

RESEARCH ARTICLE

Synthesis and characterization of BIFeO₃ Nanoparticles for supercapacitors

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ABSTRACT

In the present study, bismuth ferrite (BiFeO₃) nanoparticles were synthesized by a simple and cost-effective co-precipitation method. The synthesized materials were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, and Field Emission Scanning Electron Microscopy (FE-SEM) with Energy dispersive X-ray spectrum (EDAX). Finally, the electrochemical performance was analysed using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) analysis. From the XRD results, it was found that there was a formation of rhombohedral-structured BiFeO₃, and the average crystallite size of BiFeO₃ was calculated to be 14 nm. The FTIR analysis confirmed the existence of possible functional groups such as Bi-O & Fe-O. There was a formation of almost spherical-shaped particles in the size range of 20-40 nm as evident from FE-SEM images. The EDAX spectra of the prepared nanoparticles provided the composition of BiFeO₃. Finally, the electrochemical studies demonstrated that BiFeO₃ could be utilized as a potential electrode material for supercapacitors.

Keywords: Bismuth ferrite; co-precipitation; supercapacitors

1. INTRODUCTION

Supercapacitor namely ultracapacitors/electrochemical capacitors employ high surface area electrode materials to achieve high capacitances than conventional capacitors. They attain greater energy densities by maintaining high power density of conventional capacitors [1]. There are two charge storage mechanisms involved in supercapacitors: a) electrostatically storing the charges at the interface of the capacitor electrode as electric double-layer capacitors (EDLC) and b) Faradaically storing the charges at the electrode surface as pseudo-capacitors [2]. Pseudo-capacitors are the type of supercapacitors with metal oxide or conducting polymer electrodes as pseudo-capacitive material. The mechanism for storing charge in pseudocapacitor is a Faradaic mechanism, like oxidation-reduction reactions, involving charge transfer between electrolyte and electrode [3].

Bismuth ferrite, BiFeO₃ has captivated great attention in various applications because of its unique properties such as good oxygen ion conductivity, large energy density band gap, high refractive index, and dielectric conductivity. In addition, BiFeO₃ is non-toxic, biocompatible, &

extensively used in various applications like optical materials, gas sensors, catalysts, supercapacitors, biosensors, and solid oxide fuel cells. It has been reported to be a potential electrode in electrochemical supercapacitors due to high specific capacitance and high long-term stability of charge-discharge cycles. However, the specific capacitance behavior of BiFeO₃ was not studied in depth [4]. In the present work, bismuth ferrite (BiFeO₃) nanoparticles were synthesized by a simple, cost-effective co-precipitation method. The synthesized materials were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, and Field Emission Scanning Electron Microscopy (FE-SEM) with Energy dispersive X-ray spectrum (EDAX). Finally, the electrochemical studies were carried out using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) analysis.

2. EXPERIMENTAL METHODS

BiFeO₃ nanoparticles were synthesized by the chemical co-precipitation method. All the chemicals purchased were used without further purification. The synthesis process for 2 g of BiFeO₃ is as follows. Bismuth nitrate (Bi(NO₃)₃.5H₂O) and

ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were chosen as starting precursors. 3.101 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 6 mL of concentrated nitric acid (HNO_3). This solution was then diluted with 40 mL of double-distilled water. Later 2.5829 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 40 mL of water and dropped into the bismuth nitrate solution under constant stirring. Next 0.7672 g of sodium hydroxide (NaOH) was dissolved in 20 mL of distilled water separately and added drop by drop into the above mixture of precursors. The initial pH of the solution was found to be 2. Ammonia solution was added to bring up the value of pH to 7. A brown color precipitate was formed under constant stirring for 2 hours. The obtained precipitate was centrifuged and dried in a muffle furnace at 120°C for 2 hours. Thus obtained powder was calcinated at 500°C in a muffle furnace for 2 hours. The prepared material was subjected to various characterization techniques like XRD, SEM, FTIR, and EDAX respectively. The electrochemical performance was studied using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) analysis. The working electrode for studying the electrochemical performance was prepared by mixing the active material, carbon black, PVDF (polyvinylidene fluoride) in the weight ratio of 80:10:10 using NMP (N-methyl 2 pyrrolidone) as a solvent to form a slurry. Then 10 μL of slurry was coated onto a stainless steel electrode of area $1 \times 1 \text{ cm}^2$. Finally, the loaded active mass was calculated to be 0.8 mg. The coated slurry was air dried at 50°C overnight. The cyclic voltammetry, charge-discharge, and electrochemical impedance analysis were carried out using an SP-150 BIO-LOGIC science workstation. Three-electrode configuration was used for electrochemical characterization utilizing platinum as a counter electrode, and Hg/HgO was used as the reference electrode.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction

