CHAPTER-III

CHARACTERIZATION

3.0 Introduction to X-Ray diffraction

X – ray spectroscopy is one of the important and prominent tools for the study of structure of molecules and crystals. There are certain advantages in the use of X – ray methods as against the optical ones. X – rays have intrinsic characteristics possessing more energy than that of light as such these can easily penetrate through any opaque media. This very property will give us an interference pattern of coherent beams being diffracted from the true crystal lattice of the matter under investigation. There are many X–ray methods for the study of the crystals. But amongst them, the most useful and powerful techniques are interferometry and diffractometry. With the application of these methods, one can obtain information such as the deformation of the crystals, electronic energy density in terms of a function of width [1-4].

3.1 X-Ray Diffraction

The X-ray structure analysis is based on the phenomenon of diffraction of X-rays by a substance. X-rays are short electromagnetic waves. In the X-ray diffraction analysis, wavelengths of 0.5-2.5Å are used. The X-ray study give information about the nature and structure of the materials and also helps to know the phase present in the end product of preparation. Analysis of the X-ray data gives the values of the unit cell parameters of the system [5-7]. The slow disappearance of certain peaks and emergence of new peaks in the pattern reveals the associated structural phase changes occurring due to the variation in temperature, dopant concentration etc.
When a monochromatic X-ray falls on a crystal, whose dimensions are of the same order of magnitude as the wavelength as shown in figure 3.1 then diffraction occurs according to Bragg’s law:

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

where $d$ is interplanar spacing, $\theta$ is glancing angle, $\lambda$ is wavelength of X-ray and $n$ is the order. The 2θ values obtained from the position of the Bragg peaks from the XRD patterns are used to obtain the interplanar spacing expressed in terms of Miller indices $(hkl)$, are substituted into the above equation and a number of relations which are useful for indexing and calculating the lattice parameter are obtained. The distance between the planes $(d)$ may be found by substituting the value of lattice parameter $(a)$ and $(hkl)$ in the following equations:

1. Cubic system:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
2. Orthorhombic system: \[ d_{hkl}=\frac{1}{\sqrt{h^2 a^2 + k^2 b^2 + l^2 c^2}} \]

3. Tetragonal system: \[ d_{hkl}=\frac{a}{\sqrt{h^2 + k^2 + l^2 \left(\frac{a}{c}\right)^2}} \]

For the monoclinic and triclinic systems, which are most typical of a number of polymers, the corresponding formulae have more complex form.

The intensity and direction of X-rays that have been diffracted by a crystal are recorded by a quantum detector (a Geiger counter or a scintillation counter) or by a photographic technique.

In order to elucidate the structure of crystals, various methods are used [8, 9]. These methods include Laue’s method, the rotating crystal method and the Debye-Scherrer method (the powder technique).

### 3.2 Powder method

In this method a monochromatic beam of X-rays is made to strike a fine grained specimen in a thin walled capillary tube. The diffraction occurs simultaneously from individual crystallites that are oriented with planes having some incident glancing angle (%0) satisfying Bragg’s law. In diffractometers the sample is placed at the center and diffracted X-rays are recorded by proportional counter. When the sample is rotated through an angle 0, the proportional counter is rotated through 20. The diffractometer gives the variation of intensity of diffraction lines with diffraction angle 20.
3.3 Experimental Technique

The X-ray diffraction patterns of the samples in this present study are obtained on Philips X-ray diffractometer shown in figure 3.1.1 using CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å). The diffractograms were recorded in terms of 2$\theta$ in the range 20$^0$ – 120$^0$ with a scanning rate of 2$^0$ per minute.

![Figure-3.1.1 X-ray diffractometer](image)

3.4 Results and Discussion

3.4.1 Polyaniline

Figure 3.1.2 Shows X-ray diffraction pattern of Polyaniline. Careful analysis of X-ray diffraction of polyaniline suggests that it has amorphous natured with a broad peak centered at 2$\theta \approx 26.40^0$.  

