FABRICATION OF ROTARY FORCE-SPINNING TECHNIQUE AND SYNTHESIS OF $BiNiO_3$/PVP NANOFIBERS

A Project Report submitted for the award of the Degree of

MASTER OF SCIENCE IN PHYSICS
(UNIVERSITY OF CALICUT)

Submitted By

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DEPARTMENT OF PHYSICS

MES ASMABI COLLEGE, KODUNGALLUR
(Affiliated to University of Calicut)

JULY 2024

DECLARATION

I hereby declare that the project report entitled “Fabrication of Rotary Force-spinning Technique & Synthesis of $BiNiO_3$/PVP Nanofibers” submitted to Calicut Univer sity in partial fulfillment of the requirement of the degree of Master of Science in Physics is a record of original work done by me under the supervision and guidance of Dr. Mo hammed Rasi U P Assistant Professor, Department of Physics, Sullamussalam Science College Areekode and it has not formed the basis for the award of any Degree/Diploma or other similar title to any candidate of any University.

Place:

Date:

Signature of candidate
(FIDHA SALEEM T A)
Reg.No.

CERTIFICATE

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SCIENCE COLLEGE

This is to certify that the dissertation entitled “Fabrication of Rotary Force-spinning Technique & Synthesis of $BiNiO_3$/PVP Nanofibers” submitted to MES Asmabi College, Kodungallur, affiliated to University of Calicut, in partial fulfillment of the re quirements for the award of the degree of Master of Science in Physics is a record of original work done by Ms. FIDHA SALEEM T A(Reg. No:AIAWMPH004) dur ing the period 2022-2024 of her study in Department of Physics, MES Asmabi College Kodungallur, under my supervision and guidance.

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ACKNOWLEDGEMENT

I am highly indebted to my guide Dr. Mohammed Rasi U P, Assistant Professor, Department of Physics, Sullamussalam Science College, Areekode for his continuous sup port and timely guidance.His comments and suggestions were invaluable throughout the course of project.

I sincerely thank Mrs.Ebitha Eqbal E and all other faculty members of Department of Physics, MES Asmabi College, Kodungallur for their encouragement and able guidance at every stage of this project.

We would like to also acknowledge Dr. Benjamin Hudson Baby, Post-Doc Fellow, NIT Warangal for facilitating FE-SEM facility and thanking Department of Physics, Sulla mussalam Science College, Areekode for availing their experimental facilities.

I also thank all my friends and my family members for their constant help and support. FIDHA

SALEEM T A

ABSTRACT

Fabrication of Rotary Force-spinning Technique & Synthesis of $BiNiO_3$/PVP Nanofibers

Nanofibers of multiferroic material of special interests due to their potential applications in memory and storage applications.Bismuth based multiferroics are good candidate for this purpose due to predicted ferromagnetic and ferroelectric properties. Bismuth Ni trate (BiNiO3) is a futuristic compound in this category, which has 6s2 lone-pair effect driven non-centrosymmetry offer ferroelectric nature. Also, the presence of Fe3+ ion and magnetic exchange mechanism is contributing to the ferromagnetic character.Magneto electric properties of BiNiO3 is not explored as much. Preparation of nanofiber is bit tricky; we have utilized force-spinning setup for nanofiber production. In terms of ef ficiency and control parameters, this method is better than widely used electrospinning method. Force-spinning is a simple solution-based method for the fabrication of nanofibers with diameter in the range of nm to micrometer. It is a unique process that utilize to create multiple continuous fibres or filaments in a single operation, producing a bundle of strands with consistent dimensions and properties. For the fabrication of a nanofiber, a polymer solution is needed due to its viscous texture. The solution viscosity, spinning duration, spinning speed determines the physical, electrical and magnetic properties of the nanofibers. So, Polyvinylpyrrolidone (PVP) is used as the polymer binder.[12] In this work, we were fabricated a home-made rotary force-spinning setup (cotton-candy model), which enables the nanofibers production of a broad variety of materials in a versatile and efficient way. Using this setup, BiNiO3/PVP microfibers were prepared. Afterwards, XRD and FE-SEM were used for structural and morphological studies respectively. Fur ther optimization of BiNiO3/PVP nanofibers is required for tunable magneto-electric properties.

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Chapter 1

Introduction

Multiferroics are those materials in which ferroic orderings (ferroelectric, ferromagnetic, ferrotoroidic, ferroelastic) coexist.This term is usually used to describe magnetoelectric materials. This is because, in materials that simultaneously exhibit ferroelectricity and ferromagnetism ,the polarization can be handled by the magnetic field and magnetization of the material by the electric field and thus such materials are called magnetoelectric mul tiferroics. [11]These compounds are promising for potential applications in data storage memory devices, sensors, pressure sensitive devices.

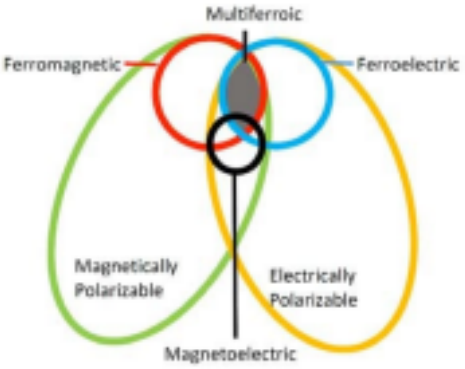


Figure 1.1: Multiferroic material

1.1 Important terms in multiferroics

1. Ferroic

   The materials which shows long range order with respect to atleast one of the macroscopic properties and it also develops a dipole with conjugate field used is termed as ferroic.There are four types of ferroics which is shown in Figure 1.2

Materials exhibiting ferroelectricity have a inherent polarization (P) that is stable and can be reversibly switched by an external electric field (E), displaying hysteresis loops, which are characteristic of ferroelectric behavior. Ferromagmetic material possesses a spontaneous magnetization M that is stable and switched hysterically by an applied magnetic field H. Ferroelastic material shows spontaneous deformation that is stable and switched hysterically by an applied stress. Ferrotoroidic state with a domain can be hysterically switched by the space-time anti-symmetric external field or toroidal field.

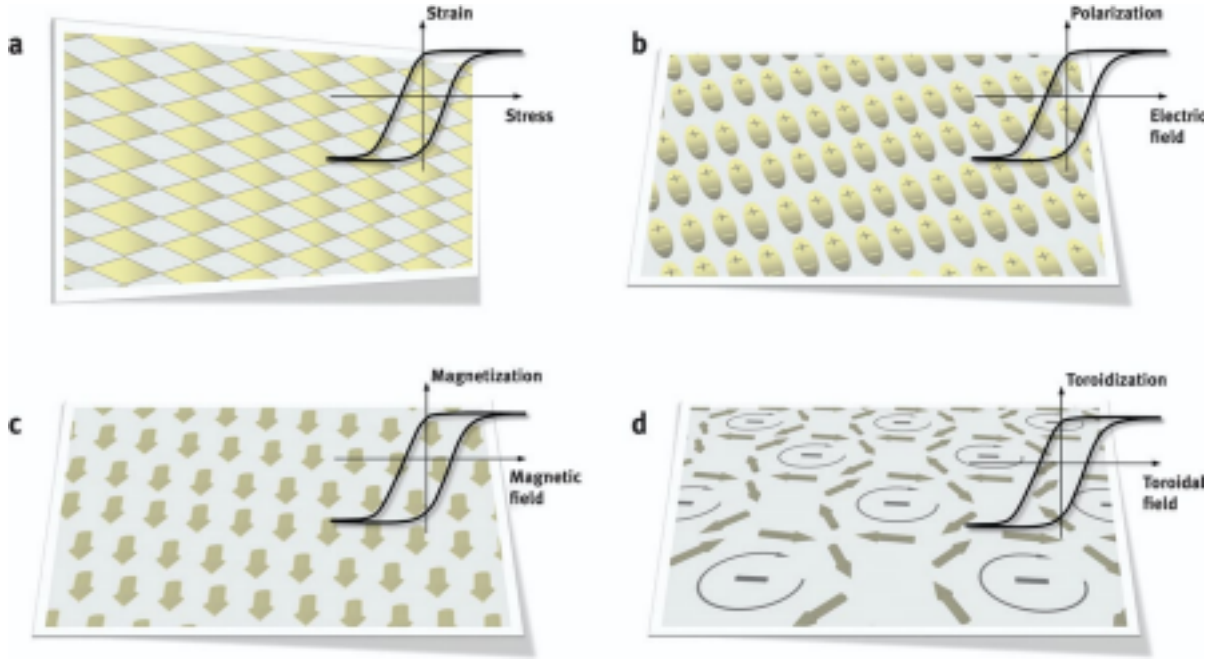


Figure 1.2: Types of ferroics, (a)ferroelasticity, (b) ferroelectricity, (c) ferromagnetism, (d) ferrotoroidicity.

2. Magnetoelectric Coupling

By using the expansion for the free energy expression, Landau theory describe the magneto electric effect in single phase material.

1.1.1 Multiferroicity due to different mechanism

Multiferroicity due to Charge Ordering:

In some material, spontaneous charge ordering that can occur below certain temperature cause inappropriate in site or the material can contain ion with different valence which after a structural dimerization transition induce ferroelectricity [17].

Some example of charge ordering multiferroic are perovskite manganites, Fe_3O_4 and $LuFe_2O_4$.

Multiferroicity due to lone pair:

Lone pair is unbounded valence electron around the host ion. This is mainly observed in $BiFeO_3$. In this mechanism the spatial asymmetry is created due to anisotropic dis tribution and high ferroelectric polarization. The ferroelectric behavior in this material is not a result of the Fe^{3+} ion (B site) displacement, but is instead primarily due to the presence of a steriochemically active lone pair on the Bi^{3+} ion (A site), which induces instability in the material. Two electrons in the 6s orbital of the bismuth ion is not in

volved in the bond.That shows the high polarizability and the observed polarization in the ferromagnetic material is very large and it also created a local dipole along plane.

Multiferroicity due to geometric effect:

Sometimes, the geometric constraints and size effect can also cause an instability in ma terial. These kind of mechanism is driven by steriochemical effect over the variation in chemical bond leads to ionic shift which result to a polar distortion and geometric ferro electricity.