Figure 1 shows the XRD pattern of BiFeO_3 nanoparticles synthesized from bismuth nitrate and ferric nitrate using the co-precipitation method at pH- 7 and calcinated at 500°C . The XRD peaks are sharp confirming the crystalline nature of BiFeO_3 . The diffraction peaks observed at 2θ of 22.480° , 32.117° , 39.559° , 45.890° , 51.526° , 57.112° , 67.178° , 71.574° , and 75.921° corresponds to (100), (110), (111), (200), (210), (211), (220), (300), and (310) planes of BiFeO_3 . All the diffraction peaks displayed

strong similarity with the reported JCPDS No. 72-2112. The study reveals the crystalline structure as the rhombohedral system with lattice parameters $a = b = c = 3.952 \text{ \AA}$. The formation of rhombohedral-structured BiFeO_3 with an additional peak of Bi_2O_3 was detected using XRD analysis.

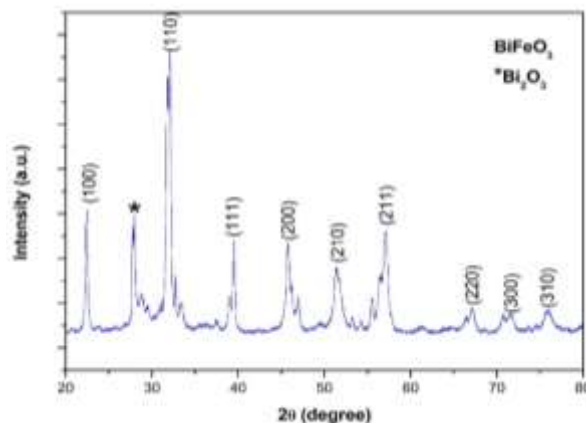


Figure 1. XRD Pattern of bismuth ferrite nanoparticles

The crystallite size (D) of the synthesized nanomaterials is calculated using Scherer's formula.

$$D = K\lambda / \beta \cos\theta \quad (\text{nm}) \quad (1)$$

where the K-shape factor is taken as 0.94, λ -wavelength of the incident beam ($\text{CuK}\alpha$ radiation), D -mean crystallite size, β -full width at half maximum, and θ -Bragg's angle. The average crystallite size of BiFeO_3 is found to be 14 nm.

The lattice density (ρ) of the BiFeO_3 nanostructure was estimated using the equation given below

$$\rho = ZM/\text{Na}^3 \quad (\text{g}/\text{m}^3) \quad (2)$$

where Z is the number of moles per unit cell, M is the molecular weight of BiFeO_3 , N is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), and a^3 is the volume of the unit cell. The calculated of BiFeO_3 lattice density (ρ) was found to be $0.2816 \times 10^3 \text{ kg}/\text{m}^3$.

The surface area (S) of prepared BiFeO_3 by co-precipitation synthesis is calculated using the formula

$$S = 6/\rho D \quad (\text{m}^2/\text{g}) \quad (3)$$

where ρ is the lattice density in g/m^3 , D is the crystallite size in nm. The surface area was found to be $152 \text{ m}^2/\text{kg}$.

3.2. Fourier Transform Infrared Spectroscopy

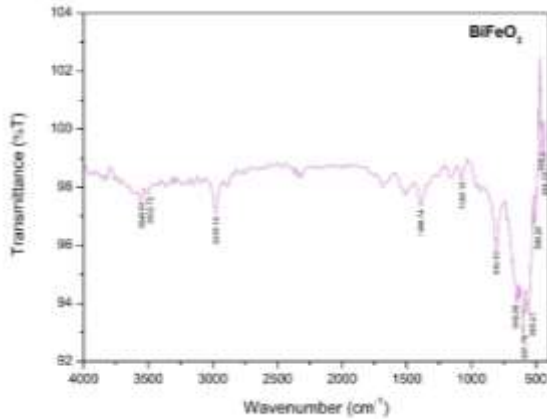


Figure 2. FTIR spectrum of BiFeO₃

Figure 2 shows the FTIR spectrum of BiFeO₃. The broad absorption bands located between 600 and 400 cm⁻¹ are due to the stretching and bending vibrations of Fe-O [5]. The BiFeO₃ has a Fe-O absorption peak at 810 cm⁻¹[6]. The peaks at 1080

cm⁻¹ are attributed to the vibration of the Bi-O bond [6]. The FTIR analysis confirmed the presence of functional groups in BiFeO₃

3.3. Morphological analysis

The morphological features of synthesized material such as particle size distribution were observed using a field emission scanning electron microscopy (FE-SEM), equipped with an energy-dispersive X-ray spectrometer (EDAX). Figure 3 depicts the FE-SEM micrographs of the BiFeO₃ nanoparticles prepared by the chemical co-precipitation method. The FE-SEM images clearly show the morphology of BiFeO₃ to be more or less spherical in shape with a size range of 20 - 40 nm with slight agglomeration.