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3.4.2 Polyaniline / ZnFe$_2$O$_4$ composites

Figure 3.1.3 shows the X-ray diffraction pattern of Polyaniline – ZnFe$_2$O$_4$ composite with 50 wt % of ZnFe$_2$O$_4$ in polyaniline. It is seen from figure that the peak of ZnFe$_2$O$_4$ indicates the crystalline nature of the composite. By comparing the XRD pattern of composite with that of PANI, the prominent peaks corresponds to $2\theta$ = 18.59°, 30.09°, 35.55°, 56.43° and 62.32° are due to (220), (311), (400) (422) and (333) planes of ZnFe$_2$O$_4$. By comparing the XRD patterns of the composite and PANI, it is confirmed that ZnFe$_2$O$_4$ (JCPDS 06-0696) has retained its structure even though it is dispersed in PANI during polymerization reaction [10].
Figure-3.1.3 X-ray diffraction pattern of Polyaniline – ZnFe$_2$O$_4$ composites

3.4.3 Polyaniline / NiZnO$_3$ composites

Figure 3.1.4 shows the X-ray diffraction pattern of Polyaniline – NiZnO$_3$ composite with 50 wt % of NiZnO$_3$ in polyaniline. It is seen from the figure that, the peaks of NiZnO$_3$ indicates the crystalline nature of the composite. By comparing the XRD pattern of composite with that of PANI, the prominent peaks corresponding to $2\theta = 18.02^0$, $24^0$, $26.5^0$, $30.7^0$ and $61.02^0$, are due to (100), (002), (101), (102) and (110) planes of NiZnO$_3$ (JCPDS card No. 04-0835 and No.05-0664). By comparing the XRD patterns of the composite, it is confirmed that NiZnO$_3$ has retained its structure even though it is dispersed in PANI during the polymerization reaction.
3.4.4 Polyaniline / CuO composites

The X-ray diffraction pattern of PANI/CuO composite is shown in figure3.1.5. There are five prominent and two less prominent peaks representing Bragg’s reflections of copper oxide. While the broad peaks representing the periodicity parallel to the polymer chains of PANI was not clearly observed at the 2θ value of 26.5 due to weak intensity in comparison to the copper oxide peak (JCPDS No.05-661). Results from both FTIR and X-ray diffraction measurements have provided additional evidence that the polymerization of PANI has been successfully obtained on the surface of the CuO composites.
Average inter chain separation can be estimated from these maxima using the relation

\[ R = \frac{5}{8} \left( \frac{\lambda}{\sin \theta} \right) \]

[11-14] where \( \lambda \) is the x-ray wavelength of CuK\( \alpha \) and \( \theta \) is the diffraction angle at the maximum intensity.

<table>
<thead>
<tr>
<th>Dopant (Primary /Secondary)</th>
<th>( 2\theta )</th>
<th>Inter Chain separation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>25.40</td>
<td>2.24</td>
</tr>
<tr>
<td>ZnFe(_2)O(_4)</td>
<td>34.34</td>
<td>1.706</td>
</tr>
<tr>
<td>NiZnO(_3)</td>
<td>28.66</td>
<td>2.007</td>
</tr>
<tr>
<td>CuO</td>
<td>25.25</td>
<td>2.207</td>
</tr>
</tbody>
</table>
3.5 Introduction to Infra Red Spectroscopy

The electrical and magnetic properties of materials depend upon their chemical composition, cation distribution and method of preparation. The vibrational, electronic and magnetic dipoles spectra can give information about the position and valance of the ions in the crystal lattice. The infrared spectrum is an important undestructive tool to describe the various ordering problems.

3.6 Experimental technique

The IR spectra of all the samples are recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. For recording IR spectra, powders are mixed with KBr in the ratio 1:25 by weight to ensure uniform dispersion in KBr pellets. The mixed powders are pressed in a cylindrical die to obtain clean discs of approximately 1 mm thickness.

The characterization of polyaniline and its composites by spectroscopic methods is important, as it gives information not only about various molecular – levels interactions but also on the type of charge carriers.

Infrared spectroscopy is a powerful tool to determine the structural changes that occurs during doping and dedoping process. Various groups have reported IR results of polyaniline, but the IR results of composites are scarce.

