STUDY OF NANOCRYSTALS USING FIBER BASED FOURIER TRANSFORM INFRARED SPECTROMETER

A project Report

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Dedicated to . . .

My parents

For providing moral support and love

&

My Wife, Meera

For her patience and encouragement

THESIS CERTIFICATE

This is to certify that the thesis entitled "**STUDY OF NANOCRYSTALS USING FIBER BASED FOURIER TRANSFORM INFRARED SPECTROMETER"** submitted by **B. Vinoth** to the Indian Institute of Technology, Madras for the award of the degree of Master of Technology is a bonafide record of research work carried out by him under my supervision. The contents of this thesis, in full or part, have not been submitted to any other Institute or University for the award of any degree or diploma.

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(Dr. Shanti Bhattacharya)

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ABSTRACT

Fourier Transform spectroscopy (FTS) is a technique for determining a spectrum of a sample by taking Fourier transform (FT) of an Interferogram. An experimental set up of Fourier Transform infrared (FTIR) spectrometer is developed based on Michelson interferometer principle for analyzing the absorption and wavelength characteristics of polymer based Nano composite materials.

Source calibration was carried out using the standard Michelson interferometer based fiber Optical spectrum analyzer. A CD pick up head were used as one of the two mirrors of the standard setup and velocity of the mirror was estimated. A polymer based nanocrystal synthesis was carried out and the characterization was done by using the standard techniques like X-Ray diffraction (XRD) method and Scanning Electron Microscope (SEM) technique. The absorption and wavelength behavior of the synthesized nanocrystal in IR region is estimated by the developed spectrometer. FTIR technique is widely used in the analysis of broad, complex or extremely weak spectra, especially in the infra-red [IR] region. As a result, the technique has been extensively utilized in the fields of molecular IR spectroscopy, astrophysics, biomedical applications etc.

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Abbreviations and notations

FTS – Fourier Transform spectrometer

FT – Fourier Transform

FFT – Fast Fourier Transform

IR – Infrared

NIR – Near infrared

UV – ultraviolet

PbS – Lead Sulphide

QD_s – Quantum dots

SNR – Signal to noise ratio

GRIN – Graded index lens

OPD – Optical path length difference

RMS – Root mean square

OSA – Optical spectrum analyzer

XRD – X-Ray diffraction

SEM – Scanning Electron Microscope

FWHM – Full width half maximum

λ – Wavelength

$\Delta\lambda$ – Spectral width

l_c – Coherence length

T_c – Time taken by the mirror to cross the coherence length

T – Time taken by the mirror to cross one complete cycle

V_m – Velocity of the mirror

F_m – Mirror actuation frequency

D_m – Distance travelled by the mirror for one complete cycle

CHAPTER: 1 – INTRODUCTION

1.1 – THESIS OUTLINE

The present thesis describes the study of lead Sulphide (PbS) nanocrystals inside Nafion polymer film. A fiber based Fourier Transform infrared spectrometer is developed based on a Michelson interferometer principle, which can be used to estimate the absorption property and wavelength behavior of the sample. Source calibration was carried out using a standard Michelson interferometer based fiber optical spectrum analyzer. A CD pick up head were used as one of the two mirrors of the standard setup and the velocity of the mirror was estimated. A polymer based PbS nanocrystal synthesis was carried out by using chemical synthesis method. To confirm the formation of PbS nanocrystals, a standard X-Ray diffraction (XRD) technique is studied for the sample and the mean size of the synthesized PbS nanoparticle size is estimated to be 9.8 nm. An optical absorption study of both the base (pure Nafion film) and the sample (PbS nanocrystals inside the nafion film) was carried out. Standard microscopic imaging techniques like scanning Electron Microscope (SEM) and confocal microscope techniques are used to view the PbS nanocrystals. The optical absorption behavior for the pure nafion film and PbS nanocrystals is studied over the range of 200 to 2000 nm. Finally the absorption and wavelength behavior of the synthesized PbS nanocrystal inside the Nafion film in IR region is estimated with the developed spectrometer.

1.2 – INTERFERENCE PRINCIPLE

Interaction (superposition) between the waves traveling in the same medium is called interference. Consider two waves, which overlap as shown in fig.1.1; constructive and destructive interferences will happen depending on the phase difference between the waves. Interference effects can happen in all types of waves, for example light, acoustic, radio and surface water waves. In this thesis, we use light wave interference [1-3].

1.2.1 – CONDITION FOR INTERFERENCE

The conditions for interference to occur in light waves are

a). Coherent Source

The phase of the two interfering waves should be constant with respect to each other. For example, if two waves are phase shifted by π, this must not change with respect to time.

b). Monochromatic source

A narrow band source should be used. Interference cannot be observed from the light emitted from incandescent light bulb because it is highly incoherent.

In constructive interference, amplification of the waves will happen, when the phase between the two waves match with each other, if the crests and crests or trough and trough of the waves coincide with each other. Consider two waves (fig: 1.1), traveling on same medium in the same directions. When these crests of two waves come into contact, the resulting amplitude will be the sum of the two waves.

Destructive interference results in the cancellation between two waves when they out of phase with each other. Consider two waves (fig: 1.2) traveling in same medium in the same direction, the resulting amplitude will be the difference of the two waves.

Consider two travelling waves moving in space

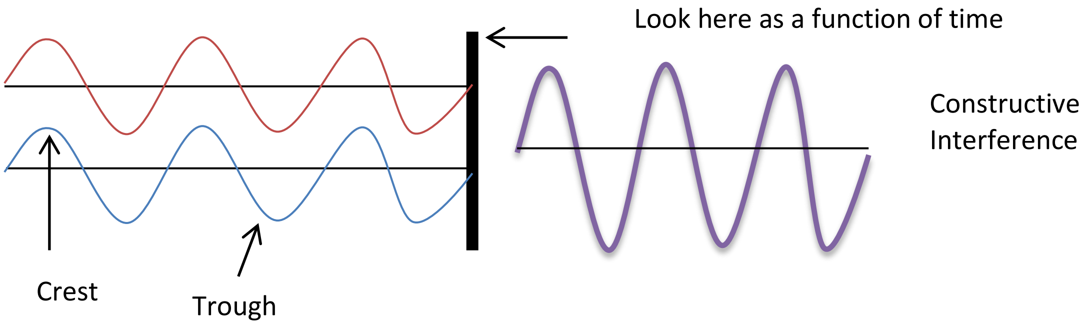

Fig: 1.1. Constructive interference of two waves

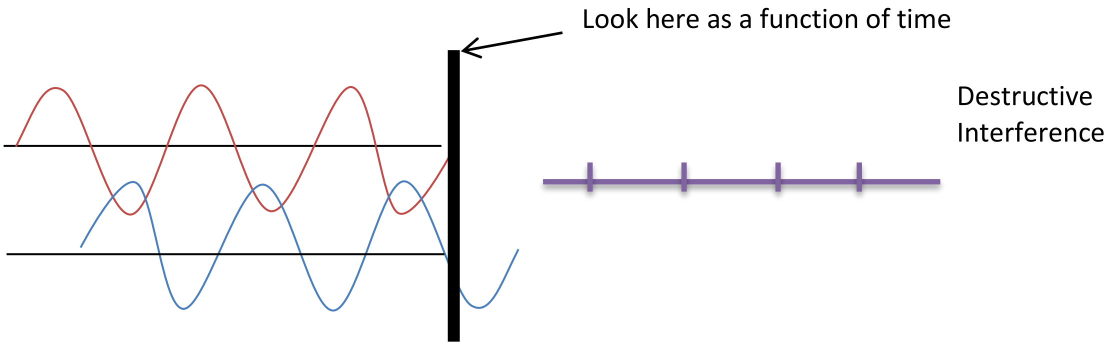

Fig: 1.2. Destructive interference of two waves.

1.3 – MICHELSON INTERFEROMETER

1.3.1 – BACKGROUND

Albert A. Michelson first set up an interferometer in 1881. With this experiment, he could explain the concept of interference, for which the setup is named Michelson Interferometer. The Michelson interferometer is a setup, which splits the amplitude of a wave into two and then overlaps them to create an interference pattern at the detector.

1.3.2 – THEORY

The Michelson interferometer technique is used to generate an interference pattern between two waves. A diagram of the typical free space schematic setup is shown in Fig. 1.3. The interferometer will work as follows; a Light beam from the source is split into two parts by using the beam splitter, a part of wave travels different optical path length than the other part of a wave. After travelling these different path lengths, the two parts of the light are combined together with the same beam splitter and the interference pattern can be seen at the detector.

The source light splits into two with the use of a 50/50 beam splitter. Of the two beams, one is allowed to fall on the fixed mirror (M_1) and the corresponding distance travelled to reach M_1 is L_1; the other signal will travel a different path length L_2 and falls on the movable mirror (M_2). Initially the setup was arranged such that zero path length difference (ZPD) existed between the beams. Once the mirror starts moving, the optical path length will vary, hence an interference pattern will be observed at the detector end.

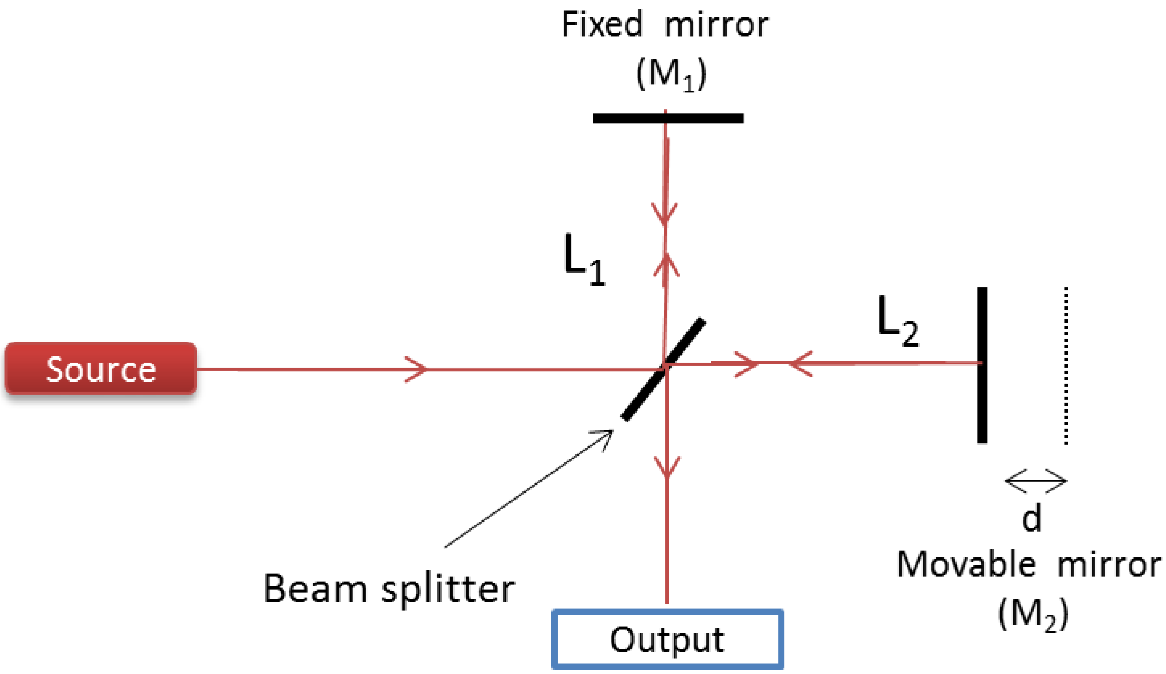

Fig: 1.3. Schematic of free space Michelson interferometer

1.4 – FOURIER TRANSFORM SPECTROMETER

Infrared spectrometers were first developed in the 1940's, using dispersive technology [1]. This had the disadvantage of low scanning speed, low throughput, low signal to noise ratio (SNR) and manual operations were needed. The range of Infrared region is 780 nm ~ 1 mm. It can be divided into near-infrared region (0.78 ~ 3 µm), mid-infrared region (3 ~ 50 µm) and far-infrared region (50 µm ~ 1 mm). To effectively utilize infrared light, initially researchers came up with a technique called infrared absorption spectroscopy. This is a technique used to determine the structures of molecules as their characteristic absorption occurs in the infrared (IR) region. Once the IR beam is passes through the sample, dipole oscillations of the molecules will take place. This causes absorption at a particular frequency since the vibrational energy transfers from the ground state to the excited state. The energy emitted could be either higher or lower depending on the sample characteristics.

After the 1950’s, the Fourier Transform Infrared (FTIR) spectrometer was developed and commercialized. Fourier Transform Infrared Spectroscopy is a spectroscopic technique which is used to analysis the absorption, emission, or scattering behavior of samples in either solid, liquid or gaseous states. Fourier Transform spectrometry (FTS) is a technique used to determine a complete spectrum of the sample by taking the Fourier transform (FT) of an obtained Interferogram. It is widely used in the analysis of broad, complex or extremely weak spectra, especially in the infra-red [IR] region. As a result, the technique has been extensively utilized in the fields of molecular IR spectroscopy and astrophysics, bio-medical applications [4-8].

1.4.1 – ADVANTAGES OF FTIR SYSTEM

The most important advantage of the FTIR system is multiplex or Fellgett advantage. In an FTS system the entire spectral region is scanned multiple times to produce a good quality spectrum. An FTS system captures an interferogram, which contains information of all the wavelengths simultaneously. FTS systems do not use a special filter or slits to limit the frequency components. A high Signal to Noise ratio (SNR) is obtained. Since no slits are used, all the radiation from the source will pass through the sample and, no tuning is required to capture a particular frequency [7, 8].