The EDAX analysis of the synthesized sample is illustrated in Figure 4. This pattern confirms that the elements in the samples are Bi, Fe, and O.

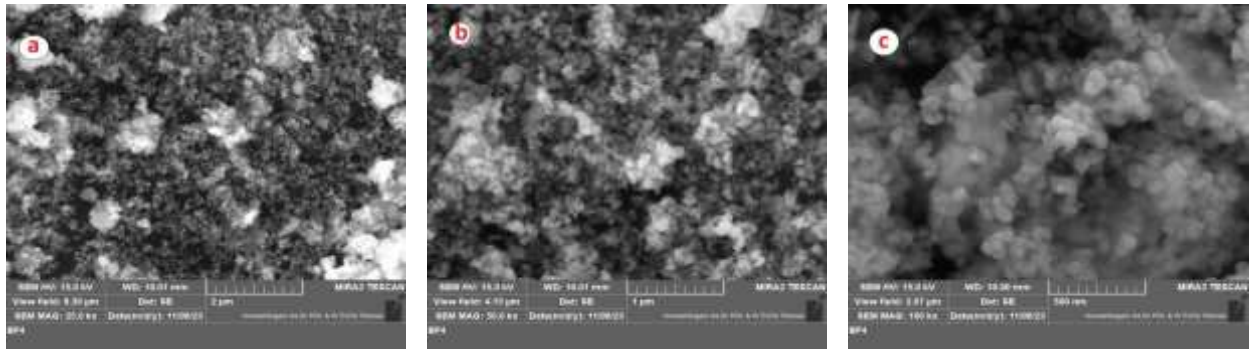


Figure 3. Field emission scanning electron microscopy

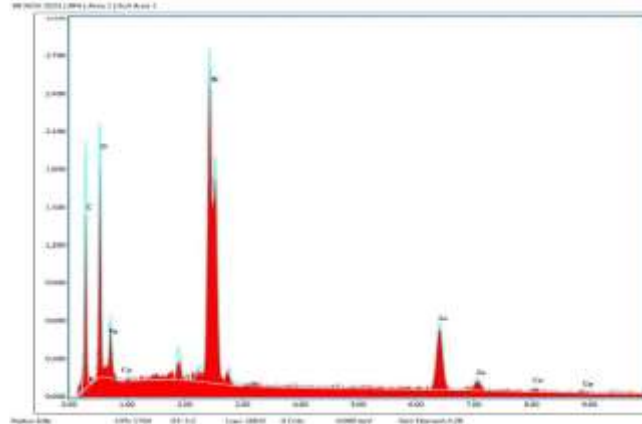


Figure 4. Energy dispersive X-ray spectroscopy (EDAX)

3.4. Electrochemical studies

3.4.1. Cyclic voltammetry

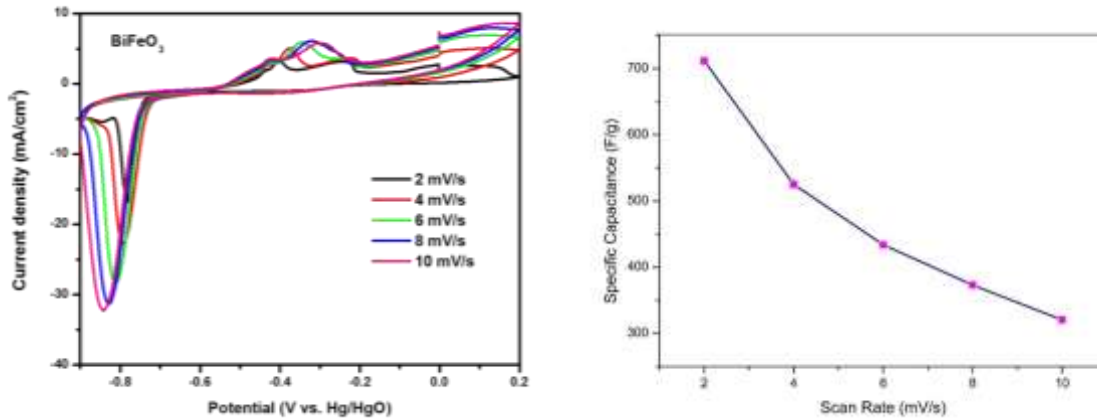


Figure 5. CV curves of BiFeO₃ and the calculated specific capacitance of BiFeO₃ at various scan rates

The cyclic voltammetry (CV) is the basic electrochemical analysis of the material where the current is recorded by sweeping the potential back and forth (from positive to negative and negative to positive) between the chosen limits. The information obtained from CV can be used to learn about the electrochemical behavior of the material. The potential at which the material is oxidized and reduced can be found.

