Chapter - 2
2.1 FERROELECTRIC AND MAGNETIC MATERIALS

Magnetic and Ferroelectric materials are the customary subjects of research area and have been leading the most significant technological advances in these days. These materials have several applications in modern technology. For example, the consumers’ electronic products are generating huge data and are stored as regions of opposite magnetic polarization in ferro-magnets. The sensors industry depends mostly on ferroelectrics materials. Many ferroelectric materials are also ferroelastic – i.e., A change in their electric polarization is accompanied by a change in shape. Consequently, they are used to convert sound waves into electrical signals in sonar detectors. In actuators they convert electrical impulses into motion.

Ferroelectricity and Magnetism are concerned with off centre structural distortions of the material and local twists. These two apparently unrelated phenomena may coexist in certain odd materials. These materials are known as multi-ferroics [4-14]. The word “electromagnetism” derives from the fact that the magnetic and electric fields are interdependent. A changing magnetic field produces an electric field, whereas an electric current, produces a magnetic field (the Biot-
Savart law). Electromagnets are coiled wire or loops, which are bulky and difficult to fabricate. It is possible to develop an electromagnet made from a nano material in another form. The magneto-electric effect in a solid—i.e., the induction of magnetization by means of an electric field and the induction of an electric polarization ($P$) by magnetic field— are observed by Pierre Curie [15]. He studied the analogy of the electromagnetic phenomena in solids and in vacuum. This analogy is significant from the standpoint of applications. The efficient control of magnetism by an electric field in a solid could help the technology of spinelectronics (spintronics) used for magnetic random access memory and magnetic storage.

2.2 FERROELECTRICITY

Ferroelectrics are the materials that have two or more equilibrium orientations of impulsive polarization vector in the absence of an external electric field. The spontaneous polarization vector may be switched between these two orientations by an electric field [16]. Two main types of a ferroelectric behavior can be distinguished – displacive and order-disorder. The displacive type behavior is due to an ion getting displaced from the equilibrium position. Hence it acquires a permanent dipole moment. At high temperatures ($T > T_C$, where $T_C$ is a ferroelectric Curie temperature), the thermal energy is sufficient to allow the ions to move randomly from one position to another, so there is no fixed asymmetry. When the temperature is below $T_C$, the ion is frozen in an off-center
position. This gives a net dipole moment. In an order-disorder ferroelectric, a dipole exists in each unit cell. But at high temperatures, they are pointing in random directions. When the temperature is lowered, the dipoles get arranged in order and become aligned in the same direction within a single domain.

Ferroelectric polarization hysteresis loop shown in (Fig.2.1) is the characteristic of ferroelectric material, which arises due to the presence of ferroelectric domains in the crystal. Application of an external DC electric field, $E > E_C$ (where $E_C$-coercive field) to a polydomain ferroelectric crystal, causes the polarization. The vectors $P$, having different orientations in different domains, to align themselves parallel to the field direction via the domain wall movement. The minimum value of the DC field, required to move the domain walls, is a measure of the coercive field. The initial value of the vector $P_s$ in a polydomain crystal increases with increasing DC field to a maximum value which is a characteristic of the material. Reversing the electric field reintroduces movement of domain walls. This results in the vector $P_s$ in different regions to be reversed. At zero current fields, the crystal will have a remnant polarization, which is smaller than the spontaneous polarization. At fully reversed field, the final $P_s$ will have the same magnitude as the original $P_s$ but with opposite sign. The hysteresis loop is a function of the work required to displace the domain walls, which is closely related to the
defect distribution in the crystal and to the energy barrier separating the different orientations.

Fig: 2.1 Hysteresis loop showing polarization switching in Ferroelectric materials.

According to their symmetry, crystals can be divided into the 32 point groups with 11 of them being centro-symmetric (non-polar) and 21 lacking an inversion center (polar). Lack of inversion center is a prerequisite for the piezoelectric behavior of the crystal. The crystal lacking a centre of symmetry will have a net 6 displacement of the negative and positive ions with respect to each other resulting in an electric dipole. For the centro-symmetric crystals, the centers of the two opposite charges will always coincide, so that there is no electric dipole generated. Out of the twenty piezoelectric classes, only ten, possessing a unique polar axis which can be spontaneously polarized, belong to ferroelectrics. Among all the ferroelectric materials, which are studied the perovskite ferroelectrics
are the most extensively and widely used. A perfect perovskite structure has a general formula of ABO$_3$, where A represents a divalent or trivalent cation, and B is a tetravalent or trivalent cation. The origin of ferroelectricity in this class of materials can be explained using the well-known example of BaTiO$_3$ (barium titanate). BaTiO$_3$ is a ferroelectric material with a perovskite structure as shown in Fig. 2.2. It is the first discovered piezoelectric ceramic [17].

