Strucutral, Electrical and Magnetic Properties of Mechanoothermally Synthesized Bi \((\text{Co}_{0.45}\text{Ti}_{0.45}\text{Fe}_{0.10})\text{O}_{3}\) Nanoceramic

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Abstract. High-energy ball mill was exploited to synthesize Bi\((\text{Co}_{0.45}\text{Ti}_{0.45}\text{Fe}_{0.10})\text{O}_{3}\) nanoceramic, followed by solid-state ceramic method. XRD (X-ray diffraction), SEM (scanning electron microscopy) and impedance spectroscopy methods were exploited to analyze elementary crystal structure, micrograph and comprehensive electrical characteristics of the as-synthesized nanoceramic. The impedance spectroscopy technique offered many exciting outcomes on the influence of grain and grain boundary on the total resistive properties of the nanoceramic. The trend of frequency dependence of a.c. conductivity follows Jonscher’s power law. The upgraded conductivity and dielectric property propose various applications in the embedded capacitors. PE loop tracer and VSM (Vibrating sample Magnetometer) were exploited to study the ferroelectric and magnetic characteristics of the synthesized nanoceramic. The B-site modified BiFeO\(_3\) (with Co and Ti) exhibit ferroelectric and magnetic behavior at room temperature.

1. Introduction

Multiferroics demonstrate more than one ferroic order (i.e. ferroelectricity, ferromagnetism and ferroelasticity). Because of numerous applications in technological fields, multiferroic materials have gained a lot of attention in the area of solid-state or high temperature physics. Perovskites, containing the very general chemical formula like ABO\(_3\), have the capability in providing the A-site or B-site or both A-site and B-site for substitution/doping with iso and non-isovalent elements. Because of such easy availability for doping on any or both sides, BiFeO\(_3\) have gained the attention of many material scientists. [1–4]. The 6s\(^2\) lone pair in Bi\(^{3+}\) is accountable for ferroelectricity and Fe\(^{3+}\)-O-Fe\(^{3+}\) super-exchange formulation is accountable for G-type anti-ferromagnetic characteristic. Though, BFO has few boundaries like, large dielectric loss, low remanent polarization and high leakage current, besides, it is not very easy to synthesize the pure phase BFO material because of its small temperature range for phase steadiness, D-M interaction (i.e. Dzyaloshinskii –Moriya) is accountable for displaying weak ferromagnetism in the crystal symmetry of BFO, however the existence of a spin cycloid at 62 nm avoids net magnetization. BFO has rhombohedral crystal structure symmetry with the R3c space group and it has a T\(_C\) (i.e. Ferroelectric Transition Temperature) around 973 K and T\(_N\) (i.e. Antiferromagnetic Transition Temperature) around 643 K [5–9]. Ilmenite-type perovskite (Titanium based) compounds, commonly expressed as M\(\text{TiO}_3\) (M= Co, Ni, Sr, Cd and Fe), have been considered as smart materials due to their multifunctional properties. For minimizing the leakage current issue, the substitution at the A, B or AB-sites of compound has been
tried and accomplished. Substitution effect in BFO with other perovskite materials of the Bismuth-site (i.e. A-site) and Iron-site (i.e. B-site) atoms such as La, Sm,Gd and Nd, Zr, Ti and Mn, for controlling the oxygen vacancies have also been tried and resulted many new outcomes. This current research work proposes that the partial co-substitution at the B-site (Co and Ti) of selected percentages of the (i.e. Fe$^{3+}$ site)bismuth ferrite, by isovalent elements directtowards theenhancement ofdielectric and magnetic properties. In the present work, polycrystalline sample of Co/Ti modified BiFeO$_3$ [i.e., Bi(Co$_{0.45}$Ti$_{0.55}$Fe$_{0.10}$)O$_3$] (BCTFO) has been prepared by High Energy Ball Mill, followed by a solid-state ceramic route. The present report discuss the study on multifunctional property of as-prepared Bi(Co$_{0.45}$Ti$_{0.45}$Fe$_{0.10}$)O$_3$ nanoceramic.

