Chapter - III

3.0. Introduction

**X-Ray diffraction (XRD) Studies**

X-ray Powder Diffraction (XRD) is one of the efficient analytical technique employed to determine crystalline structure of unknown materials. Monochromatic x-rays are used to determine the interplanar spacing of the unknown materials. The prepared samples were examined as powders with grains in random orientations to all possible crystallographic directions are scanned by the beam. The constructive interface produces reflections when Bragg condition satisfied. Hence the high of relative peak is generally indicates grains orientation in a preferred direction [1-4]. In most of the powder diffractometers systems a series of parallel plates arranged corresponding to the plane of the diffractometer with several scatter and receiving slits were employed to generate an incident beam of X-rays that are almost parallel. The soller slits are generally deployed to the incident and diffracted beam, however these will be depends on the defined system. The scatter slits may be change to control the width of the incident beam that incident on the specimen and the receiving slits may be change to monitor the width of the entering beam of the detector.

3.1. X-Ray Diffraction

The secondary diffracted beam of the X-rays interact with samples which is related to interplanar spacing of the crystalline powder samples examine represents by the “Bragg’s Law” as shown in figure 3.1 [5]:
\[ 2d \sin \theta = n\lambda. \]

Where \(d\) is the interplanar spacing, \(\theta\) is glancing angle, \(\lambda\) is the wave length of X-ray, and \(n\) is the order of the atoms. The values of \(2\theta\) obtained from the Bragg peaks position of the X-ray patterns give interplanar spacing in terms of Miller indices (hkl) and they are used to calculate the lattice parameter employing above equation.

![Figure 3.1: the reflection of X-rays by a family of atomic planes](image)

**Detectors**

Several different types of detectors have been used in XRD systems. The Scintag system is used for our prepared samples and which has a scintillation counter. The Siemens systems have scintillation counters and a large-window position sensitive detector or PSD and it covers \(8\theta\) \(2\theta\) simultaneously. Scintillation counters exist with same oldest technology available, however still widely using due to their durability, low cost and ease of use. Newer detector technologies give improved quality data, a higher degree of energy selectivity or fast delivery [6]. All detector technologies also engross tradeoffs in maintenance.
In order to illuminate the crystal structure the various methods are adopted such as Laue’s method, the rotating crystal method and the Debye-Scherrer method. In the present study, authors are used powder method to elucidate the structure of composites.

3.2. Powder method

In this method, X-rays is made of a monochromatic beam to strike a fine grained powder in a thin walled capillary tube. The diffraction take place simultaneously from every crystallites surface that are oriented along the planes having incident glancing angle (θ) satisfying the Bragg’s law. In diffractometers the prepared sample was placed at the center and proportional counter used to record the diffracted X-rays. When the sample is rotate of an angle θ, the proportional counter is rotated through 2θ. The diffractometer recorded the variation of intensity of diffraction lines as a function of diffraction angle 2θ [7, 8].

3.3. Experimental Technique

The X-ray diffraction patterns of the prepared samples were recorded by using Philips X-ray diffractometer using CuKα radiation (λ = 1.5406 Å). The diffractograms were recorded in terms of 2θ in the range 20° – 120° with a scanning rate of 2° per minute.

3.4. Results and Discussion

3.4.1. Polyaniline / ZnFe₂O₄ composites

Figure 3.2(a-d) shows the X-ray diffraction patterns of PANI, ZnFe₂O₄ and PANI/ZnFe₂O₄ nanocomposites. Figure 2(a) shows the XRD pattern of pure PANI, the peaks at 2θ=20.7° and 25.29°
which can be ascribed to the periodicity parallel and perpendicular to the polymer chains respectively [9, 10]. Figure 2(b) shows the XRD pattern of ZnFe$_2$O$_4$ nanoparticles. The peaks at 2θ values of 18.3, 29.99, 35.40, 36.90, 43.01, 53.86, 57.01 and 62.42 which corresponds to (111), (220), (311), (222), (400), (422), (511) and (440) crystal planes of cubic ZnFe$_2$O$_4$ with spinel structure [11,12]. All the peaks match with the characteristic reflection of ZnFe$_2$O$_4$ (JCPDS Card No. 22-1012). The average crystalline size of the ZnFe$_2$O$_4$ nanoparticle was determined by Scherrer’s formula and found to be 32 nm. The XRD patterns of the PANI/ZnFe$_2$O$_4$ (10 & 30 wt %) nanocomposites are shown in figure 2(c-d). The XRD patterns exhibit both the characteristic peaks of ZnFe$_2$O$_4$ and the broad diffraction peaks of PANI. These results confirm the formation of PANI/ZnFe$_2$O$_4$ nanocomposites.

