Influence of BaO doping on the structural, ac conductivity, and dielectric properties of BiFeO$_3$ multiferroic nanoparticles

M. S. Ayoub$^a$, Ibrahim Morad$^{a,b}$, H. Elhosiny Ali$^{c,d}$, M. M. Mostafa$^a$, M. M. El–Desoky$^a$,$^1$

$^a$Physics Department, Faculty of Science, Suez University, Suez, Egypt

$^b$State Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, Zhejiang University, Hangzhou 310027, China

$^c$Advanced Functional Materials & Optoelectronic Laboratory (AFMOL), Department of Physics, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, Saudi Arabia.

$^d$Department of Physics, Faculty of Science, Zagazig University, Zagazig, Egypt.

Abstract
The Bi$_{1-x}$Ba$_x$FeO$_3$ (BiBaFeO$_3$) multiferroic nanoparticles with different Ba molar concentrations were fabricated in reliance on the solid-state reaction technique. Nanostructures of the prepared samples were confirmed by X-ray diffraction (XRD) together with Fourier transforms infrared (FTIR) spectroscopy, whereas the ac conductivity, dielectric and ferroelectric features were examined depending on the RLC Bridge, and Sawyer–Tower circuit. XRD patterns displayed the creation of rhombohedral–hexagonal single-phase of BiBaFeO$_3$. The formation of BiBaFeO$_3$ multiferroic nanoparticles was confirmed by FTIR spectra. Curie temperature ($T_C$) was observed around 1121–1189 K. Ferroelectric polarization was enhanced with remnant polarization of 88.8 μC/cm$^2$ by Ba$^{2+}$ ions substitution at $x = 0.15$ mol%. Besides, ac electrical conductivities as a function of frequency as well as temperature were reported for all BiBaFeO$_3$ multiferroic nanoparticles, which exhibit a strong frequency dependence with conduction mechanism is the correlated barrier hopping (CBH) model. The obtained high polarization and Curie temperature enhance their use in information storage devices.

Keywords: Multiferroic, dielectric, Ferroelectricity, XRD

$^1$ Corresponding author (M. M. El–Desoky): mmdesoky@gmail.com
mmdesoky@suezuniv.edu.eg

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1. Introduction

Multiferroics that show a set of two anti/ferromagnetism, anti/ferroelectricity and/or ferroelastic (stress-strain hysteretic relationship) simultaneously at the similar pressure and temperature [1]. A wide variety of possible data storage applications, logic devices, sensors, and spintronic devices are the most common advantages of multiferroics [2, 3], and as the ferroelectric and ferromagnetic coupling properties allow the complex interaction among variables of these arrangements [4]. BiFeO$_3$ shows a higher Curie temperature ($T_C \sim 1103$ K) as well as higher Néel temperature ($T_N \sim 643$ K) [5]. Owing to the off-centered disruption of Fe$^{3+}$ ions formed by 6$s^2$ lone pairs of Bi$^{3+}$ ions through its non-centrosymmetric rhombohedral framework, ferroelectricity appears in purely BiFeO$_3$ [6]. At room temperature, BiFeO$_3$ demonstrates Antiferromagnetic G-type arranging because of its cycloidal spin structure with a wavelength ($\lambda \sim 62$ nm). It exists a single-phase multiferroic compound with a warped perovskite ABO$_3$ structure [7] and yet the dominant compound with ferroelectricity and antiferromagnetism intercurrent at room temperature [8].