1.5 – NANO COMPOSITE CRYSTALS

Nanoparticles have an interesting surface property, which leads to varied applications in nonlinear optics, photonics, and information storages, etc.

The name nanocrystal or nano particle or Quantum dot (QD_s) is derived from the size of the particle. Nano particles typically have a size less than 100 nm, The rise of nanotechnology has led to many new and exciting applications. Particles are can be classified into coarse, fine and ultrafine particles based on their sizes. Particles between 2.5 µm to 10 µm in size are called coarse particles. Those between 2.5 µm to 100 nm are called fine particles and those between 1 nm to 100 nm are called ultrafine particle or nanoparticles or QD_s. When moving from bulk to nanoparticles, the material behavior will change completely, depending on the size synthesized [9-10]. Synthesizing and characterizing the nanoparticles to estimate the exact size of the particle is a challenging task.

1.6 – Synthesis of Nanocrystals – an overview

Experimentally the quantum confinement effect was first observed in Copper (I) chloride doped microcrystallites in silica glass. Later QD_s effect was reported in a large number of semiconductor materials like Gallium Arsenide, Cadmium Sulphide, Zinc Sulphide, etc. Their behavior was also found to be dependent on the size of the particles [10-13].

There are two basic approaches followed for nanoparticle synthesis. They are the top down and bottom up approaches. Etching bulk material to nanoparticle is called the top down approach, whereas using a chemical synthesis (atom by atom or molecule by molecule) method is known as the molecular nanotechnology or bottom up approach. Synthesis can also be classified as physical and chemical in nature. This thesis followed a chemical synthesis method explained in Chapter 3.

Synthesis nano particles are characterized using several sophisticated pieces of equipment. In this work, we attempt to show the benefit of using an FTS system to study nano-particles.

CHAPTER: 2 – EXPERIMENTAL SETUP OF SPECTROMETER

2.1 – INTRODUCTION

This chapter describes the developed spectrometer. It consists of seven sections. The first section (2.2) explains the principle of operation of the spectrometer; the second section (2.3) describes the main components used and the source characterization; third and fourth sections (2.4 & 2.5) are about the characterization of the movable mirror and the spectrometer; fifth (2.6) is about the resolution; the sixth (2.7) section explains the error analysis and finally (2.8) is followed by the results and discussions.

2.2 – PRINCIPLE OF OPERATION

Fiber based Fourier transform Infra-Red spectrometer (FT-IR) is a technique used to determine the unknown sample characteristics by analyzing the obtained FT of the interferogram. The FTIR spectrometer design is based on a Michelson interferometer. A schematic of the experimental setup is shown in fig 2.1. A low coherence IR beam is passed through a 50/50 splitter. It splits IR light into two beams of equal power, which travel into arm2 and arm3 of the interferometer respectively. At the end of arm2, a fixed gold coated reflector

(M_1) is placed and the other arm (arm3) has a movable gold coated reflector (M_2). Once the mirror starts moving, an optical path length difference (OPD) arises between the two arms. The reflected beam from both arms reaches arm4, and the resulting Interferogram is obtained at the detector [14].

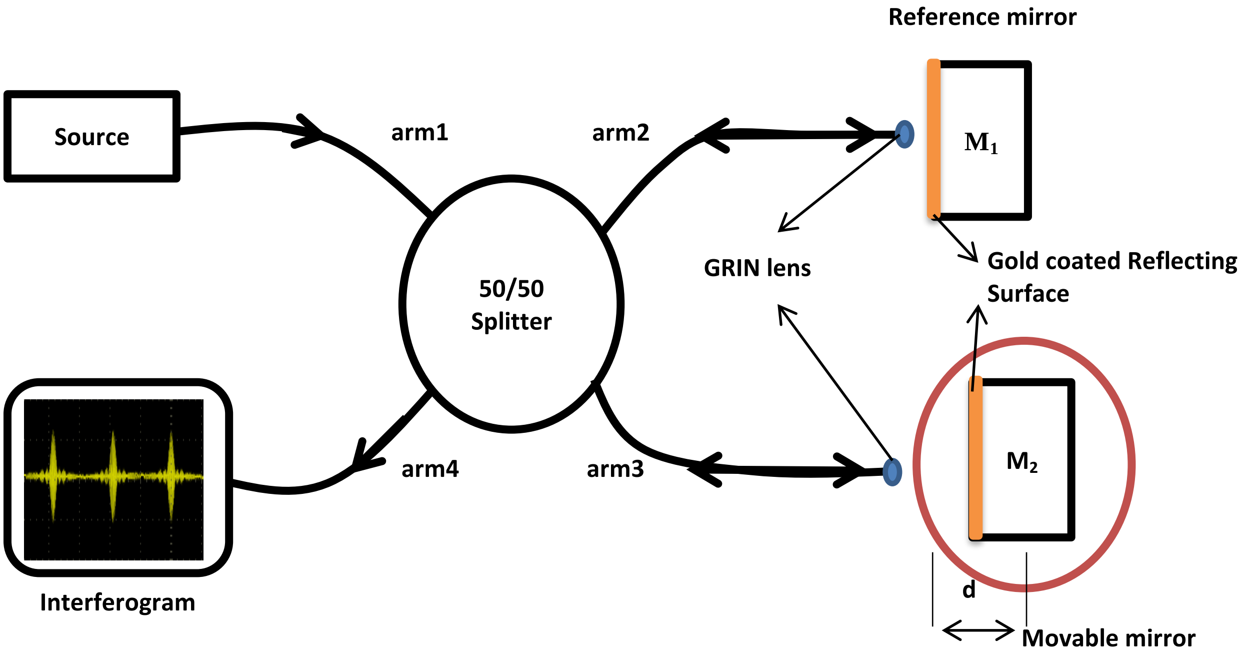

Fig: 2.1 - Schematic Diagram of All Fiber Fourier-Transform spectrometer.

The main components used to develop the fiber based Fourier transform spectrometer are discussed in detail in the next section.

2.3 – MAIN COMPONENTS IN FTIR SETUP

The following are the main components in the all fiber Fourier Transform infrared spectrometer development

1. Low coherence source
2. Single mode fiber
3. 50/50 coupler
4. GRIN lens
5. Fixed mirror (M_1) and movable mirror (M_2)

2.3.1 – LOW COHERENCE SOURCE

Lasers have very different properties compared to other light sources. One important property is that of coherence. This important feature of laser light can be expressed in terms of temporal coherence, which describes the degree of monochromaticity (narrow spectral width) of the light, and the spatial coherence, which describes the uniformity of phase across the optical wavefront. The coherence length (lc) is the average length of a light beam along which the phase of the wave remains predictable. The significance is that wave interference will be observable within a coherence length of the source, but not beyond it. Coherence length of the source is calculated (eqn. 2.1). Here the coherence length of the source was calculated by two methods. First, an Interferogram was obtained and varied, using a mirror mounted on a micrometer stage, till no pattern was seen. A typical trace is shown in fig 2.2.

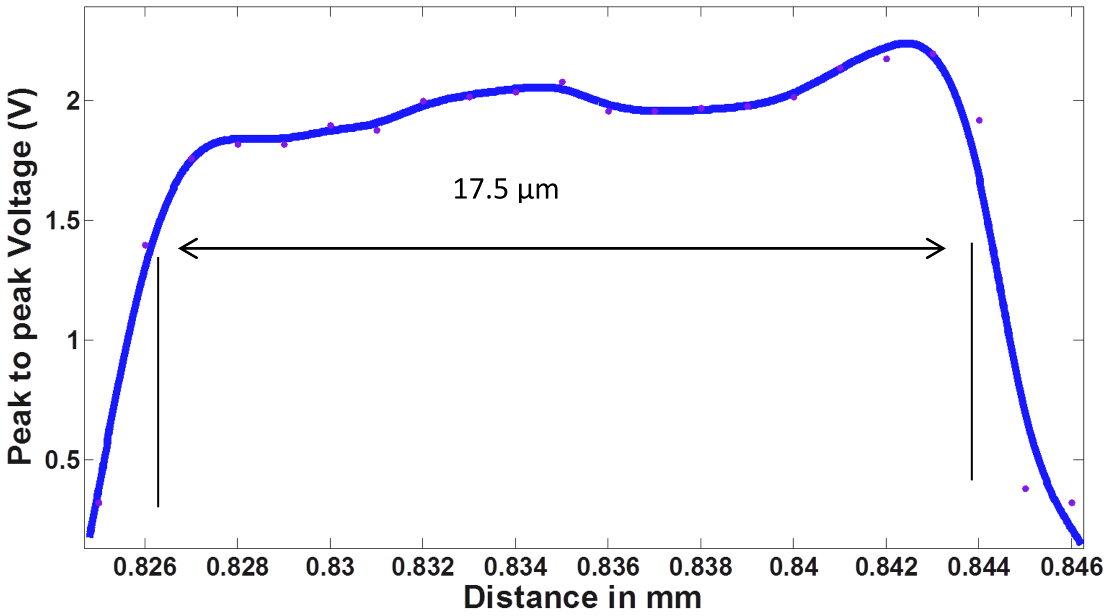

Fig: 2.2 - Distance adjustment (Manually) by using screw gauge vs obtained fringe peak to peak Voltage

From the above graph, the region where interference is observed can be seen. Using this graph, the coherence length of the source was calculated as 17.5µm. Second, the coherence length of the source was calculated by measuring the source spectral width with an optical spectrum analyzer (OSA). This is shown in fig 2.3.

From this figure, the center frequency (λ_c) is 1568.8 nm and the spectral width ($\Delta\lambda$) is 76.5 nm

The coherence length is given by [1],

$$l_c = \frac{2C \times \ln(2)}{\pi \Delta \gamma} = \frac{0.44\lambda^2}{\Delta\lambda} \qquad \text{------------- (2.1)}$$

Using the above formula, the coherence length of the source was estimated as (l_c) =14.5 µm.

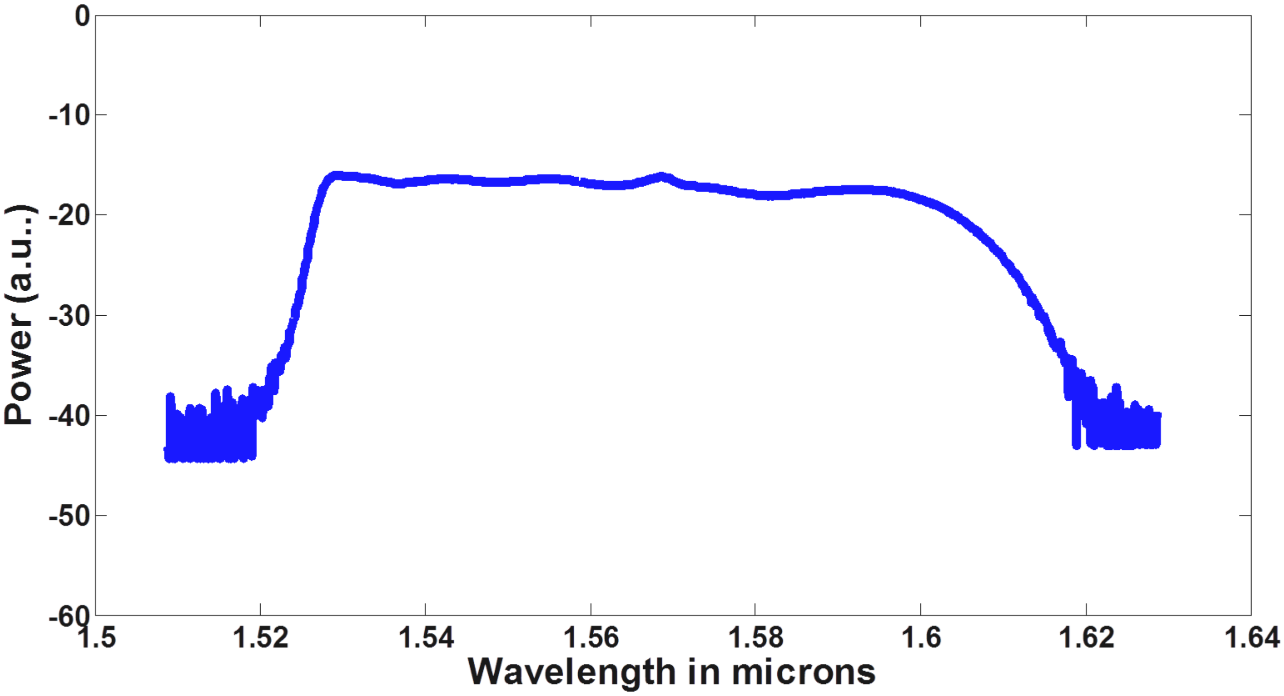

Fig: 2.3 - Spectral diagram of the broadband source captured from Optical Spectrum Analyzer

2.3.2 – FIBER USED: Single Mode Fiber SMF-24

2.3.3 – COUPLER

A 50/50 fiber coupler was used as a beam splitter in the Michelson's interferometer.

2.3.4. GRIN LENS

Graded Index (GRIN) lenses were used at the end of arm3 and arm4 for focusing of the beam on the vibrating mirror and effectively coupling the reflected beam back into the respective fiber.

2.3.5– MIRRORS

Gold coated reflectors M_1 and M_2 were placed at the end of arm 2 and arm3 as shown in fig.1. Out of these two reflectors M_1 is fixed and M_2 is movable one. A CD-pickup lens head with a mirror replacing the CD lens (fig.2.4) was used as the movable mirror. Characterization of the CD-pickup (M_2) was done and the results are discussed below.