![Perovskite structure](image)

**Fig: 2.2 Perovskite structure.**

BaTiO$_3$ has a cubic structure above Curie temperature Tc, 120 °C. Cubic BaTiO$_3$ is nonferroelectric because, the centers of negative and positive charges overlap as the ions are symmetrically prearranged in the unit cell. It has tetragonal structure below $T_c$, in which the O$^{2-}$ ions in the BaTiO$_3$ crystal are shifted in the negative C-direction, while the Ti$^{4+}$ ions are shifted in the positive C-direction. It results in an electric dipole along the C-axis. Therefore BaTiO$_3$ is ferroelectric in tetragonal structure. The behavior of the spontaneous polarization of ferroelectrics can be explained by thermodynamic (Landau-Ginzburg-Devonshire) theory [16,
In the basic Landau-Ginzburg-Devonshire theory, one assumes that the free energy may be expanded in a power series of the order parameters of the system. For a ferroelectric, the macroscopic order parameter is polarization $P$:

$$F(P,T,E) = -EP + \alpha_0 + \frac{1}{2} \alpha_1 P^2 + \frac{1}{4} \alpha_2 P^4 + \frac{1}{6} \alpha_3 P^6 + \ldots$$ 

(2.1)

Where the coefficients $\alpha_n$ are temperature dependent. This series does not contain terms in odd powers of $P$ if the un-polarized crystal has a center of inversion symmetry. The value of $P$ in thermal equilibrium is given by the minimum value of $F$ as a function of $P$; differentiating the equation above with respect to $P$ gives:

$$\frac{\partial F}{\partial P} = 0 = -E + \alpha_1 P + \alpha_2 P^3 + \alpha_3 P^5 + \ldots$$ 

(2.2)

The coefficient $a_1$ takes the form $a_1 = \gamma (T - T_0)$, where $\gamma$ is a positive constant and $T_0$ may be equal to or lower than the phase transition temperature, $T_C$. The assumed form of $a_1$ is a necessary result of mean field theory and its validity is supported by the experimentally observed Curie-Weiss law. A small positive value of $a_1$ indicates that the lattice is “soft” and close to instability. A negative value of $a_1$ indicates that the un-polarized state is unstable.

When $a_2$ is positive, we can neglect the $a_3$ term. The polarization for zero fields can be found from Eq.2.3.

$$\gamma(T - T_0)P_z + \alpha_2 P_s^3 = 0$$ 

(2.3)
So that either $P_S = 0$ or $P_S^2 = \frac{\gamma}{\alpha_2} (T_0 - T)$

For, $T \geq T_0$, $P_S = 0$ since $\gamma$ and $\alpha_2$ are positive. Therefore, $T_0$ is the Curie temperature. For $T < T_0$, the minimum of the free energy in zero field is at

$$|P| = \sqrt{\frac{\gamma}{\alpha_2} (T_0 - T)}$$

(2.4)

Which is plotted in Fig.2.3(a). Changes in the free energy and polarization at the transition temperature are continuous and it is a second order transition. When $\alpha_2$ is negative, the transition is of first order. We must retain $\alpha_3$ and take a positive value to ensure that $F$ converges. The equilibrium condition for $E = 0$ in this case is:

$$\gamma(T-T_0)P_S + \alpha_2 P_S^3 + \alpha_3 P_S^5 + ... = 0$$

(2.5)

So that either $P_S = 0$ or

$$\gamma(T-T_0) + \alpha_2 P_S^2 + \alpha_3 P_S^4 + ... = 0.$$  

(2.6)

At the transition temperature $T_C$, the free energies of the paraelectric and ferroelectric phases are equal. The existence of meta-stable phases during the phase transition is characteristic of first order transitions. Correspondingly, a sudden jump in polarization occurs at $T_C$ as shown in Fig. 2.3 (b). In the present study an attempt is made for the synthesis and characterizations of BiFeO$_3$ and BiFeO$_3$ with CrFeO$_4$ for different percent compositions discussed in chapters 4 and 5 respectively.
As per definition, a singlephase multi-ferroic [5] material is one, which consists of 2 or all 3 of the ‘ferroic’ properties: i.e., ferro-electricity, ferro-elasticity and ferromagnetism. On the other hand, the current tendency is to eliminate the requirement of ferro-elasticity, but to include the possibility of ferrotoroidic order. Furthermore, the classification of a multi-ferroic is widening to include anti-ferroic order. The magneto-electric effect is defined as the induction of polarization by means of a magnetic field and induction of magnetization by an electric field. Magneto-electric coupling may exists, whatever be the nature of magnetic and electrical order parameters. For example this occurs in paramagnetic ferroelectrics [14]. Magneto-electric coupling may occur directly between the two order parameters, or indirectly via strain. The nontrivial spin-lattice coupling in these multi-ferroics has been manifested through various forms, like linear and bilinear magneto-electric effects [19, 20], polarization change through field-induced phase transition [21, 22],
magneto-dielectric effect [8, 10], and dielectric anomalies at magnetic transition temperatures [11, 12].

Magnetoelectric multi-ferroics have all the potential applications of both their parent ferroelectric and ferromagnetic materials [23]. Specific applications, that have been proposed for such materials include multiple-state memory elements, magnetic field sensors, electric-field-controlled ferromagnetic resonance devices, and transducers with magnetically modulated piezoelectricity. The ability to couple with either the magnetic or the electric polarization offers an extra degree of freedom in the design of conventional devices. It was initially proposed that both magnetization and polarization could independently encode information in a single multi-ferroic bit. Four-state memory has recently been demonstrated [24], but in practice, it is likely that the two order parameters are coupled [20, 9]. Coupling could permit data to be written electrically and read magnetically. This is attractive, since it would use the best aspects of magnetic data storage and FeRAM (ferroelectric random access memory). At the same time, the problems associated with reading FeRAM and generating the large local magnetic fields needed to write can be avoided.