3. 4.2. XRD pattern of polyaniline / NjFe$_2$O$_4$ composites

Figure 3.3 shows the XRD pattern of the nickel ferrite nanoparticles, polyaniline and PANI/NiFe$_2$O$_4$ composites. XRD pattern of nickel ferrite (NF) shows all the peaks corresponds to spinnel ferrite phase matches well with JCPDS data 10-325. The average crystallite size of the NiFe$_2$O$_4$ was found to be 14nm. NiFe$_2$O$_4$ belongs to the class of ferrites with inverse spinel structure having structural formula Fe$^{3+}$[Ni$^{2+}$ Fe$^{3+}$]O$_4$ [13]. XRD pattern of PANI shows sharp peak at 2θ = 20° and 26° which is clear indication of the semi crystalline nature of the sample matches with those of literature [14]. XRD pattern of PANI/NiFe$_2$O$_4$ composites shows diffraction peaks as superposition of those of polyaniline and nickel ferrite nanoparticles, indicating the formation of PANI/NiFe$_2$O$_4$ nanocomposites. We conclude from the XRD results that nanocomposites have a more ordered arrangement and better crystallinity than that of pure polyaniline.
Figure 3.2: XRD pattern of PANI, ZnFe$_2$O$_4$ and PANI/ZnFe$_2$O$_4$ nanocomposites.
3.5. Infra Red Spectroscopy

3.5.1. Introduction
Over more than seventy years, Infrared spectroscopy technique has been used to analyze the structure of the prepared materials in the laboratory. An infrared spectrum produces a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations or stretching between the atomic bonds of the material [15]. Every unique materials combination of atoms cannot reproduce the same spectra by other compounds. Hence, infrared spectroscopy gives a positive identification of each industrial material. In addition, the peaks size of the spectrum indicates the amount of material present. With contemporary software algorithms, infrared spectroscopy is one of the excellent tools for quantitative analysis of materials.

Fourier transform infrared (FT-IR) spectrometry was developed in order to encounter the structural analysis problems and limitations with the dispersive instruments. The main difficulties were the slow scanning process with these instruments [16]. A solution was developed which consists of a very simple optical device known as interferometer. The interferometer produces a unique kind of signal which encoded long range infrared frequencies.

The electrical, thermal and magnetic properties of composite materials depend on their chemical composition, crystal orientation, cationic distribution and preparation methods. The vibrational of the atomic bonds, electronic arrangement and magnetic dipoles informations can get from the spectra. It also gives the information about the position and valance of the ions in the crystal lattice. The FTIR spectrum is an efficient undestructive tool to describe the various problems associated with structure of the materials.

3.6. Experimental technique
The FTIR spectra of prepared samples are recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. The samples uniform pellets was prepared by mixing of KBr in the ratio 1:25 with samples. The clean disc have prepared by pressed in a cylindrical die approximately 1 mm thickness.

Figure 3.4 shows that schematic diagram of FTIR spectroscopy
In FTIR, the polychromatic infrared source light is a black-body radiator directed to a beam splitter. The half of the light is refracted towards the fixed mirror and another half of the light is transmitted towards the moving mirror. The reflected light from both mirrors back to the beam splitter and almost 50% of the original light transmits through the sample compartment. There, the transmitted light is refocused on to the detector after absorption by the sample compartment. The difference between the two optical path lengths of the two arms of the interferometer is called the retardation. An interferogram is found by changing the retardation and measuring the signal from the detector for different values of the retardation. The interferogram will be formed when there is no sample shows the splitter efficiency and variation of source intensity with the wavelength. [17]. The maximum results obtained at zero retardation because of constructive interference in complete wavelengths, followed by formation of a number of wiggles. The maximum intensity in the interferogram shows the position of zero retardation when modulated the presence of absorption bands of the samples.