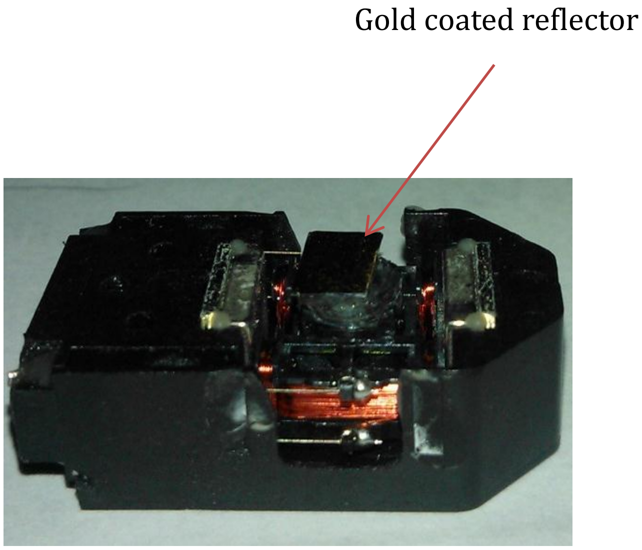

Fig: 2.4 – Image of CD-pickup head

2.4 – CHARACTERIZATION OF MOVABLE MIRROR (M_2)

A CD-pickup head from a CD drive was removed and used as a movable mirror. Initial characterization of the movable mirror M_2 was carried out so as to be able to fix the operating conditions of the mirror. The frequency; velocity of the mirror and amplitude of the mirror need to be fixed.

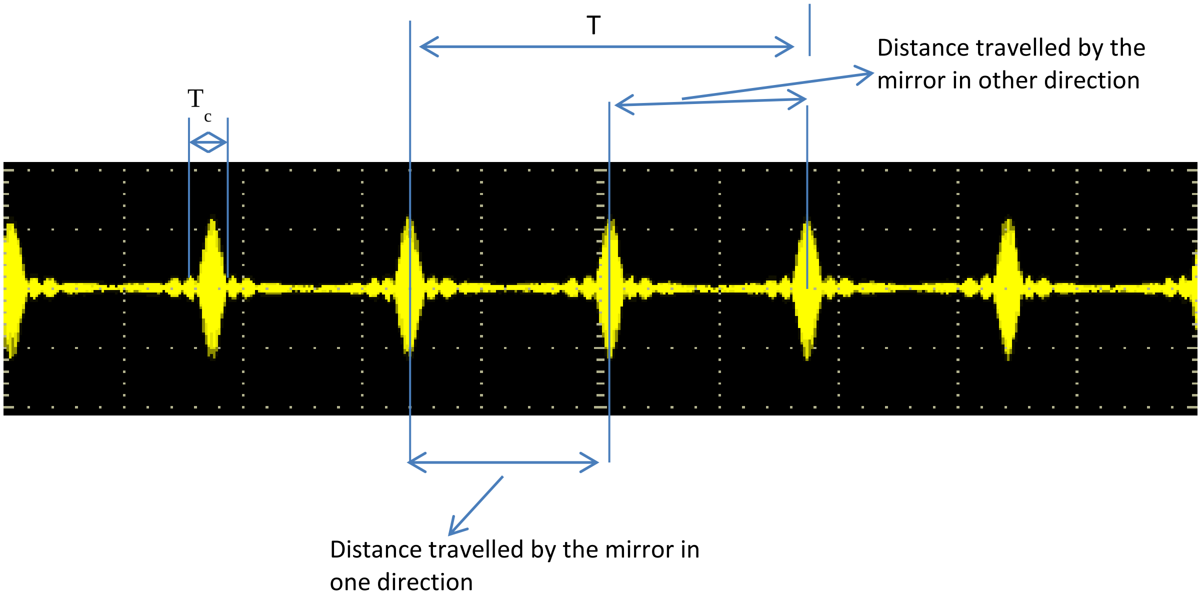

Fig: 2.5 - Obtained fringe pattern shows the time taken by the mirror to move one complete cycle (T) and the time taken by the mirror to travel the coherence length (T_c)

The characterization of movable mirror (M_2) was carried out with the help of the obtained interference fringe pattern. The velocity of the mirror is estimated in the following way.

The distance travelled by the mirror in one cycle is given by,

$$(D_m) = \frac{l_c \times T}{T_c} \,(\mu m) \qquad \text{------ (2.2)}$$

Therefore, the velocity of the mirror is given by,

$$(V_m) = D_m \times F_m \,(\mu m/sec) \qquad \text{------ (2.3)}$$

Where, l_c is the coherence length of the source (in µm), T is the time taken by the mirror to move one complete cycle (ms), T_c is the time taken by the mirror to travel the coherence length (ms) and F_m is the mirror actuation frequency (Hz)

The velocity of the mirror is calculated experimentally for different operating frequencies. This variation is given in Fig: 2.6.

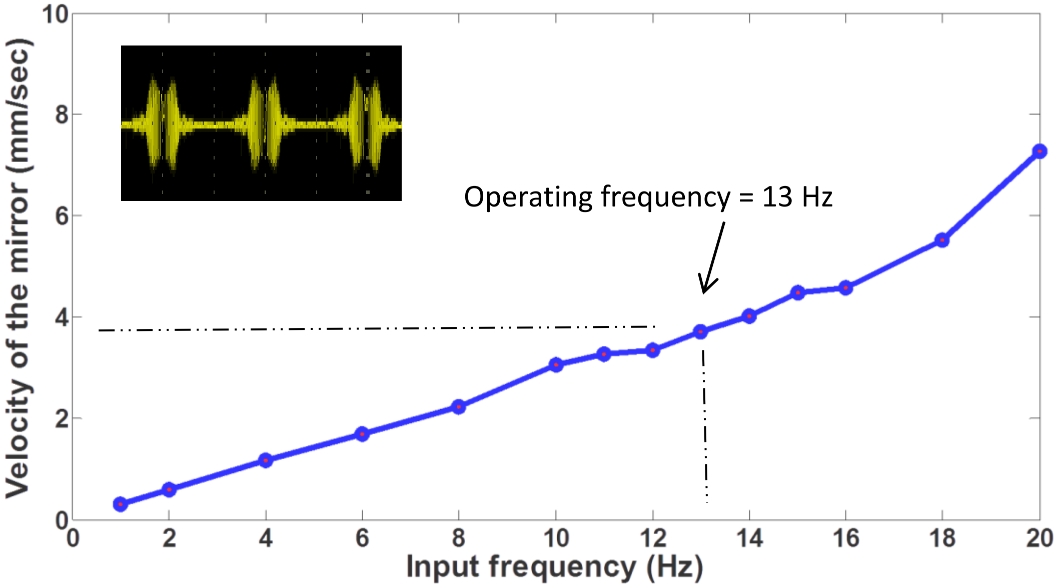

Fig: 2.6 - Mirror actuation frequency vs Velocity of the mirror. The inset shows the fringe pattern captured at different from operating frequency, where the pattern is not stable.

Here the operating frequency is fixed as 13 Hz with the mirror actuation voltage as 1 V and the corresponding mirror velocity (obtained using equation 2.3) as 3.82 mm/sec. This point was chosen, as the fringe pattern was found to be repeatable at these values.

2.5 - THEORETICAL VALUE OF RESOLUTION

Resolution in Frequency [1],

$$(\Delta F) = \frac{\text{Velocity of light}}{4 \times (\mathrm{D_m})} \qquad \text{- - - - - - - - - (2.4)}$$

Rewritting the equation (2.3)

$$\mathrm{D_m} = \frac{\text{Velocity of mirror}(\mathrm{V_m})}{\text{Mirror actuation frequency } (\mathrm{F_m})} \qquad \text{- - - - - - - - - (2.5)}$$

$$= \frac{3.821 \text{ mm/sec}}{13 \text{ Hz}}$$

$$\mathrm{D_m} = 293.92\ \mu\mathrm{m}$$

Substituting the D_m value in equation (2.4) gives,

$$\Delta F = 255.19 \text{ GHz}$$

Resolution in wavelength,

$$(\Delta\lambda) = \frac{\Delta F \times \lambda^2}{\text{Velocity of light}} \qquad \text{- - - - - - - - - (2.6)}$$

$$= 2.09 \text{ nm} \qquad \approx 2 \text{ nm}$$

The theoretical value of resolution was calculated as 2 nm. This can therefore, be taken as the minimum possible resolution of the developed spectrometer.

2.6 – CHARACTERIZATION OF SPECTROMETER

The spectrometer was initially calibrated using known wavelengths as input. Fig. 2.7 shows the variation in FT frequency, when the mirror was vibrated at different frequencies.

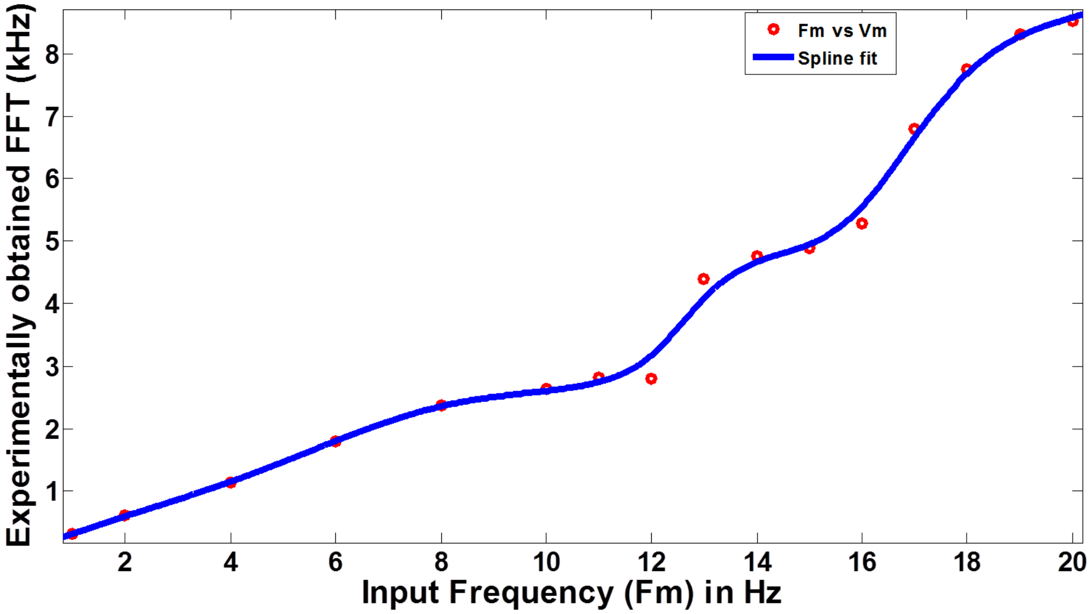

Fig: 2.7 - Mirror actuation frequency vs FFT.

Fig: 2.6 and fig: 2.7 confirm that different actuation frequencies will result in different FFT values.

The obtained fringe pattern when using a broadband source is shown in fig: 2.8, the corresponding time domain data was acquired from a Mixed signal Oscilloscope (MSO). Its FFT was calculated using Matlab and fig: 2.9 shows the same.

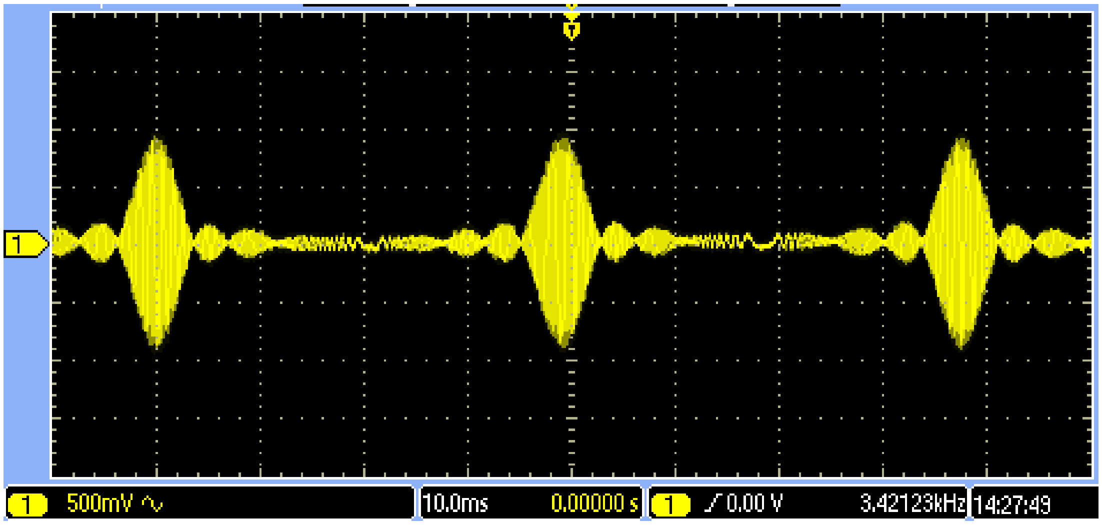

Fig: 2.8 - Obtained Fringe pattern with input mirror actuation frequency of

13 Hz with 1 V peak to peak.

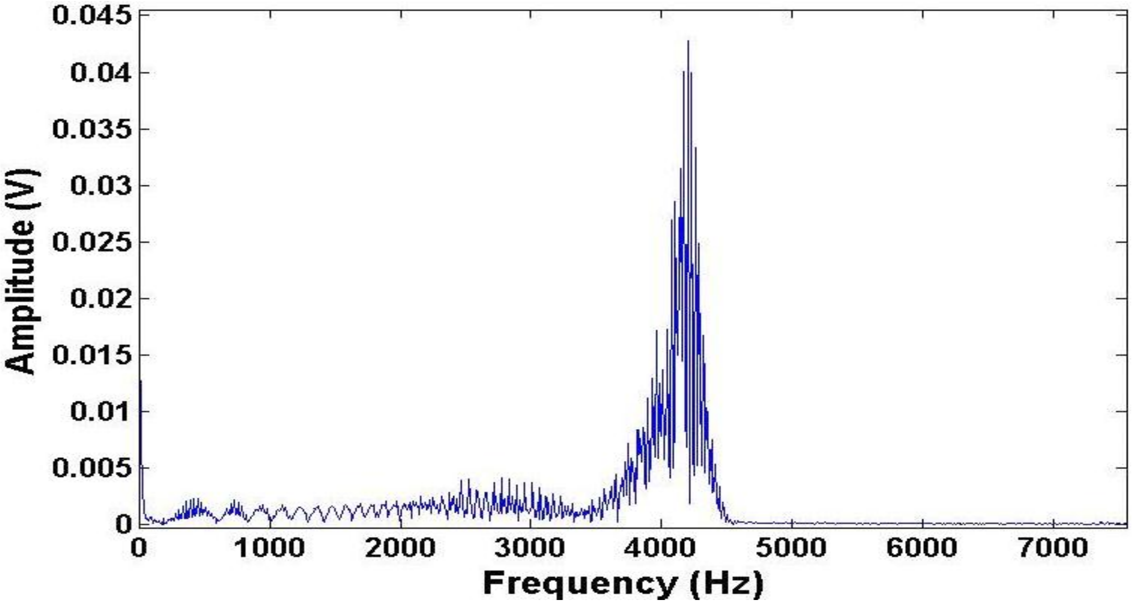

Fig: 2.9 – FFT plot corresponds to fig: 2.8

Once the Fast Fourier Transform (FFT) frequency is known, we can obtain the corresponding wave length by using the following identities.