In the early 1894, Curie [15] claimed that symmetry conditions enable the bodies containing asymmetric molecules to be polarized in a magnetic field and, magnetized in an electric field. The existence of
magneto-electric materials was first experimentally observed in an un-oriented Cr$_2$O$_3$ crystal by Astrov in 1960 [25]. Rado and Folen then revealed the anisotropic nature of the magneto-electric effect in oriented Cr$_2$O$_3$ crystals [26, 27]. Smolensky et al [28] experimentally proved the existence of magneto-electric effect in a solid solution of PbFe$_{2/3}$W$_{1/3}$O$_3$-Pb$_2$MgWO$_6$. Zhdanov et al. independently confirmed the existence of magneto-electric perovskite materials based on a study on the PbTiO$_3$-BiFeO$_3$ and BiFeO$_3$ [29-31] systems. Later, a magneto-electric effect was revealed in other structures and more and more systematic studies were undertaken [7, 34, 32].

BiFeO$_3$, with its magnetic and electrical properties has created interest as the material with many applications. It was expected to form a new type memory by the combination of ferromagnetic and ferroelectric properties. Tabares-Munoz et al [33], observed the ferroelectric/ferroelastic single domain using polarized light microscopy. After this observation, the controversy surrounding the ferroelectric nature in BiFeO$_3$ was solved. BiFeO$_3$ is reported to exhibit about a weak ferromagnetic ordering and eight structural transitions [34, 35]. The neutron diffraction studies are conducted at room temperature. This revealed that BiFeO$_3$ has compensated anti-ferromagnetic ordering ($T_N$ ~397°C) with a cycloidal spin arrangement, which is disproportionate with its lattice [36]. In BiFeO$_3$, the ferroelectric phase is stable up to
836°C. It is very difficult to observe ferroelectric loop at room temperature because of the low resistivity of the sample. The measurements are done at 80KV by Teague et al [37], to enhance the resistivity and observe a hysteresis loop. They obtained a loop on a single crystal, with a spontaneous polarization of 3.5 μC/cm^2 in the (100) direction.

The existence of Bi$_2$Fe$_4$O$_9$ as an additional impurity phase in spite of adopting the improvised method suggested by Sosnowska et al [37] and Achenbach et al [38] is represented by several investigations. Synthesis by microwave-hydrothermal technique is reported to give rise to pure binary oxide [39]. Forming a solid solution of BiFeO$_3$ with other ABO$_3$ type of perovskites helps to reduce the impurity and enhances the resistivity [40, 41]. This enables the study of physical properties of BiFeO$_3$ rich phases and extrapolation of the data to the pure compound.

In present work, an attempt is made to study the effect of sintering temperature on electrical and structural properties of BiFeO$_3$ ceramics, prepared using sol-gel technique. This is discussed in chapter-4 in detail.

2.4 CrFe$_2$O$_4$ - BiFeO$_3$ Perovskite Multiferroics

It is emphasized that the Multiferroics are a rare class of materials, since ferro-electricity and ferromagnetism make them an exclusive group. Presently, they are a hot research area in view of the many novel applications. Equilibrium contributions of the two phases like ferrite and
ferroelectric form magneto-electric composites. These materials are used in sensors, transducers, switching devices and data storage [42]. In addition to the potential application as magneto-electric devices, they are likely to find applications as microwave absorption materials also due to magneto-electric coupling [43]. Perovskite-type BiFeO$_3$ is one of the multi-ferroics with both ferroelectric ($T_c=1103 \text{K}$) and G-Type antiferromagnetic ($T_N=643 \text{ K}$) nature [44-47]. In BiFeO$_3$, Bi-O orbital hybridization (or covalence) due to Bi $6s^2$ lone pair is responsible for the ferroelectric instability, while Fe-O-Fe anti-symmetric Dzyaloshinskii-Moriya exchange gives rise to a complicated magnetic order [48]. The low resistivity of the BiFeO$_3$ ceramics is mainly caused by existence of Fe$^{2+}$ and oxygen deficiency [49]. The selection of ferrite and ferroelectric materials depends on factors like high magnetostriction coefficient, piezoelectric coefficient, high dielectric permeability and poling strength. CrFe$_2$O$_4$ is an IIB-type half-metal material. Its molecular magnetic moments are about 5.6$\mu_B$ which is higher than that of Fe$_3$O$_4$, 4.0$\mu_B$ [50].

From a theoretical study of cation distribution of CrFe$_2$O$_4$, it is observed that it has Fe$^{3+}$ at tetrahedral site, Fe$^{2+}$ and Cr$^{3+}$ at octahedral site [51]. Till now, scholars have synthesized nano-composites of ferrites (CuFe$_2$O$_4$, CoFe$_2$O$_4$ and ZnFe$_2$O$_4$) with PZT/BaTiO$_3$/BiFeO$_3$ both in bulk and thin films in order to enhance the multi-ferroic properties [52-54]. An important property is the coupling between electrical and magnetic
dipole. The coupling can be induced by magneto-electric effect. Understanding the coupling between the magnetic and dielectric properties of nano-composites is a hot area of research. The ultimate goal of controlling the magnetic/dielectric state using electrical/magnetic field requires that both these properties are coupled. The magneto-electric couplings of most of the materials are normally weak at room temperature. Hence, it is difficult to find a material with a large magneto-electric effect at room temperature. To find out the materials which have large magneto-electric effect at room temperature a lot of research is started now [55, 56].