The considerable oxygen vacancies amount formed as a result of the extremely Bi volatile aspect together with the several Fe valance states (Fe$^{2+}$ and Fe$^{3+}$) cause the material to lose its ferroelectric properties due to a high leakage current [9]. The high leakage current is a large barrier in applications of BiFeO$_3$ [10]. The doping approach was recommended as a better way to boost multiferroic properties by reducing the leakage current or minimizing the second phase to eliminate this problem [1]. Thus, substitution cations such as (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) at the Bi$^{3+}$ site as well as (Co$^{3+}$, Cr$^{3+}$, Mn$^{3+}$) cations at the Fe$^{3+}$ site may improve the ferroelectric possessions of BiFeO$_3$ [11-13]. These replacements give rise to strengthen the ferroelectric properties along with the change in BiFeO$_3$ crystal symmetry. In this paper, Bi$_{1-x}$Ba$_x$FeO$_3$ (0.10 $\leq x \leq 0.25$ mol%) multiferroic nanoparticles were successfully synthesized and the Ba$^{2+}$ ions substitution effect on the structural, electrical, dielectric, and ferroelectric characterizations of BiFeO$_3$ have been investigated in details.

2. Experimental
Nanostructure multiferroic samples Bi\(_{1-x}\)Ba\(_x\)FeO\(_3\); (x = 0.1 - 0.25 mol%) were fabricated by solid-state reaction method. The raw materials were containing Bi\(_2\)O\(_3\)(99.99%), BaCO\(_3\), and Fe\(_2\)O\(_3\)(99.99%) were weighted with a Stoichiometric ratio. The raw chemical powders were well mixed and continuous ground through an agate mortar for 210 min. The as-prepared samples were gently pressed till produced a pellet form. First, the pellet samples sintered at 873 K with a 4 K/min heating rate in an open atmosphere for 360 min. Subsequently, the samples were reground for 90 min. The last sintering process was be exhausted at 1123 K for 180 min in the air with the last heating rate. The as-synthesized nanoparticle samples were characterized by XRD via Diano Corporation of target Co–K\(_\alpha\) to confirm the utilization of solid reaction and the single-phase achievement. By employing type, A Jasco-FT/IR-4100 in the 250 cm\(^{-1}\) to 1000 cm\(^{-1}\) range, the IR spectra were reported. Dielectric constant and ac electrical conductivity as a function of the frequency range from 100 kHz to 1 MHz and from 5 kHz to 1 MHz were tested from room temperature (RT) up to 1200 K as a function of the temperature using the RLC Bridge (Microtest model 6377). In addition, through a Sawyer–Tower circuit, ferroelectric hysteresis loops were estimated. The RT polarization against the electric field (P–E) hysteresis loops were collected at 50 Hz.

3. Results and discussion

3.1 Characterization

3.1.1 X-ray diffraction (XRD)

Fig. 1 represents the XRD patterns of the Bi\(_{1-x}\)Ba\(_x\)FeO\(_3\) multiferroic nanoparticles with different Ba molar concentrations. Fig. 1 (a) displays a strong reflection to (110), (024), (012), (214), and (202) that referred to as the rhombohedral–hexagonal unit cell belonging to the R3c space group. The Debye–Scherrer (Eq.1) formula has been employed to evaluate the mean crystallite size denoted by (D) [14-16].

\[
D = \frac{k \lambda}{\beta \cos \theta}
\]  

The extra little intensities secondary phase is listed as Bi\(_2\)Fe\(_4\)O\(_9\) and BaFe\(_2\)O\(_4\) and by the Ba\(^{2+}\) ions addition substitution, the Bi\(_2\)Fe\(_4\)O\(_9\) impurity peaks have vanished. The
diffraction peaks of (104) and (110) merge towards one peak at \( x = 0.15 \) to examine the influence of barium content mostly on structure, with the increasing replacement of \( \text{Ba}^{2+} \) ions, as could be shown in Fig.1 1(b).

The mean crystallite size value possesses a minimum value at \( x = 0.15 \), it is showing that the maximum distortion in the system displayed at \( x = 0.15 \) [14]. The prepared sample crystallite sizes are listed in Table 1. The lattice parameters \((a \text{ and } c)\) were calculated according to the hexagonal distortion of the rhombohedral structure and listed in Table 1. It is noted that with rising barium concentration complying with the well-known Vegard law, the lattice parameters growing substantially [17], enhancement in the unit cell volume \((V)\), and the density decreases with increasing barium content as recorded in Table 1.