$$\mathrm{FFT} = \frac{2 \times \mathrm{V_m}}{\lambda} \ (\mathrm{kHz}) \qquad \text{- - - - - - - - - (2.7)}$$

The unknown wavelength is therefore,

$$(\lambda_{\ (\mathrm{unknown})}) = \frac{2 \times \mathrm{V_m}}{\mathrm{FFT}} \ (\mathrm{nm}) \qquad \text{- - - - - - - - - (2.8)}$$

Where, V_m is the velocity of the mirror.

The time domain signal data is captured by using MSO and the FFT is calculated by using matlab, the smoothing and the fitting is done by using cftool option in matlab and the results are shown in fig: 2.11 & 2.13

2.7 RESULTS AND DISCUSSIONS

Different wavelengths given as input to the spectrometer and the back calculated wavelengths are tabulated below.

Different wavelengths like 1530 nm, 1550 nm and 1570 nm (assumed as unknown wavelength) were used to calibrate the spectrometer and the corresponding average Fast Fourier Transform (FFT) of 10 iterations was measured, calculated and tabulated (table 2.1) below.

Table: 2.1 – FFT and Calculated wavelengths for different input wavelengths.

Input wavelength (nm)	Average FFT of 10 iterations (kHz)	Back calculated wavelength (nm)
1530	5.008	1525.6
1550	4.959	1540.6
1570	4.825	1583.4

Two different wavelengths were coupled together using a 50/50 coupler and fed to the input of the spectrometer. The resulting interferogram is shown in Fig. 2.10.

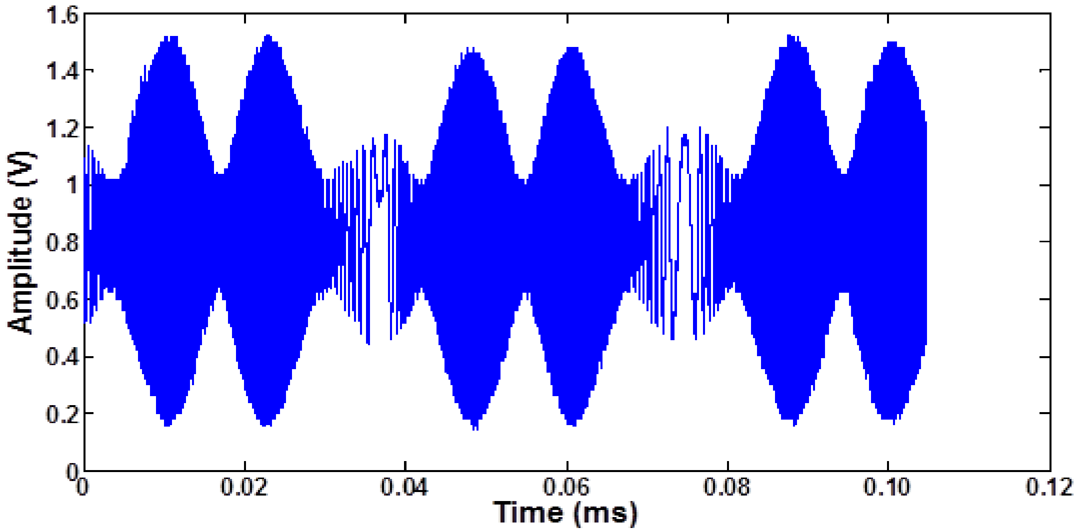

Fig: 2.10 - Obtained Interferogram of when two different wavelengths 1525 nm and 1550 nm , are present simultaneously.

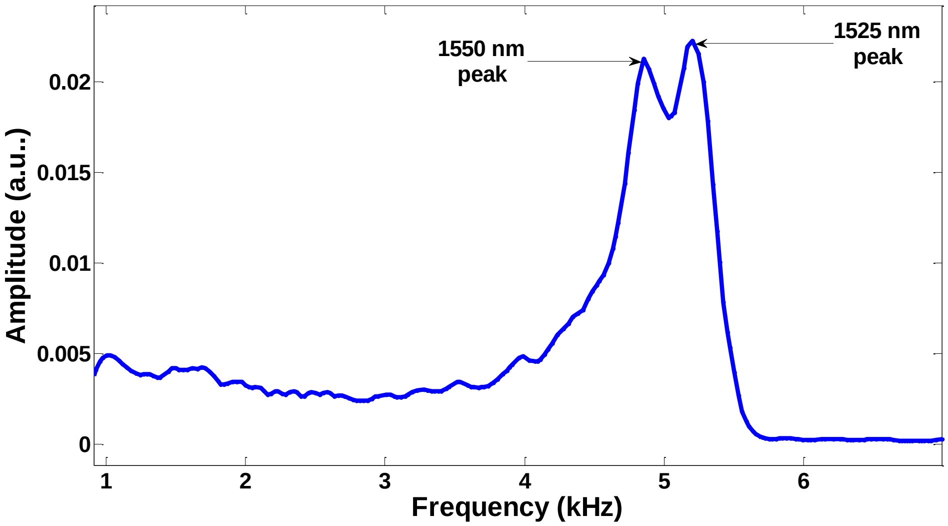

Fig: 2.11 Obtained FFT plot of fig: 2.10

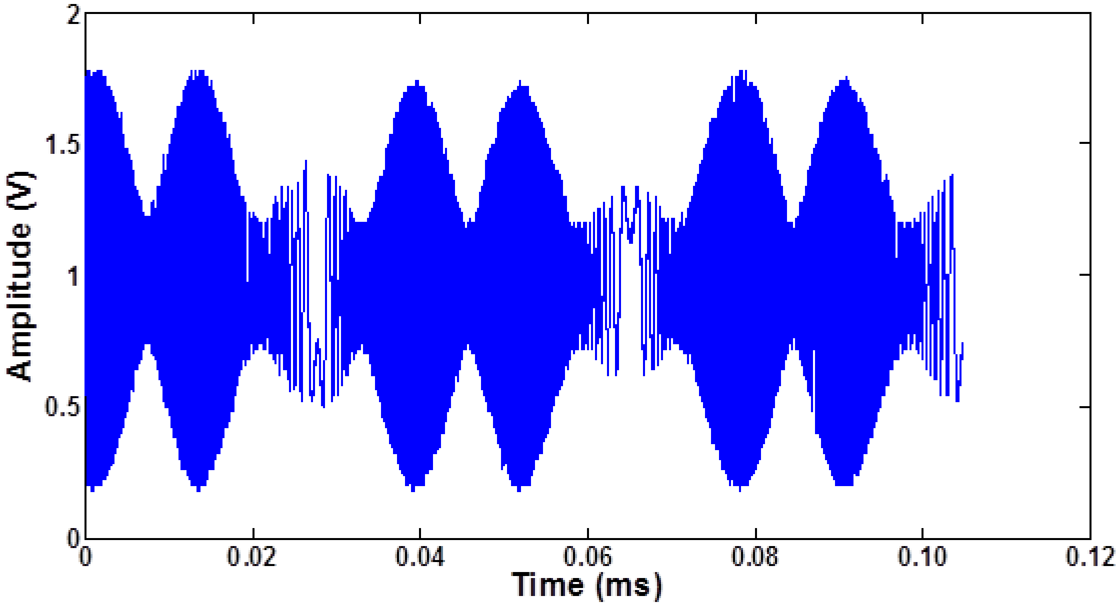

Fig:2.12 - Obtained Interferogram of when two different wavelengths 1550 nm and 1575 nm , are present simultaneously.

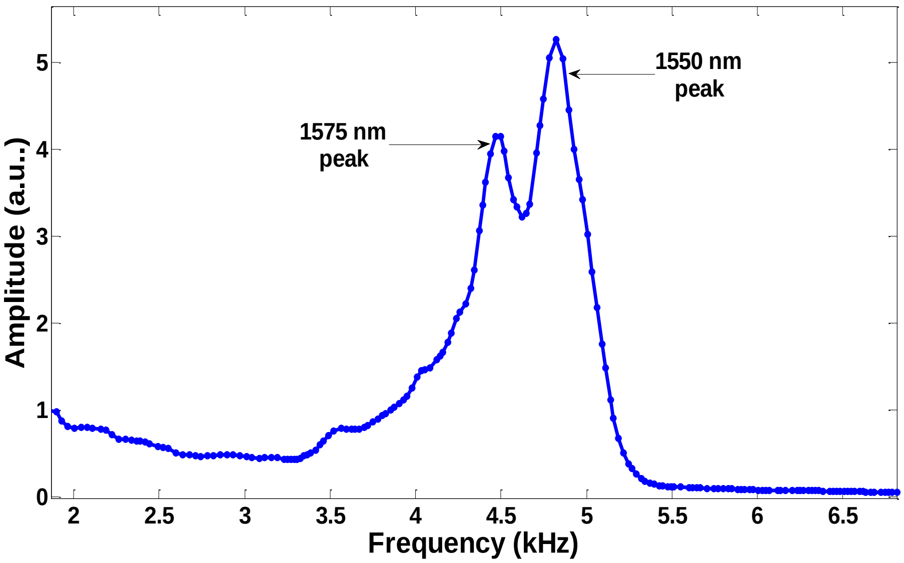

Fig: 2.13 - Obtained FFT plot of fig: 2.12

2.7.1 – Error Analysis

The possible parameter which affects the calculated wavelength will be the velocity of mirror. The minimum possible error in the velocity of mirror and the back calculated wavelength corresponds to the CD-pickup mirror were calculated and shown below.

From the known following formula,

$$\text{Wavelength } (\lambda) = \frac{2 \times V_m}{FFT} \text{ (nm)} \qquad \text{- - - - - - - (2.9)}$$

From equation (2.9) we can write,

$$\text{Velocity of mirror, } Vm = \frac{\lambda \times FFT}{2} \quad (\mu m/sec) \qquad \text{- - - - - - (2.10)}$$

To find the minimum error in velocity differentiate equation (2.10), will give

$$\Delta V_m = \frac{1}{2}\,(\lambda \times \Delta FFT + FFT \times \Delta\lambda) \qquad \text{- - - - - - - (2.11)}$$

To find the minimum error in back calculated wavelength, differentiate equation (2.9),

$$\Delta\lambda = 2\,\left(\frac{\mathrm{FFT} \times \Delta \mathrm{V_m} \ - \mathrm{V_m} \times \Delta\mathrm{FFT}}{\mathrm{FFT}^2}\right) \qquad \text{- - - - - - - - (2.12)}$$

2.7.2 - Calculations

The known values are shown below

Source wavelength	(λ) =	1550	nm
Velocity of the mirror	(Vm) =	3.820	mm/s
Average over 10 iterations	(FFT) =	4.90	kHz
Change in source wavelength	($\Delta\lambda$) =	0.50	nm
Change in FFT	(ΔFFT) =	10^{-9}	Hz

Substitute the known values in equation (2.11) will give the possible error in mirror velocity,

$$\Delta V_m = 0.5 \times (1550 \text{ nm} \times 10^{-9} \text{ Hz} + 4.90 \text{ kHz} \times 0.5 \text{ nm})$$

$$= 1.23\ \mu\text{m/sec}$$

Now the error in back calculated wavelength can be obtained from the equation (2.10)

$$\Delta\lambda = 2\ [(4.90 \text{ kHz} \times 1.23\ \mu\text{m} - 3.82 \text{ mm} \times 50 \text{ kHz})$$

$$= 0.5 \text{ nm}$$

The maximum possible error in the velocity of mirror was estimated as 1.23 µm/sec (0.03%) and the corresponding error in the calculated wavelength was estimated as 0.5 nm (0.03%)

CHAPTER: 3 – POLYMER BASED SYNTHESIS OF PbS NANOCRYSTALS

3.1 – Introduction

Nanomaterials have numerous advantages over the same material in bulk form; this is because of the particle size. Properties like the electric band gap, light interaction and the conductivity are quite different for materials in the form of nanoparticles [15,16]. As these properties vary with size, it becomes important to be able to control the size of the particle. This is achieved using templates. Typically templates and are made from polymers, zeolites or ceramic substrates. By using anyone of these as a template, one can obtain a stable matrix of nanoparticles.