Very few papers have been reported on CrFe$_2$O$_4$-BiFeO$_3$ spinel-perovskite nano-composite. Therefore in the present a systematic study is carried out on structural, dielectric, magnetic and magneto-electric properties of nano-composites $x$CrFe$_2$O$_4$-$(1-x)$ BiFeO$_3$ with $x = 0.00, 0.10, 0.20, 0.30$ and $0.40$ synthesized by solgel technique and discussed in chapter - 5 in detail.

2.5 CARBON NANOTUBES

As discussed in the introductory chapter-1, the Carbon Nanotubes (CNTs) are first invented by Iijima [2] in 1991. Later they have fascinated almost all the scientists and researchers because of their unique properties like mechanical properties i.e., structural perfection, high strength and stiffness, low density, small in size [57-59]. They are stronger and superior than, when compare with the performance of any
other materials like steel, tungsten carbide, alloys of carbon etc. They also possess high thermal, electrical, optical and tremendous electronic properties [60] with greater quality which any other materials cannot exhibit.

2.5.1 TYPES OF CARBON NANOTUBES

The atomic graphite structure looks like one-atom thick sheets of planar network of interrelated hexagonal rings of carbon atoms. In normal graphite, carbon sheets are located on top of one another, allowing them to easily slide. Therefore, graphene sheets are very soft, and greasy. They may be used as lubricant. When a graphene sheet is rolled into cylindrical shape and edges joined together, it forms CNT. Graphene sheets are placed in such a way that only the tangents of the graphitic planes come into contact with one another. Hence, their properties are more like that of a carbon molecule.

Nanotube consists of only one atom thick. One graphite tube known as a Single Walled Nanotube (SWNT) and a number of concentric tubes are known as Multiwall Nanotubes (MWNTs). Fig.2.4 (a, b & c) shows graphite sheet, single-walled tube and multi-walled tubes respectively. These tubes appear as planes, when viewed with a TEM (transmission electron microscope). The SWNTs appear as two planes. Whereas MWNTs appear as more than two planes and may be observed as series of parallel lines. Because the graphene sheets can be rolled in
different ways, there can be different types of CNTs. The three different types of CNTs are Zigzag, Armchair and Chiral.

![Graphene sheet](image1)
![SWCNT](image2)
![MWCNT](image3)

**Fig: 2.4 Images of (a) Graphite sheet (b) Single-wall (c) Multi-walled CNTs.**

![Single graphene layer](image4)
![Graphene sheet rolled in tubes](image5)

**Fig: 2.5 Images of (a) Single graphene layer (b) Graphene sheet rolled into nanotubes.**

### 2.5.2 CARBON NANOTUBES’ STRUCTURE

To study the CNTs atomic structure, one can imagine, taking the graphite structure, and removing one of the 2-d planes, which is a graphene sheet. A single graphene sheet is shown in Fig.2.5 (a). A CNT is can be viewed as a rolled-up graphene strip, which forms a closed cylinder. A speciality of the CNTs structure is the orientation of the
hexagon carbon ring in the honeycomb lattice relative to the CNT axis. The direction of the hexagon carbon ring is taken almost arbitrarily without any distortion of the hexagon except for the distortion due to curvature of the CNT. This provides many structures for the CNTs.

The basic vectors $a_1 = a (\sqrt{3}, 0)$ and $a_2 = a (\sqrt{3}/2, 3/2)$ create the graphene lattice, where $a = 0.142\text{nm}$ is the carbon–carbon bond length. Assume that A and B are the two atoms in the graphene unit cell. In cutting the rectangular strip, a circumferential vector, $C = na_1 + ma_2$ may be defined. From this, the CNT radius is obtained as $R = C/2\pi = (\sqrt{3}/2\pi) a(\sqrt{n^2 + m^2 + nm})$. Two special cases may be observed as shown in Fig.2.5(b): (1) When the circumferential vector lies along one of the two basis vectors, then the nanotube is termed as ‘zigzag’ type (Fig.2.5(b)), which generates a $(n, 0)$ zigzag nanotube. (2) When the circumferential vector is along a direction exactly between the two basic vectors $(n = m)$, then the nanotube is termed the ‘armchair’ type. This is also shown fig.2.5 (b). A nanotube with arbitrary chirality $(n, m)$, is obtained if the strip generated by $m = n$.

The SWCNTs, which consist of single layer of graphene strips and could, form multi wall nanotubes. However, they are found in other closely related shapes and forms, as shown in Fig.2.5 (a & b). The individual tubes in the bundle are attracted to the neighbouring ones.
This attraction is due to the van der Waals interactions between the tubes. This distance between tubes may equal to the inter-planar distance of graphite, 3.34 Å. An MWCNT is formed by concentric graphitic layers with or without closed caps at both ends. These layers are weakly bound by van der Waals forces. Since the graphene interlayer spacing is 3.34Å, the concentric layers in the MWCNTs are also separated by the same distances. Thus, the successive concentric layers will differ in the circumference by $2\pi \times 3.34 \sim 21\text{Å}$. An armchair MWCNT will have an interlayer distance between successive concentric layers of 3.4Å.

