Chapter - 6
6.1 OBJECTIVE

Goal of this work is subdivided into a small number of objectives. These objectives are specified as follows:

1. Growth of CNTs by two different methods
   (i) Vapor Phase Growth (Acetylene) Method
   (ii) Thermal Chemical Vapor Deposition (Xylene) method.
2. Characterization and comparison of synthesized CNTs by FE-SEM, TEM, XRD, FTIR, VSM and R-T analysis.
3. To see the effect of magnetic field on the resistance (MR studies) of CNTs.
4. Comparison of three Nanomaterials which are considered for experimental study in this research work.

6.2 EXPERIMENTAL METHODS

6.2.1 Growth of Carbon Nanotubes

Carbon nanotubes are grown by two different methods, one by using Xylene (Thermal Chemical Vapor Deposition method) as a carbon source while other using Acetylene (Vapor Phase Growth Method) as a
carbon source. For both the methods iron as catalyst and ferrocene as iron precursor are used.

Fig: 6.1. Line diagram of the atomizer used to grow carbon nanotubes

6.2.2 Thermal CVD Method

The apparatus mainly consisted of a simple atomizer that had two inlets: one for the carrier gas Ar/H₂ and the other for the liquid reactant. Approximately the ferrocene with 6.5 mol% was dissolved to get a feed solution with \( \sim 0.75 \) At% Fe/C ratio, in xylene. It was fed into the atomizer continuously through the dripper, which had a flow control wheel, into a tubular quartz reactor (diameter 30mm, length 60cms) (Fig:6.1 & Plate:6.1). The reactants were held in an injector and gave out through a pine needle into the dripper. Ar/H₂ gas flow was optimized in such a method that the liquid was able to reach the centre of the furnace. H₂ is required for the reduction of xylene. To produce catalyst Fe particles, which can generate nanotube growth, ferrocene, whose catalyst main particles (sublimation temperature is 140°C) has been shown to be a high-quality precursor. Xylene was selected because the hydrocarbon source boils (boiling point, \( \sim 140°C \)) under the decomposition temperature of ferrocene (\( \sim 190°C \)).

The liquid feed was passed through a medical nebulizer, which was used as an atomizer, attached to the quartz tube (preheated to the desired temperature), into the furnace. The atomizer was inserted into the tube and the junction was properly insulated to air by a Teflon tape in order to prevent oxidation of iron. Contact with oxygen can also lead to a minor flame. The tube was heated using a cylindrical furnace with a
precise temperature control. The liquid leaving the tube quickly volatilized at the temperature and sweep up into the zone of reaction of the furnace by a stream of argon with 5% hydrogen. The furnace temperature (750–900°C), feed rate (0.5-2mL/min) and sweep gas flow pressure (1-2 kg/cm²) are used to examine the growth conditions meant for high purity associated MWCNTs, keeping the ferrocene/xylene ratio (6.5mol %) constant. The grown parameters are optimized to obtain the final sample. The final sample is at following conditions; 825°C temperature, 1.5mL/min feed rate, 1.5kg/cm² Ar/H₂ gas pressure. When the reaction was complete, the furnace is allowed to cool up to room temperature in stream of Air or Hydrogen. During growth, nanotubes begin to form in the vapor phase, and then deposit on the quartz tube walls.

The sample formed inside the tube was immediately annealed to remove left out iron in the form of its oxide at the experimental temperature. After the room temperatures were attained, the sample was found to form a cylinder along the tube axis and it be supposed to carefully scratched out.

**6.2.3 Vapor Phase Growth Method**

Apparatus used in this method is same as we have used in Thermal CVD method but the difference is of carbon source, now we have used Acetylene as a carbon source in place of Xylene. Ferrocene is used as
iron precursor and put at the inlet of the tube. In this method we have also optimized the growth condition by changing growth parameters; reaction temperature and Acetylene flow rate. The temperature is changed from 800-900°C and acetylene pressure to 0.2-0.5Kg/cm². To obtain the inert atmosphere in the tube to prevent oxidization of ferrocene and fire, flow the Ar gas before the flow of acetylene. In the reaction zone both ferrocene and acetylene decomposes to form CNTs. Final conditions for carbon nanotube growth is 900°C temperature and 0.2 Kg/cm² acetylene partial pressure. As growth conditions matched then get black carbon nanotube powder in the reaction zone and that is carefully peeled off for further characterization.