There are two principal advantages for an FT spectrometer compared to a scanning (dispersive) spectrometer.

1. The advantage of multiplex or Fellgett's arises from all wavelengths is collected concurrently. This may result in a higher Signal-to-noise ratio for a swipe scan-time or a shorter scan-time for a defined resolution.

2. The high throughput or Jacquinot's is another advantage. This is because the interferometer throughput is determined by the diameter of the source beam.

3. The less sensitivity to stray light cones.

While a disadvantage is that FTIR cannot use the advanced electronic filtering techniques that often makes its signal-to-noise ratio inferior to that of dispersive measurements.
The FTIR spectra of polyaniline and its composites give information about various molecular levels interactions but the type of charge carriers.

3.7. Results and Discussions

3.7.1 FTIR of PANI – ZnFe$_2$O$_4$ Nanocomposites

Figure 3.5 shows the FTIR spectra of pure PANI, ZnFe$_2$O$_4$ and PANI/ZnFe$_2$O$_4$ nanocomposites. Figure 3.5 (a) shows the FTIR spectra of pure PANI. The characteristic peaks of PANI occur at 1564, 1478, 1301, 1244, 1137 and 808 cm$^{-1}$. The peaks at 1564 and 1468 cm$^{-1}$ are attributed the characteristic C=C stretching of the quinnoid and benzenoid rings, the peaks at 1301 and 1244 cm$^{-1}$ are assigned to C-N stretching of the benzenoid ring, the peak at 1137 cm$^{-1}$ which is considered to be the measure of degree of electron delocalization and 808 cm$^{-1}$ corresponds to the N-H out of plane bending in rocking mode. Figure 3.5 (b) shows the FTIR spectra of ZnFe$_2$O$_4$ nanoparticles. The main peaks 555 cm$^{-1}$ is due to intrinsic stretching vibrations of the metal at the tetrahedral site and 464 cm$^{-1}$ is due to octahedral-metal stretching vibrations. Figure 3.5 (c-e) shows the FTIR spectra of PANI/ZnFe$_2$O$_4$ (10, 30 & 50wt %) nanocomposites respectively. The peaks of the composites shift to lower wave numbers. This indicates that there is some interaction between ZnFe$_2$O$_4$ nanoparticles and PANI backbone.
3.7.4 FTIR spectra of polyaniline / NiFe₂O₄ composites

Figure 3.6 (a-c) shows the FTIR spectra of the nickel ferrite nanoparticles, polyaniline and PANI/NiFe₂O₄ composites. The transmittance bands ν₁ and ν₂ around 611.12 cm⁻¹ and 465.90 cm⁻¹ in NiFe₂O₄ are attributed to the stretching vibration of tetrahedral and octahedral group complexes of ferrites, respectively [18]. The bands at 1578.39 and 1487.89 cm⁻¹ in pure PANI are the characteristics bands of nitrogen quinoid and benzoid forms due to the conducting state of the polymer. In PANI/NiFe₂O₄ nanocomposites, there are characteristic bands of NiFe₂O₄ located around 600 cm⁻¹ and 400 cm⁻¹, indicating the well wrapping of NiFe₂O₄ nanoparticles with PANI in the PANI/NiFe₂O₄ composites. The interaction of nickel ferrite with polyaniline is confirmed from IR spectra of the nanocomposites.
Figure 3.5 (a-e) FTIR spectra of PANI, ZnFe$_2$O$_4$ nanoparticles and PANI/ZnFe$_2$O$_4$ nanocomposites
3.8. Scanning Electron Microscopy (SEM)

3.8.1. Introduction

The Micro structural studies on material provide information about:

1. Grain size of the samples
2. Interstitial area per unit volume
3. Phase dimensions of composites
4. Phase distribution
5. Density of dislocated ions or atoms
6. Precipitation volume fraction and
7. Surface to volume ratio of the composites etc.