### 2.6 Research and Development of Single and Multi Walled Carbon Nanotubes

So far, the experimental research on properties of CNTs is mainly confined to their static mechanical properties like strength, bending, buckling; Young’s and Shear moduli, electromechanical coupling, mechanical resonance, and some thermal properties. The mechanical behaviors of CNTs have been the area of research of experimental studies and studies of elastic continuum modeling and Molecular Dynamics. While studying MWCNTs, reliable understanding of the tube geometry before transferring the data into properties is very important. The CNTs’ structure can be studied thoroughly by MD simulations, microscopy and spectroscopy. The CNTs deformation in buckling, bending and torsion
can be simulated by MD methods but the sizes of the CNTs are restricted due to the computational expenses. Elastic models cannot be applied to nanotubes. This is because of the presence of interlayer van der Waals forces. A lot of research is devoted to know the behavior of CNTs under various conditions like bending, buckling and twisting. So many methods are available for finding the properties of CNTs. Some investigators used Molecular Dynamics, some others used Van der Waal equations and few others used numerical methods like Finite Element Analysis (FEA). The scope of the present work restrict to establishment of the properties by conducting experimental work on synthesis and characterization of CNTs and simulation work by an FEA approach by modeling the structures and the deformation of SW- and MW- CNTs. these are discussed in detailed in the chapters 6, 7 and 8.

2.7.1 Atomistic Simulation and Experimental studies of Single and Multi walled CNTs.

The small dimensions of CNTs, which are of few nanometers diameter and lengths in microns, pose challenges for experimental observation of properties and mechanical behaviors. The positioning of CNTs in suitable configuration for testing and the achievement of desired loading is very difficult. The measurement and characterization of the mechanical deformation at the nanoscale length is also a difficult task. However, several scholars have been attempted to measure the elastic modulus of CNTs experimentally.
Both SWCNTs and MWCNTs give significant promise for utilization as catalysts, as strong and super-stiff nano-fibers and as components of electrical, electronic and thermal devices [61, 62]. In spite of the applications of CNTs in many areas like technology and science, thorough understating of their mechanical behaviors is not available in literature. Hence, the design and optimization of CNTs are presently difficult. According to Chopra et al. [63] CNTs may completely crumple along the length. Treacy et al [64] used transmission electron microscopy (TEM) to study the thermal vibration of cantilevered MWCNTs inside. They obtained a mean modulus of elasticity 1.8TPa with a scatter from 0.400 to 4.150TPa. Krishnan et al [65] who made a similar study reported, Young’s modulus varying between 0.9TPa to 1.70TPa with an average value of 1.25TPa, using TEM. They observed thermal vibration of single walled CNTs. However, the length and diameter of samples of the CNTs used in the technique used by Krishnan et al. and Treacy et al. were limited to those that did not result in neither too small nor too big thermal vibrations, which were necessary for reliable TEM detection.

Wang et al [66] got the modulus of elasticity as 1.28 ± 0.59TPa without considering the diameter of MWCNT. It was used in atomic force microscopy (AFM) as a cantilevered beam for the analysis of bending. Salvetat et al [67] proposed that the Young’s modulus can be determined by depositing the CNTs on a membrane. A CNT across pores and formed
a clamped beam and they used AFM to apply load on the suspended CNT caused a deflection on the CNT based on applied force. They found Young’s modulus as 0.81±0.41TPa. Lourie and Wagner [68] used micro-Raman spectroscopy to observe the cooling-induced compression of CNTs enclosed in an epoxy matrix. Young’s moduli were resulting from a concentric cylinder replica for thermal stresses and were in fine concurrence with the experiment of Treacy et al [64]. Poncharal et al [69] obtained Young’s modulus between 0.1 and 0.73TPa. They used MWCNTs as cantilever in an electric field to induce mechanical deflection which could be excited at their resonant frequency.

Muster et al [70] performed detailed structural investigations by using scanning force microscopy. Their study revealed the striking flexibility of SWCNTs and Young’s modulus of about 1TPa was estimated for MWCNTs. The bending tests were conducted using atomic force microscope on cantilevered CNTs and obtained young’s modulus of 1.28TPa by Wong et al [71]. Falvo et al [72] observed periodic buckling of CNTs and found local strain as large as 16% could be sustained without separating a CNT. Lourie et al [73] conducted experimental study of various deformation and fracture modes of SWCNTs embedded in a polymeric film. Williams et al [74] reported the characterization of torsional oscillators using MWCNTs as spring elements and found that the CNTs were stiffened by repeated flexing. Yu et al [75] investigated the
sliding between nested shells of MWCNTs using mechanical loading step working inside the scanning electron microscope. They observed a smooth pullout moment and stick-slip moment for the two separate MWCNTs. They determined the shear strength between shells and estimated the surface energy of the shell of the MWCNTs. Yu et al [76] connected end to end of the MWCNT onto the opposing tips of the two AFM cantilever probes and subjected to tensile load until it broke and found Young’s modulus in the range of 0.27 – 0.95TPa.