The standard polymer template which is generally recommended for nanoparticle synthesis is Nafion because of it is optical transparency. It is commercially available as films. Nafion has thermal stability upto 200^0C [17-18]. The most accepted nafion model is an ionic cluster model (fig: 3.1), although researchers are still trying to understand its structure.

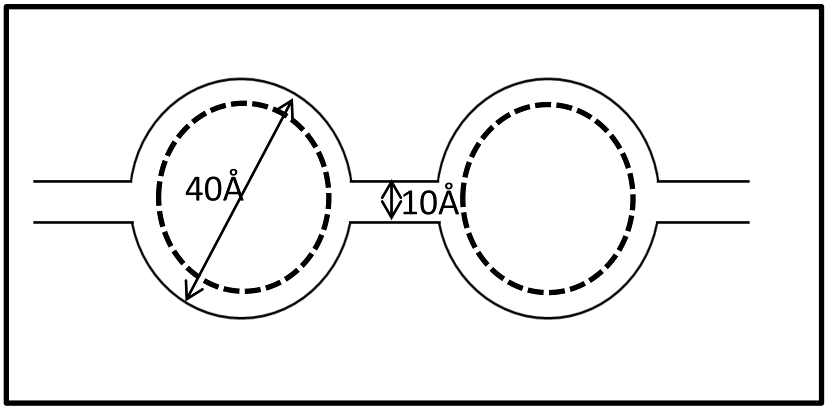

Fig: 3.1 – Cluster model for Nafion

3.2 – EXPERIMENT DETAILS

3.2.1 - CHEMICALS REQUIRED

Distilled water, Nitric acid (HNO_3), Lead (II) acetate trihydrate ($[CH_3COO]_2$ Pb), Thioacetamide (C_2H_5NS), Nafion film.

3.2.1 – EXPERIMENTAL PROCEDURE

Commercially available Nafion film with thickness of 0.18mm film is cut into 1 x 1 cm^2 area and boiled in nitric acid to remove all the impurities. The film is then washed with distilled water and dried with an air blower. The cleaned film looks completely transparent. 0.2M of lead (II) acetate trihydrate in 20 ml solution and an equimolar solution of Thioacetamide are made separately. Prepared solutions were mixed carefully and the nafion film was immersed in it. Two different samples were synthesized by changing the immersion properties as given in Table 1. As the PbS content increases, the color of the film varies (Fig: 3.2).

Table: 3.1 – Shows the sample prepared at different conditions

Sample name	S1	S2
Temperature	Room temperature	70^0 C
Immersion time (min)	10	60

The following figure shows the captured image of the film after synthesis of nanocrystals under different conditions.


(a) (b)

Fig: 3.2 – Color change in Nafion film on different immersion time

(a) Sample S1, (b) Sample S2

The sample S2 turns completely dark because of large amount of PbS deposition on it. Therefore, this sample cannot be tested with the developed spectrometer as it is designed for transmitted light from the sample (more details given in section 4). Hence, sample S1 is used for all the remaining experiments.

3.2.2 – MOLARITY CALCULATION

The number of moles of a solute per liter of a solution is the definition of concentration. The unit of concentration is molarity. In order to obtain a particular concentration, we need to calculate how many grams of salt are needed to get X molarity concentration.

$$\text{Gram needed per liter} = \mathrm{X} \times \text{molecular weight of the salt}$$

The atomic weights for the various elements involved are 207.2 for lead (Pb), 12 for carbon, 1 for hydrogen and 16 for oxygen. The molecular weight of lead acetate is therefore, calculated as,

Molecular weight of Lead acetate ($[CH_3COO]_2Pb$) = (12+3+12+32) × 2 + 207.2

= 325.2 g

Weight needed for 0.2M of Lead acetate in 20 ml = 0.2 × 325.2 × 20 ml

= 1.3 g

Therefore, dissolving 1.3 grams of lead acetate in 20 ml of water will lead to 0.2 molar concentration of lead acetate solution.

Similarly for Thioacetamide, the molecular weight is calculated using the atomic weights of nitrogen (14) and sulfur (32):

Molecular weight of Thioacetamide (C_2H_5NS) = 12 × 2 + 1× 5 + 14 + 32

= 75 g

Grams needed for 0.2M of Thioacetamide in 20 ml = 0.2 × 75 × 20 ml

= 0.3 g

Dissolving 0.3 grams of Thioacetamide in 20 ml of water will create a 0.2 molar concentration of Thioacetamide solution.

3.3 – CHARACTERIZATION TECHNIQUES

Once the experiment is completed, it is necessary to check whether nanoparticles were generated in the film or not. There are several standard characterization techniques and tools that are used, such as X-ray diffraction and imaging using a scanning electron microscope.

3.3.1 – X-ray diffraction (XRD) method

X-ray diffraction method is the standard method which is used to estimate the mean size of the synthesized nanoparticles [21]. X-ray measurements were carried out using an XD-D1 Schimadzu Horizontal Diffractometer using Cu-K_α radiation as the source (wavelength of 1.54Å). It has a maximum operating power range of 600 W with 30 kV voltage and 20 mA current with a 3^0 slit width. For the analysis, samples should be kept on a glass plate which is held in a sample holder for X-ray analysis. It is operated at a scan speed of 0.02^0 scan per step per second.

The mean size of the nanocrystals is calculated from the obtained X-ray diffraction data using Scherrer formula [21].

$$\mathrm{D} = \frac{0.9\lambda}{\beta\cos\theta} \qquad ------(3.1)$$

Where D is the diameter of the nanocrystal (nm), λ is the wavelength of the X-ray, β is the full width half maximum (FWHM), of the obtained peaks, in radians and θ is the Bragg angle.

3.3.2 – SCANING ELECTRON MICROSCOPE

Scanning electron microscope (SEM) is generally used as the microscopic imaging technique used to determine the nanocrystal size. In an SEM, a high velocity electron beam is incident on the sample [22]. Sample molecules will interact with the electrons and produce back scattered electrons that can be captured to yield an image [22]. With the resulting image, the shape and size of the nanoparticles can be easily determined. The main drawback of this method arises if the sample starts charging due to the incident electrons. In that case, the developed image will not have good resolution. A Quanta 3D FEG (FEI) SEM was used to take images of the synthesized nanoparticles.

3.3.3 – OPTICAL ABSORPTION SPECTROSCOPY

Optical absorption spectroscopy is a spectroscopic technique which is used to analyze the absorption characteristics of a sample, in the wavelength region of interest. We used a CARY 5E UV-VISIBLE-NIR spectrometer. The source used in this spectrometer is a Deuterium lamp for the UV region and a tungsten lamp for the visible and IR regions. For samples in solution form, air was considered as a reference and for film samples the core film will be considered as reference. The resulting spectrum will be wavelength versus Intensity.

3.4 RESULTS AND DISCUSSIONS

X-ray diffraction was used to determine the nanoparticle size and confirm the formation of PbS nanoparticles in the Nafion film. First the XRD of pure Nafion is taken and is shown in fig.3.3. The X-ray diffraction measurement of pure Nafion film is taken in range from 10^0 to 65^0 and shows a broad peak at 17^0. The output of the X-ray diffraction is given in terms of twice the angle θ.

Fig: 3.3 – XRD pattern of pure Nafion polymer film

X-ray diffraction of the sample S1 is taken in the 2θ range starting from 20^0 till 60^0, as shown in Fig. 3.4. The resulting spectrum has peaks at 26.1^0, 30.2^0 and 43.2^0 respectively. This corresponds to reflections from the (111), (200) and (220) planes of cubic PbS [23]. From the obtained peaks, the Full width half maximum (FWHM) can be estimated. Using equation 3.1, the size of the nanoparticle is determined:

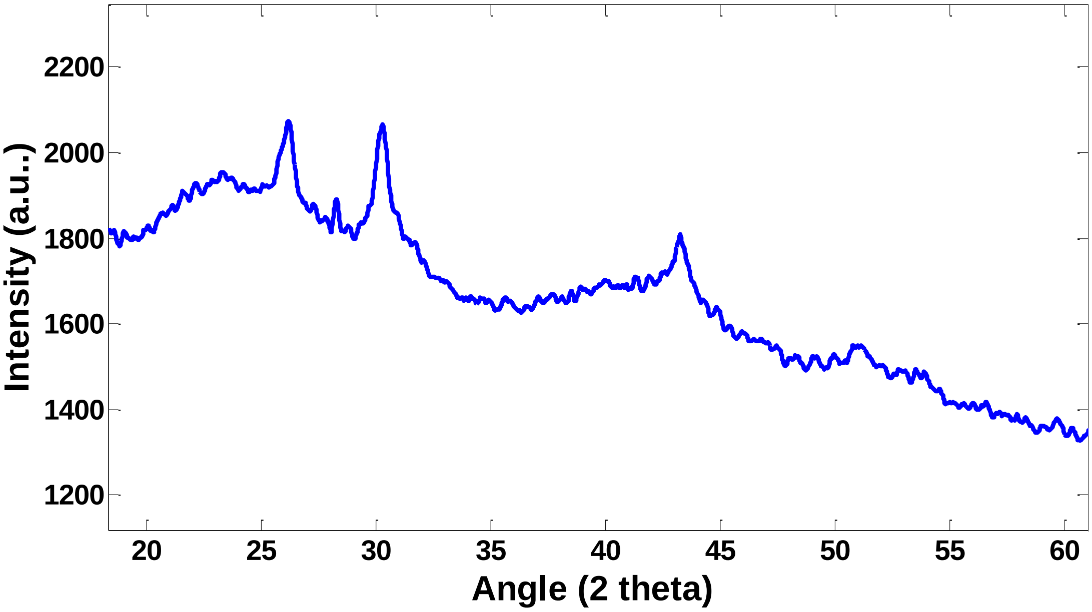

Fig: 3.4 – XRD pattern of Sample S1

3.4.1 – Calculations

From fig 3.4, we can obtain the following parameters:

$$2\theta = 26.11^o \Rightarrow \theta = 13.055^o$$

$$\theta = 0.22785 \text{ rad}$$

$$\text{FWHM } (\beta) = 0.83^o = 0.01448 \text{ rad}$$

By substituting these values in equation 3.1, the mean size of the nanoparticle size was estimated to be 9.8 nm.

3.4.2 – SEM AND CONFOCAL MICROSCOPE IMAGES

Scanning electron microscope (SEM) images are captured with different zoom settings. Fig 3.5 shows nanocrystal formation in the Nafion film, with a magnification of 60X.

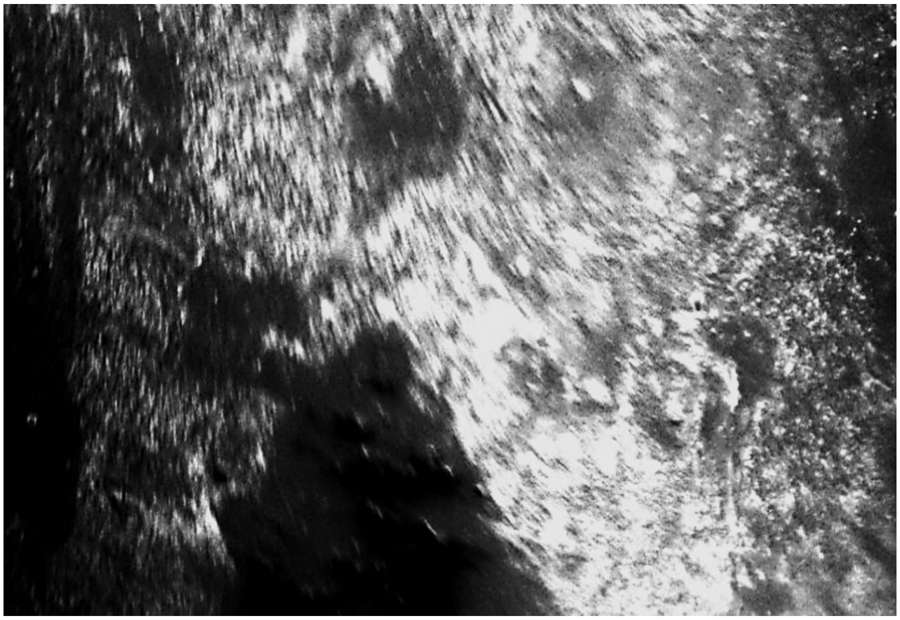

Fig: 3.5 – SEM image of Sample S1 shows nano crystal formation in the Nafion film

The same image at higher magnification is shown in fig 3.6.

