RAMAN CHARACTERIZATION OF STRUCTURAL PROPERTIES OF THERMALLY MODIFIED NANOGRAFITE.

Muhammad Ali

Supervisor: Tatiana Makarova

Master’s Thesis in Physics, Department of Physics, Umeå University
ABSTRACT

Raman spectroscopy is highly sensitive to study the structural properties of nanographite (NG) materials. An experiment was conducted to assess the spectrum of multi-shell nanographite at different temperature and laser treatments. Four samples with different temperature were used. The range of temperature used was 1500-1650 °C. All samples were subjected to different laser treatments like 488, 514, 633 and 785 nm respectively. The spectrum of nanographite was observed by using the Raman spectroscopy. The 1st and 2nd order spectra of NG were evaluated by using the Voigt analysis. The variations in the intensities of D and G bands were analyzed. The decrease of D band width with heat treatment was observed. The peak 1523 cm\(^{-1}\) exhibited more and more reduction with increase in temperature treatments. Temperature induced the conversion of nanodiamond to nanographite.
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If all infinite resources of water are turned in ink and all the wood turned in to pens even then it is impossible to express His affections, generosity, bounteous blessings and neutifulness, because the words are bound, knowledge is finite and time is limited. I must bow my head to offer my humblest and sincerest thanks to "Almighty Allah" Who enabled me to perceive and pursue higher ideas of life.

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1. INTRODUCTION

The carbon nanostructure with a well developed $\pi$-electron system like nanotubes, nanographite and turbostractic carbons has been a subject of special interest. Nanofibers, nanoribbons, nanohoops, nanocones, nanohorns, nanoonions and graphene are regarded as carbons structure with nanometer size. It is generally accepted that the ability of multishell diamond like carbon to maintain the exceptionally high charge/discharge rates without a considerable loss of capacitance is due to its hexahedral structure and small particle size, resulting in a high curvature. The increased capacitance achieved are related to the moderately high surface area of curved graphic shells, combined with the high charge–discharge rate capabilities and high electrical conductivity makes diamond like carbon attractive for high-power applications[47]. In graphite, atoms are strongly bonded within the sheet but the layers can slip easily over each other due to weak force between them. Therefore the graphite is used as a dry lubricant, as pencil or standard material for scanning probe in microscopy etc. When the large numbers of defects are introduced in the graphite then it behaves like hard material. The pyrolytic graphite and carbon fibers are extremely strong and heat resistant (about 3000 °C) materials. Such types of materials are used for jets and missiles, high temperature reactors, electric motor brushes, reinforced plastics etc. Due to this wide range of applications graphite has been studied for last sixty years [5].

Graphite and diamond are the most naturally occurring chemical elements of carbon. There are many forms of carbon known as allotropes that can be considered as pure forms of carbon but arranged in a different crystal lattice. These forms include hexagonal graphite, rhombohedral graphite, diamond, buckminsterfullerene and amorphous carbon. The chemistry of graphite and diamond is same but with different crystalline structure (polymorphs) [1]. Diamond like Carbon (DLC) is a metastable form of amorphous carbon. It contains a significant fraction of $sp^2$ and $sp^3$ type C bonds. The DLC can be insulator with high resistivity if it is structurally very close to the tetrahedral amorphous carbon or $ta-C$ on plots of bonding ratio with hydrogen content. It is very interesting that if DLC prepare in the medium cobblestone version then electricity can pass through it (Conductor). This process results in the formation of DLC which behaves like a semiconductor [1,3].
The multishell nanographite (MSNG) particles are usually produced by the annealing of detonation nanodiamonds (grain size ~5 nm) in inert atmosphere or in vacuum causing the transformation of nanodiamond to multishell nanographite. Nanodiamond begins to graphitize at about 1500 °C. The MSNG were obtained by the heat treatment at 1500, 1550, 1600 and 1650 °C of nanodiamond particles lead to their conversion to the mixture of quasi-spherical carbon onion and multishell polyhedron nanographite [6].

Raman effect was discovered by an Indian Physicist Chandrasekhara Venkata Raman who won the Nobel Prize in 1928. Raman spectroscopy is powerful technique that can be used for characterization of carbon nano materials. Raman is suited to detect the small change in the structural morphology of the carbon nano materials. Raman spectroscopy is also used to characterize the material composition and to analyze the specific phonon mode energy. It is traditionally carried out at wavelength in blue 488 nm and green 514 nm spectral regions but multi-wavelength Raman studies are increasingly used. It has been a considerable improvement in the field of multi-wavelength Raman spectroscopy in carbon systems. Raman measurement needs very little sample preparation and rapid nondestructive spectrum can be easily achieved. Raman spectroscopy is very good to investigate the crystallinity of micro and nano materials through the phonon confinement effect. The phonon confinement effect occurs with the lifting of phonon momentum selection rule \( q=0 \) for the Raman scattering process. This phenomenon occurs when the crystalline domain becomes very small and it effects as both the frequency shift and an asymmetrical broadening of phonon modes. The intensity of Raman scattering is proportional to the number of density of interacting media.

In this thesis chapter 2 presents the theoretical information about graphite, nanographite and Raman spectroscopy for characterization of \( sp^2 \) and \( sp^3 \) nanocarbons. Additionally the information about the dispersion of D and G band are also expressed in this chapter. In chapter 3 sample synthesis and experimental work is described. All the results and discussion are expressed in chapter 4 and chapter 5 gives the summary and conclusion about this thesis.
2. THEORY

2.1 Graphite:

Carbon is an element of group IVA in the periodic table having the electronic configuration $1s^2$, $2s^2$, $2p^2$. Graphite is the most stable allotrope of carbon materials. The graphite is very fine conductor of heat and electricity and has highest natural strength and stiffness as compared to any other material. It is one of the lightest in all reinforcing agents and has high natural lubricity.

The $sp^2$ hybridization undergoes due to one $s$-orbital and two $p$-orbitals in the carbon atom [7]. One electron in $2s^2$ state is stimulated and combines with the $2p$ orbital to form the $3sp^2$ orbital and one unhybridized delocalized (free) $p$-orbital electron (Fig. 2.1).