In another experiment, Yu et al [77] considered a fully collapsed MWCNT and observed a different twisted and collapsed MWCNT by using AFM. A tensile strength of 0.15TPa and Young’s modulus of 0.9TPa was estimated by Demczyk et al [78] during their experiment on pulling and bending tests on individual CNTs in-situ in a TEM. They observed that no clear decrease of cross-sectional area earlier to the failure. The result pointed out that individual CNT may fail as really defect-free materials. Cao et al [79] observed super-compressible froth-like behavior in the self-supporting layers of CNTs joint vertically. Under compression, they formed zigzag buckles that may perhaps fully unfold to their actual length when load is released. In most of the experiments, bending of the CNTs studied using beam theory and elastic modulus is deduced. In several applications, it is seen that the bending stiffness, EI, of the SWCNT or MWCNT is given by the standard expression,
\[ EI = E \left[ \frac{\pi}{4} \left( R + \frac{h}{2} \right)^4 - \left( R - \frac{h}{2} \right)^4 \right] \]  

(2.7)

where \( R \) = tube’s mean radius, \( t \) = tube’s total wall thickness, and \( E \) = Young’s modulus. The wall thickness of the SWCNT is taken as \( t = 0.314 \text{nm} \), which is the equilibrium spacing between two graphitic layers.

The wall thickness of an \( N \)-layered MWCNT is given as \( t = 0.314N \) nm. Iijima et al [80] used high resolution electron microscopy (HREM), and observed single kinks in 0.8 and 1.2nm diameter SWCNTs for large bending angles. Several researchers observed that the MWCSNTs display multiple buckling patterns during bending. During the bending of MWCNTs, Iijima et al [80] used five-walled CNTs in HREM and observed single kink; then, by increasing load for further bending, they observed double kinks without change in distances between respective walls for high degree angles of bending. Falvo et al [81] bent MWCNTs using the FM’s tip. They explained that the MWNTs could be twisted frequently through large angles, without causing fracture. On the inner-side of the bend of the tube, small regularly distributed buckles are observed. As the tube is bent in the opposite direction, the location of the buckles is shifted. They appear in regions where they were not observed before. Also they have disappeared from the previous locations.

Bower et al [82] studied MWCNTs in polymer matrices using TEM. In strained composites, when MWCNTs were bent to large curvatures it is
seen that local CNT wall buckling is taking place. Poncharal et al [83] have also measured local buckling of MWCNTs in bending. From TEM images, it is observed that the buckling wave length is dependent on radius of the CNT. The buckling wavelength of the outer wall spreads to the inner walls. The interwall spacing does not change in buckling. This indicates the effect of strong van der Waals interactions between the MWCNT walls. The small dimension of CNTs poses on the measurement of mechanical properties. Their positioning in a suitable testing configuration, achievement of the desired loading and the characterization and measurement of deformation are all difficult [84]. Hence theoretical investigations are necessary. Two main classes of theoretical methods are atomistic simulation and continuum mechanics. Although the theoretical investigation is not the substitution for the experiments, it provides useful guidelines for subsequent investigations and interpretations of the properties of CNTs.

From the last 8-12 years, SWCNTs and MWCNTs have created strong research endeavor in the search of their mechanical properties. Many studies have been made on MD simulations and Electronic simulations like ABACUS, on the deformations and structures of CNTs. The results indicate that, if wall modulus and thickness are properly defined the nanotube walls may be treated as elastic shells without much
lose of accuracy. The results also revealed that, at a certain level, SWCNTs could be treated as beams of effective bending stiffness.

Robertson et al [85] studied energies of many SWCNTs with radii <0.9nm using both theoretical and experimental methods. They understood that CNTs hold internal strain energy per carbon atoms comparable to the unstrained graphitic sheet which has an inverse square (1/R²) dependence on CNT radius. It is not sensitive to other properties of lattice structure, even when tube radius is 0.35nm. This result agrees well with the results using continuum elasticity theory. They assumed the wall thickness to be 0.314nm, which is equal to the graphite inter-planar spacing. They compared their results to the results obtained from beam theory. Later, many investigators expressed the curvature strain energy as a function of CNT radius [86-92]. The atomistic simulations substantiated the observation that the SWCNTs follow classical elasticity theory in their behavior. The corresponding relation is \( U_R = \frac{1}{2} D/R^2 \), where \( U_R \) = internal energy/unit area of the CNTs due to its cylindrical nature, \( R \) = tube radius and \( D \) = sheet bending stiffness. These calculations point out that those CNTs hold an initial “internal stress” distribution due to their finite radius. This differentiates them from the state of their stress-free condition.
Yakobson et al [93] conducted many MD simulations for CNTs under bending, buckling, axial compression and torsion. Wide simulations of SWCNTs for different diameters, lengths and helicities had been carried out for each loading mode. They observed simulation results in the form of final and intermediate deformed configurations, strain energy as a function of deformation of axial compression, bending and torsion angles of the applied boundary conditions. They had observed the strain energy increased quadratically with increase in buckling curvature. Using molecular dynamics method, the bending of SWCNTs is studied by Iijima et al [94]. Their theoretical simulations seem to verify results of Yakobson et al [93]. They had observed previously that the strain energy increased quadratically with the bending angle. Thus the bending response of the CNT might be treated as that of an effective beam.