6.3 PURIFICATION OF CNTs

As formed carbon nanotubes have impurities of catalyst particles and amorphous carbon. The raw particles, amorphous carbon, and multi-shell carbon material were first heated in Ar/H₂ atmosphere to remove them. After room temperature was attained, the powder form of the tubes was collected. For purification purposes it was dissolved in 6M nitric acid for 12hrs, and after washing it with distilled water, black powder putted in to the oven at 150°C for drying. After drying the sample heated in the nitrogen environment at 300°C for 4 hours. The final product is now ready for characterization.
6.4 RESULTS AND DISCUSSIONS

6.4.1. FESEM and EDAX Analysis

In this research work, synthesis of Carbon nanotubes (CNTs) is done by Vapor phase growth and Thermal chemical vapor deposition (CVD) methods. The FE-SEM (FEI-QUANTA 200 ESEM FEG) micrograph images the surface morphology of the samples prepared by two methods. They are presented in Fig. 6.2 and 6.3. CNTs grown by Vapor phase growth method at 900°C and by Thermal chemical vapor deposition (CVD) method at 825°C are shown in the Fig. 6.2(a) and (b). Fig. 6.2(a) clearly indicates highly aligned, bundled CNTs obtained in Vapor phase growth method but CNTs grown by Thermal CVD method are not well aligned as shown in Fig. 6.2(b). The micrographs taken at lower magnification shown in the Fig.6.3(a), 6.3(c), and Fig.6.3(b) 6.3(d) are prepared by Vapor phase growth and Thermal CVD method respectively. Fig.6.3 (a, c) shows high yield of CNTs and negligible proportion of amorphous carbon but the sample in Fig.6.3 (b, d) grown by Thermal CVD method yield was not high and also have high proportion of amorphous carbon. For purification purpose we flow nitrogen over the CNTs synthesized by vapour Phase growth method. Fig.6.4 (b) shows that Nitrogen flow over the sample has remarkable effect on the removal of amorphous carbon and effect on residual catalyst particle can see in TEM micrograph.
The chemical compositions of the synthesized samples are clearly indicated by the Energy Dispersive Analysis of X-ray (EDAX) presents in Fig.6.5. It is to be noted that the percentage of catalyst Fe in the sample prepared by Vapor phase growth method is less than as prepared by Thermal CVD method, indicating high purity of the CNTs. The focused EDAX on a single tube for each sample clearly indicates the highest Wt% and At% of C in the sample prepared by Vapor phase growth method at 900°C with Acetylene and 825°C with xylene. Best optimized temperatures are 900°C and 825°C for vapor phase growth and thermal CVD methods respectively, showing the highest yield of CNTs. Average length of CNTs is around 75μm for acetylene method and 60μm for xylene method and diameters range of 30-55nm. Also the outer diameter of CNTs calculated ranges from 35 to 85 nm. The FE-SEM and EDAX investigation revealed that the CNTs grown by the Vapor phase growth method are well aligned, high yield and highly purified as compared to CNTs grown by Thermal CVD method. Therefore, acetylene is better hydrocarbon source as compared to xylene.
Fig: 6.2 FE-SEM images of (a) CNTs prepared by vapor phase growth method (b) CNTs prepared by Thermal CVD method.
The average length of the nanotubes was around 75 µm with Figure 6.3 FE-SEM images of (a) & (c) high yield and aligned CNTs prepared by Vapor phase growth method (b) & (d) CNTs prepared by Thermal CVD method
Fig: 6.4 FE-SEM images of (a) CNTs as prepared (b) CNTs after flow of Nitrogen