![Figure 2.1: $sp^2$ hybridization of carbon atoms.](image-url)
The $sp^2$ bonded carbon atoms are densely packed in the planar hexagons sheet. This planar atomic sheet is called the graphene. The carbon-carbon bond length in the graphene is about 0.142 nm. The graphene sheet stacks to form the graphite with the interplanar spacing of 0.335 nm as shown in figure 2.2. These graphene layers loosely bonded and have the twice spacing distance than the Vander Waals radius of carbon. This bonding arrangement results due to the $sp^2$ hybridization of carbon electronic orbitals. The hybridized fourth valence electron is paired with another delocalized electron to the adjacent plane from Vander Waals bond. Graphite can conduct the electricity due to the vast electron delocalization within the layers of graphite. The valance electron is freely moved within the planes of layers, so electricity can conduct within the planes of the layers of graphite. It means that phonon can propagate very quickly along the tightly bonded planes but slower to move along one plane to another plan. [8].

Figure 2.2: Structure of graphite and graphene [49].
Graphene layers stack in different ways to form the graphite hexagonal lattice and rhombohedral lattice.

2.2 Hexagonal graphite:

The hexagonal graphite is formed by the stacking layers of graphene in sequence of ABABAB. The planar layers are stacked in such a way that the atoms of hexagon lie exactly above or below of nearest atoms and the center of the hexagons in the neighboring atoms. It belongs to the P63/mmc (D46h) space group. Such type of graphite is bulk or flat and thermodynamically stable form of graphite. By using the mechanical treatment, the hexagonal shape can be converted to rhombohedral form and this form can be return to hexagonal structure when it is heated to above 1600 K [8].

2.3 Rhombohedral (beta) graphite:

The rhombohedral has stacking order of ABCABC. This type of graphite does not exist in nature in pure form. It is found only in combined form with the hexagonal graphite and it is thermodynamically unstable form of graphite [8].

2.4 Polycrystalline graphite:

Hexagonal graphite which described above has no defect and naturally this form of graphite is seldom. But in case of polycrystalline different forms like Pyrolytic graphite, carbon fiber, carbon matrix composites, carbon black and vitreous carbon are all reported. They graphite can exhibit a random orientation, more or less preferred orientation, or a highly oriented texture as in some pyrolytic graphites. Their planar may not be perfectly to each other as compared to the hexagonal graphite. The large cluster type is often found in pyrolytic graphite that is more uniformly ordered, free of defects and planar layers are more parallel to each other [8].
Figure 2.3: Structure of (a) Hexagonal and (b) Rhombohedral graphite crystal. The view is perpendicular to the basal plane [8].

2.5 Nanographite:

The term nanodiamnod is used for a variety of diamond based materials at nanoscale. Nanodiamonds are produced by the explosive detonation and have mean size distribution about 5 nm. The natural diamond is hydrophobic but nanodiamond is hydrophilic. Nanodiamond core comprises of $sp^3$ orbital structure and it is surface contain $sp^3$ orbital structure. Therefore the surface also has dangling [9]. Nanographite samples are prepared by the heat treatment of nanodiamond. The nanodiamond particles (5 nm) are heated at different temperatures i.e., 1500 °C, 1550 °C, 1600 °C and 1650 °C leads to their conversion of mixture quasi-spherical carbon onions and multi-shell polyhedral nanographites.
Figure 2.4: Chemical formula of trinitrotoluene (TNT) and hexogen structure [48].

This heat treatment changes the structural properties of the materials. The quasi-spherical and polyhedral nanographite structures initially found in the detonation-synthesized nanodiamond heat-treated at high temperatures. The nanodiamond to nanographite transformation starts from the surface of nanodiamond layers. Then graphitization front propagates into the diamond core. The annealing temperature and time duration determines how much amount of carbons atoms transferred from $sp^3$ to $sp^2$ hybridization [6].
2.6 Raman Spectroscopy:

Raman spectroscopic techniques are used to study the vibrational, rotational and other low frequency modes. The shift in wavelength is unique for every material that is called as fingerprints of materials. Raman affect is due to the interaction of electromagnetic field of incident beam with the sample material. When a laser beam falls or strikes on the sample material it may interact with it in different form like an absorption, scattering or reflection. Here Raman affects deal with the scattered situation [10].

![Diagram of Raman spectrometer showing essential features](image)

**Figure 2.5:** Schematic diagram of Raman spectrometer showing essential features [11].

When the laser light is incident on the molecule or atom, the incoming phonon interacts with the phonon in the atom or molecules. The laser beams scattered from the molecules or atom can suffer the Rayleigh scattering, Stokes scattering or Anti-stokes scattering. A large fraction of laser light scattered that is called Rayleigh scattering. In Rayleigh the emitting photon has same energy as an incident photon. The inelastic scattering of photon known as the Raman effect. A few are shifted to higher energy wavelengths (Anti-stokes scattering) but most are shifted to lower frequencies (stokes scattering) [10]. When the phonons in molecule or atom are in ground state, they interact with the incident phonon and excited into the virtual or the real transition state at high energy. Due to instability, phonon tends to back its initial state and emitting a photon of same energy (Rayleigh scattering). A few electrons fall back to the higher energy state just above the ground state by emitting the photon of lower energy that is called stokes scattering. The incident laser beam may be also excited the phonon from the above state of their ground state. In
this situation electron falls back to the ground state emitting a photon having more energy than the incoming photon. This process is rare and called as anti-stokes scattering [12].