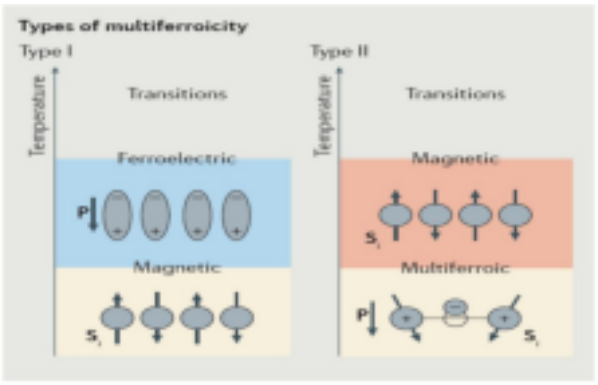
For example in h-$RMnO_3$ (R = Sc, Y, In or Dy - Lu).

Multiferroicity due to spin driven mechanism:

Magnetic order can break the inversion symmetry. In this case the multiferroic with spin ordering induced ferroelctricity in which the coupling between magnetic order and ferroelectricity is obvious, or we can say that the modification should necessarily acompany a change of magnetic or ferroelectric structure and property. It is electric polarization induced by magnetic ordering.

1.1.2 Types of Multiferroics

- If the magnetic and ferroelectric ordering for a material behaves independently that means the source of ferroelectric ordering and magnetic ordering are different, de noted as type 1.
- The magnetoelectric coupling in type-1 multiferroics is usually quite feeble, indicat ing a weak correlation between magnetic and ferroelectric behaviors.
- In general mechanism which driven the multiferroicity in type 1 multiferroic are charge charge ordering mechanism, lone pair mechanism and geometric ferroelec tricity mechanism.



Nanofibers

Figure 1.3: Types of Multiferroicity

- In type-2 multiferroics, the ferroelectric and magnetic transitions coincide, resulting in a material that exhibits both properties simultaneously.
- The magnetoelectric coupling in type-1 multiferroics is typically very weak, suggest ing a relatively independent coexistence of magnetic and ferroelectric properties, with minimal cross-talk between the two.
- In general spin driven mechanism is responsible for type 2 multiferroics.

1.2 Nanomaterials

Nanomaterials are of technological interest due to the potential of their dimension that offers wide variety of application in different fields.

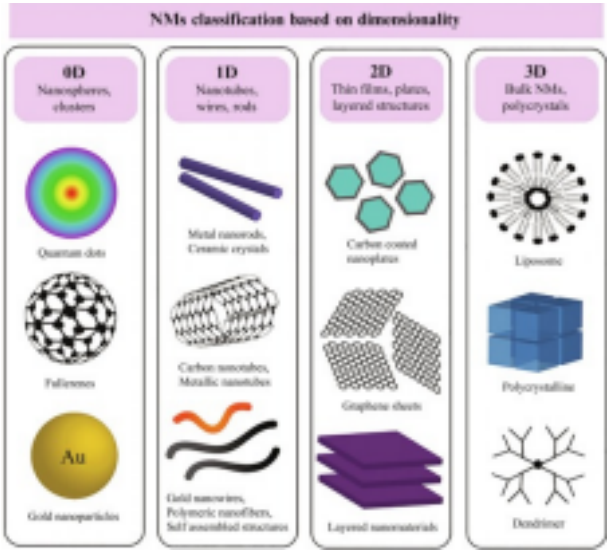


Figure 1.4: Different types of nanomaterials [3].

There are different types of nanostructures.Some of the important nanostructures are given below.

• Nanocrystals

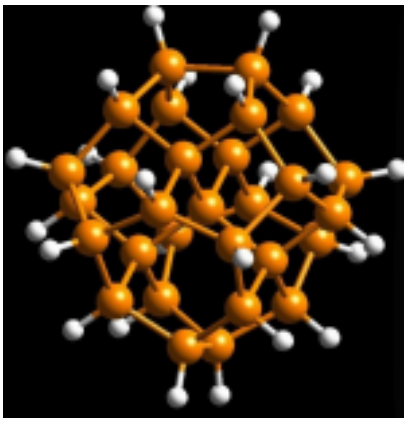


Figure 1.5: Nanocrystal

These are tiny ,small crystals made of semiconducting materials that have potential applications.These are a subtype of nanoparticles that possess a crystalline structure throughout their volume.

• Nanowires

Nanowires are nanostructures that are in the form of a wire with the diameter in nanoscale.These are 1-D materials with lateral quantum confinement of electrons.It can be made of different materials like inorganic, organisms, metallic,etc.Their unique properties includes enhanced electrical, thermal, and optical behaviors, quan tum confinement effects, high aspect ratios (length-to-width ratio), discrete values of electrical conductance, surface area-to-volume ratio, making them excellent for chemical sensing and detectors.

• Nanofibers

Nanofibers are a type of nanostructure that have a diameter in the nanoscale, typi cally between 1-100 nanometers (nm). These fibers have a high aspect ratio, charac terized by lengths that can vary significantly, spanning from just a few micrometers to several millimeters. Nanofibers possess distinctive characteristics, including high porosity and a high surface-to-volume ratio, making them valuable for various ap plications. These nanofibers can be fabricated using a range of methods, such as electrospinning, melt-blown spinning, self-assembly, and sol-gel processing, allowing

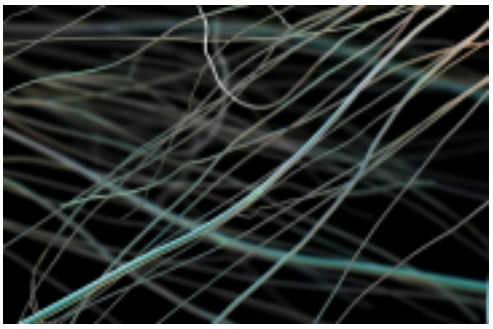
Nanofibers 

Figure 1.6: Nanofiber

the creation of nanofibers with enhanced properties and structures. This versatil ity enables their use in a broad spectrum of fields, from biomedical applications to advanced materials development.

• Nanorods

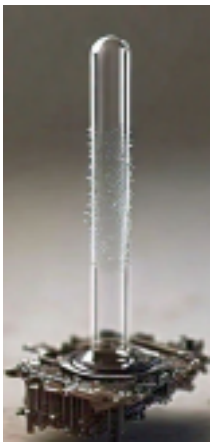


Figure 1.7: Nanorods

Nanorods are nanostructures with a rod-like shape, typically with a diameter in the range of 1-100 nanometers (nm) and a length that can vary from a few hundred nanometers to several micrometers. They have unique optical, electrical, and mag netic properties.Their properties can be tailored by controlling their size, shape, composition, and surface chemistry.

• Nanopowders

Nanopowder is a type of powder that contains nanoparticles, which are parti cles with at least one dimension in the nanoscale. The properties of nanopowder can vary depending on the size, shape, composition, and surface

chemistry of the nanoparticles it contains.

Figure 1.8: Nanopowder

• Nanofilms

A nanofilm is a thin film with a thickness in the nanoscale range. Nanofilms have unique properties that differ from their bulk material counterparts. Various methods can be employed to deposit nanofilms, including Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), Sol-Gel processing, and other techniques. The properties of nanofilms can be tailored by controlling their thickness, composition, and surface chemistry.

• Nanosheets A nanosheet is a two-dimensional nanostructure with a thickness ranging from 1 to 100 nm. Some examples of nanosheets are Graphene, silicon nanosheets, Carbon nanosheets, PbS sheets,etc[14].

1.3 Motivation Of The Work

• $BiMO_3$ (M=Fe,Co and Ni) is a magnetoelectric material that exhibits multiferroic properties.

• Researchers have focused more on $BiFeO_3$ and $BiCoO_3$, while there have been fewer studies on $BiNiO_3$.

• The discovery of $BiNiO_3$ as a transition metal oxide with some properties has also great interests.

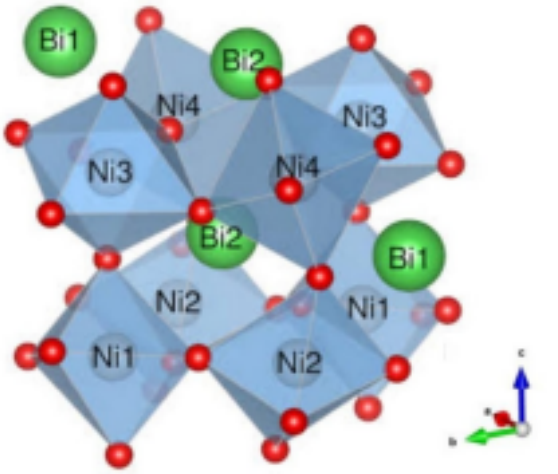
• Can replace lead based multiferroics,which is toxic.

• This complex oxide can be synthesised in an easy way because their constituent elements are abundant.

• Applications in the field of pressure sensitive devices.

1.4 Material of Interest

Bismuth Nickel Oxide ($BiNiO_3$)



Nanofibers

Figure 1.9: Triclinic perovskite structure of $BiNiO_3$ [9].

• Bismuth nickel oxide is a triclinic perovskite ($a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90^o$)

• It acts like an insulator as the oxidation state of Ni in the compound is +2 contrary to expected state +3.

• The synthesis of Bismuth Nickel Oxide is suggested under high

pressure. • Molecular weight of $BiNiO_3$ is 315.67 g/mol.

• Experimental and theoretical works and researches on this compound is very less.

In Bismuth Nickel oxide ($BiNiO_3$), Bismuth and Nickel exists in +3 and +2 oxidation state respectively [8].

$$[Bi^{+3}Ni^{+2}O^{-2}{}_3]$$

Nanofibers

• Fibers, at a size ranging from micro-to-nanometer, have been developed intensively in engineering material for a wide range of applications.One of the

broadest appli cations of nanofibers is in the medical field.

- The fibers at this range have many advantages as it has a very high ratio of surface area to unit volume,low density, high porosity and high flexibility.These character istics increases its applications.
- Large specific surface area,which gives them unique advantages in the gas sensing, supercapacitors and photocatalysis [15].

1.5 Objectives

- Design and construct an force-spinning setup with precise control over parameters such as rpm, flow rate, and collector distance.
- Synthesize BiNiO3 nanorods via electrospinning using precursor solutions containing appropriate metal precursors.
- Characterize the crystal structure and morphology of the nanorods/fibers using XRD, SEM, and TEM.
- Measure the magnetic properties using VSM to assess magnetoelectric coupling. • Investigate electronic properties through XPS and conductivity measurements. • Explore magnetoelectric coupling by varying external magnetic and electric fields.