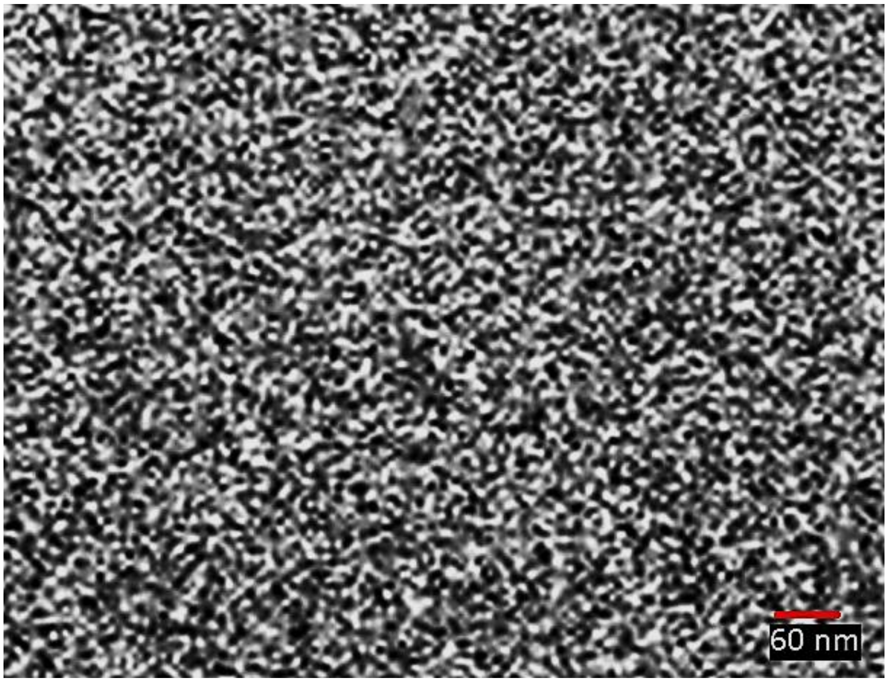

Fig: 3.6 – Higher magnified image of sample S1

The following captured image from a confocal microscope shows the formation of PbS nanocrystals inside the Nafion polymer, but the image has poor resolution and all further imaging was carried out using an SEM only.

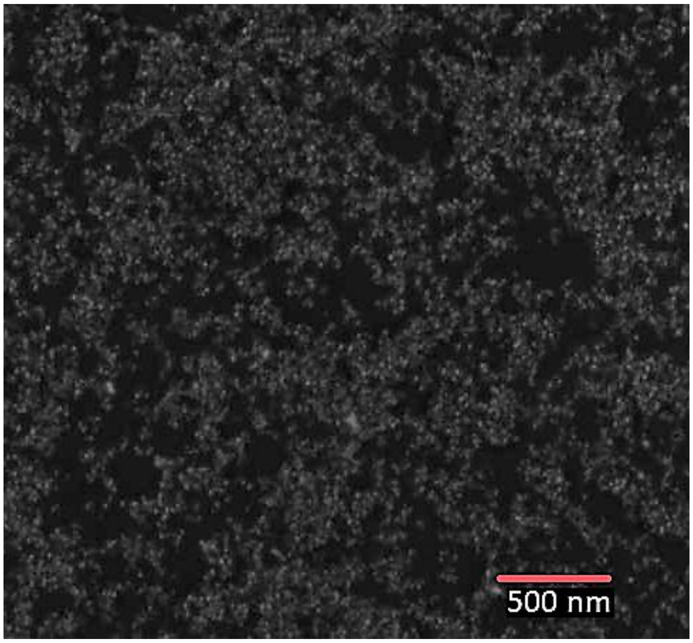

Fig: 3.7 – Confocal microscopic image of sample S1

3.4.3 – OPTICAL ABSORPTION SPECTROMETER

To analysis the optical absorption of the PbS nanoparticles, a standard absorption spectrometer is used. First the absorption of pure Nafion polymer is carried out and the resulting spectrum is shown fig 3.8. The resulting spectrum clearly shows that there are no specific absorption peaks from 200 nm to 1800 nm.

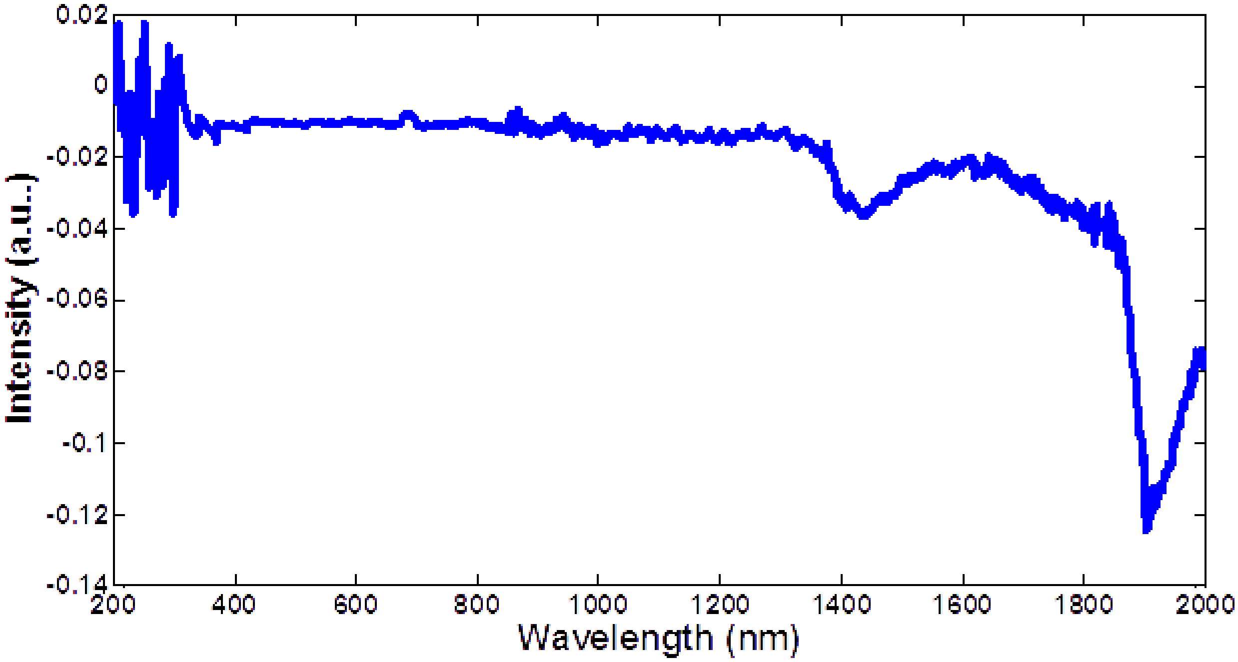

Fig: 3.8 – Optical absorption spectrum of pure Nafion film

The experiment is repeated with the synthesized PbS nanocrystals. Pure Nafion is kept for reference, so that the Nafion effect will be cancelled out. The absorption spectrum of the PbS nanocrystals is shown fig: 3.9. The resulting spectrum shows a strong absorption region in the visible range.

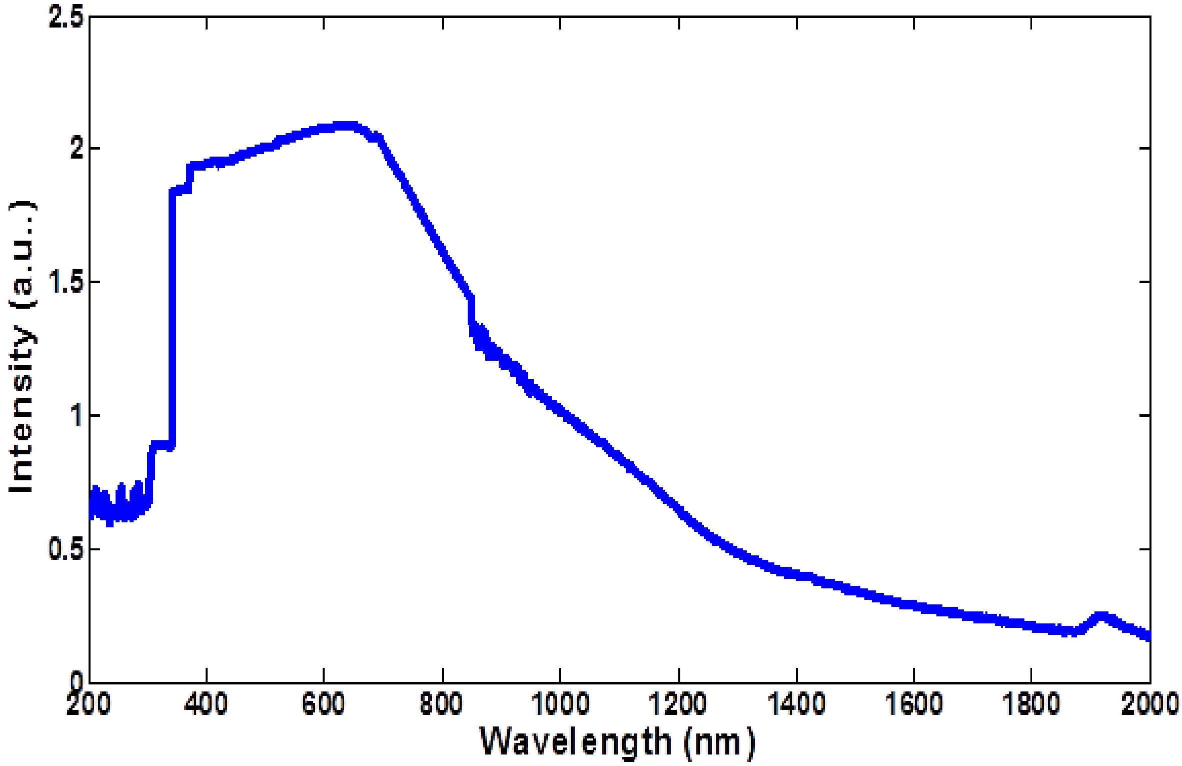

Fig: 3.9 – Optical absorption spectrum of PbS nanocrystals

Even though there are no peaks or special features in the IR region, we decided to analyse the sample with the developed Fourier Transform spectrometer.

RESULTS OVERVIEW

Equimolar (0.2M) solutions of lead acetate and Thioacetamide are made separately. By careful mixing of the above two solutions, synthesis of PbS nanocrystals inside a Nafion polymer is done for different conditions. Several experiments are carried out to confirm the formation of PbS nanocrystals and also to estimate the mean size of the nanocrystals. SEM and confocal images give confirm the presence of the Pbs nanocrystals inside the Nafion film. The mean size of the nanocrystals is determined using X-ray diffraction to be 9.8 nm. An optical absorption study is carried out for pure Nafion film. The optical absorption is carried out on the synthesized PbS nanocrystals. Strong absorption occurs in the range 400 nm to 800 nm. There is minimum optical absorption in the IR region.

CHAPTER: 4 – NANOCRYSTAL ANALYSIS WITH FTS SETUP

4.1 Introduction

To analyze the sample in the developed spectrometer, a free space sample arm is created, as shown in fig 4.1. The source light has to pass through the sample and the transmitted light is coupled into the fiber and used as the input light of the spectrometer.

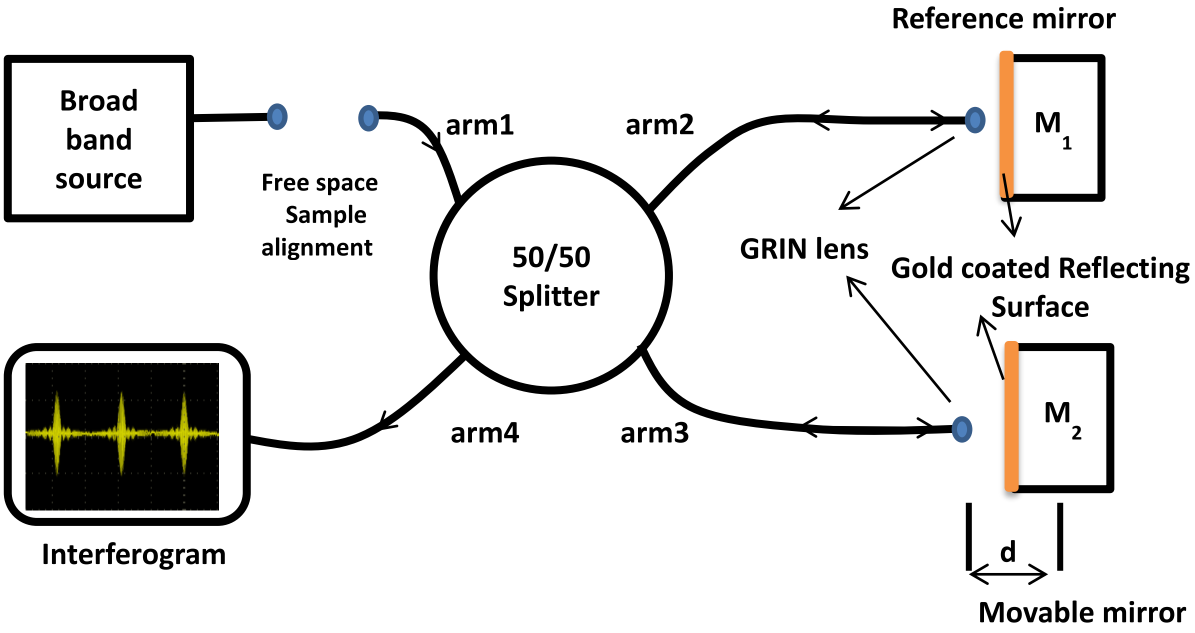

Fig: 4.1. Schematic of experimental setup with free space sample alignment

With the newly created free space sample alignment, all types of transparent samples can be analyzed.

4.2 – RESULTS AND DISCUSSIONS

The Nafion polymer with synthesized nanocrystals was kept in the sample arm. The resulting interferogram was recorded and the corresponding fast Fourier transform was calculated for different input wavelengths.

The FFT curves for input wavelengths of 1525 nm, 1550 nm and 1575 nm are shown in figures 4.2 to 4.4 respectively.