Stokes scattering is most common than anti-stokes scattering because mostly electrons exist on the ground state at normal temperature. In Raman spectroscopy, stokes scattering is used mostly because anti-stokes scattering is less intense than stokes scattering. The shift in wavelength of stokes and anti-stokes scattering compared to the incoming photon wavelength to vibrational energies of molecules that is called Raman shift [12].

\[
P = \alpha E
\]

(1)

Where \( \alpha \) is the polarizability of the molecules. If a molecule is vibrating then polarizability depends on the vibrational frequency of molecules. In classical mechanics \( E \) and \( P \) of the
molecules are oscillating during the interaction process. The oscillating function of electric field depends on the frequency of light,

\[ E = E_o \cos 2\pi v_o t = E_o \cos \omega_o t \]  

(2)

Where \( v_o \) is the frequency of light and \( E_o \) is an interacted electric field with the molecules in time \( t \). Putting value of \( E \) in the equation (1), new equation will be

\[ P = \alpha E_o \cos \omega_o t \]  

(3)

The polarizability changes due to motion of nuclei in the molecules [13]. This term can be shown by an expression depending on the internal vibrational mode \( q \) that is equation as

\[ q = q_o \cos \pi v_{vib} t \]  

(4)

Where \( v_{vib} \) presents the eigenfrequency of nuclei. The equation for series \( \alpha \) is presented as

\[ \alpha = \alpha_0 + \left( \frac{\delta \alpha}{\delta q} \right) q + \text{higherorderterms} \]  

(5)

Now inserting the equation (5) into (3), the new complex equation for dipole moment is produced that is

\[ P = (\alpha_0 E_o \cos \omega_o t) + \frac{1}{2} E_o q \frac{\delta \alpha}{\delta q} [\cos(\omega_0 + \omega_{vib})t + \cos(\omega_0 - \omega_{vib})t] \]  

(6)

In this equation the first term represents the equilibrium condition of the molecules and second term \( \omega_0 - \omega_{vib} \) and \( \omega_0 + \omega_{vib} \) expression are the stokes and anti-stokes shifts respectively [14].
2.7 Raman spectroscopy for characterizing $sp^2$ and $sp^3$ nanocarbons:

Graphite and diamond are the famous allotropes of carbon with wide range of disordered forms. Raman spectroscopy is quite sensitive to these structures in which the translation symmetry takes place in polycrystalline or grain size. It is powerful method to describe the characterization of carbon material that needs little or no sample preparation becomes a suitable choice for Raman spectroscopy [15]. It is very sensitive to short range disorder carbon material and can also expose the different forms of amorphous carbons. Carbon materials itself from different compounds undergo different structural changes in the original material due to rearrangement of the atoms through different hybridization. The carbon materials are integrated with the linear chain of C-C atoms forming the monomers and polymers. This type of homonuclear bonds show very weak or no polarization due to high symmetry mostly found in the polymer system. The vibrational mode will be symmetrical if molecules contains the centre of symmetry and infra red forbidden. The existence of $\pi$-states in carbon materials with the $sp^2$ bonds have very long range polarizability, leading to a large Raman cross section making Raman spectroscopy a suitable choice [16].

Diamond is the crystalline form of carbon and belongs to the face centered cubic lattice. Its Raman active phonon is a single, triply degenerate zone centered vibrational mode which is attributed to C-C single bonds between $sp^3$ hybridized carbon atoms in the cubic structure. This mode is only Raman active with first order band appearing at 1332 cm$^{-1}$ as a sharp line.

Graphite is the stacked sheet of carbon atoms in the basal planes arranged in the $sp^2$ tetragonal configuration. Graphite has two dimensional hexagon shapes with the fourth electron in the $\pi$-orbital and perpendicular to the weakly bonded hexagon sheets [15]. Graphite has a high degree of disorder due to strong C-C bonding. It will be sufficient to consider the graphene layers for the physical properties of graphite because of weak interaction between the layers. The symmetry of graphite is shown in figure 2.7.
Figure 2.7: Graphite lattice in (a) top and (b) side view. $\alpha_1$, $\alpha_2$ and $\alpha_3$ span the unit cell of graphite [17].

The graphite has the six normal modes at $q=0$, these modes can combined in phase ($\Gamma_{\text{vib},2D} \otimes A_{1g}$) or out of phase ($\Gamma_{\text{vib},2D} \otimes B_{1u}$) to obtain the phonon vibration symmetry of graphite [17]. The phonons vibration symmetry of graphite are given by

$$
\Gamma_{\text{vib},3D} = 2A_{2u} \oplus 2B_{2g} \oplus 2E_{1u} \oplus 2E_{2g}
$$

(7)

How the graphite modes split into higher frequency out of phase and lower frequency in phase vibration are shown in figure 2.8.

The irreducible representation for the brillouin zone (BZ) center optical modes can be decomposed into

$$
\Gamma = A_{2u} + 2B_{2g} + E_{1u} + 2E_{2g}
$$

(8)
Figure 2.8: Phonon eigenvectors of graphene and graphite. Every phonon eigenvector of graphene gives rise to two vibrations of graphite. For example, the in-phase combination of the two layers for the $E_{2g}$ optical mode of graphene yields $E_{2g} \otimes A_{1g} = E_{2g}$ and the out-of-phase combination $E_{2g} \otimes B_{1u} = E_{1u}$. Next to the graphite modes we indicate whether they are Raman (R) or infrared (IR) active and the experimentally observed phonon frequencies [17].

The Raman active modes are $2E_{2g}$ were observed at 42 and 1582 (G) cm$^{-1}$ (Nemanich and Solin 1979). The maids at $A_{2u}$ and $E_{1u}$ have been observed at 867.8 and 1588 cm$^{-1}$ (Nemanich et al. 1977) and one of the two optically inactive $B_{2g}$ modes were observed at 127 cm$^{-1}$ by neutron scattering (Nicklaus et al. 1972). The other $B_{2g}$ mode corresponds to out of plane atomic displacement observed in the Raman spectrum of pyrolytic graphite edge planes. The peak is possible when the Raman inactive mode $B_{2g}$ becomes Raman active due to crystalline point group symmetry by a slight rearrangement of the lattice structure near the edge (Kawashima and Katagiri 1999). According to these results, a sharp peak observed at 864 cm$^{-1}$ for He-Ne laser (633 nm) excitation and 864 cm$^{-1}$ in the case of 780 nm laser excitation when an incident photon is polarized at 90 degrees to the basal plane [18].

Raman spectroscopy of nanographite structure increased due to the measles relativistic properties of electron conduction in a single layer of graphite [19, 20]. The plane size $L_a$ of crystallites can be determined by using the Raman spectrum of nanographite. The local arrangement of atoms in
nanographite has defined the edges as an armchair or zigzag shape. This local arrangement of atoms can determined by the disorder induced bands in the Raman spectrum of nanographite. This spectrum can be used if the nanographite sample presents the stacking order or turbostratic structure.