The characteristics of the cations on the A-sites and the B-sites, for example, frequently cause common distortions, such as cation groupings inside the octahedra and octahedra inclining. Generally, the distortion degree can be estimated by A-site in ABO\(_3\) perovskites. The tolerance factor \((t)\) [18, 19] was determined by using the following Eq.2

\[
t = R_A + R_O / \sqrt{2}(R_A + R_O)
\]  

(2)

where \( R_A, R_B, \) and \( R_O \) are the A, B, and oxygen ions ionic radii, respectively.

The effective ionic radius of the A-site cation is calculated by

\[
R_{A(\text{eff})} = R_{Bi^{3+}} \times (1 - x) + R_{Ba^{2+}} \times (x)
\]  

(3)

where \( R_{Bi^{3+}} \) and \( R_{Ba^{2+}} \) are the Bi\(^{3+}\) and Ba\(^{2+}\) ions ionic radii, respectively.

The data displayed in Fig. 2 indicated a tolerance factor increase as barium content increases as a result of the larger Ba\(^{2+}\) ions ionic radius. The tolerance factor values display the twisted structure of the rhombohedral. These results have a good matching with XRD analysis. The tolerance factor rose because of the ionic radii difference of the A-site cations \((\text{Bi}^{3+} = 1.17 \text{ Å}, \text{Ba}^{2+} = 1.42 \text{ Å})\) by growing the barium amount throughout the BiFeO\(_3\) lattice. The development in the tolerance factor implies there is an increase in distortion. As a result of increasing the ionic radius of the A-site cation scale, this distortion resulted from the inclination of the octahedron. Therefore, the atomic distances were predictable to be changed due to the change in ionic radii because
of the replacement trivalent cation \( \text{Bi}^{3+} \) instead of divalent one \( \text{Ba}^{2+} \) according to the above Eqs. 2 and 3.

### 3.1.2 Fourier transform infrared (FTIR) spectra

FTIR transmission bands of BiBaFeO\(_3\) multiferroic nanoparticles are shown in Fig. 3. An abnormal vibration band of about 630 cm\(^{-1}\) \((\square_1)\) is fulfilled for BiBaFeO\(_3\) multiferroic nanoparticles. In this region, a comparable vibration band was monitored for Ceria substituted BFO [20] Since the vibration of Ba-O seems mostly in the region of low frequency. The 630 cm\(^{-1}\) band refers to strong metal-oxygen M–O\(_6\) bending vibration [21] Such vibration band is an impurity phase possibility as a minor impurity phase has been seen in replacement XRD. The strong 441 cm\(^{-1}\) \((\square_4)\) and 576 cm\(^{-1}\) \((\square_2)\) absorption bands are owning to Fe–O bending and stretching vibration, respectively, being the octahedral \(\langle\text{FeO}_6\rangle\) characteristic vibration. The broad vibration band at 538 cm\(^{-1}\) \((\square_3)\) is a consequence of the presence of \(\langle\text{BiO}_6\rangle\) octahedral coexisting together with \(\langle\text{FeO}_6\rangle\) [22, 23]. The band at 360 cm\(^{-1}\) \((\square_5)\) is categorized as the bending vibration mode of O–Fe–O [24]. The spectra of 302 cm\(^{-1}\) \((\square_6)\) could be arises from the iron ions bending vibration, which is much less that of stretching. As the direct effect of Ba\(^{2+}\) ion substitutions, the bending vibration emerges from the spinning of the \(\langle\text{FeO}_6\rangle\) octahedron. The adjustment in the A-site cation radius, simply put, causing a tilting of \(\langle\text{FeO}_6\rangle\) octahedron.