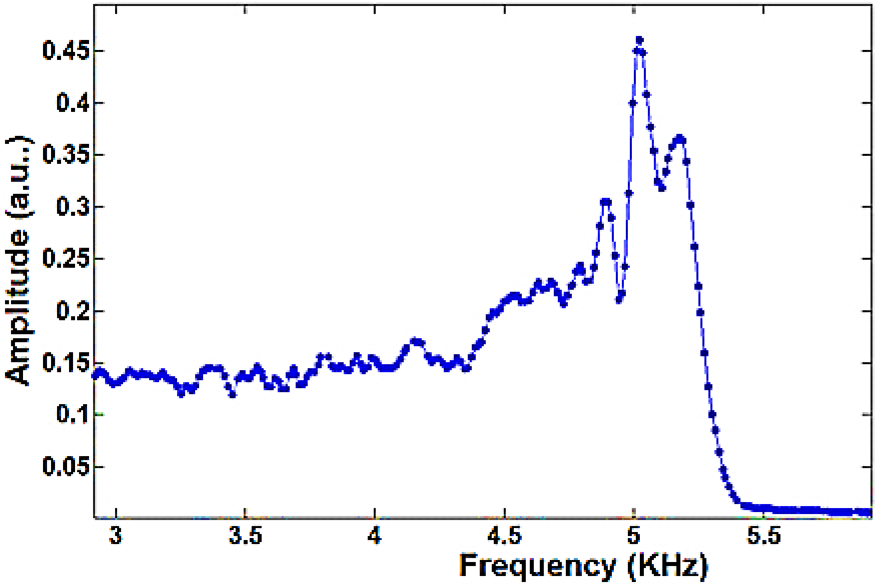

Fig: 4.2- FFT plot of sample S1 at a wavelength of 1525 nm

From the plot, three peaks are visible. The peaks are tabulated (table4.4) and the width (FWHM) of the each peak is measured.

Table: 4.1 Width (FWHM) of the three peaks corresponds to the plot: 4.2

First peak **Δλ (nm)**	**Second peak** **Δλ (nm)**	**Third peak** **Δλ (nm)**
22	21	21

The source wavelength is set as 1550 nm and the corresponding FFT response of the nanocrystals is plotted below,

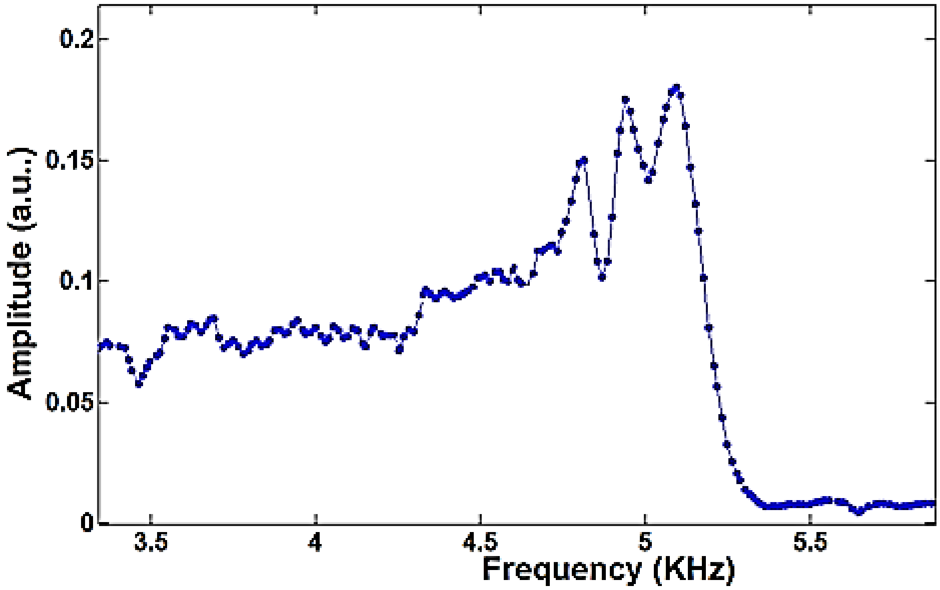

Fig: 4.3- FFT plot of sample S1 at a wavelength of 1550 nm

Again the FWHM is measured and tabulated.

Table: 4.2 Width (FWHM) of the three peaks corresponds to the plot: 4.3

First peak **Δλ (nm)**	**Second peak** **Δλ (nm)**	**Third peak** **Δλ (nm)**
21	25	30

Now the source wavelength is set at 1575 nm and the corresponding FFT response of the nanocrystals is plotted. Interestingly, like 1525 nm and 1550 nm there are also three different peaks with FWHM as noted and shown in table 4.3.

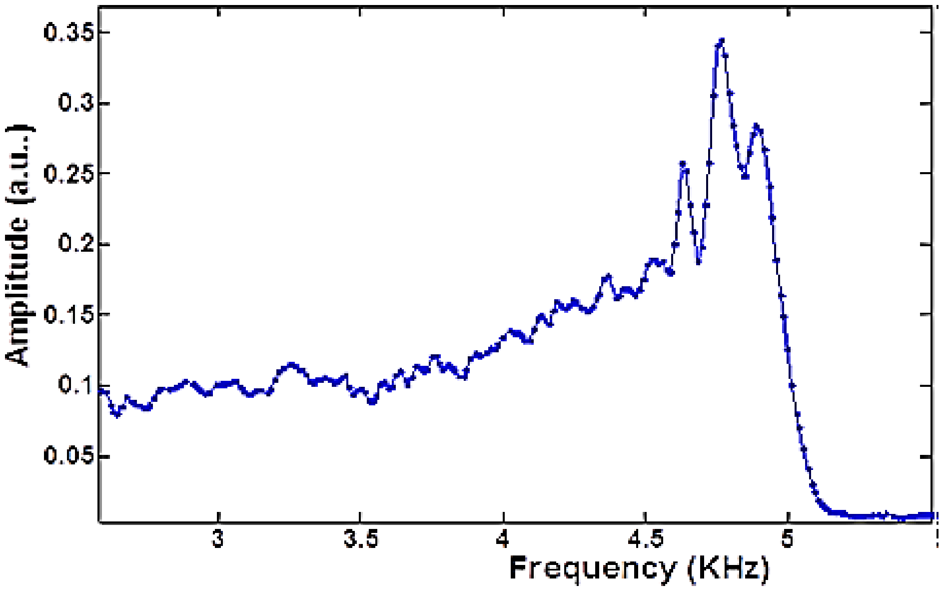

Fig: 4.4 - FFT plot of sample S1 at a wavelength of 1575 nm

Table: 4.3 Width (FWHM) of the three peaks corresponds to the plot: 4.4

First peak Δλ (nm)	Second peak Δλ (nm)	Third peak Δλ (nm)
24	34	25

From the obtained FTS plots (figures 4.2 - 4.3) for different input wavelengths, the three corresponding FFT peaks are obtained and the corresponding wavelengths are back calculated and given in table 4.4.

Table: 4.4 – Back calculated wavelengths of the FFT peaks for different input wavelengths

Input Wavelength (nm)	**Experimentally obtained values**			**Back calculated wavelengths**		
	FFT 1 (kHz)	**FFT 2 (kHz)**	**FFT 3 (kHz)**	**λ_1 (nm)**	**λ_2 (nm)**	**λ_3 (nm)**
1525	4.893	5.029	5.174	1560	**1520**	1480
1550	4.7	4.93	5.079	1625	**1555**	1504
1575	4.621	4.866	4.952	1650	**1570**	1542

An interesting phenomenon is observed. Although the input is a narrowband source, the transmitted spectrum of the PbS nanocrystals produces side bands, at higher and lower wavelengths.

To verify that this effect is caused only because of the PbS nanocrystals and has not arisen due to some other artifacts, the same FTS experiment was carried out with the pure undoped Nafion polymer film. The resulting spectrum is shown in Fig 4.5.

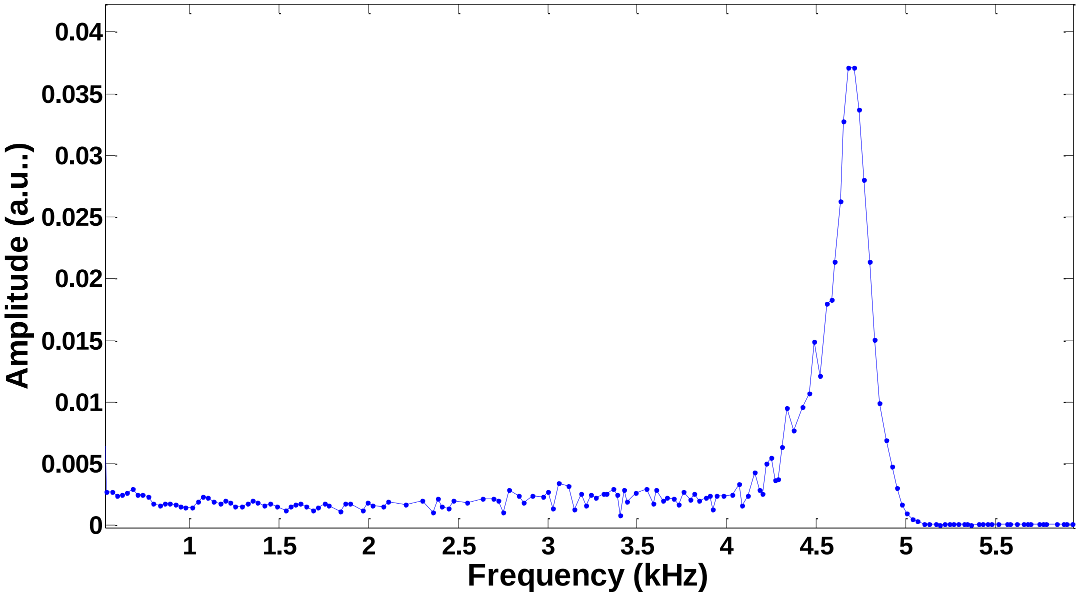

Fig: 4.5 - FFT plot of pure Nafion film at a wavelength of 1575 nm

Similar plots were obtained at a source wavelength of 1550 nm and 1525 nm.

Studies on the Nafion film clearly show that the extra peaks seen in the previous experiment are only because of the PbS nanocrystals.

To further verify the FTS results, a standard fiber based optical spectrum analyzer (Agilent 86141B) is used. The experiment carried out is shown in fig 4.8

The same input source wavelengths as used in earlier experiments were given as input so as to be able to compare both the results.

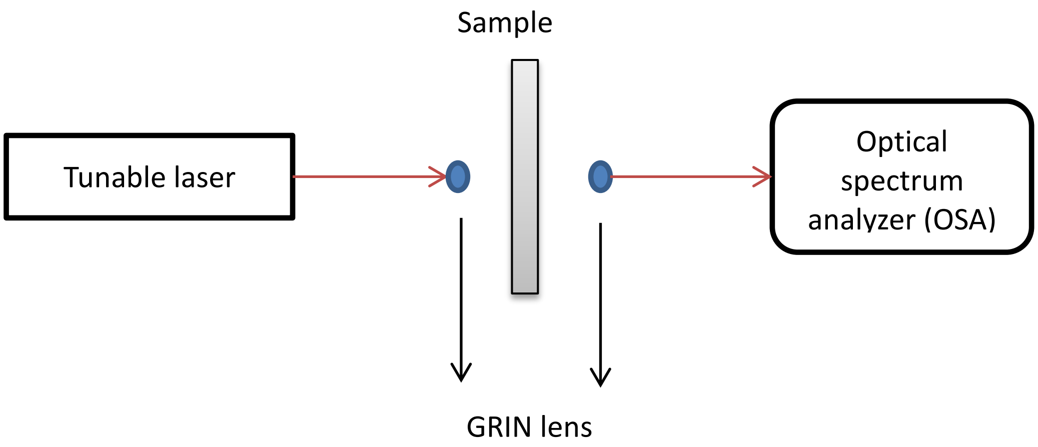

Fig: 4.6 – Schematic of optical spectrum analyzer (OSA) setup

Initially pure undoped Nafion polymer was tested. The results, shown in figures 4.9 to 5.1 confirm what was observed earlier with our FTS system.