2. Experimental
Bi(Co$_{0.45}$Ti$_{0.45}$Fe$_{0.10}$)O$_3$ ceramic compound (lead free) was prepared by a High Energy Ball Mill, pursued by anSSR (solid-state reaction) methodology. Stoichiometric quantities of highly pure oxide powders, i.e., cobalt oxide (99.5%), bismuth oxide (99.99%), iron oxide (99.5%) and titanium oxide (99.8%) were firstly stir together in a mortar & pestle manually in air mediaand later in methanol medium. Further, it was followed by ball-milling with zirconium oxide grinding jar for effective milling/grinding time of 30 h through high energy planetary ball mill (Retsch-PM 200, Germany). The ratio of mass to the balls was kept 1:10 at 400 rpm in the toluene medium. Subsequently, after 30 h of milling time, ball-milled powder was calcined comparatively at lower temperature (973 K) with already reported mixed oxide technique [10]. Through XRDanalysis (Rigaku, Japan) exhibiting, CuKα radiation (wavelength, $\lambda = 1.5405$ Å) in a widespread range of Bragg’s angle (20° to 80°) and at a very slow scan speed, single-phase of the powder material was formed. Surface morphology and preliminary elemental analysis was carried out by Field Emission Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy technique respectively, at room temperature. KBr hydraulic press was utilized to form pellet(diameter =12 mm and thickness $\approx$ 1.2mm) of material, followed by sintering process at a controlled temperature of 1023 K for 6 h to yield its denser form in the air medium. Using high quality silver paste, electrodes were made on sintered pellet for dielectric and electrical measurements, followed by heating at 200 K for 4 h to eliminate the PVA (binder) and humidity from the synthesized pellet. Both electrical and dielectric measurements were achieved over an extensive frequency ranges from 1 kHz – 1 MHz and temperature ranges from 298K–573K, by operating a computer-controlled Phase Sensitive Multimeter (PSM-1735, Newton4th Ltd, UK). PE loop tracer and VSM (vibrating sample magnetometer) were deployed to measure the ferroelectric and magnetic characteristic of synthesized nanoceramic at room temperature.

3. Results and Discussion
3.1. Structural Study
Figure 1 displays the plot of room-temperature XRD data for Bi(Co$_{0.45}$Ti$_{0.45}$Fe$_{0.10}$)O$_3$ ceramic, ball milled for 30 h of effective milling time. To attain the crystallographic information of the synthesized compound at room temperature, X-ray diffractometer was used. The basic crystalline nature and phase analysis of Bi(Co$_{0.45}$Ti$_{0.45}$Fe$_{0.10}$)O$_3$ compound was carried out by least-square refinement, applying the XRD data in ‘POWDMULT’ software[11]. Obtained parameters were, $a = 18.133 Å$, $b = 8.21 Å$, $c = 12.73 Å$ and S.D.$ = 0.010$ with orthorhombic crystal symmetry. The value of parameters obtained are summarized in the Table 1. The crystallite size (D) of the as synthesized compound was calculated by using the Debye-Scherrer formula:

$$D = \frac{k \lambda}{\beta \cos \theta}$$

where $\beta$ (FWHM of a reflection peak) at the Bragg angle (2θ) and the wavelength ($\lambda$), k =0.89=Scherrer constant and D = Crystallite size. The value of average crystallite size was found to be 35.70 nm for the Bi(Co$_{0.45}$Ti$_{0.45}$Fe$_{0.10}$)O$_3$. Furthermore, tolerance factor ($T_F$) value, for perovskite family (ABO$_3$) is depend on succeeding equation; [12]
$T_F = \frac{\langle R_A \rangle + R_O}{\sqrt{2} \langle R_B \rangle + R_O}$

where $\langle R_A \rangle$, $\langle R_B \rangle$, $R_O$ represents the mean ionic radii of A(bismuth), B(cobalt, titanium, iron) and O (Oxygen) respectively. Calculated outcome of the tolerance factor is 0.83 for Bi(Co$_{0.45}$Ti$_{0.45}$Fe$_{0.10}$)O$_3$ that proposes much degree of deformation, for ideal perovskite compound the value of tolerance factor is one [10][13].