The Raman spectrum of nanographite is divided into first and second order spectrum. The first order spectrum lies in the range of 200-2000 wave number (cm\(^{-1}\)), where the 200-900 wavenumber (cm\(^{-1}\)) is the low energy region. The second order spectrum lies in the range of 2000-3400 wavenumber (cm\(^{-1}\)).

The first order spectrum is characterized by the D-band at 1350 cm\(^{-1}\). This D-band is related to the disorder induced in the nanographite and it is assigned to the \(k\) point of \(A_{1g}\) symmetry. [21].

![Figure 2.9](image.png)

**Figure 2.9:** The Raman spectroscopy to characterize the diamond like carbons [22].

The first allowed band at 1580 cm\(^{-1}\) is called the G band that is originated from doubly degenerated vibrational mode \(E_{2g}\). It occurs in the first Brillouin zone at the cross of (iLO) and (iTO) phonon branches at the \(\Gamma\) point. [21].
Figure 2.10: First order Raman spectrum of nanographite [22].

The intensities of Raman spectra of nanographite are dependent on the ratios of D (1350 cm\(^{-1}\)) and G (1580 cm\(^{-1}\)) band intensities and structural properties of nanographite. The D and G band ratio can be used to measure the crystalline size \(L_a\) of nanographite. This ratio is inversely proportional to the crystalline size \(L_a\) of nanographite [23]. The Raman spectrum can be used to measure the order occurring along the c axis and second order D and G-band is sensitive to the degree of graphitization of the material [23].

According to the Tuinstra and Koenig relation with the coefficient belonging to Knight and White:

\[
L_a (nm) = 4.4 \text{ nm } \frac{I_D}{I_G} \text{ (at green laser 514nm)}
\]

The crystalline size can also calculated by using the Cancado formula at different laser energy.

\[
L_a (nm) = \frac{560}{E^4 (I_D/I_G)^{1.7}}
\]

Where \(E\) is the excitation laser energy used in the Raman experiment in eV units.

The D band mode also appears in the second order spectrum of nonographite at about 2700 cm\(^{-1}\) and has the double peak structure. The shape and position of the 2D peak is very good tool for analyzing the stacking sequence of nanographite. The difference in the peak position in the second ordered spectrum of single or multilayer graphene is useful to how many layers of graphene are in the stacking sequence [24].

The 2450 cm\(^{-1}\) band and the 2D band corresponds to \(q=0\) and fully dispersive \(q=2k\) respectively. This band is assigned to an overtone mode of longitudinal optical phonon (LO) from the dispersion
and frequency of phonons \[25\] G+D at 2940 cm\(^{-1}\). The 2936 cm\(^{-1}\) is assigned to a combination of the zone centre mode 1592 cm\(^{-1}\) and the zone boundary mode at 1358 cm\(^{-1}\) \[26\]. The 2960 cm\(^{-1}\) is a band that becomes more intense with decreasing crystalline size \[27\]. The C-H stretching at 2925-2970 cm\(^{-1}\) are absorption peaks in the C-H vibration region. The 2925 cm\(^{-1}\) is assigned to \(sp^2\)-CH\(_2\) bonds that are asymmetrically Raman active. The 2970 cm\(^{-1}\) corresponds to CH\(_3\) bond asymmetrically Raman active. 3000 cm\(^{-1}\) is assigned to \(sp^2\) C-H bonds \[28\]. The 2D’ band at 3250 cm\(^{-1}\) is suppressed with decreasing crystallite size \[29\]. The 3480 cm\(^{-1}\) maybe assigned to O-H stretching of surface of hydroxyls generated from absorption of the trace of amount of moisture \[30\].

2.8 The dispersion of D and G bands:

A variety of four different excitation energies are used to characterize the Raman spectra of nanographite. The Raman modes are assigned on the double resonance Raman effect. In many Raman modes of nanographite there is presence of frequency inconsistency between the stokes and anti-stokes lines. These frequency inconsistency values are highly dependent on the excitation energy in which the D band values are change from positive to negative. The frequency of the D band shows two important spectral features. First, the frequency of the D band is highly dispersive for different \(sp^2\) carbon materials and shift with excitation energy at a rate of 44 to 53 cm\(^{-1}\) over wide excitation energy (\(\varepsilon_L\)). Secondly the stokes (\(\omega_s\)) and anti stokes (\(\omega_{As}\)) component of the D band in graphite materials have different frequency and this difference in frequency is equal to the product of the phonon energy (\(\hbar \omega_s\)) of D band and its laser energy difference. The similar spectral property exists for the overtone of D band is called the 2D or G´mode and other dispersive mode \[7, 13\].

The dispersion modes may have different values for different graphite materials. For example, by 1.96 eV excitation, the frequency of D modes in graphite whisker and single wall carbon nanotubes are 1333 and 1323 cm\(^{-1}\) respectively. The stokes Raman spectra can provided the probe of first order dispersive modes, because the frequency of higher order modes are the sum of frequency of its fundamental modes. The frequency \(\omega_s\) of the first order or higher order stokes mode can be detected by the frequency \(\omega_{As}\) of the corresponding anti-stokes mode by the excitation \(\varepsilon_L\). For example, the anti-stokes frequency of the 2D’ mode by 2.54 eV excitation is 3235 cm\(^{-1}\), then can get the stokes frequency of the 2D’ mode by the 2.94 eV (2.54 eV + \(\hbar \omega_{2D'}\))
excitation is 3235 cm$^{-1}$. Therefore the anti-stokes modes provide us more information on the excitation energy dispersion properties of dispersion Raman modes. So, the dispersion properties of anti-stokes Raman modes allow us to probe the phonon dispersion relation of the graphite materials by using the double resonance anti stokes process.
3. EXPERIMENTAL SECTION

3.1 Sample synthesis:

Multishell nanographite (MSNG) particles were produced by the annealing of detonation nanodiamonds (grain size ~5 nm) in argon flow. The MSNG nanographite is prepared by the heat treatment of nanodiamonds. This was done in the Department of Technology, Tokyo Institute of Technology, Enoki Laboratory, and described in the paper “Magnetic and EPR studies of edge-localized spin paramagnetism in multi-shell nanographites derived from nanodiamonds” by V.Yu. Osipov, A.I. Shames, T. Enoki, K. Takai, M. Endo, T. Hayashi, Y. Kaburagi, A.Ya. Vul. Diamond and Related Materials, 18, 220. Below are the main points of this paper.