3.7 Results and Discussions

The occurrence of various bands in IR spectra may be attributed due to the following factors.
Characterization

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1610, 1593 and 1503</td>
<td>C = C stretching</td>
</tr>
<tr>
<td>1550 and 1500</td>
<td>C = N stretching</td>
</tr>
<tr>
<td>1040, 960 and 790</td>
<td>C – N stretching</td>
</tr>
<tr>
<td>1050</td>
<td>N – H bending deformation</td>
</tr>
<tr>
<td>726 and 1326</td>
<td>C – H bending deformation</td>
</tr>
</tbody>
</table>

3.7.1 Polyaniline

Figure 3.2.0 shows the FTIR spectra for pure Polyaniline. The characteristic absorption peaks are found to be at 2922 cm⁻¹ is due to the C-H stretching, 1566 cm⁻¹ corresponds to C = C stretching vibration of quinoid ring, 1548 cm⁻¹ for C=N bond stretching, 1494 cm⁻¹ corresponds to stretching vibration of benzenoid ring, 1406 cm⁻¹ is the characteristic vibration mode of C - H bonding of aromatic nuclei, 1302 cm⁻¹
assigned to the stretching of C-N bonds of aromatic amines, 1140 cm\(^{-1}\) an strong band which considered to be the measure of degree of electron delocalization 796 cm\(^{-1}\) corresponding to the N-H out of plane bending in rocking mode. 734 cm\(^{-1}\) and 684 cm\(^{-1}\) are due to the out of plan blending of C-H bond in aromatic ring, respectively.

### 3.7.2 Polyaniline / ZnFe\(_2\)O\(_4\) composites

Figure 3.2.1(a-f) shows the FTIR spectra of polyaniline/ZnFe\(_2\)O\(_4\) composites at different percentage (10, 20, 30, 40 and 50 wt. %). The absorption peaks are found to be at 3441 cm\(^{-1}\) correspond for N-H stretching vibration, 1581 cm\(^{-1}\) corresponds to C = C stretching vibration of quinoid ring, 1481 cm\(^{-1}\) corresponds to stretching vibration of benzenoid ring, 1300 cm\(^{-1}\) is for the stretching of C-N bonds of aromatic amines, 1240 cm\(^{-1}\) for the C-N stretching of benzenoid ring, 1140 to 1145 cm\(^{-1}\) corresponds to C-H in plane of aromatic rings found to be an strong band which considered to be the measure of degree of electron delocalization, and other bands like 802 cm\(^{-1}\), 738 cm\(^{-1}\), and 686 cm\(^{-1}\) are due to the out of plan blending of C-H bond in aromatic ring, respectively. The samples show characteristic absorptions bands of Zinc ferrite, the absorptions bands at 507 cm\(^{-1}\) is due to the intrinsic vibration of Zn\(^{2+}\) which is present in tetrahedral positions and around 415 cm\(^{-1}\) which corresponds to the vibration of octahedral group of Fe\(^{3+}\)O\(^{-2}\), which confirm the formation of the polyaniline / Zinc ferrite composites [15].
3.7.3 Polyaniline / NiZnO₃ composites

Figure 3.2.2 (a-f) shows that the FTIR spectra of PANI/NiZnO₃ composites of 10 wt %. The characteristic absorption peaks is found to be at 3433 cm⁻¹, 1556 cm⁻¹, 1487 cm⁻¹, 1302 cm⁻¹, 1236 cm⁻¹, 1140 cm⁻¹, 800 cm⁻¹, 738 cm⁻¹, 584 cm⁻¹, 509 cm⁻¹ & 422 cm⁻¹ respectively. The peaks at 3433 cm⁻¹ is corresponds to N-H stretching vibration 1556 cm⁻¹ is for stretching vibration of C=C bonds of quiniod rings,
Characterization........

1487 cm\(^{-1}\) is corresponds to C=C stretching vibration of benzoniod ring, 1302 cm\(^{-1}\) is due to the stretching of C-N bonds of aromatic amines 1236 cm\(^{-1}\) corresponds to C-N stretching of benzoniod ring 1140 cm\(^{-1}\) corresponds to C-H in plane of aromatic rings is found to be a strong band which is considered to be the measure of degree of electron delocalization 800 cm\(^{-1}\), 738 cm\(^{-1}\) & 584 cm\(^{-1}\) are due to the out of plane bending of C-H bond in aromatic ring. The composites also show the absorption bands at 509 cm\(^{-1}\) is due to the intrinsic vibration of Ni\(^{2+}\) which is present in tetrahedral position and around 422 cm\(^{-1}\) is vibration of octahedral group of Zinc which conform the formation of PANI/NiZnO\(_3\) composites.

