatra, S.R.; Sahu, B.; Badapanda, T.; Pattanaik, M.S.; Kaushik, S.D.; Singh, A.K. Optical, dielectric relaxation and conductivity study of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> ceramic. *J. Mater. Sci. Mater. Electron.* 2016, 27, 3645–3652. [CrossRef]
- 29. Mariyappan, C.R.; Govindaraj, G.; Ramya, L.; Hariharan, S. Synthesis, Characterizationand electrical conductivity studies on A<sub>3</sub>Bi<sub>2</sub>P<sub>3</sub>O<sub>12</sub> (A-Na.K) materials. *Mater. Res. Bull.* **2005**, *40*, 610–618. [CrossRef]
- 30. Joanscher, A.K. A new understanding of the dielectric relaxation of solids. *J. Mater. Sci.* **1981**, *16*, 2037–2060. [CrossRef]
- Behera, A.K.; Mohanty, N.K.; Satpathy, S.K.; Behera, B.; Nayak, P. Effect of rare earth doping in impedance modulus and conductivity properties of multiferroic composites: 0.5 BiLaxFe<sub>1-x</sub>O<sub>3</sub>-0.5 PbTiO<sub>3</sub>. *Acta Metall. Sin.* 2015, 28, 841–857. [CrossRef]
- 32. Funke, K. Jump Relaxation in Solid Electrolytes. Prog. Solid State Chem. 1993, 22, 111–195. [CrossRef]
- Behera, B.; Nayak, P.; Choudhary, R.N.P. Impedance spectroscopy study of NaBa<sub>2</sub>V<sub>5</sub>O<sub>15</sub> ceramic. J. Alloy. Compd. 2007, 436, 226–232. [CrossRef]
- Dridi, R.; Saafi, I.; Mhandi, A.; Matri, A.; Yumak, A.; Lakhdar, M.H.; Amlouk, A.; Boubaker, K.; Amlouk, M. Structural, optical and AC conductivity studies on alloy ZnO-Zn<sub>2</sub>SnO<sub>4</sub>(ZnO-ZTO) thin films. *J. Alloy. Compd.* 2015, 634, 179. [CrossRef]
- 35. Ranjan, R.; Kumar, P.; Kumar, N.; Behera, B.; Choudhary, R.N.P. Impedance and electrical modulus analysis of Sm modified Pb(Zr0.55Ti0.45)<sub>1-x/4</sub>O<sub>4</sub> ceramics. *J. Alloy. Compd.* **2011**, *509*, 6388–6394. [CrossRef]

- Jia, W.; Hou, Y.; Zheng, M.; Xu, Y.; Zhu, M.; Yang, K.; Cheng, H.; Sun, S.; Xing, J. Advances in lead free high-temperature dielectric materials for ceramic capacitor application. *JET Nanodielectr.* 2018, 1, 3–16. [CrossRef]
- 37. Lanbing, F.; Danping, S.; Yanming, H.; Laijung, L. Low dielectric loss and good thermal stability of Eu and Ti codoped K0.5Na0.5NbO<sub>3</sub> ceramics. *J. Mater. Sci. Mater. Electron.* **2015**, *26*, 7159–7164. [CrossRef]
- 38. Sebastian, M.T.; Ubic, R.; Jantunen, H. Low loss dielectric ceramic material and their properties. *Int. Mater. Rev.* **2015**, *60*, 392–412. [CrossRef]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).