Prolonged (up to 2 h) heat treatment at 1500, 1550, 1600 and 1650 °C of nanodiamond particles (5 nm) leads to their conversion to the mixture of quasi-spherical carbon onions and multi-shell polyhedral nanographites. This treatment changes structural properties of nanodiamonds.

Figure 3.1: The HRTEM images of nanographite with quasi-spherical carbon onions shape [6].

According to the high-resolution transmission electron microscopy (HRTEM) observation, the annealing at T>1600 °C transfers the nanodiamond particles into the quasi-spherical carbon
onions after the few minutes of process (Fig 3.1a) and no traces of nanodiamond cores were detected in the sample. Some onion-like particles which made up to 6-8 defective quasi-spherical graphitic shells are enclosed into one another with an average inter shell spacing of 0.34–0.39 nm. One of such particle is marked by arrow in figure 3.1 a. The smallest diameter 0.83 nm of the shell indicated by an arrow in figure 3.1 (a) that is as the small as the diameter 0.71 nm of the C_{60} molecules. Further graphitization produces the polyhedral multi shell nanographite particles with an empty core as the heat-treatment temperature or annealing time were increased (Figure 3.1d) [6].

3.2 Experimental work:

The experiment was conducted in physics department of Umea University. The samples were studied by the Renishaw1000 micro-Raman spectrometer by using the three different lasers; green, red and infrared laser.

Table.3.1 Lasers available in the Raman spectroscopy

<table>
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<th>Color</th>
<th>Laser</th>
<th>wavelength</th>
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<tr>
<td>Green</td>
<td>Argon ion</td>
<td>514 nm</td>
<td>2.41 eV</td>
</tr>
<tr>
<td>Green</td>
<td>Argon ion</td>
<td>488 nm</td>
<td>2.54 eV</td>
</tr>
<tr>
<td>Red</td>
<td>Helium-Neon</td>
<td>633 nm</td>
<td>1.96 eV</td>
</tr>
<tr>
<td>Infrared</td>
<td>Diode</td>
<td>785 nm</td>
<td>1.57 eV</td>
</tr>
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</table>

Raman spectrometer has the 5x, 20x, 45x and 50x lenses. In this experiment mostly 20x and 50x lens were used for the characterization of nanographite. Raman spectrometer was calibrated with Si wafer at about wavelength 520 cm\(^{-1}\).
All the samples were placed on the Si substrate for measurements. Each sample was measured at three different points to get the structural information of nanographite by using the argon laser. Similarly also measurements were done with Helium-Neon and diode lasers. The origin 8.5 and PeakFit software was used for analysis of spectra. In the PeakFit software the Voigt function was used to analyze the peaks in the spectra of samples.
4. RESULTS AND DISCUSSION

The D and G band at ~1350 cm$^{-1}$ and ~1590 cm$^{-1}$ indicates the presence of $sp^2$ phase. The D band is the disordered graphitic lattice (graphene layer edges) with the $A1_g$ symmetry. The presence of D peak is defined as the rate of the disorder and shape. The G peak reflects more graphitic planes [31]. Here disorder means the presence of elastic scattering sources for phonon and electron systems. The perfect crystal with finite size (with size smaller than the mean free path of electrons or phonons) shows the D band, here the domain boundaries can be considered as the defects or disorder that is scattering the phonon and electron. The G peak is shifted to ~1582 cm$^{-1}$ at temperature 1650 °C that is graphitic lattice with $E_{2g}$ symmetry. The D´ peak at ~1618 cm$^{-1}$ is also produced in sample 1650 °C. The dispersion peak at ~1360 cm$^{-1}$ is the extra peak in first order spectra of nanographite [32].

The 1st order Raman spectra of nanographite approximately have the same result of green laser at energy 2.41 eV as explained at energy 2.54 eV. The D peaks (disordered induce band) appeared at ~1343 and ~1345 cm$^{-1}$ respectively and bands at ~1596 and ~1595 cm$^{-1}$ were very close to the G band for nanocrystalline graphite as shown in figure 4.2. This G band has a higher frequency than the G peak of oriented pyrolytic graphite at ~1582 cm$^{-1}$ as produced in sample 1650 °C. This means that sample 1650 °C has more planner, oriented and more graphite like structure. At temperature 1650° C, the D´ peak was ~1612 and ~1615 cm$^{-1}$ at 488 and 514 nm respectively. The presence of D peak determined the amount of disorder and G peak determined perfection of graphene layers. Both temperatures (1500 and 1600 °C) showed different increasing and decreasing trend in both bands at different laser treatments (i.e. 488 and 514.5 nm). However, more intensity was observed in D band when subjected to wavelength of 514 nm laser treatment under both temperatures. But under influence of 488 nm laser treatment both peaks behave differently on above mentioned temperatures. So in this regard G peak showed higher intensity at 1500 °C while at 1600 °C, no significant difference in both bands was recorded. Under 1550 and 1650 °C, both peaks also behave differently when subjected to 488 and 514 nm. At 1550 °C both peaks were at same level by applying laser wavelength 488 nm while a little bit increase was observed in G peak. However, when material was subjected to 514 nm laser treatment, a little bit more intensity in G band was recorded under both (1550 and 1650
°C) temperatures. This means that there is higher perfection of graphene layers present. So, overall it was concluded that the graphene bands are temperature as well as laser dependent.