Figure-3.2.2 (a-f) FTIR spectra of PANI/NiZnO\(_3\) composites of different weight percentage
3.7.4 Polyaniline / CuO composites

Figure 3.2.3(a-f) shows the FTIR spectra of PANI and PANI/CuO composites of different weight percentage (10, 20, 30, 40 and 50 wt%). The FTIR spectra (figure-a) show the pure PANI. The characteristic important peaks are found at 1566 cm\(^{-1}\) corresponds to C = C stretching vibration of quinoid ring, 1548 cm\(^{-1}\) for C=N bond stretching, 1494 cm\(^{-1}\) corresponds to stretching vibration of benzenoid ring, 1406 cm\(^{-1}\) is the characteristic vibration mode of C - H bonding of aromatic nuclei, 1302 cm\(^{-1}\) assigned to the stretching of C-N bonds of aromatic amines, 1140 cm\(^{-1}\) an strong band which considered to be the measure of degree of electron delocalization, 796 cm\(^{-1}\) corresponding to the N-H out of plane bending in rocking mode respectively.

The important peaks of PANI/CuO composites (figure- b) of different weight percentage (10, 20, 30, 40 & 50 wt%) are found to be in between 1572-1552 cm\(^{-1}\) is due to the C = C stretching vibration of quinoid ring, 1460 -1481 cm\(^{-1}\) corresponds to stretching vibration of benzenoid ring, 1246-1304 cm\(^{-1}\) is assigned for stretching of C-N bonds of aromatic amines, 1118-1143 cm\(^{-1}\) is due to a strong band which considered to be the measure of degree of electron delocalization and 501-599 cm\(^{-1}\) is due to the stretching vibration of M-O in composites.
3.8 Introduction to Scanning Electron Microscopy (SEM)

The micro structural studies on material provide information about:

1. Grain size of specimen
2. Amount of interfacial area per unit volume
3. Dimensions of constituent phases
4. Amount of Distribution of phase
5. Dislocation density
Some of the techniques employed for microstructure analysis are scanning electron microscopy, optical microscopy, field ion microscopy, field emission microscopy, X-ray microscopy and electron microprobe analysis. Of these, SEM is an extremely versatile technique for providing structural information over a wide range of magnifications, with an added advantage of 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 sintered in the form of pellets (to measure grain size) are investigated using Phillips XL30 ESEM scanning electronic microscope (SEM). The samples in the form of pellets are mounted on an aluminum platform, where conducting gold is sputtered on the sample to avoid charging at the sample surfaces. They were examined under SEM and selected areas were photographed.

3.10 Results and Discussions

SEM technique is applied primarily for the visualization of the sample surfaces, especially for the study of surface morphology, domains, pin hole defects and patterns. The images are formed by the interaction of electrons with samples in vacuum. The scanning electron micrographs of the samples in a system of polyaniline and its composites are presented in figures 3.3.0 to 3.3.3.
3.10.1 Polyaniline

SEM micrograph of conducting polyaniline synthesized by chemical oxidative method is shown in figure 3.3.0. It can be clearly seen that the micrograph of polyaniline is branched and homogeneous. Since Hydrochloric acid is used as protonic acid in the preparation of polyaniline, the presence of microcrystalline structure can be seen. Conducting polymers are very sensitive to the temperature, due to the interaction between electron and the sample, considerable amount of heat is generated which causes the development of mall crackening in the sample during SEM recording. A granular morphology of the microcrystalline structures was measured and found to be about 312 nm in diameter for polyaniline which is consistent with other reports [16]. The contrast in the image is a result of differences in scattering from different areas of the surface as a result of geometrical differences.

![SEM image of pure PANI](image)

**Figure-3.3.0 SEM image of pure PANI**

3.10.2 Polyaniline / ZnFe$_2$O$_4$ composites

Figure3.3.1.(b) shows the Scanning Electron Micrograph of 10 wt. % of PANI/ZnFe$_2$O$_4$ composite where highly agglomerated cube like structure are seen. The crystallinity of the ZnFe$_2$O$_4$ decreases with the addition of PANI in it. It is found
Characterization......
that zinc ferrite particles were homogeneously distributed throughout polyaniline matrix. The average grain size is found to be 600 nm.