Chapter 2

Experimental Methods

2.1 Methods for Nanofiber production

Nanofibers can be synthesised by different methods and some of these methods are men tioned below[1].

2.1.1 Electrospinning

Electrospinning is a fiber production method that utilizes electric force to draw

charged threads of polymer solutions or melts, resulting in fibers with diameters in the nanometer scale.Initially a high voltage is applied to a liquid droplet, causing the body of the liquid to become charged[18]. Electrostatic repulsion counteracts the surface tension, stretch ing the droplet.A stream of liquid erupts from the surface at a critical point called the Taylor cone.The jet then dries in flight.The mode of current flow changes from ohmic to convective, causing the charge to migrate to the surface of the fiber.The jet undergoes a whipping motion, triggered by electrostatic repulsion at minor bends in the fiber, leading to its extensive elongation.The elongated jet is deposited on the grounded collector.

Principle of Electrospinning

The electrospinning process involves an electrodynamic mechanism where a liquid droplet is electrified, generating a jet that undergoes stretching and elongation to pro duce fibers. The basic setup is straightforward, making it widely accessible in laboratories. The essential components include a high-voltage power source, a syringe pump, a spin neret (typically a blunt-tipped hypodermic needle), and a conductive collector.During electrospinning, a pendant droplet forms at the spinneret due to surface tension, and subsequently, electrification causes the droplet to deform into a Taylor cone shape. The

process can utilize either direct current (DC) or alternating current (AC) as the power source. This deformation leads to the ejection of a charged jet, ultimately resulting in fiber formation.The jet initially extend in a straight line and undergo vigorous whipping motion because of bending instabilities.As the jet undergoes stretching and thinning, it rapidly solidifies, resulting in the formation of solid fibers that are deposited onto the grounded collector.[16]

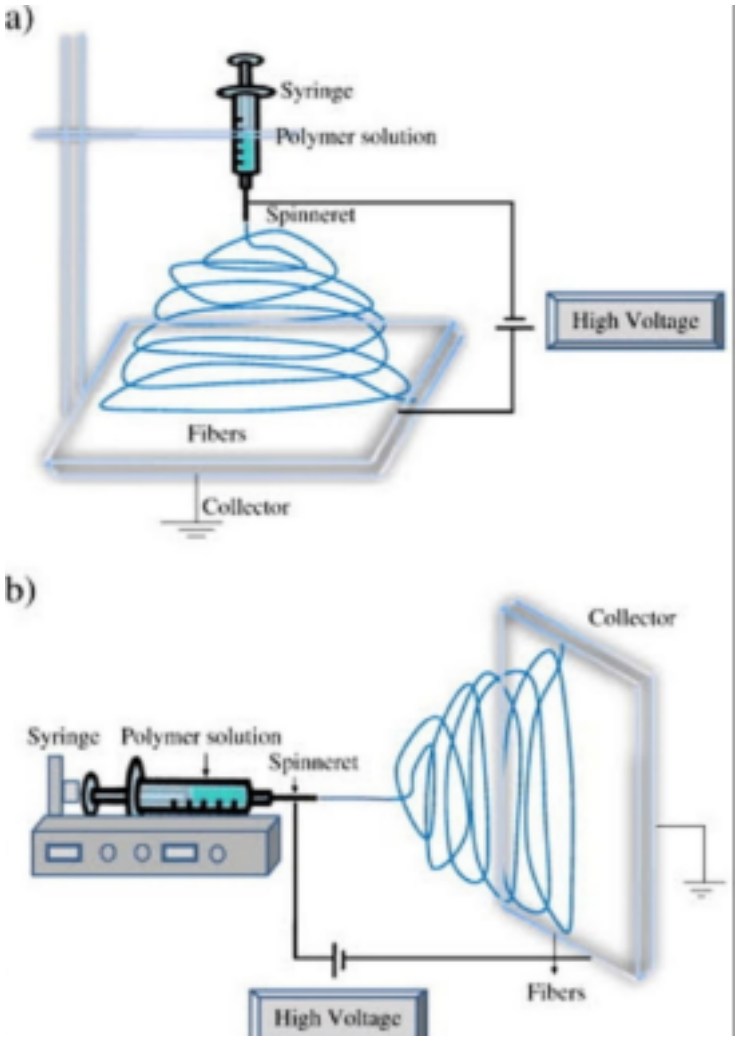


Figure 2.1: A Schematic diagram of Electrospinning Apparatus

2.1.2 Template synthesis

Template synthesis is a technique used to fabricate nanofibers by depositing materials onto a template, such as porous membranes, nanoporous structures, lipid bilayers, or biomolecular templates like DNA or peptides.[10]The process involves three key steps:

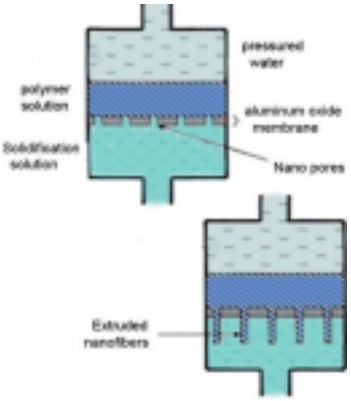


Figure 2.2: Template synthesis of Nanofibers

1. Material deposition onto the template surface.
2. Formation of a layer or shell around the template.
3. Template removal, resulting in a free-standing nanofiber.

This method offers precise control over nanofiber dimensions, length, and composition, making it an adaptable approach for creating nanofibers with tailored properties.

2.1.3 Freeze-drying synthesis

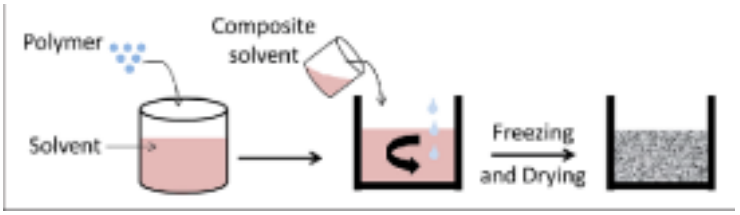


Figure 2.3: Depiction of freeze-drying synthesis

Freeze-drying synthesis, or lyophilization, is a method used to fabricate nanofibers by: 1. Dissolving a material or polymer in a solvent.

2. Freezing the solution, creating a solid matrix
3. Removing the solvent through sublimation under vacuum, leaving behind a solid material
4. Collecting the resulting nanofibers, which have a controlled diameter, length, and composition.

This technique is particularly useful for sensitive materials that require gentle processing conditions, and is commonly applied in fields like pharmaceuticals, biotechnology, and food processing[5].

2.1.4 Sonochemical synthesis

Sonochemical synthesis is a unique method that utilizes high-intensity ultrasound waves to generate nanofibers through chemical reactions[7]. This process involves:

1. Creating a solution with the desired material or polymer.
2. Exposing it to powerful ultrasound irradiation.
3. Inducing chemical reactions that form nanofibers.
4. Controlling the fiber structure and morphology.

This innovative approach enables the synthesis of various nanofibers, including polyani line, with tailored properties for specific applications.

2.1.5 Centrifugal synthesis

Centrifugal synthesis, also known as forcespinning technique or Centrifugal jet spinning is a revolutionary technique that fabricates nanofibers with high efficiency, low costs, and large-scale production capabilities. The process involves:

1. Employing a DC motor-driven system to extrude a polymer solution through a spinneret
2. Utilizing centrifugal force to draw the solution into continuous

nanofibers 3. Collecting the resulting nanofibers on a dual-collector

system

This groundbreaking method has far-reaching potential in various applications, includ ing the development of nanofibrous scaffolds for bone tissue regeneration and beyond[19].

2.1.6 Rotary Force-spinning Technique

Electrospinning is popular for the production of nanofibres,but it is not the ideal method because it has a low production rate.This method uses very high voltage. The limitations of traditional methods can be overcome by utilizing Rotary Forcespinning, a cutting-edge technique that offers high productivity, improved jet stability, eco-friendliness, and elim inates the need for high voltage, enabling the rapid production of fibers with enhanced efficiency and sustainability.

Eventhough electrospinning is the most popular method to produce nanofibers it has some limitations like larger time of production, use of high voltage,etc. To overcome these issues,we found that RFS is a better solution to get more nanofibers within short time using centrifugal effect instead of high voltage. The high rotational speed of RFS ensures that the solution will run out rapidly compared to the time-consuming electrospinning. Therefore, the use of RFS technique can improve the selection of material, increase the production rate, and lower the cost of fibers synthesis through eco friendly processes[2].

In the Rotary Forcespinning (RFS) technique, a rotating container holds the solution, which is then forced out through tiny holes in the reservoir, creating a continuous flow of fibers as the solution is ejected.The electric field which is used to attract the fibers in the electrospinning process is replaced by the centrifugal force of motor rotation for a force-spinning technique. From elementary physics, the centrifugal force (F) depends on the quantities : mass (m), rotational speed (ω) and radius (R) and they are related by the formula of $F=m\omega 2R$. The centrifugal force becomes the main factor in the produc tion of fibers because as the force increases,the stretch of this force causes the solution to turn into fibers. There are three main systems of the RFS technique: a motor system, a collector, and a heating system that controls the temperature and humidity around the motor.

The steps in the RFS method in producing fibers are as follows :

1. Initiation of the jet to stimulate the flow of the polymer solution through the holes in the container,
2. Jet extension to increase the surface area of the polymer solution flow which is driven out from the reservoir through the holes (elongation process),
3. Solvent evaporation and solidification processes.