Table 4.1 Crystalline sizes \( L_a \) according to Tuinstra and Cancado at different laser energies

<table>
<thead>
<tr>
<th>Samples</th>
<th>Green (2.54 eV)</th>
<th>Green (2.41 eV)</th>
<th>Red (1.96 eV)</th>
<th>Infrared (1.57 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ratio ( (I_D/I_G) )</td>
<td>Cancado (nm)</td>
<td>Ratio ( (I_D/I_G) )</td>
<td>Tuinstra (nm)</td>
</tr>
<tr>
<td>1500</td>
<td>1.78</td>
<td>7.5</td>
<td>0.99</td>
<td>4.3</td>
</tr>
<tr>
<td>1550</td>
<td>1.26</td>
<td>10.62</td>
<td>1.60</td>
<td>7</td>
</tr>
<tr>
<td>1600</td>
<td>1.36</td>
<td>9.81</td>
<td>0.94</td>
<td>4.1</td>
</tr>
<tr>
<td>1650</td>
<td>1.38</td>
<td>9.68</td>
<td>1.35</td>
<td>5.9</td>
</tr>
</tbody>
</table>

The results calculated by using the Tuinstra and Cancado formulas gave quite different values. The green laser exhibited different values of \( L_a \) at different temperatures. It was suggested that \( I_D/I_G \) depends strongly on the excitation laser energy used in the Raman experiment. Tuinstra formula is only valid when we conduct an experiment by using the laser level 514 nm (2.41 eV) [33, 34]. The green laser (514 nm) shows that the samples at 1500 and 1600 °C have small crystalline size as compared to samples at 1550 and 1650 °C. It is related to the large \( sp^2 \) hybridization in samples at both (1550 and 1650 °C) temperatures. The green laser has shorter wavelength that can only probe the surface of the materials. The red and infrared laser gave the larger crystalline size values because they can probe the depth of nanographite due to larger wavelength.
Figure 4.1 The 1st order spectra of all samples with the blue laser (488nm).
Figure 4.2 1st order spectra of samples after peak analysis in the PeakFit at 1500-1650 °C.
Figure 4.3 The 1st order spectra of all samples with the Green laser (514nm).
Figure 4.4 1\textsuperscript{st} order spectra of samples after peak analysis in the PeakFit at 1500-1650 °C.
Figure 4.5 The 1st order spectra of all samples with the Red laser (633 nm).
**Figure 4.6** 1st order spectra of samples after peak analysis in the PeakFit at 1500-1650 °C.
**Figure 4.7** 1\textsuperscript{st} order spectra of all samples with the infrared laser (785 nm).
Figure 4.8 1\textsuperscript{st} order spectra of samples after peak analysis in the PeakFit at 1500-1650 °C.
Table 4.2 The FWHM of D and G bands at different laser energies

<table>
<thead>
<tr>
<th>Samples</th>
<th>Blue (2.54 eV)</th>
<th>Green (2.41 eV)</th>
<th>Red (1.96 eV)</th>
<th>Infrared (1.57 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Band width (FWHM), cm⁻¹ for D band</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>104</td>
<td>50</td>
<td>68</td>
<td>80</td>
</tr>
<tr>
<td>1550</td>
<td>73</td>
<td>89</td>
<td>62</td>
<td>73</td>
</tr>
<tr>
<td>1600</td>
<td>55</td>
<td>51</td>
<td>88</td>
<td>75</td>
</tr>
<tr>
<td>1650</td>
<td>56</td>
<td>41</td>
<td>61</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>Band width (FWHM), cm⁻¹ for G band</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>70</td>
<td>78</td>
<td>80</td>
<td>61</td>
</tr>
<tr>
<td>1550</td>
<td>78</td>
<td>81</td>
<td>63</td>
<td>68</td>
</tr>
<tr>
<td>1600</td>
<td>72</td>
<td>76</td>
<td>69</td>
<td>67</td>
</tr>
<tr>
<td>1650</td>
<td>40</td>
<td>43</td>
<td>61</td>
<td>60</td>
</tr>
</tbody>
</table>

The full wave half maximum (FWHM) of D bands behave differently at 514 nm. A variation in FWHM at different temperature was noticed at different laser treatments as shown in above table. However, more decrease in FWHM of D band was recorded at 1650 °C. The decrease in FWHM of D band means that there is less disorder in the material. The nanographites at this temperature (1650 °C) behave in same manners at all laser treatments. The FWHM of G band also decreases and this decrease ranges from 78 cm⁻¹ to 43 cm⁻¹ at 514 nm. This decreasing trend in FWHM of G band was similar under all laser treatments which are mentioned in the above table. In basal planes the characterization level of graphitization is linked with specific parameters of nanocarbons like FWHM of both D and G bands. This means that there is a higher degree of graphitization if D and G bands are more constrict. The FWHM of G-band and $I_D/I_G$ ratio for multi-shell nanographites are almost highest compared to other graphitic materials with well developed π-electronic system. The crystalline sizes of the nanographites at different temperatures are extremely small as compared to other graphitic materials with well-developed π-electronic network [1].

The dispersion peak of D band on red laser (633nm) was produced at ~1309, ~1319, ~1316 and ~1321 cm⁻¹ as mentioned in figure 4.4. These disorders induced peaks are slightly lower than the
as observed by Tan et al. (2011) for turbostratically stacked structures (TS). The G band peak positions are different in all samples but they are very close to the ~1590 cm\(^{-1}\). The D and G band positions are changed on red laser (633 nm). It is related to the change of wavelength of the laser treatments and temperature variations. At 1650 °C red laser induced D´ peak was at ~1619 cm\(^{-1}\) that is strongly referred to the more oriented and microcrystalline graphite structure [35].

Raman spectrum of nanographite with infrared laser (785nm) is shown in figures 4.8. The D and G bands appeared at ~1300 cm\(^{-1}\) and ~1598 cm\(^{-1}\) respectively. The spectra with the infrared laser (785 nm) of all samples showed similar trend with a little bit differences in peaks. For example, the D peaks of have the lowest peaks value than the D peaks at green (488 nm and 514 nm) and red laser (633 nm). But the trends of G bands were approximately same at all mentioned laser treatments. Here the intensity of D band is also greater than the intensity of the G band in all samples of nanographite (figures 4.8). The peaks related to nanodiamonds are very well seen in Raman measurements. They are not only seen at the green laser line and also observed at red and infrared laser.