![Figure 1. XRD plot of Synthesized nanoceramic compound](image)

**Table 1.** XRD parameters

| No. | 2 Theta | I   | I/I$_0$ | I/I$_0$ | D$_{obs}$ | D$_{cal}$ | h | k | l | Difference | Crystallite size (nm) |
|-----|---------|-----|---------|---------|-----------|-----------|---|---|---|------------|----------------------|
| 1   | 21.62   | 2154| 17.16198| 17      | 4.1069    | 4.1055    | 0 | 2 | 0 | -.007      | 31.77                |
| 2   | 23.26   | 3689| 29.39208| 29      | 3.8209    | 3.8199    | 1 | 2 | 1 | -.006      | 43.13                |
| 3   | 24.78   | 2495| 19.87889| 20      | 3.5898    | 3.5886    | 2 | 2 | 1 | -.009      | 49.18                |
| 4   | 27.76   | 7714| 61.46124| 61      | 3.2109    | 3.2108    | 5 | 1 | 1 | -.000      | 46.68                |
| 5   | 30.26   | 12551| 100 | 100 | 2.9511    | 2.9515    | 0 | 2 | 3 | .005       | 37.17                |
| 6   | 32.96   | 8504| 67.75556| 68      | 2.7152    | 2.7183    | 5 | 2 | 0 | .038       | 36.26                |
| 7   | 39.74   | 2844| 22.65955| 23      | 2.2662    | 2.2670    | 8 | 0 | 0 | .015       | 32.85                |
| 8   | 41.68   | 1360| 10.83579| 11      | 2.1651    | 2.1648    | 0 | 2 | 5 | -.006      | 32.59                |
3.2. Micro structural and elemental study

The SEM image of Bi(Co$_{0.45}$Ti$_{0.45}$Fe$_{0.10}$)O$_3$ nanoceramic is represented in Figure 2, which displays that the synthesized compound has average grain size of ≈ 250 nm and are homogeneously spread over the surface. Further, the uniformly distributed shape, size and nature of the particles show the presence of polycrystalline nature. Grains are regularly spread on the surface of the pellet and dimensions, spreading trend and cavities in the grains evidently advised higher density of pellet. Figure 2 also displays EDX spectrum (elemental analysis) of synthesized nanoceramic. EDX outcome displays the occurrence of primary materials and atomic ration near to stoichiometric concentration of Bi, Co, Ti, Fe and O in the synthesized ceramic compound.

![Figure 2. SEM image and EDX spectra of Synthesized ceramic compound](image)

3.3. Temperature and Frequency Dependent Dielectric Study

Figure 3 discloses the variation of dielectric parameters with temperature (298–573 K) at selected frequencies of 1 kHz, 10 kHz, 50 kHz, 200 kHz, 500 kHz and 1 MHz for Bi(Co$_{0.45}$Ti$_{0.45}$Fe$_{0.10}$)O$_3$. 

|    | 9    | 10   | 11   | 12   | 20   | 3    | 4    | 1    | -.004 | 33.31 |
|----|------|------|------|------|------|------|------|------|-------|-------|
| 9  | 47.26| 52.48| 55.7 | 57.14| 2555 | 19.69564| 2571 | 22.07792| 1.9217 | 1.9215 |
| 10 | 2472 | 1697 | 2271 | 22   | 20   | 1.7426 | 1.6106| 1.6103| 1.9217 | 1.9215 |
| 11 | 13.52083| 19.69564| 19.69564| 1.6487| 1.6487| 1.6487| 1.6487| 1.6487| 1.8817| 1.8817 |
| 12 | 13.52083| 19.69564| 19.69564| 1.6487| 1.6487| 1.6487| 1.6487| 1.6487| 1.8817| 1.8817 |
|    |      |      |      |      |      |      |      |      | 7    | 6    |
|    |      |      |      |      |      |      |      |      | .013 | .002 |