The variability in the locations of the bands in the FTIR spectrum is due to the alteration in the bond lengths and sometimes angles. As stated in the XRD section, these variations are well recognized and illustrated by the reliance of the lattice parameters on the content of barium. The shift in the expansion of the band is noticeable from the FTIR spectra; the spectral nature and intensity changes on Ba-doped BiFeO\(_3\) suggest a structural alteration. The optical phonon frequency \((\square_7)\) and Debye temperature \(\square_8\) could be estimated from FTIR spectra utilizing the reported absorption band [25], which owning to bending and stretching Fe–O vibrations bonds. by utilizing the equation

\[
c = \lambda v_o = \frac{v_0}{v'}
\]

where \(\square_7\) is the optical phonon frequency. The Debye temperature \(\square_8\) could be calculated according to the relation [26]
\[ h\nu_0 = k_B\theta_D \]  

(5)

The estimated optical phonon frequency and Debye temperature values are presented in Table 2.

3.2 Dielectric constant

3.2.1 Temperature–dependence

Including all multiferroic BiBaFeO\(_3\) nanoparticles, the variance of the real part dielectric constant (\(\varepsilon'\)) with an absolute temperature in the range of 300 K to 1200 K in response to frequency is demonstrated in Fig. 4.

The data in Fig. 4 shows that \(\varepsilon'\) value increases very slowly with increasing the absolute temperature and afterward increases rapidly as far as the transition temperature and then decline again. Two factors are affecting \(\varepsilon'\) and polarization. The first one is the effect of the electric field associated with the applied frequency, which leads to the ordering of the electric dipoles. Thus, the polarization and the dielectric constant increased. The second factor is the thermal effect, which leads to the disorder in the oriented dipoles, and consequently a decrease in the polarization as well as \(\varepsilon'\). Moreover, \(\varepsilon'\) increases swiftly escorted by increasing temperature upwards a maximum \(T_c\). This enhancement because of the large free dipoles number caused by high thermal energy and aligned in their direction by the field effect. Besides, after \(T_c\), the gradual reduction in the values of \(\varepsilon'\) is owing to the thermal energy, which is overlarge and resists the electric field's influence.

On account of substitute Bi\(^{3+}\) ions regarding Ba\(^{2+}\) ions, the enhance of \(\varepsilon'\) occurs according to the concentration of barium and the off-center distortion will decline since Ba\(^{2+}\) ions do not contain a lone pair. In addition, oxygen vacancies are formed, determining the octahedral oxygen collapse \(<\text{FeO}_6>\) [27, 28].

Besides, an aberration has indeed been taken place in the dielectric curve. The alternatives in the unusual peak position as a consequence of Ba\(^{2+}\) ions substitutions are shown in Fig. 4, which seems in the antiferromagnetic change vicinity. The abnormal dielectric peak displays the coupling between the properties of both the antiferromagnetic and dielectric as a magnetic transition effect on the electric order was foreseen by the Landau–Devonshire theory [29]. The ferro elastic state will be influenced by an antiferromagnetic
transition from the spin-ordered state to the disordered state, resulting in the first-order transition [30], then it would interrupt the organized electrical dipoles [31]. In the intended accurate multiferroic material system, this strong connection between electrical polarization and magnetic order is significant [29].

Figure 5 represents the variation of Curie temperature \( (T_C) \) based on barium addition. As illustrated in Fig. 5, the result demonstrates an increasing tendency with the content of barium up to \( x = 0.15 \) mol\% followed by decreases to \( x = 0.25 \) mol\%. The maximum Curie temperature \( T_C = 1189 \) K for \( x = 0.15 \) mol\% may be attributed to maximum distortion and minimum crystallite size [27, 32] as shown in XRD results and Table 1. In contrast, the drop in \( T_C \) through rising the barium content could be responsible for the establishment of oxygen vacancies in the system that will alter the long-range ferroelectric order and interrupt it [33]. At \( x = 0.15 \) mol\%, \( T_C \) increased more than 86 K from its initial value (undoped BiFeO\(_3\)).