The peaks around 470 and 625 cm\(^{-1}\) were observed in turbostratic stakes. In the nanographite these peaks belongs to the density of phonon states (PDOS) in the LA and TA mod branches [36]. The peak position 620 cm\(^{-1}\) has shifted upward by 8 cm\(^{-1}\), 4 cm\(^{-1}\), 13 cm\(^{-1}\)and 15 cm\(^{-1}\) at temperature 1500 °C, 1550 °C, 1600 °C and 1650 °C respectively as it was observed at 620 cm\(^{-1}\) by Osipov et al. (2011). The appearance of dispersion peaks around 830 cm\(^{-1}\)was described as PDOS. It is assigned to the intra-valley out of plane tangential optical (oTO) phonon branches, it is counterpart with the auto phonon close to the \(\Gamma\) point and its activity is due to the plane curvature [37]. This peak has shifted downward by 15, 17, 20 and 16 cm\(^{-1}\) in samples at 1500, 1550, 1600 and 1650 °C respectively as was presented at 840 cm\(^{-1}\)by the Osipov et al. (2011). These peaks in the lower region frequency have very weak intensities. The first peak has higher frequency while the second and third peaks have lowest frequency that is observed in the carbon onions. These peaks are related to the relaxation of the Raman selection rule that might be caused by the curvature of graphene planes in the shell [38].
Figure 4.9 Second order Raman spectra at energy 2.41 eV.
Figure 4.10 Second order Raman spectra at energy 2.54 eV.
Figure 4.11 Second order Raman spectra at energy 1.96 eV.
The second ordered Raman spectra of four different samples of nanographite at energy 2.41 eV and 2.54 eV are shown in figures (4.9, 4.10) respectively. These spectrums are to the overtone caused by the defects resulting from double resonance Raman process. It was fitted by several Voigt curves. The 2D band originates from a two phonon double resonance Raman process [39]. Sometimes the 2D band is also named as G band as it is a second most well-known band of graphite [40]. Here it is referred as 2D band because it is the second order overtone of the D band. The 2D band at 2680 cm\(^{-1}\) and 2679 cm\(^{-1}\) was recorded as overtone of the disorder induced band at 1343 cm\(^{-1}\) in sample at temperature 1500° C and 1550° C. The peaks 2686 cm\(^{-1}\) and 2699 cm\(^{-1}\) which were produced are the overtone of the disordered at 1345 cm\(^{-1}\) at temperature 1600 °C and 1650 °C respectively. The D+G modes were observed at 2941 cm\(^{-1}\), 2931 cm\(^{-1}\), 2932 cm\(^{-1}\) and 2947 cm\(^{-1}\) at previously nominated temperatures. The presence of D+G bands indicates the structural disorder in the sample as well [31].

The peak at 2489 cm\(^{-1}\) (at 2.41eV) linked to the blend of oTo phonon and iLo phonon near the \(\Gamma\) point by a strong curvature of graphene sheet in the study of nanographite particles. This band shifted upward 13 cm\(^{-1}\) and 18 cm\(^{-1}\) in samples at 1500 °C and 1600 °C respectively and 20 cm\(^{-1}\) in materials at 1550 °C and 1650 °C as observed by Osipov et al. (2011) in diamond related materials at 2469 cm\(^{-1}\). The strong curvature of graphene sheets was also observed at other (2.54 eV and 1.96 eV) laser treatments but the peaks showed a little bit deviation from peak which produced at 2.41 eV. The 2D’ bands were also studied there at different points 3223, 3253, 3231 and 3242 cm\(^{-1}\) at different temperatures as shown in figure 4.9. These modes are related to scattering of non center optical phonons in the brillioun zone. It has a mixed character as it is neither longitudinal nor transverse optical or acoustic [41]. The 2G bands were produced at 3122, 3124, 3123, and 3175 cm\(^{-1}\). The modes at 2848, 2839, 2819 and 2863 cm\(^{-1}\) are natural with positive dispersion can be assigned to the combination of D and 1518, 1526, 1524 and 1525 cm\(^{-1}\) peaks respectively.

The peak at 1172-1195 cm\(^{-1}\) can be certified to hexagonal diamond or sp\(^3\) rich phase. The structure consists of both sp\(^2\) and sp\(^3\) bonding diamond like structure connected by the chain of different length and composition [31, 42]. As our samples are produced from nanodiamonds, this band may be due the disordered graphitic lattice, poylene, ionic impurities and can be assigned to the C=C and C-C stretching vibrational modes of a polyene like structure [43].
The bands were shifted in all samples to the higher position as observed at 1170 cm⁻¹ by Osipov et al. (2011). Then the 1170 cm⁻¹ band can be assigned to a local vibration mode of TPA-like chains which is most likely, weakly coupled with other phonon modes of the NG particle [31]. The bands of these peaks also become wider than observed by Osipov et al. (2011). All the peaks showed positive dispersion at different laser photon energies. However, these peaks are laser specific. It means peaks centered at different points at different laser photon energies. As mentioned above that these peaks showed variations at different laser photon energies. For example, sample which has temperature 1550 °C showed increasing and decreasing trend in peak with respect to different laser treatments. An increasing trend in peak was noticed at 1.57, 2.41 and 2.54 eV energy levels respectively. While at 1.96 eV a significant decrease in peak was recorded. But the other peaks having temperature 1500 °C and 1600 °C showed a little bit opposite trend as compared to peak with 1550 °C. Such as both peak showed increasing trend at 1.57 and 2.41 eV energies respectively. While a decreasing trend was observed at 1.96 and 2.54 eV energies levels respectively.

Figure 4.12 The 1172-1195 band position at different laser energies.
The variation of D band values with respect to laser energies. The D bands depicted approximately a linear positive dispersion relation. At energies 1.57, 2.41 and 2.54 eV the peaks levels were approximately at same points while at energy 1.96 eV peaks range was 1309-1321 cm\(^{-1}\). Such as the lowest peak was observed at 1500 °C and highest peak was produced at 1650 °C. All of this it is concluded that the ranges of peaks are temperature specific at laser photon energy 1.96 eV. At 1650 °C another band which we called D’ band was also noticed at all given treatments of laser. It may be due to the defects that is why D’ band is produced only in this sample. The large amount of disorder and resultant decrease in plain domain size (La) of the \(sp^2\) could give rise to the D bands.
The 2D band showed positive dispersion relationship. An increasing trend was observed in bands. At 1.96 eV peaks range was 2616-2648 cm\(^{-1}\). The ranges of peaks were 2680-2699 cm\(^{-1}\) and 2693-2705 cm\(^{-1}\) at 2.41 eV and 2.54 eV respectively.