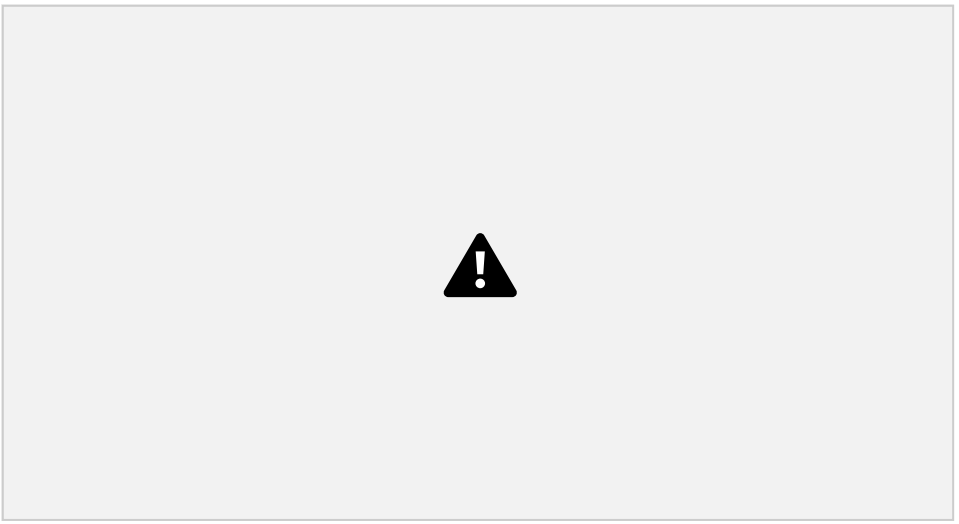


Figure 2.4: Working of a Rotary Force-spinning Machine

The RFS technique leverages centrifugal force to stretch and form fibers, offering a cost-effective method for fiber production. By tuning key parameters like solution concentration, flow rate, and surface tension, this technique enables efficient fabrication of fibers at a significantly lower cost.

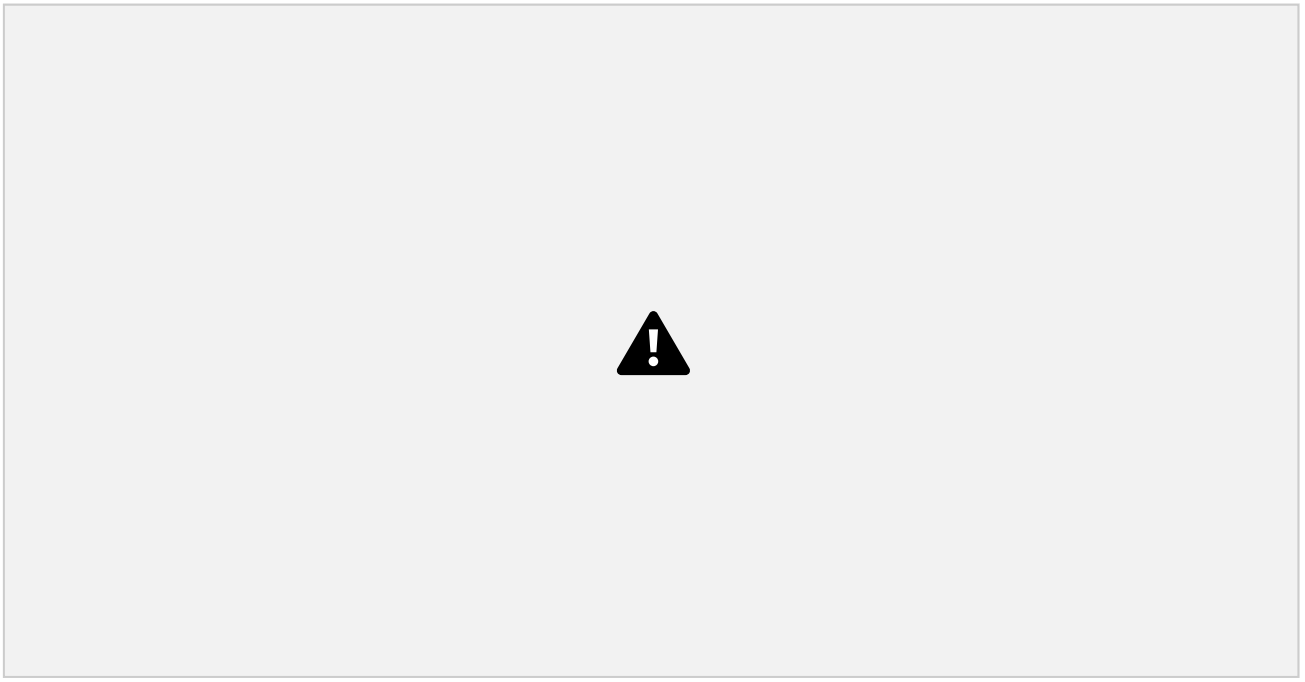


Figure 2.5: Force-spinning machine and the fibers collected at collector after the spinning

2.2 Characterization Techniques

2.2.1 Structural Characterization

• X-ray diffraction (XRD):

The analysis of crystal structure and atomic spacing has been revolutionized by the widespread adoption of (XRD) as a fundamental research technique. XRD's versatility and accuracy have made it an indispensable tool in various fields, including materials sci ence, chemistry, physics, and biology.It is a versatile non destructive analytical technique to analyze the physical properties such as phase composition, orientation of powder,crystal structure[6].XRD (X-ray diffraction) is a highly valuable technique for structural analysis, offering numerous benefits:

• Non-invasive analysis: XRD preserves the sample's integrity for further investiga tion.

• Crystal structure elucidation: XRD determines lattice parameters, unit cell dimen

sions, and space groups.

- Phase identification: XRD accurately detects and distinguishes various phases, in cluding polymorphs and solvates.
- Material quality assessment: XRD evaluates crystallinity and purity.
- Defect analysis: XRD detects lattice strain and defects, providing insights into material behavior.
- High-throughput capabilities: Modern XRD instruments enable rapid and auto mated analysis.
- Real-time studies: XRD allows for in situ and operando analysis of structural changes during chemical reactions and phase transitions.
- Complementary insights: XRD complements other analytical techniques, providing a comprehensive understanding of materials.

By leveraging these advantages, XRD plays a vital role in unraveling the structural prop erties of materials.

PRINCIPLE OF XRD MEASUREMENT

X-ray diffraction is based on the constructive interference of monochromatic x-rays and crystalline sample.When two or more waves overlap and combine in phase, their peaks and troughs align, resulting in constructive interference. This phenomenon ampli fies the waves' amplitude and intensity, creating a new wave with increased energy. In essence, constructive interference is the reinforcement of waves that are in sync, leading to a stronger and more intense combined wave.For the conditions satisfying bragg's law,the incident ray interferes the sample constructively.

Bragg's law is as follows ;

$$2\,d \sin\theta = n\,\lambda$$

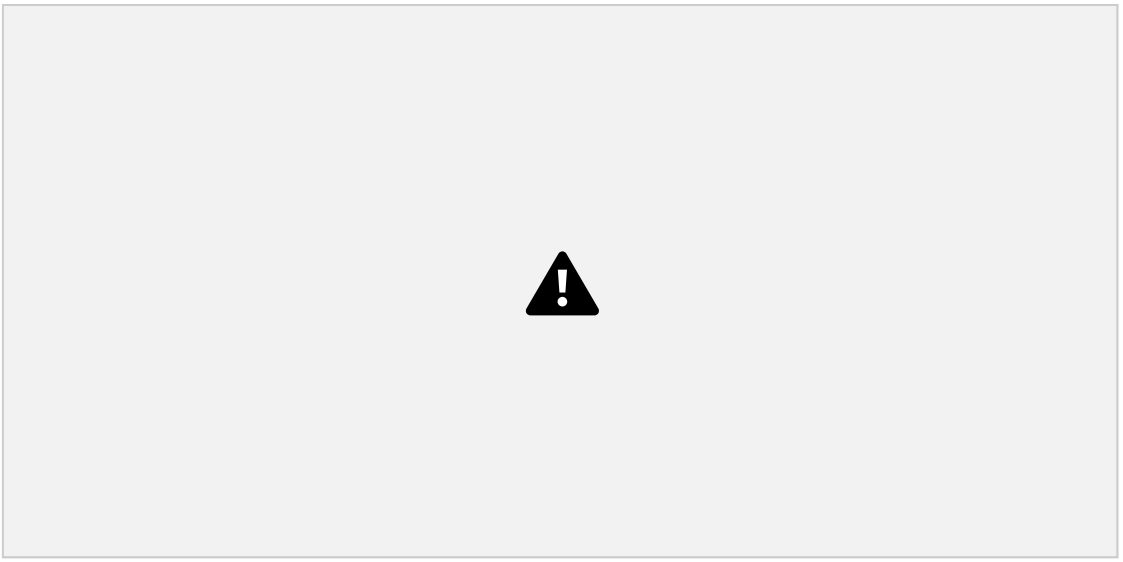


Figure 2.6: Schematic representation of XRD Principle

There are some other techniques used for structural analysis, aside from XRD like Nuclear Magnetic Resonance (NMR) Spectroscopy determines molecular structure and dynamics,Fourier Transform Infrared (FTIR) Spectroscopy, Raman Spectroscopy,Small Angle X-ray Scattering (SAXS), Wide-Angle X-ray Scattering (WAXS),Neutron Scatter ing,etc.

These techniques provide valuable insights into the structural properties of materials, complementing XRD and offering a more comprehensive understanding.

2.2.2 Morphological Studies

• Field emission scanning electron microscopy(FE-SEM):

FESEM is an advanced technology used to study the morphology of the sample.It pro vides the topographical and elemental information about the object.It is one of the most versatile and well known analytical techniques for observing and analysing the surface of specimen. Unlike conventional optical microscope, electron microscope offers more advan tages which includes high magnification, great resolution ,large depth of focus and ease of sample preparation ,observation and analysis.

WORKING PRINCIPLE

The electrons generated from the electron gun enter on the surface of specimen

and inelastic interaction with atoms in the specimen produces variety of signals that contains the information about the surface morphology and composition.The specimen generates many low energy secondary electrons.The intensity of secondary electrons is governed by the surface topography of the sample. The surface topography of the specimen is reconstructed by detecting the variations in secondary electron emission as the primary electron beam scans across the sample, creating a spatial map of electron intensity that reveals the surface features and morphology.[13]

Working Principle

- In the Scanning Electron Microscope (SEM), electrons replace light to generate an image.
- The process begins with the production of a focused electron beam at the micro scope's apex, achieved by thermally exciting a metal filament.
- The beam then traverses the microscope's column, guided by electromagnetic lenses that refine and direct its trajectory, ultimately converging onto the sample to probe its surface features.
- Once it hits the sample, other electrons (back scattered or secondary) are ejected from the sample.
- The detectors capture the backscattered or secondary electrons emitted by the sam ple and convert them into an electrical signal, which is then transmitted to a display screen, analogous to a conventional TV screen, where it is rendered as a visual image, providing a detailed representation of the sample's surface morphology.