|    |      |      |      |      |      |      |      |      | 24.93 |
|    |      |      |      |      |      |      |      |      | 24.93 |
Corresponding to the basic characteristic of dielectrics, existing analysis discloses the upsurge in dielectric constant dispersion spectrum concurrently with increasing signature at all designated temperature. The dielectric constant outcome decreases with an increment in the frequency. BCTFO [i.e. Bi(0.45Co0.45Ti0.1O3)O3] has high dielectric constant at low frequencies which decreases concurrently in the high-frequency range. The polarization (i.e. ionic, dipole and interfacial polarization) exist in the low-frequency region. An increment in the frequency is accountable for vanishing polarization in the material. As an outcome, the value of dielectric constant decreases gradually. Additionally, Figure 4 shows dielectric parameter (i.e. tan δ and εr) with frequency dependence at selected temperatures. Outcome of such plots decreases with increasing the frequency[14][15]. The synthesized compound does not demonstrate any phase transition in the experimental temperature range (298 K – 573 K). Hence, the examination of dielectric properties is the signature of perceiving the structural and ferroelectric phase transition. Also, for BCTFO compound, both dielectric parameters depending upon temperature and frequency are summarized in the Table 2 and Table 3 respectively.
Figure 4. Frequency dependent dielectric plots

Table 2. Temperature dependent dielectric parameters

| Milling Time | Temp. (K) | Dielectric Parameters | Frequency |
|--------------|-----------|-----------------------|-----------|
|              |           |                        | 1 kHz     | 10 kHz | 50 kHz | 200 kHz | 500 kHz | 1 MHz |
| 30 h         | 298       | $\varepsilon_r \times 10^3$ | 0.4109 | 0.3952 | 0.3899 | 0.3863 | 0.3829 | 0.3795 |
|              |           | tan$\delta$            | 0.0607 | 0.0200 | 0.0134 | 0.0150 | 0.0200 | 0.0271 |
| 573          |           | $\varepsilon_r \times 10^3$ | 0.6888 | 0.5350 | 0.4815 | 0.4570 | 0.4389 | 0.4265 |
|              |           | tan$\delta$            | 1.2843 | 0.2862 | 0.1260 | 0.0845 | 0.0789 | 0.0811 |

Table 3. Frequency dependent dielectric parameters

| Milling Time | Frequency | Dielectric Parameters | Temperature |
|--------------|-----------|-----------------------|-------------|
| 30 h         | 1 kHz     | $\varepsilon_r \times 10^3$ | 298K | 323K | 373K | 473K | 573K |
|              |           |                        | 0.4109 | 0.4001 | 0.4082 | 0.4876 | 0.6930 |
3.4. Electrical impedance spectroscopic study

With the intention of identifying the electrical and physical characteristics of prepared ceramic sample, electrical, impedance spectroscopic studies are essentially needed. This unique method demonstrates to be advantageous for establishing a co-relation among electrical and structural properties of multiferroics materials[16][17][18]. Figure 6 portrays the Nyquist plot (\(Z' v/s Z''\), where \(Z'\) and \(Z''\) are real and imaginary part respectively) for Bi(Co\(_{0.45}\)Ti\(_{0.45}\)Fe\(_{0.10}\))O\(_3\) at selected temperatures. The Complex Impedance Spectroscopy technique (CIS) is a significant nondestructive method to investigate the electrical characteristics of synthesized compound over a widerange of temperature and frequency. Few impedance components (resistive and capacitive parameters) of the compound leads to a sequence of semicircles as soon as portrayed on a Nyquist formulism. Normally, the frequency dependence of the dielectric characteristics of a compound could defined as the subsequent terms:

Complex dielectric constant: 
\[
\varepsilon' = \varepsilon'' - i\varepsilon'' = \varepsilon\ 
\]

Complex Impedance: 
\[
Z' = Z' - jZ'' = R_\epsilon - \frac{j}{\omega C_{\ell}} \ 
\]

Phase sensitive multi-meter was exploited to collect the complex impedance data of the prepared material and further it was analyzed. For data collection i.e., output response (both real and imaginary components), an ac-signal was employed among the circular shaped and silvered pellet. In conformity with the study, the semicircles are off-centre, and consequently, replicates a non-Debye type relaxation progression appeared for examined compound[19][20]. This characteristic property is considered as a result of the contribution of the possible liberation of space charge [21].