![Fig: 6.4 FE-SEM images of (a) CNTs as prepared (b) CNTs after flow of Nitrogen](image1)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CK</td>
<td>95.89</td>
<td>99.09</td>
</tr>
<tr>
<td>FeK</td>
<td>04.11</td>
<td>00.91</td>
</tr>
<tr>
<td>Matrix</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig: 6.5(a) EDAX analysis of CNTs prepared by Vapor phase growth method

![Fig: 6.5(a) EDAX analysis of CNTs prepared by Vapor phase growth method](image2)
6.4.2 Analysis using XRD and EDAX

The XRD technique was used to characterize the crystalline structure of the samples. XRD patterns of the CNTs prepared by vapour phase growth and Thermal CVD are presented in Fig. 6.6 (a) and (b) respectively. It is observed that the characteristic diffraction peak (002) of
MWCNTs located at $2\theta = 26.0^\circ$ in both samples consistent with the reports [181]. Comparing the relative intensities of C (002) and other impurity peaks, we can clearly see that the most prominent peak is C (002) that confirms the sample prepared is carbon nanotubes. The CNT sample prepared by Thermal CVD method has some additional peak due to presence of amorphous carbon and metal catalyst but sample prepared by Vapor phase growth method is relatively pure. It is also seen the effect of nitrogen flow over the sample prepared by Acetylene method. Fig. 6.7(a) and (b) clearly shows the effect of nitrogen flow, some impurity peaks in XRD pattern have been suppressed after the nitrogen flow. This confirms that CNTs have been purified due to flow of nitrogen.
Fig: 6.7 XRD analysis of (a) CNTs before nitrogen flow (b) CNTs after nitrogen flow

6.4.3 Fourier Transform Infrared (FTIR) Analysis

To characterize the functional elements immersed by carbon nanotubes FTIR is used. Fig. 6.8 shows (a) Tubes grown by acetylene method, and (b) Tubes grown by xylene method in the FTIR spectra range of 400–4000 cm$^{-1}$. Fig 6.8(a) Shows dominant peaks at 463.62, 602.23, 1615.37, 3414.10 cm$^{-1}$ which also corresponds to C–H, –CH=CH–(cis), CNT, C–H$_x$ respectively and (b) Shows dominant peaks at 476.08, 613.84, 1615.37, 3414.10 which corresponds to C–H, –CH=CH– (cis), CNT, C–H$_x$ respectively [182, 183]. The weak signals at 400-700 cm$^{-1}$ is consistent with stretching vibrations of C-H and –CH=CH–(cis). The strong signals at
1615.37 attributed C=C stretching vibrations of CNTs. The peak in 3400-3500 range ascribed to the partial conversion from sp² to sp³-hybridized carbon as an effect of the interaction between carbon and hydrogen atoms on the CNTs walls [184].

![Graph of FTIR analysis of (a) CNTs prepared by Vapor phase growth method (b) CNTs prepared by Thermal CVD method.](image)

*Fig: 6.8 FTIR analysis of (a) CNTs prepared by Vapor phase growth method (b) CNTs prepared by Thermal CVD method*

### 6.4.4 Vibrating Sample Magnetometer (VSM) Analysis

Room temperature Magnetization measurements of pure carbon nanotube bundles were carried out by vibrating sample magnetometer (VSM). Fig.6.9 had shown the M–H loop of pure carbon nanotubes grown from acetylene–ferrocene and xylene-ferrocene mixtures. M–H loops obtained with a saturation magnetization of 9.2emu/g and 10.77emu/g
for acetyleneferrocene and xyleneferrocene mixtures respectively. Since the diameter of the average catalyst particle is small 2–13nm [185], a reduction in the value of magnetization saturation is expected compared to the bulk value 222 emu/g. It is significant that the iron nanoparticles of the carbon nanotubes are satisfactorily big to make them ferromagnetic. Therefore, it is proposed that the ferromagnetism of the iron nanoparticles is responsible for the alignment of the nanotubes, if prepared by the pyrolysis of ferroceneactylene mixtures [186].