Field Emission Scanning Electron Microscopy (FESEM) is a powerful tool for morphol ogy analysis, which involves the study of a material's surface shape, size, and structure. The process begins with sample preparation, where the sample is fixed to a substrate or mounted on a stub. Next, high-resolution images of the sample's surface morphology are produced, allowing for detailed examination of surface features at magnifications of up to 100,000 times. With a resolution of around 1-2 nanometers, fine details can be visualized, and elemental analysis can be performed using Energy-Dispersive X-ray Spec troscopy (EDS) to identify the sample's elemental composition. Additionally, FESEM can create 3D images of the sample using techniques like stereo imaging or 3D reconstruction, providing a comprehensive

understanding of the material’s morphology.

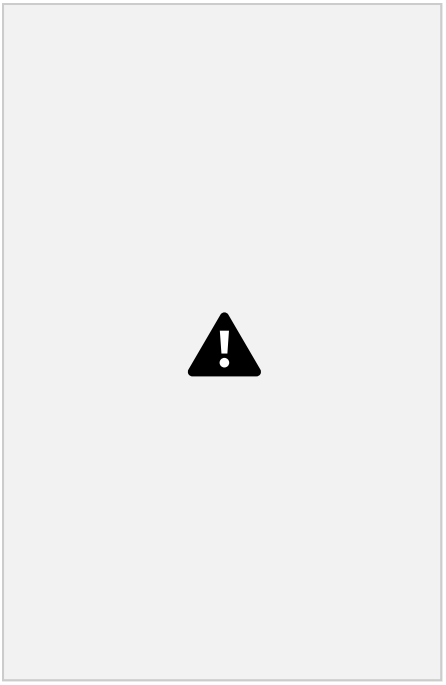


Figure 2.7: Schematic diagram of SEM

Field Emission Scanning Electron Microscopy (FESEM) offers several advantages over traditional Scanning Electron Microscopy (SEM), including higher resolution (achieving spatial resolution as low as 1.5 nanometers, surpassing SEM’s capabilities by three to six times), improved image quality with reduced electrostatic distortion, simplified sample preparation with minimal requirements and no need for conducting coatings on insulating materials, lower accelerating voltages that reduce sample damage and charging, increased depth of field, and a narrower probe beam that provides improved spatial resolution and reduced sample damage.

SEM (Scanning Electron Microscopy) is a powerful tool for morphology analysis, pro viding high-magnification images with exceptional detail,in-depth surface analysis, re vealing texture, composition, and properties, accurate measurements of shape, size, and surface features and valuable insights into structural organization, composition, and prop erties.It also provides detailed visualization of cellular and tissue structures. By leveraging these capabilities, scientists can gain a deeper understanding of the morphology of various materials and biological samples.

Chapter 3

Fabrication of Rotary Force-spinning Technique & Synthesis of

$BiNiO_3$/PVP Nanofibers

3.1 Fabrication of Low cost Home-made Force-spinning Machine

To design a home made arrangement of force-spinning, it is necessary to have some impor tant parts such as a rotating motor, a collector ,etc. Initially a square box is made with the glass as the five faces and the base of box with wood.A hole is made on the centre of the base and a rotating motor (DC motor) is fixed on it.Then, a container with multiple holes on the wall is fixed to the motor. As the motor rotates,the container also rotates. To build a forcespinning machine, it is necessary to gather materials like a DC motor, power supply, controller, wooden box with glass as faces ,shaft, bearing, switch,container to hold solution and a base to keep container connected with motor.

Initially,attach the shaft to the motor.Connect the motor to the power supply and controller. Mount the plate and motor on a stable base. The motor is connected to the base at which the container kept. The base of the wooden box should be made of wood or hardened material so that we can use the base to fix the motor. Enclose the setup in a box or container.When the power is on, motor rotates and the container also rotates with the motor.It is okay to use a variable power supply for speed control.Add a switch for safety and convenience.Ensure proper balancing and alignment for smooth operation. For building a professional-grade spin coater ,it may require more expertise and specialized materials.

The motor’s positive and negative is connected through a switch to the DC power source. When the power is on ,using appropriate voltage, the motor started to rotate on turning the switch on.When the polymer solution is poured into the rotating container, the fibers are ejected out from the container through the holes.Then the fiber can be collected from container after it gets dried.

This method of force-spinning is taken from the idea of cotton candy machine. This method of force-spinning is used in cotton candy machine to produce very tiny, elongated fibers of cotton candy. A cotton candy machine model is shown below.

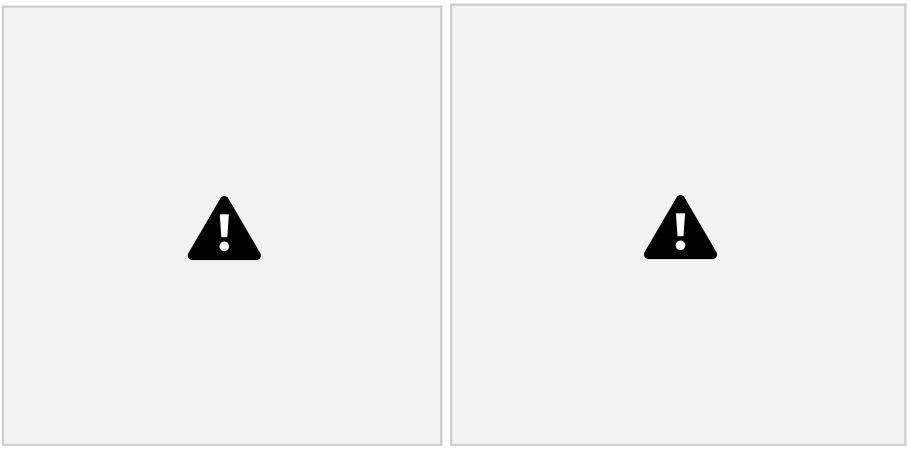


Figure 3.1: Cotton Candy machine model collecting candy fibers

Modelling of a new force-spinning machine from the idea of cotton candy machine is shown below.[4]