| 1 MHz | \(\tan\delta\) | \(\varepsilon_r(\times10^3)\) | \(\tan\delta\) |
|-------|----------------|--------------------------|----------------|
|       | 0.0607         | 0.3795                   | 0.0271         |
|       | 0.0241         | 0.3899                   | 0.0056         |
|       | 0.0500         | 0.3899                   | 0.0056         |
|       | 0.1756         | 0.3937                   | 0.0223         |
|       | 1.2843         | 0.4265                   | 0.0811         |

Figure 5. Frequency dependent dielectric plots
3.5 Temperature dependent conductivity study

The outcome of ac-conductivity ($\sigma_{ac}$) was figured out exploring the dielectric data into an equation $\sigma_{ac}(\omega) = \omega \varepsilon_0 \varepsilon_r (\tan \delta)$ (where sign denotes their typical meaning) [22]. Figure 7 leads the dissimilarity of ac-conductivity over an extensive range of frequencies (from 1 kHz to 1 MHz) at certain temperature (298 K to 573 K) of the Bi(Co<sub>0.45</sub>Ti<sub>0.45</sub>Fe<sub>0.10</sub>)O<sub>3</sub> [23].
The resultant of ac conductivity is nearly persistent at particular frequency at lower temperature. These activation energy outcome is the characteristic of oxygen vacancies diffusion [24]. The conductivity graphs can be fitted, using an empirical expression of $\sigma_{ac}(\omega) = \omega \sigma_\alpha + P\omega^\beta$, recognised as the universal power law of Jonscher [25]. Herein $\sigma_\alpha$ signifies the frequency-independent quantity that provides dc-conductivity ($\sigma_{dc}$), $P$ is a thermally activated term and $\beta$ is the frequency-dependent exponent and its value lies within $(0< \beta < 1)$. The beginning of frequency dependence conductivity lies within the relaxation phenomena because of mobile charge carriers [26].

3.6 Ferroelectric and Magnetic properties

Figure 8 (inset) depicts P–E loop and M-H loop of BCTFO compound obtained at room temperature. For P–E loop, applied electric field was 10 kV/cm.The existence of non-saturated polarization might be due to the heavy leakage current, occurring because of the inconsistent valance of Fe (i.e. Fe$^{3+}$ to Fe$^{2+}$)[27][28][29]. In this current study, we could not perform P–E loop experiment at higher electric field because of the conductive property of the synthesized compound. To examine the ferromagnetic characteristic (magnetic field v/s magnetization) of BCTFO sample, M-H loop data was collected with an operated magnetic field of ±20 kOe at room temperature by exploiting VSM (Vibrating Sample Magnetometer). Moreover, for the examined material, the trend of M-H loop depicts linear dependence of magnetic field upon magnetization. However, the existence of high remnant magnetization and un-saturated hysteresis loops proposes the characteristic of high ferromagnetic tendency in BCTFO compound [14].

Figure 8. P–E loop and M–H loop of synthesized compound
4. Conclusion

In this work, High-energy ball mill was exploited to synthesize polycrystalline Bi(Co0.45Ti0.45Fe0.10)O3 nanoceramic, followed by solid-state ceramic method. XRD technique confirmed the existence of single-phase orthorhombic crystal structure symmetry and EDX results were in well agreement with atomic concentration of the system. The crystallite size (average) was estimated to be 35.70 nm from the major peaks of BCTFO. Structural analysis shows that the structural change was observed with the substitution of Co/Ti. Impedance studies confirmed the presence of dielectric relaxation of non-Debye type. The ac-conductivity plots confirmed the Jonscher’s universal power law at selected temperatures. Additionally, Nyquist outcome has depicted the existence of semi-circular arc at higher temperature. Co-substitution of Co/Ti has been found useful, as it reduces the dielectric loss and increase the magnetic property which is useful for possible multifunctional applications of BiFeO3.

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Conflict of interest

The authors declared that they have no conflict of interest.

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