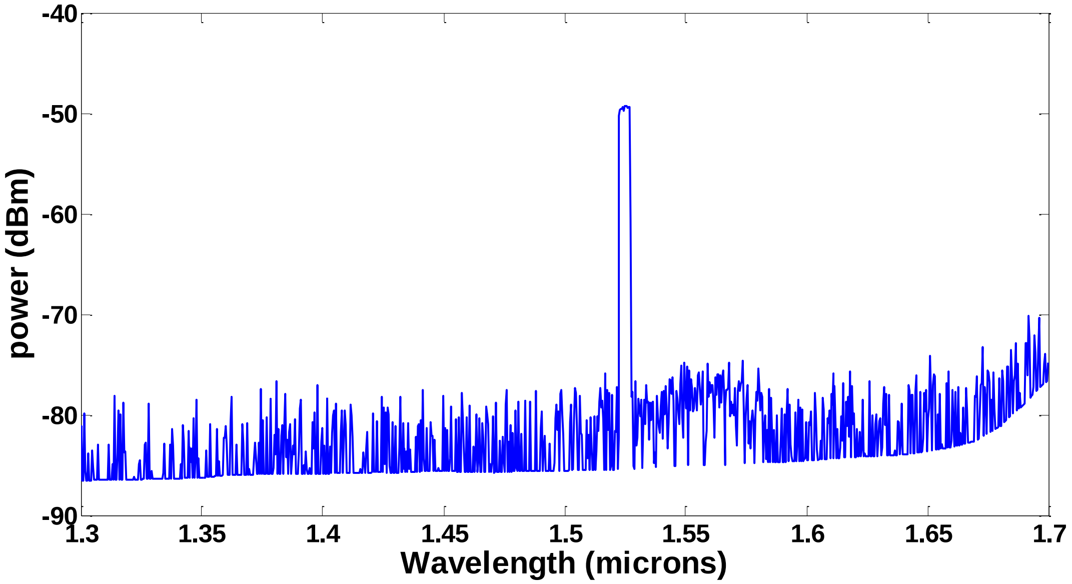

Fig: 4.7 – OSA spectrum of pure Nafion polymer at a wavelength of 1525 nm

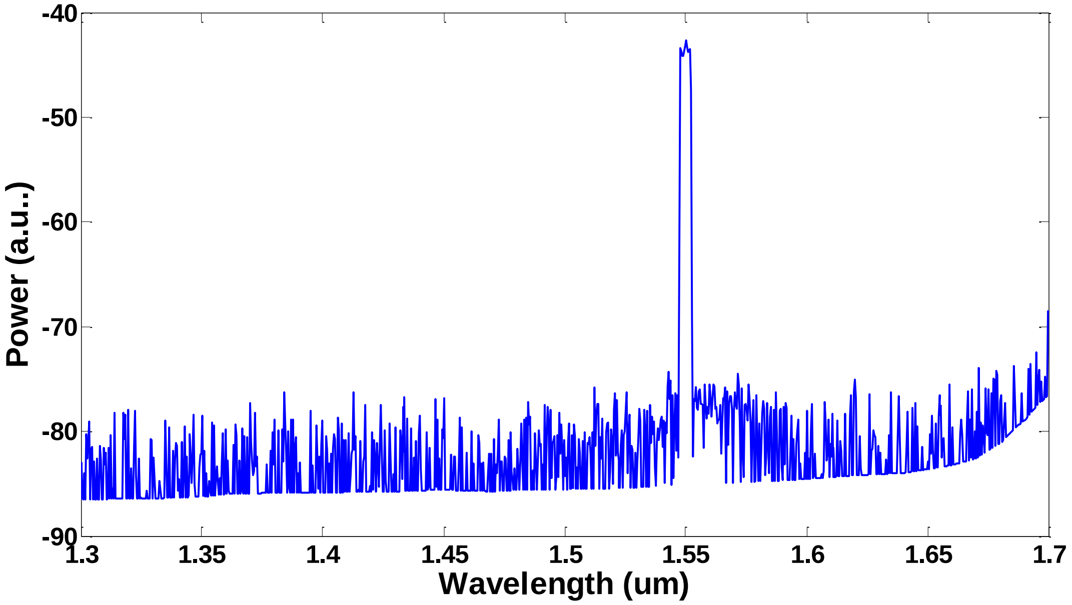

Fig: 4.8 – OSA spectrum of pure Nafion polymer at a wavelength of 1550 nm

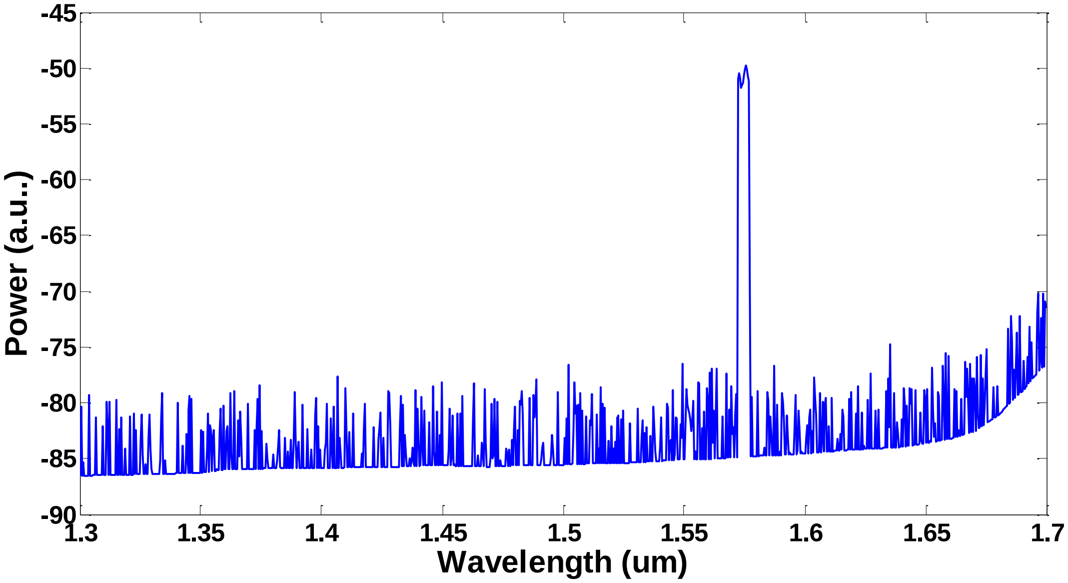

Fig: 4.9 – OSA spectrum of pure Nafion polymer at a wavelength of 1575 nm

The PbS samples were then tested. The results at 1525 nm are shown in fig. 4.12.

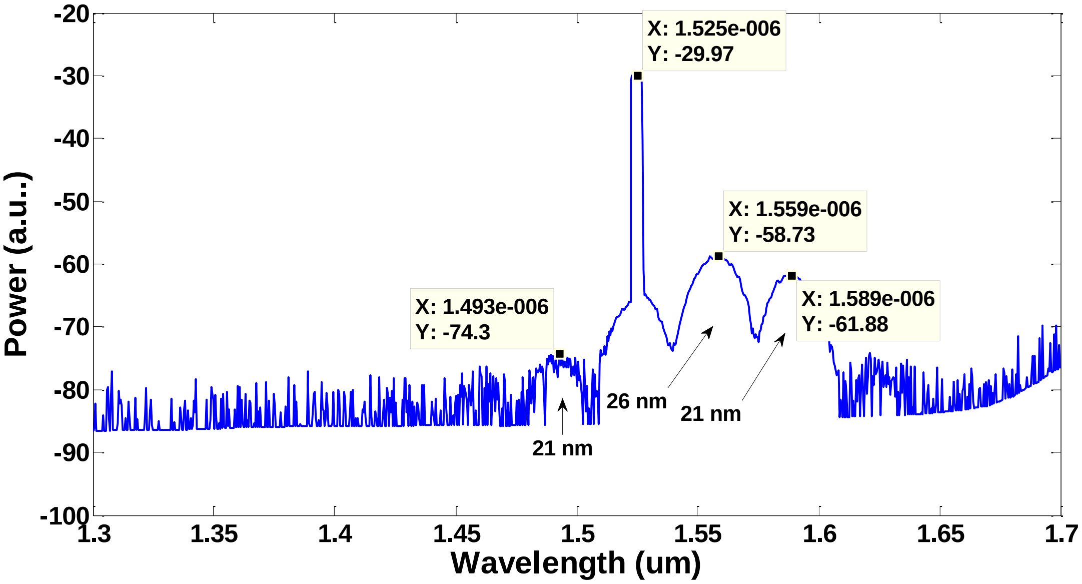

Fig: 4.10 – OSA spectrum of sample S1 at a wavelength of 1525 nm

The OSA output shows a number of peaks similar but not identical to the FTS results. The experiment is repeated for the remaining two wavelengths and the plots are shown in figures 4.13 and 4.14.

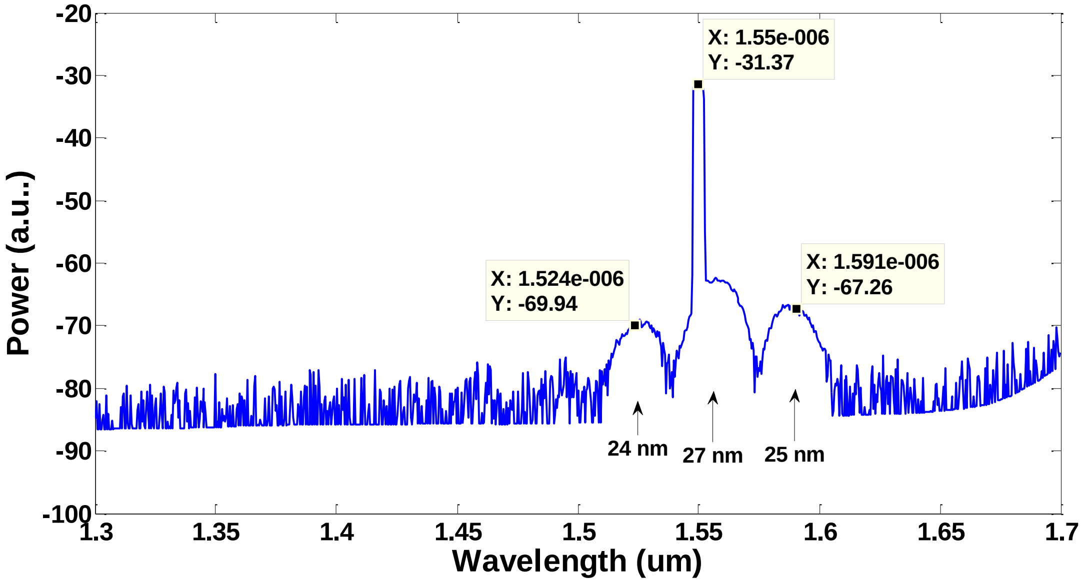

Fig: 4.11 – OSA spectrum of sample S1 at a wavelength of 1550 nm

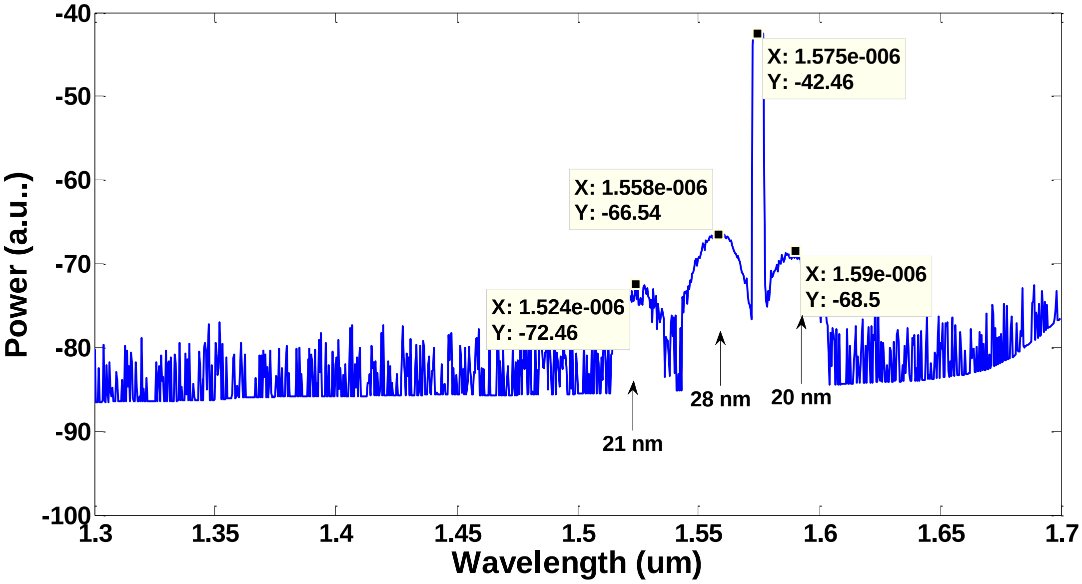

Fig: 4.12 – OSA spectrum of sample S1at a wavelength of 1575 nm

The OSA results confirm that the extra peaks are due to the PbS nanocrystals only. It is also observed that the spectral width almost matches the FTS results although the peak wavelengths are not similar. This could be due to the fact that the FTS and OSA experiments are conducted at exactly the same points of the sample. The whole experiment is carried out by masking the sample to ensure the experiments are carried out at the same location but due to the size of the beam, the exact location may still vary slightly.

CHAPTER: 5

CONCLUSION & FUTURE WORK

A study of synthesized PbS nanocrystals using the developed fiber based Fourier transform spectrometer is carried out. Synthesis of PbS nanocrystals inside Nafion polymer film is carried out by chemical synthesis. Standard characterization methods like XRD, SEM and confocal microscopic imaging techniques were carried out to characterize the nanocrystals. The estimated mean size of the synthesized PbS nanocrystals is 9.8 nm. In the FTS setup, it was observed that for a single narrow wavelength, PbS nanocrystals generated higher and lower wavelengths. The analysis is carried out for three different wavelengths and the same phenomenon was observed in all cases.

At present the physics behind the observed phenomenon is not understood. To confirm that the effect is only because of the PbS nanocrystals, an same FTS experiment is carried out with the pure undoped Nafion polymer film. The experiment gave similar results.

Further, the PbS samples were studied with and optical spectrum analyzer. Again a pure undoped Nafion polymer film at different input wavelengths was tested initially. There were no extra peaks visible. The pure Nafion polymer film is replaced with the PbS nanocrystals and the resulting spectrum shows the extra peaks which includes the source wavelength. This proves that what we observed with the FTS is not an artifact of the system.

Initially we thought that this could be a Raman Effect of the PbS nanocrystals. By using a FT-Raman spectrometer, the behavior of the PbS nanocrystals was observed. The resulting spectrum did not give any peaks. Therefore, we concluded that the effect is not because of the Raman Effect.

The future work will be to understand the physics behind the observed phenomenon .At present, a digital signal oscilloscope is used for acquisition of the time domain data and the corresponding FFT process is done by Matlab. To make the FTS setup faster and more compact, this process could be done with a data acquisition board.