The temperature dependence of \( \tan\theta \) for BiBaFeO\(_3\) multiferroic nanoparticles as a function of frequency is pointed out in Fig. 6. Dielectric loss is the dissipation of energy in the dielectric system and is considered to be proportional to the dielectric constant's imaginary part (\( \tan\theta = \varepsilon''/\varepsilon' \)). The general trend of the data is \( \tan\theta \) has lower values at low temperatures for all samples and increases with increasing temperature and then decreases sharply at higher temperatures. \( \tan\theta \) shows an anomaly near antiferromagnetic Néel temperature for BiBaFeO\(_3\) multiferroic nanoparticles. The theory of Landau–Devonshire for phase transitions anticipated this kind of dielectric observation in magneto-electrically organized mechanisms as a consequence of disappearing magnetic order mostly on electric ordering [34].

3.2.2 Frequency–dependence

The dependency of the real part of dielectric constant \( \varepsilon' \) on frequency in terms of temperature is demonstrated in Fig. 7. For all samples, the real part of the dielectric constant possesses the most considerable value at lower frequencies and decreases sharply with increasing frequency, and then, at higher frequencies, turns to be practically constant. This circumstance is attributed to the relaxation of the space charge effect [35]. The lattice
deformations, vacancies of oxygen and bismuth, and faults in the interfaces as well as within the grains are the space charge’s sources in BiFeO$_3$ [36]. Space charges can properly track the applied field at low frequencies whereas these space charges cannot have enough time to typically be subjected to gradual relaxation in the high-frequency area [35, 36]. In addition, various polarization types, including mechanical, atomic, ionic, and interfacial, refer to the dielectric constant. Even so, only electronic polarization applies to higher frequencies [37], which as well leads to reduce the dielectric constant at higher frequencies. The barium content has a clear effect on the real part of the dielectric constant as provided in Fig. 7, whereas, the $\varepsilon'$ value provides the highest value at $x = 0.15$ mol%. The enhancement in the real part of the dielectric constant could be attributed to maximum distortion as shown in XRD results [27]. Besides, the increase in replacement of divalent Ba$^{2+}$ ion in trivalent Bi$^{3+}$ ion place leads to the oxygen vacancies establishment for preserving system neutrality [38]. These would be the established sources reliable for the real part of dielectric constant decay as they induce dc conductivity [20]. Accordingly, $\varepsilon'$ is decreased. The dielectric loss tan$\varepsilon$ depending on the frequency at different temperature is illustrated in Fig. 8 For all samples, at lower frequencies, the tan$\varepsilon$ has a maximum value and decreases suddenly with increasing frequency, and then turns into nearly constant at higher frequencies, and this is considered the general behavior.

3.3 Ferroelectric hysteresis loop

Figure 9 illustrates the measured ferroelectric hysteresis loops ($P$–$E$) for the multiferroic BiBaFeO$_3$ nanoparticles at a constant frequency (50 Hz) and RT. All ferroelectric parameters such as maximum polarization ($P_{\text{max.}}$), remnant polarization ($P_r$), and coercive field ($E_c$) are listed in Table 3. From the loops' pattern, it appears that the resistivity nature of the loops. The maximum remnant polarization $P_r = 88.8 \mu\text{C/cm}^2$ was achieved at concentration $x = 0.15$ as listed in Table 3. The polarization improvement could be a consequence of the crystallite size minimum and maximum distortion as mentioned in XRD results. It could be presumed from Fig. 9 that, in all samples, the leakage current is insignificant [39]. However, a large applied electric field is required.
The estimated polarization value is higher than that announced for BiFeO₃ doped with Ba [33, 39-41].

3.4 ac conductivity

Ac conductivity could be obtained by the following equation

\[ \sigma_{ac} = \varepsilon_0 \varepsilon' \omega \tan \delta \]  

where \( \sigma_{ac} \) is ac conductivity, \( \varepsilon_0 \) refers to the permittivity of free space, \( \varepsilon' \) is the real part of the dielectric permittivity, \( \tan \delta \) is the loss factor and \( \omega \) represents the applied angular frequency.