Yakobson et al [93] fitted the results of MD and ab initio studies of Robertson et al [85], into elastic shell theory. They determined values of effective modulus of elasticity, the effective wall thickness of CNT and the Poisson’s ratio to predict the SWCNTs deformation. They predicted, using classical shell theory, the critical strain at the beginning of buckling due to bending, axial compression, and torsion as a function of SWCNTs [94]. They found that, between the shell theory and the molecular dynamic predictions a synergism, which is significant. They concluded that, the
shell theory may be used to estimate the critical deformations at which the buckling occurs, by properly choosing the wall stiffness parameters.

The elastic properties of 2D hexagonal structure are isotropic. Here, the wall is approximated using the parameters the flexural rigidity $D$, the Poisson’s ratio and the in-plane stretching stiffness $C$. The surface integral of the parabolic form of the local deformation gives strain energy of a linear elastic shell. This method can be adapted for a graphic tubule also. For this, the values of stretching stiffness and flexural rigidity are identified by comparing with the experimental studies and ab initio methods of CNT at small strains [85]. They obtained $C=59eV/atom=360J/m^2$ (for graphite $C=58.2eV/atom$) and $D=2.23eVÅ^2/atom$. From CNT simulations the poison’s ratio $\nu = 0.19$ was taken. The same value of $\nu$, the poison’s ratio was observed from elastic constants of single crystal graphite experimentally [95, 96]. From classical shell theory, using the standard relations, the effective wall stiffness properties $E_{wall} = 5.5TPa$, & $T_{wall} = 0.066nm$ are obtained. It is seen that, when $t_{wall} = 0.340nm$ and the modulus $E_{wall} = 1.06TPa$, the wall bending stiffness is given by the relation:

$$D = \frac{t_{wall}^3E_{wall}}{12(1-\nu^2)}$$

(2.8)

This is much larger, compared to the bending stiffness assumed from the rolling energy calculations in atomistic simulations.
The accuracy of the wall thickness and the effective Young’s modulus as calculated by Yakobson et al. [93] are confirmed by later studies. The strain energy of the deformed SWCNT is also found agreeing with shell theory. Zhou et al [97] obtained Young’s modulus and strain energy based on electronic band theory. This was calculated using a tight binding model. By taking account of the occupied band electronics, they computed the total energy. The total energy was then divided into the rolling, the compression and the bending energies. They obtained $E_{\text{wall}} = 5.1\text{TPa; } t_{\text{wall}} = 0.074\text{nm}$ by fitting the three energy values with estimates deduced from continuum elasticity theory. The Local Density Approximation model was projected by Lenosky et al [98]. Using this model Tu and Ou-Yang [99] developed the complete energy relation of deformed SWCNT in the continuum limit. They found this model to be dependable with classic shell theory for the wall stiffness pair $(E_{\text{wall}} = 4.70\text{TPa; } t_{\text{wall}} = 0.075\text{nm})$. Kundin et al [100] calculated the poison’s ratio inplane and bending stiffnesses of CNTs using ab initio energy calculations. The value of $\nu$ was computed from the reduction in diameter of the CNTs under simulation. They compared the in-plane stiffness and the bending stiffness relations for isotropic continuum shells to the ab initio results, and obtained the values $E_{\text{wall}} = 3.859\text{TPa; } t_{\text{wall}} = 0.0894\text{nm}$. The possibility of the application of elastic shell theory to CNTs is thus demonstrated.
Born and Huang [101] derived elastic constants based on the potential energy of a crystal system. The potential energy was expressed as a function of the atomic displacement from their equilibrium position. Martin [102] proposed elastic constants for crystal system, where the energy density is the sum of several interactions. Martin's approach is also called the Cauchy-Born hypothesis. Using the Cauchy-Born rule Zhang et al [103, 104] proposed a nanoscale continuum theory. The theory was used to study problems of the elastic modulus of SWCNTs [104] and the fracture nucleation in SWCNTs under tension [103].

CNTs are made up of curved atomic layers. They pose a big challenge in the simulation of CNTs using Cauchy-Born rule. This application may cause inconsistency in the mapping. By introducing the concept of exponential mapping from differential geometry, Arroyo and Belytschko [105] corrected this inconsistency. Odegard et al [106] present an alternative continuum approach. A representative volume element of the chemical structure of graphene is substituted with an equivalent truss and a continuum model is developed. The mechanical response of nanotubes is explained using classical beam theories in several experimental studies. Harik [107] used the beam assumption and analyzed the applicability of continuum beam models and continuum shell theories to study the mechanical behavior of SWCNTs. Using dimensional analysis, he identified the applicable non-dimensional
parameters, which control the onset of NT buckling and the change of buckling modes. He also identified the structural parameters characterizing CNTs. He concluded that the beam theory can be used only for SWCNTs with very small diameters.

The validity of Bernoulli Euler beam bending theory in inferring the Young’s modulus of MWCNTs is studied by Govindjee and Sackman [108]. While using beam theory to interpret bending data it is necessary to consider the discrete nested shell structure of the MWCNT. Ru [109,110] studied the effect of van der Waals forces on axial buckling of a double-walled CNT. To study the infinitesimal buckling of a double-walled nanotube under axial compression, he analyzed a simple elastic shell model. The van der Waals interaction is assumed to be a linear function of the change in inter-layer spacing and taken as a pressure. It is found that the interaction of CNTs is largely controlled by the van der Waals forces. This is especially true for MWCNTs. It is observed that the continuum theories which are linked to atomistic models give reliable results. The formulation of the problem is very complicated and involved compared with the finite element approach. However, computational details and results are still confidential.