In second order spectra it was concluded that the peaks were laser as well as temperature specific. Remarkable variations in levels of bands were also recorded with respect to different temperatures. At 1.96 eV, the peak with 1500 °C centered at lowest value while sample with temperature 1650 °C centered at highest peak level. The peaks with temperature 1500 °C and 1550 °C exhibited the lower most peak points at laser energy 2.41 eV. However, at laser energy 2.54 eV all peaks were originated at same point except the peak having temperature 1650 °C. It was noticed that peak with temperature 1650 °C occupied highest peak values in the graph. The graph of second order spectra showed the variations in peaks with respect to temperature but this trend was clearly observed at 2.41 eV. Such as at this level of laser energy, the peak points showed increasing trend with an increase in temperature.
Figure 4.15 The D+G band position with respect to laser energies.

The structural disorder can be indicated additionally by the presence of D+G bands. The graph in the figure 4.15 shows different pattern of D+G peaks at different laser photon energies and different temperatures. The band with temperature 1650 °C presented the highest peak values at 1.96 eV and 2.41 eV. While at 2.54 eV energy level, a deviation in trend of peaks was noticed. At this energy level (2.54 eV) the band with 1600 °C exhibited the maximum peak value. The overall pattern of the D+G bands in graph showed that the bands are temperature specific at different laser photon energies.

Table 4.3 The amorphous carbon ratios in nanographite at laser energy 2.41 eV and 2.54 eV

<table>
<thead>
<tr>
<th>Samples</th>
<th>1500</th>
<th>1550</th>
<th>1600</th>
<th>1650</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser energy 2.41 eV</td>
<td>$I_{1516}/I_D$</td>
<td>$I_{1526}/I_D$</td>
<td>$I_{1524}/I_D$</td>
<td>$I_{1525}/I_D$</td>
</tr>
<tr>
<td>Ratio</td>
<td>0.31</td>
<td>0.57</td>
<td>0.26</td>
<td>0.08</td>
</tr>
<tr>
<td>Laser energy 2.54 eV</td>
<td>$I_{1542}/I_D$</td>
<td>$I_{1527}/I_D$</td>
<td>$I_{1524}/I_D$</td>
<td>$I_{1522}/I_D$</td>
</tr>
<tr>
<td>Ratio</td>
<td>0.68</td>
<td>0.27</td>
<td>0.18</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The dispersion peak 1525-1542 cm$^{-1}$ can be assigned to the amorphous carbon. It exists in the form of interstitial defects outside the planes of aromatic rings with $sp^3$ links or to odd-membered
ring structures which are also expected in the nanographite particles [31]. According to the Dallas the presence of five membered or seven membered rings with vibration modes at 1529 cm\(^{-1}\) and 1531 cm\(^{-1}\) linking the nanocrystalline aromatic regions is explanation for this band appearance [44]. The ratio of this band and relative intensity of D or G band peaks indicated the relative contact of amorphous carbon in the disordered graphite. The values of ratio \(I_{1518-1542}/I_D\) for different samples presented in table 4 indicate the reduction of amorphous carbon contact with increasing of temperature 1500 to 1650 °C with heat treatment detonation nanodiamonds. The downward shift is caused by bond angle disorder present in the \(sp^3\) bonded fractions, which forces the graphene sheet to be nonlinear or it may be due to the decrease of holes carriers in the sample [45].

**Figure 4.16** The band positions between 1525-1542 at different laser energies.

The figure 4.16 shows the ratio of amorphous carbons at different temperatures with respect to laser treatments. The peaks with temperature 1550 and 1600 °C showed variations in the level of peaks at different laser photon energies. The peak with temperature 1550 °C exhibited the maximum value at laser energies 1.96, 2.41 and 2.54 eV. But at energy 1.57 eV highest value was observed in peak of 1600 °C. While an opposite trend was noticed in peak with temperature 1600 °C. However, peak with 1650 °C exhibited a different trend. It showed the minimum peak values at all laser treatments except the 1.96 eV. These lowest peak intensities indicated that
higher temperature improved the perfection of graphene sheets and reduced the concentration of point like defects in nanographite.

**Figure 4.17** Raman spectra of D and G bands of nanographite at 514 and 488 nm.
Figure 4.18 Raman spectra of D and G bands of nanographite at 785 and 633 nm.
The figure 4.17 and 4.18 shows the pattern of D and G bands at laser wavelength 514 nm, 488 nm and 633 nm, 785 nm respectively. At 514 and 488 nm the width of D bands constricts more and more from lower to higher temperature. Such as the peak with temperature 1500 °C was less narrow as compared to peak at 1650 °C. The constriction of the peak at higher temperature showed the more perfection of particles of nanographite. The peaks at 785 and 633 nm also showed the deep valley but the behavior was irregular with respect to temperature.
5. SUMMARY AND CONCLUSIONS
Raman spectroscopy is a very useful technique to characterize the structural properties of nanocarbons. This experiment was conducted to analyze properties of nanographite. The structural properties of nanographite were noticed at different temperature as well as laser treatments. Different laser treatments were applied to nanographite to assess the structural properties and perfection of nanographite. Positive results were observed by characterizing the nanographite. The range of perfection varies with variations in the temperatures. However, more perfect form of nanographite with well arranged graphene sheets was gained at highest temperature treatment. So from this experiment it was concluded that more perfection in nanographite could be acquired by giving heat treatments.

It was concluded:
I. Temperature-induced changes from nanodiamonds to nanographite at all temperature, particularly observed in sample with temperature 1650 °C which showed more planner, oriented and graphite like structure.
II. Temperature-mediated reduction in integrated intensity of 1523 cm\(^{-1}\) strongly linked with the improvement of crystal perfection of graphene sheets near the edges and mitigation of point like defects.
III. Slight decrease of D band width with heat treatment temperature was resulted which means that particles become less defective and more crystalline.
IV. The strong curvature of graphene sheets in second order spectra were additionally noticed at different temperatures.
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