Figure 5 shows the CV curves of BiFeO₃ in the potential range from -1.0 to 0.2 V. There is a pair of redox peaks observed which elucidates the pseudo capacitive behavior and these redox peaks are due to the oxidation and reduction reactions take place in the material. The CV curves revealed an oxidation peak at -0.3 V and a reduction peak at -0.87 V during the anodic/cathodic scan. The reduction peaks are due to the reduction of Bi (III) to Bi-metal and the oxidation peak is due to the oxidation of Bi metal to Bi (III), respectively.

The specific capacitance of the material is calculated using the following formula:

$$C_{sp} = \frac{\int I dv}{2 \times v \times m \times \Delta V} \quad (4)$$

where ΔV represents the potential window (V), m stands for the mass of electroactive material (mg), and v for scan rate (mV/s), while $\int IdV$ stands for the area under the CV curve. The estimated specific capacitance (C_{sp}) values of BiFeO₃ were 711, 525, 433, 373, and 320 Fg⁻¹ at 2, 4, 6, 8, and 10 mVs⁻¹ respectively and also provided in figure 5. The capacitance of the material is found to be decreased

with increasing scan/sweep rates and it was due to the number of active sites that actively participated in the redox reactions was low at higher scan rates.

3.4.2. Charge-discharge studies

The galvanostatic charge-discharge (GCD) profile recorded at various current densities ranging from 2.0 to 5.0 mAcm⁻² is shown in Figure 6. A nonlinear discharge curve is seen at all current densities that indicate the occurrence of the electrochemical redox process and agrees with the CV results. As seen from the figure, a higher discharge time is observed for the material at low current density and the discharge time decreases with increasing current density.

The specific capacitance of the material can be calculated using the following formula:

$$C_{sp} = \frac{I \Delta t}{m \Delta v} \quad (5)$$

where Δv represents the potential window, I stands for current density (mA/g), m stands for the mass of electroactive material (mg), and Δt stands for discharge time (s). From GCD studies, C_{sp} values of BiFeO₃ were calculated to be 3161, 2077, and 807 Fg⁻¹ at the current density of 2, 2.5, and 5 mAcm⁻² respectively. The specific capacitance is larger at lower current density and decreases with increasing current density. It is worth mentioning that the synthesized material exhibited reversible electron transfers, which may account for its excellent electrochemical performance. Also from the figure, the C_{sp} values decreased with an increase in current

density because, at high currents, only the outer surface of the electroactive material contributed to the redox reaction to proceed. Hence the specific

capacitance values decreased upon increasing the current density.

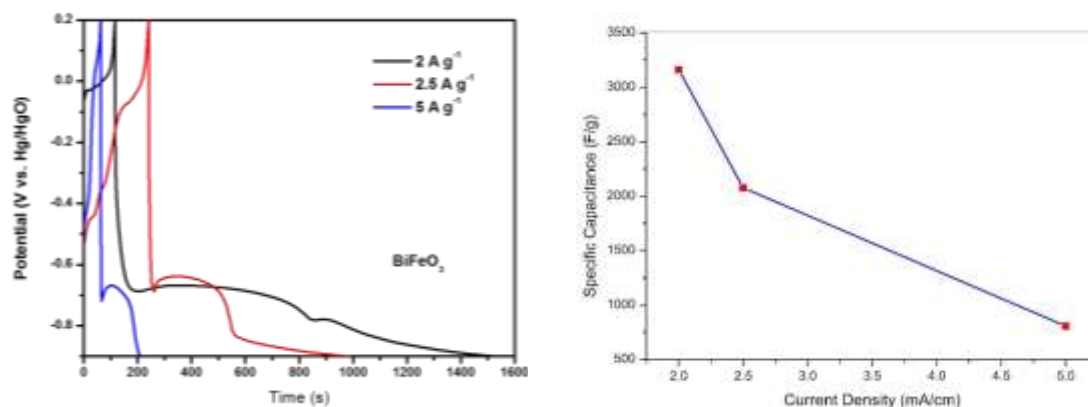


Figure 6. Galvanostatic charge-discharge curve at various current densities and specific Capacitance at various current density

4. CONCLUSION

BiFeO₃ powders were successfully synthesized through the chemical co-precipitation method. Structural and morphological analysis was carried out by XRD, FTIR, FE-SEM, and EDAX. The formation of rhombohedral-structured BiFeO₃ with an additional peak of Bi₂O₃ was detected using XRD analysis. Crystallite sizes deduced from XRD analysis were found to be 14 nm. Possible functional groups such as Bi-O & Fe-O were confirmed from FTIR. There was a formation of more or less spherically shaped particles in the size range of 20-40 nm. The synthesized BiFeO₃ exhibited a specific capacitance of 711 Fg⁻¹ at 2 mVs⁻¹ by CV studies and 807 Fg⁻¹ at 5 mAcm⁻² current density by GCD. Hence BiFeO₃ could be utilized as a potential electrode material for supercapacitors.

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