3.4.1 Temperature–dependence

The ac conductivity versus the reciprocal of absolute temperature for different BiBaFeO₃ multiferroic nanoparticles at a fixed frequency (300 kHz) is shown in Fig. 10. It has the maximum conductivity was observed at \( x = 0.15 \) mol%. The ac conductivity is strongly temperature-dependent overall temperature range. Two factors are affecting \( \sigma_{ac} \) in the high-temperature region; the first is the increase in the lattice vibrations, which leads to the electron lattice scattering. The second factor is more trapped charges are liberated at higher temperatures.

3.4.2 Frequency–dependence

Fig. 11 indicates the frequency–dependence of ac conductivity from 5–1000 kHz for BiBaFeO₃ multiferroic nanoparticles as a function of temperature. The data shows that the ac conductivity increases with increasing frequency due to the pumping force, which pushes the charge carriers within the different conduction states. In addition, the maximum ac conductivity was observed as expected at \( x = 0.15 \) mol%. Frequency-dependent conductivity measured under an ac electric field for many nanomaterials solids have been found through Jonscher’s universal power law [26, 42]

\[ \sigma_{ac} = \sigma(\omega) - \sigma_{dc}(0) = A\omega^s \]
where $\sigma_{dc} (0)$ refers to the frequency-independent dc conductivity, $A$ is the constant dependent on the temperature which decides the dispersion magnitude, and $'s'$ is an exponent factor that exists within the range $0 \leq 's' \leq 1$ denotes the interaction degree between both mobile ions and the lattice.

The variation of $'s'$ with temperature is varied for different conduction mechanisms. The exact nature of the charge transport mechanism can be confirmed by observing the variation of $'s'$. In the electron tunneling process, the exponent factor seems independent of temperature, while in the small polaron process it rises accompanied to rising temperature. Besides, in the large polaron process, it increases first and then decreases with decreasing temperature. According to the correlated barrier hopping (CBH) model, the $'s'$ value just reduced gradually with increasing temperature. The conduction mechanisms are represented according to the dependence of $'s'$ on absolute temperature $T$ (Fig.12). The value of $'s'$ is got with the slope of $\ln \sigma_{dc}$ versus $\ln \square$ through the region of high-frequency (Fig. 11). The degressive of $'s'$ with the increase of temperature is observed from Fig. 12. The trend of $'s'$ with $T$ is nearly the same for all samples but with different values. The experimental results Fig. 12 agrees with the predictions of the CBH model.

**Conclusion**

The multiferroic Bi$_{1-x}$Ba$_x$FeO$_3$ nanoparticles have successfully with different Ba concentrations have prepared by solid-state reaction technique. The structure of the multiferroic nanoparticles lattice belonged to the rhombohedral–hexagonal unit cell. The BiBaFeO$_3$ density was varied from 7.76 to 8.17 g/cm$^3$ with Ba contents. The increase of tolerance factor with increase barium content, because of the larger ionic radius of Ba$^{2+}$ ions. For all multiferroic BiBaFeO$_3$ nanoparticles, the FTIR spectra provide two strong absorption bands supplying the Fe-O bond bending and stretching vibration absorption. The dielectric properties of the samples were affected by the Ba$^{2+}$ ions substitution as well as the crystalline structure of the samples. Curie temperature of BiBaFeO$_3$ registers an increase of 86 K more than undoped BiFeO$_3$. It was found that the substitution of Ba$^{2+}$ ions have a clear effect on the ferroelectric properties of BiFeO$_3$. Moreover, Ba$^{2+}$ ions
addition could improve all ferroelectric parameters at room temperature such as $P_{\text{max}}$, $P_r$ and $E_c$. The maximum enhancement in ferroelectric properties was found for $x = 0.15$ mol% with a remnant polarization of 88.8 $\mu$C/cm$^2$. Ac conductivity exhibits a strong dependence on the frequency with the conduction mechanism in the CBH model. The strong coupling between electrical and magnetic properties is necessary for a true multiferroic nanoparticles system. The obtained results believe that the BiBaFeO$_3$ nanoparticles are a potential candidate for information storage.

**Acknowledgment:**

The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University for funding this work through the research groups program under grant number R.G.P.2/103/41.

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