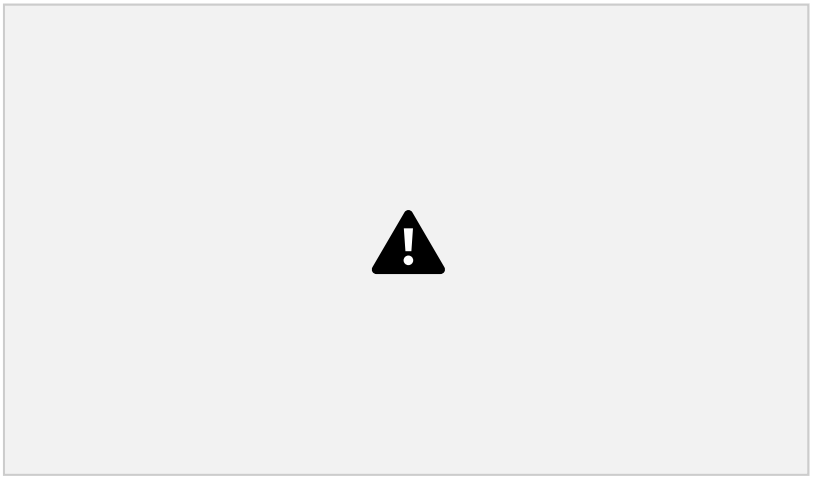


Figure 3.2: Schematic representation of force-spinning machine

3.1.1 Forcespinning machine

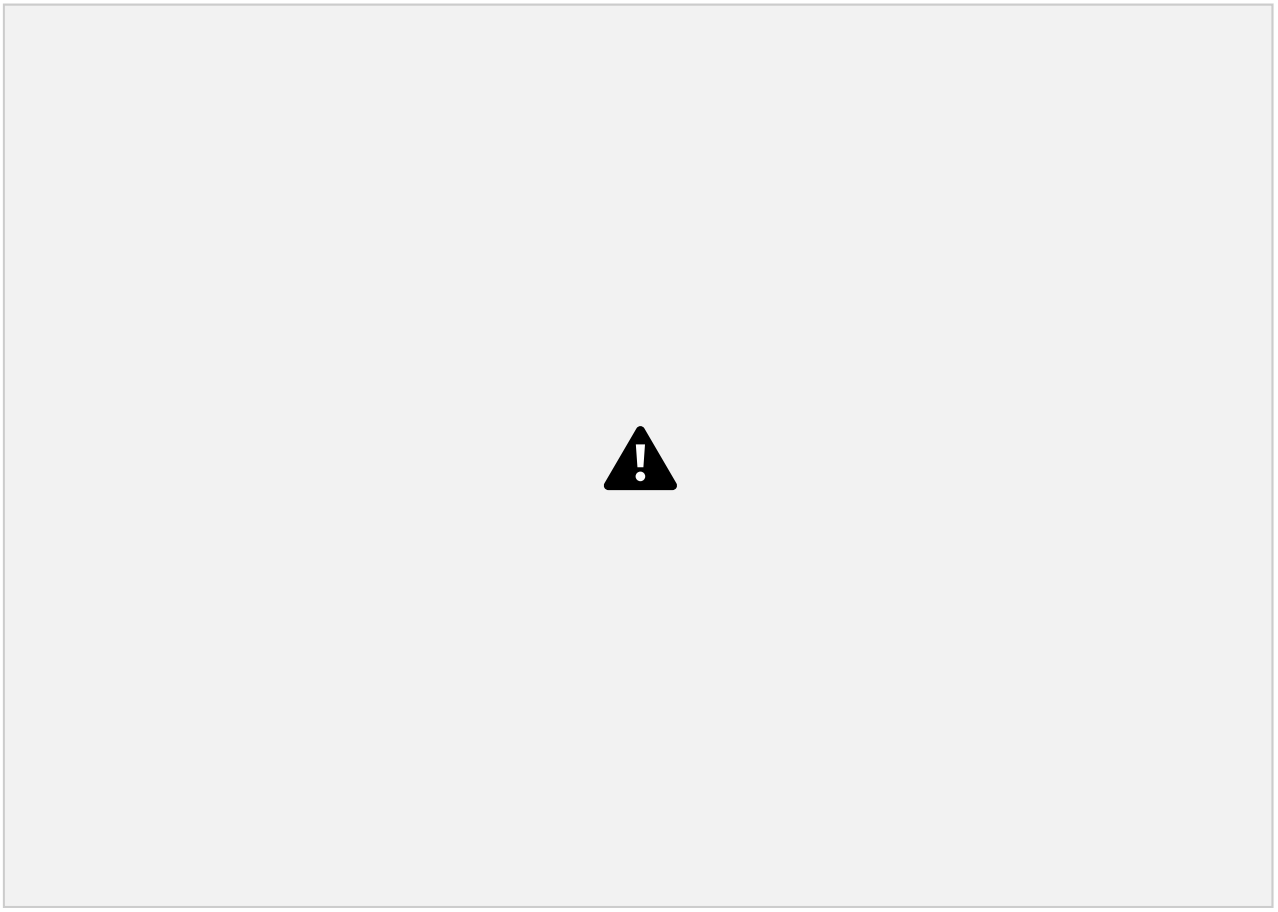
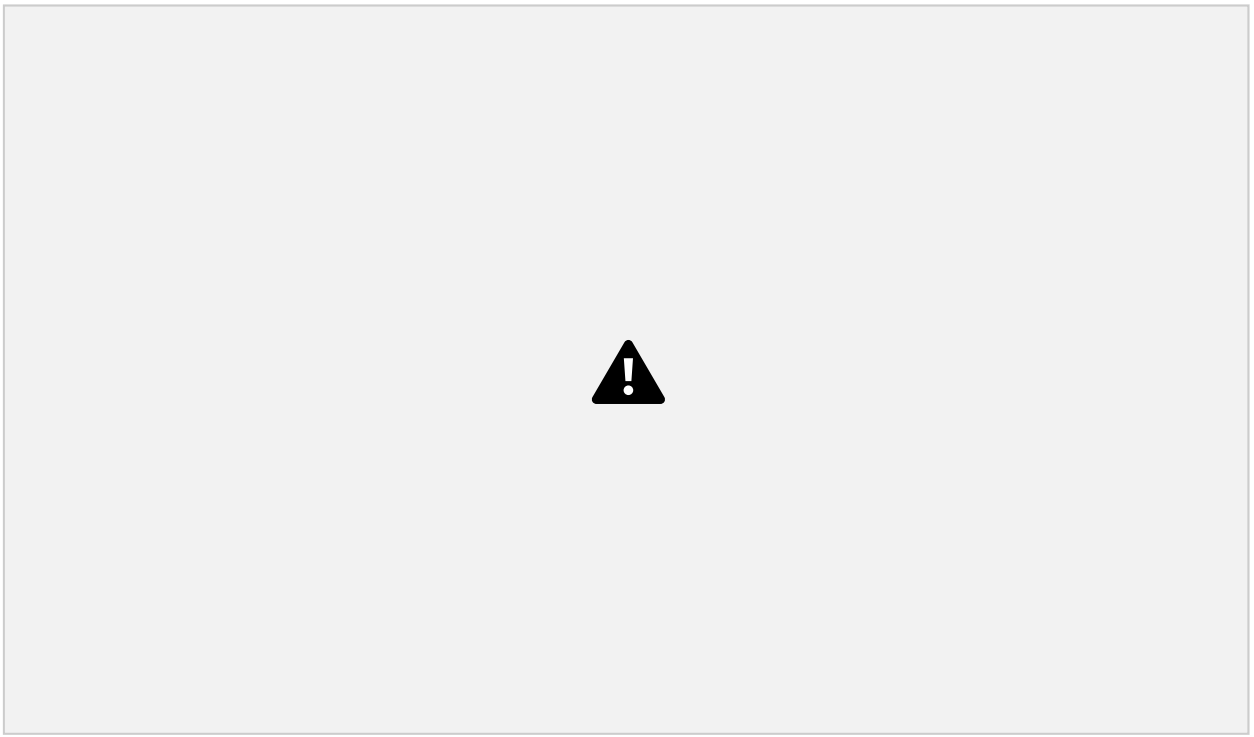


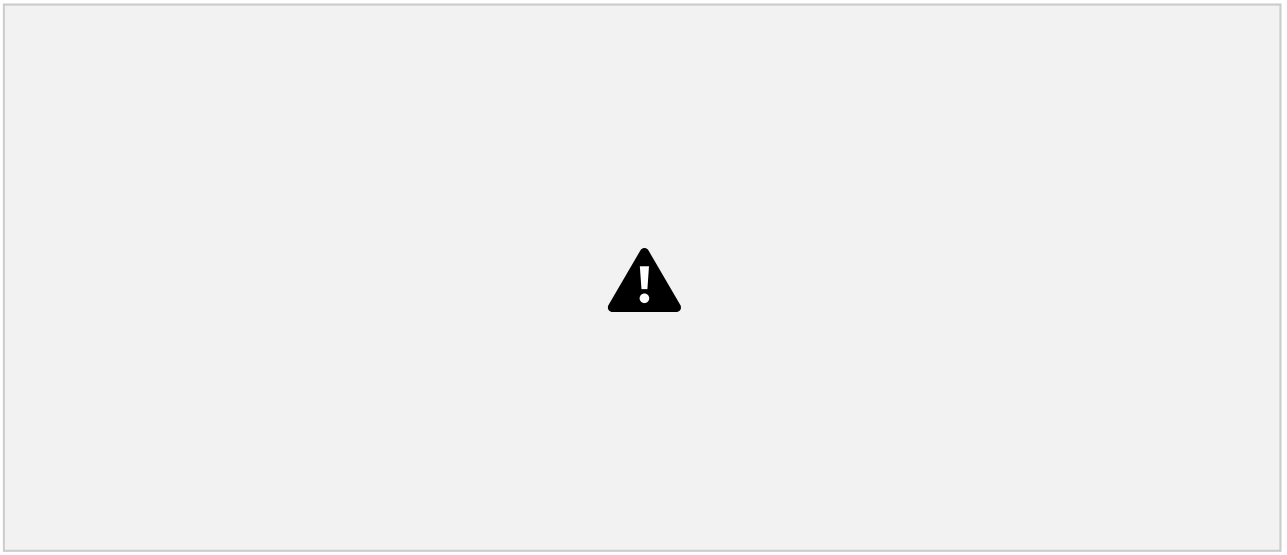
Figure 3.3: Image of force-spinning machine setup constructed

A force spinning machine is constructed as a box with all glass faces, except for the wooden base. A motor is fixed to the base and connected to a rotating container. A thick platform is utilized to provide stability and support for the motor, ensuring safe and controllable rotation. This platform stabilizes the motor, making its rotation secure and manageable.The DC motor is regulated by a switch for safety purposes. The experiment can be repeated by either adjusting the duration of rotation or varying the rotations per minute (RPM).When a polymer solution is poured into the container and the motor is activated, nanofibers are generated. The nanofibers are collected around the container, but sometimes they stick to the glass faces. To facilitate easy collection, all the glass faces are covered with aluminum foil, causing the nanofibers to stick to the foil instead. This allows for simple and efficient collection of the nanofibers from the foil.



The sample of $BiNiO_3$ powder can be prepared as shown above.The preparation of $BiNiO_3$+PVP polymer solution via the combustion method involves a multi-step process that yields a homogeneous solution containing $BiNiO_3$ nanoparticles coated with a PVP polymer matrix. Initially, $Bi(NO_3)_3$ (Bismuth nitrate) and $Ni(NO_3)_2$ (Nickel nitrate) in equal ratios are dissolved in a minimal amount of ethanol to form a clear solution, en suring complete dissolution of the metal precursors by continous stirring. The solution is then heated to a high temperature for the next few hours (typically ranging from 70°C to 80°C) on a hot plate, initiating a rapid combustion reaction,yields its powder.Then grinding it in the mortar, we get light bluish green $BiNiO_3$ powders. This powder is then used for characterization technique like XRD.

During this process, the metal nitrates decompose, and $BiNiO_3$ nanoparticles are formed through a self-sustaining combustion reaction.Subsequently, PVP (Polyvinylpyrroli done) is added to the solution, and the mixture is stirred rigorously for 1 hour at 40°C to achieve a uniform dispersion(gelly like solution of pale green colour).Concurrently, PVP decomposes and coats the $BiNiO_3$ nanoparticles, generating a polymer matrix that encap sulates the nanoparticles. The resulting $BiNiO_3$ + PVP nanoparticles are then dispersed in ethanol to form a stable solution. This combustion method facilitates the rapid synthe sis of $BiNiO_3$+ PVP polymer solution with a uniform nanoparticle size distribution and

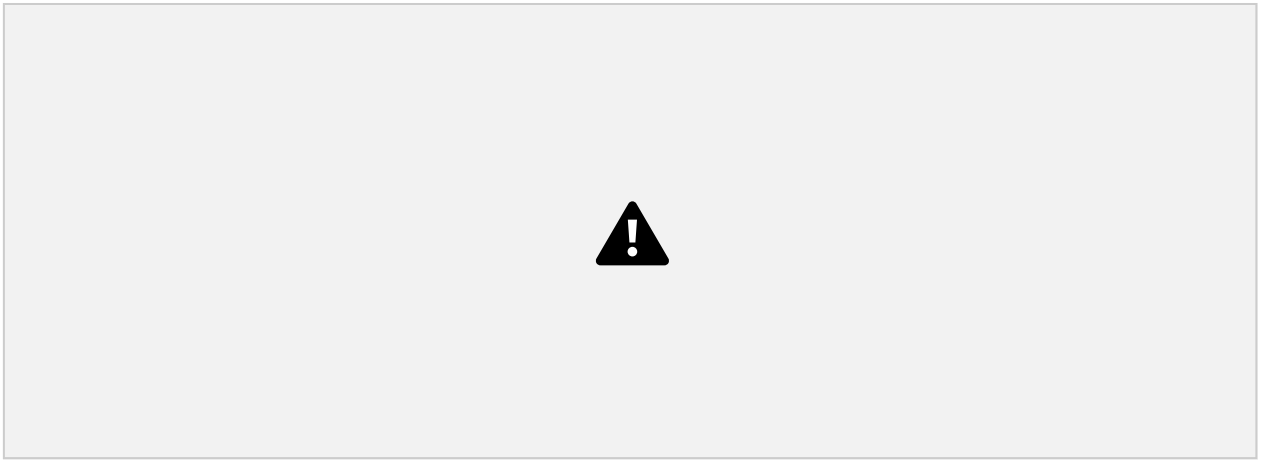


controlled chemical composition, making it an attractive approach for large-scale produc tion and applications in various fields.
Then,this solution is poured into the forcespinning setup,rotated for 2-3 minutes gives mesh like nanofiber around the walls of container.