![M-H curve of CNTs prepared by Vapor phase growth and Thermal CVD method](image)

*Fig: 6.9 M-H curve of CNTs prepared by Vapor phase growth and Thermal CVD method*
6.4.5 Resistance Vs Température (R-T) Analyses

R-T measurement of the pure carbon nanotubes pellet were performed by Four probe method in the liquid nitrogen (N\textsubscript{2}) environment in the temperature range 77K to 303K. The typical value of current was 1mA and magnetic field applied was 2.5K Gauss. For R-T measurement we have made a pellet of pure carbon nanotubes. According to the hexagons arrangement, CNTs are either semiconducting or metallic, based on their chirality and diameter [186]. The ‘armchair’ nanotubes are always metallic; however, the chiral and zigzag can be either semiconducting or metallic. Hence, based on the CNT unit cells alignments, each CNT has characteristic band gap and energy barriers for electrons to overcome. Therefore, the overall bulk R-T is measured for behavior of pure CNTs is shown in the Fig.6.10. At zero applied field the resistance is decreases uniformly from liquid nitrogen temperature to normal (room) temperature. It is clearly observed from the graph that overall behavior of CNTs is Semiconducting. When applied a low magnetic field of 2.5K Gauss to the sample there is no effect on resistance but and behavior remains semiconducting.
In order to calculate the band gap ($E_g$) of carbon nanotubes pellet, first calculated the resistivity ($\rho$) of the sample. Dimensions of the pellet are 10 x 8 x 1 mm$^3$ and the distance between two voltage probes was around 2mm. Then calculated the conductivity ($\rho$) from resistivity and it is known that for a semiconductor, slope of the graph between log ($\rho$) and 1000/T gives the band gap. Fig. 6.11 shows the graph between log ($\rho$) and 1000/T and the calculated value of slope is 825.34. By equating slope value to $E_g$/2k, calculated the band gap having value $E_g = 0.141$eV. The calculated band gap has well matched with the reported band gap $E_g$ ranges from 0.12 to 0.17eV [186].
6.5 Comparison of Nanoceramics and Carbon Nanotubes

Synthesis and characterization of the three nanomaterials taken for study viz;

- Pure BiFeO$_3$, a nanoceramic material,
- $x$CrFe$_2$O$_4$-(1-$x$) BiFeO$_3$ which is a nanoceramic composite material, and
- Carbon Nanotubes (CNTs) which is a single element Nanomaterial.

All of them have applications as memory devices, dielectric conductors and in electronic circuits. A comparative statement has been prepared to show all three nanomaterials studied and their co-related
properties in the table 6.1. From this table it is seen that all three nanomaterials have lot of similarities in structure, processing, coupling, properties etc which are studied experimentally. All of them have same applications also.