PANI/ZnFe$_2$O$_4$ composite of 20 wt. % is shown in figure 3.3.1(c). The composite is highly clustered, spherical in shape and have interlinked to each other. The decrease in the inter-granular distance between the grains helps in charge transfer mechanism. The average grain size is found to be 1.5µm.

Figure3.3.1 (d) shows the 30 wt. % of PANI/ZnFe$_2$O$_4$ composite. The images shows a highly crystalline granular flake like networking structure arranged in soccer shape and is well interlinked between each other. The average grain size is found to be 230 nm to 340 nm.

Figure3.3.1 (e) show that the 40 wt. % of PANI/ZnFe$_2$O$_4$ composite which is highly agglomerated and spherical in shape of about 0.5µm in granular size.

PANI/ZnFe$_2$O$_4$ composite of 50 wt. % is shown in figure 3.3.1(f). It is observed that the ferrites particles are not well bonded with the polyaniline due to increasing in the percolation limit to the ratio of filler concentration of the matrix.

From the figure3.3.1 (a - f), it is found that, there were lot of change in the morphology of various wt% of ZnFe$_2$O$_4$ in PANI matrix’s. The changes in the morphology were favorable for the transport mechanism in PANI / ZnFe$_2$O$_4$composites [17].
3.10.3 Polyaniline / NiZnO$_3$ composites

Figure-3.3.2(b) shows that scanning electron micrograph of 10wt % of PANI/NiZnO$_3$ composites were highly agglomerated, irregular in shape and non porous in nature. The crystalline of PANI increase with addition of NiZnO$_3$. It is clearly observed in the micrograph cavity is formed; this may be due to the Ni$^{2+}$
Characterization

which gain the electron from polymer chain. The average grain size is found to be
2 μm.

Figure-3.3.2(c) shows that the SEM image of 20wt % of PANI/NiZnO$_3$
composites. The grains are highly clustered, porous and spherical in shape. The
average grain size is found to be 1.3μm.

Figure-3.3.2 (d) Shows that the SEM image of 30 wt % of PANI/NiZnO$_3$
composites. The composites are formed a flake like structure with an average grain
size of about 700 to 830nm.

Figure-3.3.2 (e) shows that the SEM image of 40wt % of PANI/NiZnO$_3$
composites. The grins are clustered, spherical in shape. The composites matrix was
found to be porous and average grain size is found to be about 1.7μm.

Figure-3.3.2 (f) shows that the SEM image of 50wt % of PANI/NiZnO$_3$
composites. The particles are arranged in flake like, as well as some are spherical in
shape. It is observed that the two flakes are connected in between by granular shaped
particles. The average size is found to be 1.3μm.
Figure-3.3.2 (a-f) SEM images of PANI and PANI/NiZnO₃ composites of different weight percentage (10, 20, 30, 40 and 50 wt%)
3.10.4 Polyaniline / CuO composites

The SEM image of 10 wt % of PANI/CuO composites shown in figure 3.3.3 (b) shows the grains are highly agglomerated, irregular in shape but they are well interconnected to each other. The average grain size was found to be 0.22μm.

Figure-3.3.3 (c) shows the SEM image of 20 wt % of PANI/CuO composites. The grains are irregular in structure, some of them are elongate and some are spherical in shape. The particles are individual and are separated with each other. The average grain size was found to be 0.37μm.

The SEM image of 30 wt % of PANI/CuO composites is shown in figure 3.3.3 (d). It is observed from the image that all grains are irregular in structure arranged one above the others. The average grain size was found to be 0.43μm.

Figure-3.3.3 (e) shows the SEM image of 40 wt % of PANI/CuO composites prepared at room temperature. It is seen from the image the grains are clustered, have low porosity. The average grain size was found to be 0.47μm.

Figure-3.3.3 (f) shows the SEM image of 50 wt % of PANI/CuO composites prepared at room temperature. It is found that from the image the grains are high agglomerated, have porosity and good interconnectivity between the particles. The average grain size was found to be 0.53μm.

By comparing the figure (a-f), it can be conclude that the gradual increase in granular size and change in morphology helps the transportation of charge particles through the carbon back-bone of polymer chains [18].
Figure-3.3.3 (a-f) SEM images of PANI and PANI/CuO composites of different weight percentage (10, 20, 30, 40 and 50 wt %)
**Characterization**

**REFERENCE**


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