Srivastava et al [111] investigated nano-plasticity of SWCNT under compression using generalized tight binding MD and ab initio method. They found the graphitic geometry collapsed to a localized diamond-like
pyramid. The critical stress and the shape of the resulting plastic deformation were computed and found to be comparable with experimental results. Ozaki et al [112] used al O (N) tight-binding method to perform MD simulation on SWCNTs’ axial deformation. They showed that under large strain, stress was remarkably sensitive to helicity and that a zigzag CNT and an armchair CNT were the stiffest under tension and compression, respectively. Kolmogorov and Crespi [113] found that the well-defined geometry and extreme structural anisotropy of a MWCNT brought qualitatively new features to the nano-scale tribology. Tu ZC and Ou-Yang [114] took the total energy expression of the deformed SWCNT as the continuum limit from the local density approximation model. This was proposed by Lenosky et al [115]. The energy was seen to be consistent with the value, estimated from the shell theory. From this, modulus of elasticity and the effective wall thickness of CNT were obtained. Gao et al [116] reported that a DNA molecule could be spontaneously inserted into CNT in a water solute environment Via MD simulation. Buehler et al [117] investigated the SWCNTs subject to compression loading and found a shell-rod-wire transition of the mechanical behavior of CNT with increasing aspect ratio.

Buehler et al [118] revealed that wire-like CNTs could form attracting each other through vdW forces. The folding-unfolding transition could be explained by entropic driving forces that dominated
over the elastic energy at elevated temperature. Zou et al [119] reported that SWCNTs could coaxially self-assemble into MWCNTs in water due to natural insertion of smaller tubes into larger ones. Xiao et al [120] investigated nonlinear elastic properties and axial instability of SWCNT. They showed that SWCNTs were hardened under compression but softened in tension. The critical strains of CNTs were inversely proportional to their diameters when the local buckling occurred. Sears and Batra [121] performed molecular mechanics simulation on axial and torsional deformations of SWCNTs to find modulus elasticity, shear modulus and equivalent thickness. Liew et al [122] studied the axial buckling of CNTs employing Brenner et al.’s ‘second generation’ empirical potential [123]. Further, Liew et al [124] investigated the tensile properties of CNTs and obtained the stress-strain responses and the mechanical properties for 1 to 4-walled CNTs. The plastic deformation under Stone-Wales defects and brittle fracture under bond breaking are also presented.

Liew et al [125] studied the CNT bundles and presented the critical strains, failure and buckling loads. Shibutani and Ogata [126] evaluated the bending and torsion of SWCNTs using MD simulation. A cantilever beam type SWCNT loaded by a force at other free end, and it displays local buckling close to the fixed end. After buckling under torsion, an irregular plane fuzzy structure was produced and its harshness was
Weaker than its original structure. Wang et al [127] simulated the torsion of CNTs via MD simulation. The results showed that the shear modulus increased with as the radius of the CNT and changed from 370 to 500GPa. After buckling, the whole section collapsed like a dumbbell and the atoms moved with off-plane displacements. The asymmetric distribution of the system energy induced the buckling of the structure.

Liu et al [128] studied the interlayer lattice registry effect on the formation of fully collapsed SWCNTs via atomistic simulation. Jiang et al [129] applied MD to study energy dissipation of the cantilever-type CNT beam oscillators. Wong et al [130] performed MD simulation to obtain Young’s modulus varying in the range of 1.25 to 1.48TPa. They showed the zigzag CNT’s modulus of elasticity was more than the armchair CNT. The results showed that there were two buckling modes for SWCNTs and the critical stress varied with length in two buckling modes. In the above literatures, much simulation was concerned on the Young’s modulus. The classical mechanics definition for Young’s modulus $Y$, is often taken as

$$Y = \frac{1}{V_0} \frac{\partial^2 E_s}{\partial \varepsilon^2} \bigg|_{\varepsilon = 0}, \tag{2.9}$$

Where $V_0 =$ equilibrium volume, $E_s =$ strain energy and $\varepsilon =$ axial strain. In essence, a SWCNT is a hollow cylinder with its volume $V_0$ given by $V_0 = 2\pi L R t$, where $L =$ length, $R =$ radius, and $t =$ wall thickness.
The atomistic simulation has very good performance on the study of fracture, strength, failure, size effect, etc., of CNTs. It is used to gain basic understanding of the behavior of the materials at the nanoscale. It is difficult to scale up the results since a large number of degrees of freedom are involved. For example, the 4-walled (20,20), (15,15), (10,10), and (5,5) MWCNT with aspect ratio 9.1 contains 1.5097 atoms, and the calculation took two months to complete on SGI origin 2000 system [131]. Modern computer power allows modeling domains with a maximum of a billion atoms. This corresponds to only a small cube of material 1µm in size [132]. This limits the computation of CNT to a large extent. Due to these reasons, MD simulation alone cannot predict the properties and responses of macroscopic materials from the nano- and micro-structures.