The experimental procedure was repeated by modifying either the molar concentration of $BiNiO_3$ or the weight percentage of PVP. The outcomes of both sets of experiments are presented in the table below for comparison and analysis.

i)With the weight percentage of PVP held constant, we investigated the effect of changing the molar concentration of $BiNiO_3$.

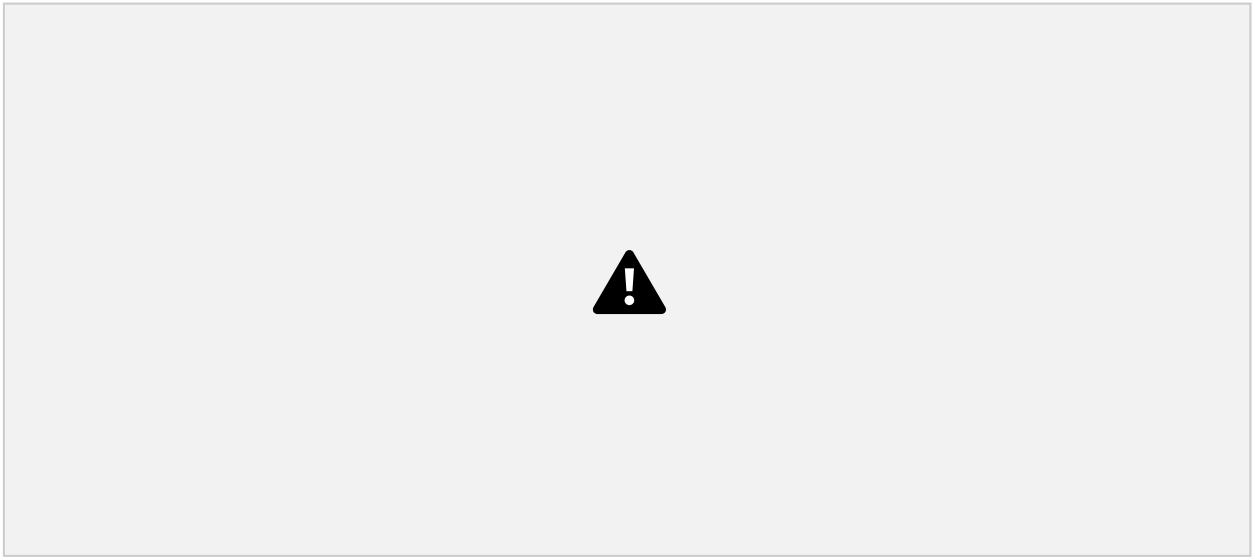
Table 3.1: Table showing effect of change in molar concentration of $BiNiO_3$



ii)Under conditions of constant molar concentration of $BiNiO_3$, we investigated the

Fabrication of Rotary Force-spinning Technique & Synthesis of $BiNiO_3$/PVP Nanofibers effect of change in weight percentage of PVP.

Table 3.2: Table showing effect of change in weight percentage of PVP



Chapter 4

Results And Discussion

Characterization of PVP/$BiNiO_3$ Nanofibers

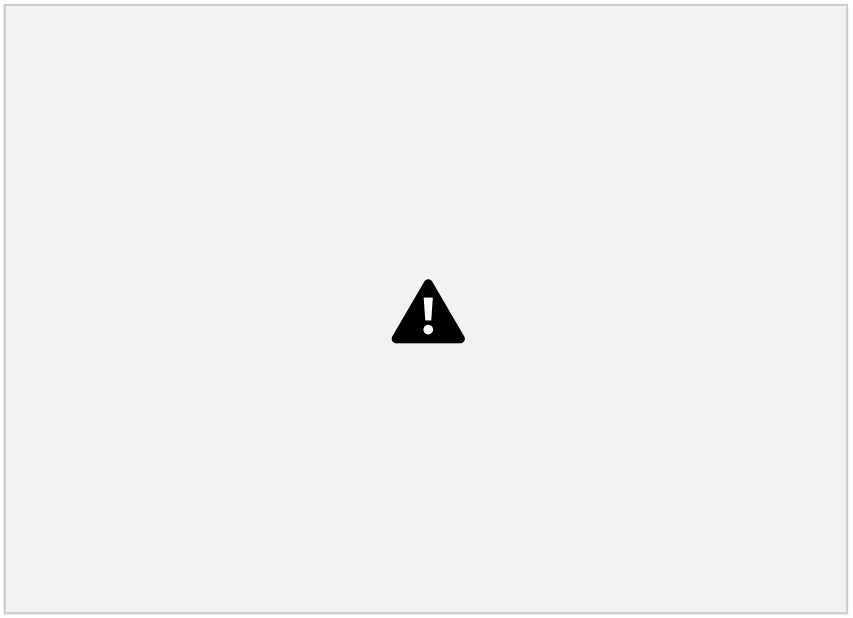
4.1 Structural Analysis

4.1.1 XRD Analysis

The XRD pattern of the BiNiO3 nanoparticle synthesized by

combustion method is shown in figure. X-ray diffraction (XRD) is commonly employed to investigate the crystallography of a sample by analyzing the diffraction patterns produced when X-rays interact with a crystalline material, re searchers can determine details such as lattice structures,crystal phases, and interplanar spacing, optical properties, crystalline size and morphol ogy. It's a powerful technique for understanding the arrangement of atoms within solids.X-ray Diffraction (XRD) is a powerful analytical technique that provides valuable insights into the structural properties of materi als, offering detailed information on unit cell dimensions,crystal structure, phase composition, phase identification, lattice parameters.

By analyzing the diffraction patterns, XRD helps researchers and sci entists understand the atomic arrangement, crystal structure, and phase distribution within the sample, making it an essential tool in materials science and research.



Nanofibers

The average particle size (D) can be determined from the Debye-Scherrer formula is given by,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (4.1)$$

where,

D=crystalline size

θ =glancing angle

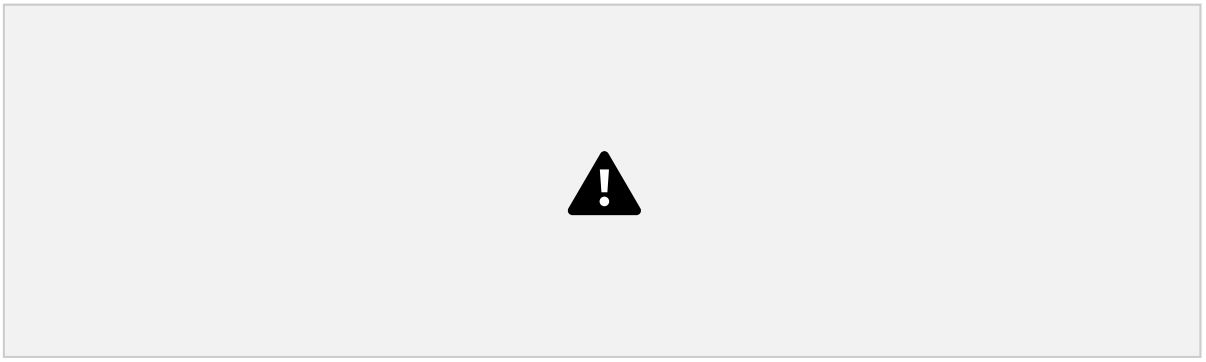
λ = wavelength of the X-ray radiation

β =full width at half maximum to the diffraction peak.

The spectrum exhibits a combination of sharp and broad peaks, indi cating a mix of crystalline and amorphous phases.The presence of BiNiO3 is evident from the characteristic peaks at 2θ values around 30-40° and 50-60°.The PVP component is likely responsible for the broad hump cen tered at $2\theta \approx 20°$, indicative of its amorphous nature.Additional peaks may suggest the presence of intermediate phases or impurities.The coexistence of BiNiO3 and PVP phases suggests a composite material with potential for synergistic properties. The amorphous PVP phase may influence the material's optical, electrical, or mechanical properties.

The XRD spectrum of BiNiO3 (Bismuth Nickel Oxide) is characterized by sharp peaks, attributable to its crystalline structure, high crystallinity, and relatively large crystal size. The material's crystal structure is well defined and ordered, with a low density of defects and a high-symmetry configuration, resulting in sharp diffraction peaks. This sharp spectrum is indicative of a well-defined crystal structure, making BiNiO3 a suit able candidate for a range of applications, including optoelectronic devices, magnetic storage, catalysis, and sensors.

The XRD spectrum of PVP (Polyvinylpyrrolidone) is characterized by a broad diffraction pattern, attributable to its amorphous nature and lack of crystalline structure. The disordered molecular arrangement and ran dom spatial orientation of PVP molecules contribute to the broadening of the diffraction peaks. Furthermore, the polydispersity of PVP's molec ular weights and potential presence of impurities or additives can also broaden the spectrum. Instrumental broadening effects, including beam divergence, sample size, and detector resolution, additionally contribute to the observed broad spectrum. While the broad spectrum presents chal lenges in resolving distinct peaks, it nevertheless provides valuable insights into PVP's structural and property characteristics.



The peaks at 2θ value 20.340° ,20.060° ,21.260° ,11.660° ,11.380°

corre 29

sponds to the intensity of 1000.00 ,956.52 ,956.52 ,934.78 ,920.29 respec tively.The peak corresponding to each 2θ is found using Qualx.

a. Crystalline size

To calculate the crystalline size and average crystalline size from the XRD data, we can use the Scherrer equation. The Scherrer equation is limited to nano-scale crystallites. We can calculate average

crystalline based on XRD data using the Scherrer equation.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (4.2)$$

where,
D=crystalline size (nm)
k=0.9 Scherrer size (nm)
β =FWHM (radians)
θ =peak position (radians)

b. Interplanar(d) spacing

Interplanar spacing or d spacing from the XRD data can be calculated using the Bragg's equation is given by,

$$n\lambda = 2d\sin\theta$$

or,

$$d = \frac{n\lambda}{2\sin\theta} \quad (4.3)$$

where,

λ =1.5418 A° (Wavelength of incident X-ray) θ = peak position (in radians)
n=1 (order of diffraction)
d=interplanar spacing or d spacing (in A°) 30

4.2 Morphological Analysis

4.2.1 Field emission scanning electron microscopy (FE-SEM)

A Scanning Electron Microscope is type of electron microscope that scan the surface of the microorganisms using a beam of low energy electron to focus and examine specimen.FE-SEM is an advanced technology used to capture the micro or nano structure image of the material specimen.The SEM has advantages of providing a huge depth of focus due to the short wavelength of the primary electron beam used,a larger imaging field of view and 3D image or topography of the sample than the TEM.