There are several other techniques to determine for the microstructure by optical microscopy, scanning electron microscopy, field emission microscopy, field ion microscopy, X-ray microscopy and electron microprobe analysis. Among all techniques, SEM is much superior and an extremely versatile method for structural information with high magnifications with depth of focus (~100 – 200 Å). The SEM has provided its potentiality to reveal the aspects of grain size, shape and orientation of pores, inclusions etc.

3.9. Experimental Technique

The powder morphology of polyaniline and its composites sprinkled on the copper grid (to measure grain size) and examined by employing Phillips XL30 ESEM scanning electronic microscope (SEM). The samples in the form of powers are mounted on a copper grid platform and sputtered a conducting gold on it to avoid charging over the composite surfaces. Further the selected area where examined under SEM to take the images. The block diagram of the SEM is shown in figure 3.7. In a SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode because of its high melting point and lowest vapor pressure among all the metals [19]. Therefore, Tungsten is normally used in electronic emission for SEM instruments. Other types of electron emitters include lanthanum hexaboride (LaB$_6$) cathodes, tungsten single crystal emitters or zirconium oxide emitter however it is necessary to upgrade the vacuum system and field emission gun.
The electron beam has an energy ranging from 0.5 keV to 40 keV, is focused by two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam generally go be pairs of detector plates or scanning coils in the electron column. The final lens normally deflect the beam in the $x$ and $y$ axes so that it scans in a raster over a rectangular selected area of the composites surface [20].

When the samples interact with primary electron beam, the electrons lose energy due to repeated random scattering in all direction and absorption within a capillary surface of the composite known as the interaction volume may be less than 100 nm to around 5 µm. The amount of the interaction volume of composite surface depends on the landing electron's energy and the atomic number of the composites and its molecular density. The energy exchange between the sample surface and electron beam generates the reflection of high-energy electrons because of elastic scattering and emission of secondary electrons due to an inelastic scattering and the emission of electromagnetic radiation which can be examined by detectors. The beam current absorbed by current. The various type of electronic amplifiers are used to enhance the signals to display on the cathode ray tube. The image may be captured by photography from a high resolution cathode ray.
Figure 3.7 shows the block diagram of Scanning Electron Microscope

3.9.1. Results and Discussions

SEM technique is employed basically to understand the surface morphology domains, grain size, pin hole defects and grain patterns. The images are integrated by the interaction of electrons with surface of the in vacuum. The scanning electron microscopic image of polyaniline and its composites are shown in figures 3.8 to 3.9.
**3.9.3. SEM image of PANI and PANI /ZnFe$_2$O$_4$ composites**

The morphology of the PANI was studied by scanning electron microscope (SEM). SEM image of zinc ferrite shows in figure 3.8 (a) and it is observed that the particles are not agglomerated but well interconnected. The SEM micrograph of the PANI in fig 3.8(a) indicates the big globular agglomerates with smooth surface. Scanning electron microscope (SEM) was employed to visualize the shape and size to confirm the nanocrystalline nature of the ZnFe$_2$O$_4$. Fig 3.8(c) shows the SEM image of PANI-ZnFe$_2$O$_4$ composites and found that the grains are well interconnected, which will be improve the transport property.
Figure 3.8 (a-c) SEM image of (a) ZnFe$_2$O$_4$ (b) PANI (c) 30 wt % of PANI/ZnFe$_2$O$_4$ composites

Figure 3.9 (a, b & c) shows the SEM image of (a) pure Nickel ferrite prepared by citrate method and it is observed that the particles are spherical in shape, well interconnected to each other. The average size of the particles is calculated by using linear intercept method and its size were found to be 800 nm. The polyaniline image shows the opal tube like morphology with the size of 1 μm as shown in figure 3 (b). It is noticed that the polyaniline grows on the surface of ferrite in unidirectional form small rod like structure as seen in figure 3 (c).
Figure 3.9 SEM image of NiFe$_2$O$_4$, PANI and PANI – NiFe$_2$O$_4$ composites

Reference