**Table 6.1 Comparison of Nanoceramics and Carbon Nanotubes**

<table>
<thead>
<tr>
<th>Material Parameter</th>
<th>BiFeO$_3$ Nanoceramic</th>
<th>$x$CrFeO$_3$ – (1-$x$) BiFe$_2$O$_3$ Nanoceramic composite</th>
<th>Carbon Nanotubes (single element)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (using basic materials the nonmaterial has been prepared)</td>
<td>Fe(NO$_3$)$_3$.9H$_2$O (Ferric nitrate), Bi(NO$_3$)$_3$.5H$_2$O (bismuth nitrate), citric acid and ethylene glycol</td>
<td>Fe(NO$_3$)$_3$.9H$_2$O (Ferric nitrate), Bi(NO$_3$)$_3$.5H$_2$O (bismuth nitrate), Cr(NO$_3$)$_3$.9H$_2$O (chromium nitrate), ethylene glycol &amp; citric acid</td>
<td>For Vapor phase method: Xylene + Ferrocene with H$_2$ gas pressure</td>
</tr>
<tr>
<td>Structure</td>
<td>Rhombohedral perovskite structure chemical formula ABO$_3$ belong to R3c class, with Rhombohedral lattice parameters $a_R$ =5.63 Å and $a_R$=59.35°.</td>
<td>Hexagonal arrangement semiconductor or metallic 2 to 30 concentric graphitic layers</td>
<td>For CVD method: Acetylene + Ferrocene with H$_2$ gas pressure</td>
</tr>
<tr>
<td>Process and Temperature range</td>
<td>Sol-gel 650 - 950°C</td>
<td>Sol-gel 400 - 700°C</td>
<td>Vapor Phase Growth Method: 750-900°C</td>
</tr>
<tr>
<td>Phase transition temperature</td>
<td>814°C Second order Transition</td>
<td>900°C for Vapor Phase Growth Method and 825°C for CVD method</td>
<td>Thermal CVD: 825°C, H$_2$ gas pressure = 1.5kg/cm$^2$.</td>
</tr>
<tr>
<td>Coupling</td>
<td>Magneto-electric coupling occur directly between the two order parameters, or indirectly via strain</td>
<td>Electromechanical coupling occur directly via strain</td>
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<td></td>
</tr>
<tr>
<td>Properties</td>
<td>These are single phase multi-ferroic material, have 2 or 3 ‘ferroic’ properties like ferro-electricity, ferro-elasticity and ferromagnetism. Structural perfection, good strength, low density, good thermal, electrical, optical and excellent electronic properties with greater quality.</td>
<td>Structural perfection, high strength and stiffness, low density, stronger and superior, High thermal, electrical, optical and electronic properties with greater quality.</td>
<td></td>
</tr>
<tr>
<td>Size</td>
<td>Particle size ~100 nm Sample size 10 x 8 x 1 mm³</td>
<td>Particle size: Length = ~75μm Dia = 30-55nm, for Acetylene method. Length = 60μm, Dia = 35 - 85 nm for Xylene method.</td>
<td></td>
</tr>
<tr>
<td>Band gap</td>
<td>$E_g = 2.8 \text{ eV}$ Standard value $E_g = 0.18 - 2.8 \text{ eV}$</td>
<td>$E_g = 0.141\text{ eV}$ Standard value 0.12 to 0.17eV.</td>
<td></td>
</tr>
<tr>
<td>Applications</td>
<td>Sensors, transducers, switching devices and data storage, magneto-electric devices, microwave absorption materials, Consumers electronic products, Actuators, multiple-state memory devices magnetic field sensors, electric-field-controlled ferromagnetic resonance devices, and transducers with magnetically modulated piezoelectricity.</td>
<td>Sensors, transducers, switching devices and data storage, magneto-electric devices. May lead all future carbon electronics. Model nano-devices, field effect transistors, metallic wires, electro-mechanical displays and sensors,</td>
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</table>
6.6 SUMMARY

In the summary, Growth of pure carbon Nanotubes have been carried out by vapor phase growth (acetylene) and thermal CVD (xylene) methods. After optimizing the growth parameters for both the methods, the MWNTs have been obtained. Best optimized temperatures are 900°C and 825°C for vapor phase growth and thermal CVD methods respectively, showing the highest yield of CNTs. Average length of CNTs is around 75μm for acetylene method and 60μm for xylene method and diameter range of 30-55nm in both methods. Various characterization studies; FE-SEM, TEM, XRD, VSM and FTIR analysis revealed that Acetylene is better hydrocarbon source for carbon nanotube growth as compared to xylene. R-T analysis of carbon Nanotubes pellet is done by four-probe method shows semiconducting behavior and band-gap calculated is 0.141eV.

In this research work, for synthesis and characterization purpose, three nanomaterials have been studied. A comparative statement has been prepared to show all three nanomaterials and their co-related properties in the table 6.1. From this table all three nanomaterials have lot of similarities in structure, processing, coupling, and properties etc which are studied experimentally. All of them have same applications also.