Figure 4.1: FE-SEM image of $BiNiO_3$/PVp fibres in two diffrent regions The device is employed at an acceleration voltage of 4.00 kV with the 31

magnification ×950 in high vacuum. The live time was 100.00 seconds

while the real time is 110.94 seconds.Dead time is 9.00 % and the count rate is 1637.00 CPS.

The device is employed at an acceleration voltage of 4.00 kV with the magnification ×950 in high vacuum. A graph of energy (in keV) is plot ted against intensity (counts) in which all the constituting elements (Car bon,Bismuth, Nickel, Oxygen) exists is shown above.

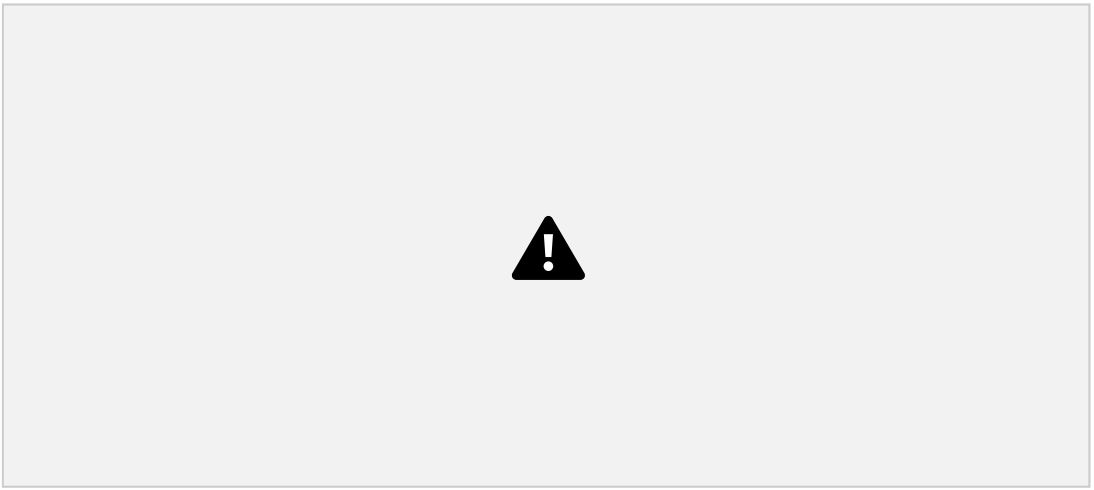
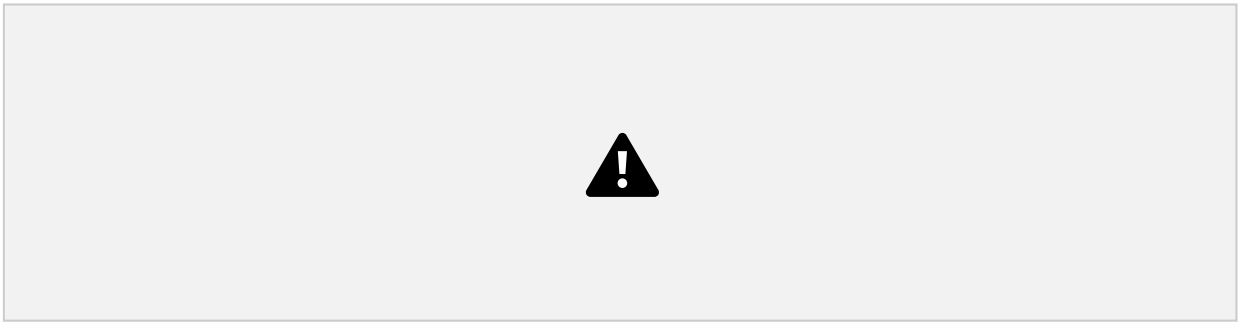


Figure 4.2: EDAX elemental analysis of $BiNiO_3$/PVP Fibers

EDAX (Energy-Dispersive X-ray Spectroscopy) is a versatile analytical tool that reveals the elemental composition of materials, enabling the iden tification and quantification of elements, including trace elements. This technique plays a crucial role in various applications, including material characterization, failure analysis, quality control,etc.

Table 4.1: Breakdown of constituting elements in compound



The table provides a detailed breakdown of the constituting elements in the compound, including their respective atomic and mass percentages. Specifically, it lists the element symbol, atomic percentage, and mass per centage for each element present in the compound, offering a comprehensive overview of the compound's composition.

Various samples are prepared by varying the molar concentration of $BiNiO_3$ in a PVP solution. The molar concentration of $BiNiO_3$ is system atically changed to create a series of samples with different concentrations, specifically 0.25M, 0.5M, 1M, and so on. The resulting samples are then collected and characterized.

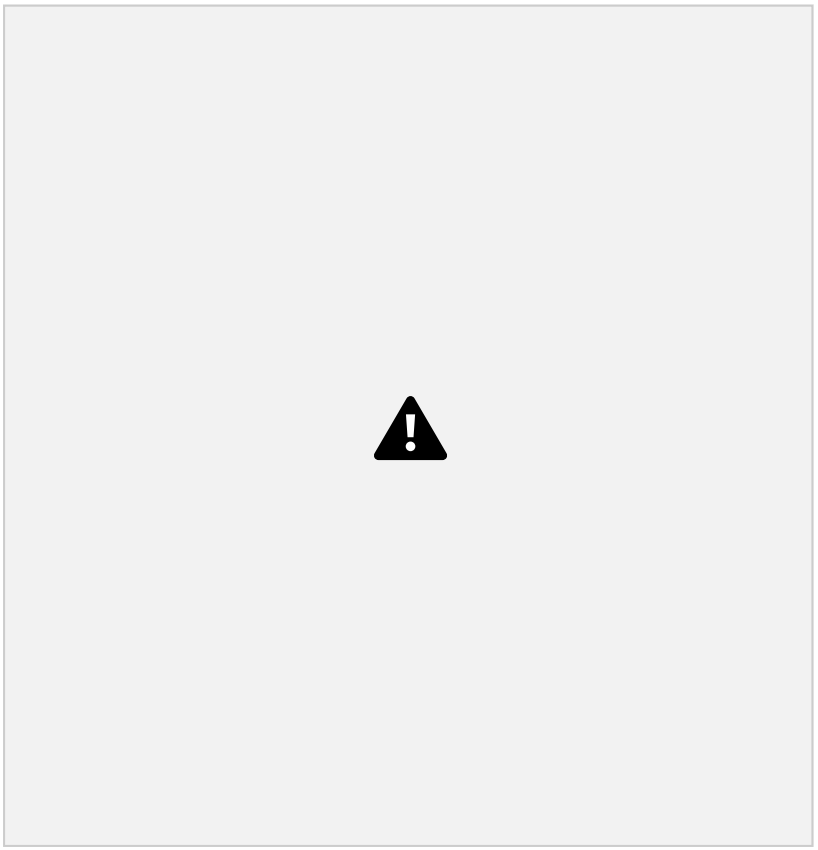


Figure 4.3: Fibers collected around the container after forcespinning 33

Mapping of the sample for 20μm and 50μm is shown.The long elongated nanofibers can be identified.Each element in the compound are identified by each colours and is also marked for better understanding of how the elements are distributed among the sample.

Figure 4.4: EDS mapping image of $BiNiO_3$/PVp fibres in two diffrent regions 34

SEM image of the $BiNiO_3$/PVP nanofibers for 20μm and 50μm is anal ysed.Considering the SEM image of 20 μm, the image is like viscous,watery texture.It may be due to the hygroscopic property of pvp. The experiment is conducted at normal room temperature and atmospheric pressure.As $BiNiO_3$ is very sensitive to pressure,there is a chance to vary the property when it prepared under atmospheric pressure.Another reason is may be due to the hygroscopic property of polyvinylpyrrolidone.

$BiNiO_3$ is a ceramic material, and when combined with Polyvinylpyrroli done (PVP) powder, it's likely that the mixture is wet at normal tempera tures due to the hygroscopic nature of PVP.PVP is a polymer that readily absorbs moisture from the air, making it a humectant. When combined with $BiNiO_3$, the PVP can absorb moisture and create a wet or humid environment, even at normal temperatures. This is because PVP has a strong affinity for water molecules, which can lead to the absorption of atmospheric moisture. For proper optimization, it might be worth investi gating ways to control the humidity or moisture content in the mixture to achieve the desired outcome.

Chapter 5

Conclusion

Primary goal of this work is to design and construct a low cost home made setup of force-spinning. Force-spinning is a better alternative for the highly sophisticated complex method of electro-spinning. Our setup is innspired from the cotton candy machine uses the same idea and produces long ,thin fibers. Our home-made setup greatly useful for the production of nanofibers. Secondly, we were produced $BiNiO_3$/PVP nanofibers us ing this homemade setup of force-spinning (cotton-candy model). $BiNiO_3$ can be embedded with PVP to attain good nanofiber nature. for that, $BiNiO_3$ is prepared in bulk using sol-gel method, which is said to be diffi cult due to the requirement of high temperature and high pressure synthe sis. XRD data demands further optimization of $BiNiO_3$ and agglomerated nanofiber structure observed in SEM analysis may be due to larger concen tration PVP's hygroscopic nature.

These results are prelimiary, extensive investigation is required to explore the potential of this combination. In corporation of a multiferroic material ($BiNiO_3$) in a organic polymer ma trix(PVP) have a lot scope towards the application in spintronics. In he lical π-conjugated materials based on supramolecular nanofibers has been shown spin filtering more than 85 % at room temperature. This opens a lot future prospects for organic- inorganic nanofibers for spintronic-based memory devices.

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