SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF NANOSTRUCTURED THERMOELECTRIC MATERIALS

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF
NANOSTRUCTURED THERMOELECTRIC MATERIALS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Materials Science and Engineering

by
Jason Brooks Reppert
December 2009

Accepted by:
Dr. Apparao M. Rao, Committee Chair
Dr. Kathleen Richardson
Dr. John Ballato
Dr. Jian Luo
ABSTRACT

Bismuth in the bulk form is a semimetal with a rhombohedral structure. It has a small band overlap between the conduction and valence bands and a highly anisotropic electron effective-mass tensor. Thermoelectric materials, in which one of the three dimensions is in the nanometer regime, exhibit unique quantum confinement properties and have generated much interest in recent years. Theoretical investigations have suggested that nanowires with diameters $\leq 10$ nm will possess a figure-of-merit $ZT > 2$. Prior to this study, it has been shown that Bi nanowires with small enough diameters ($\sim 10$ nm), prepared via the pulsed laser vaporization method, undergo a transition from a semimetal with a small band overlap to a semiconductor with a small indirect band gap. Infrared absorption and UV-visible measurements were used to confirm this semimetal-to-semiconductor phase transition.

In this thesis, we report the synthesis and optical characteristics of a variety of various potential thermoelectric materials including bismuth, nickel sulfide and cadmium sulfide. The infrared absorption in our Bi nanorods is blue-shifted in energy when compared to the corresponding spectra in bulk Bi, and when cooled down to liquid nitrogen temperatures, group theory suggests a strong temperature dependence in the Bi band structure. We also find that the Bi nanorod suspension displays excellent optical limiting properties at both 532 and 1064 nm excitations in the nanosecond laser pulse regime.

We have also synthesized nickel sulfide nanoparticles with an average size of 5 nm by a one-step solid phase reaction. The intensity-dependent nonlinear transmission study was carried out using a 7 ns Nd:YAG laser at 532nm using Z-scan, and the
nonlinear scattering was found to be the dominant mechanism for the observed response. Importantly, the modified Z-scan method allowed us to measure two competing mechanisms simultaneously - the optical limiting and saturable absorption in surface-modified nickel sulfide nanoparticles suspensions.
DEDICATION

I want to dedicate this thesis to my parents, Cindy and Dennis Reppert. Without your love and support over the years, this would not be possible. Thank you so very much.
ACKNOWLEDGEMENTS

First, I would like to thank my advisor, Dr. Apparao M. Rao for his guidance, help and friendship over the past 4.5 years. Not only has he taught me the techniques needed to succeed in the lab, but he has also offered valuable lessons about life. Also, thank you for your friendship and being my mentor throughout my graduate career. Next, I would like to recognize some work and ideas done in this thesis would not have been possible without the meaningful insights given to me through various intellectual discussions with Dr. Malcolm Skove and Dr. Jian He. In addition, I would also like extend thanks to my lab mates for their guidance and friendship.

Finally, I would like to thank my loving wife for supporting me through the years. Without her love and support, I would not be where I am today.
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GLOSSARY

TE: Thermoelectric

ZT: Figure-of-merit

$S$: Seebeck coefficient

$\sigma$: electrical conductivity

$\rho$: electrical resistivity

$\kappa$: thermal conductivity

$\kappa_L$: lattice conductivity

$\kappa_e$: electrical conductivity

$S^2\sigma T$: power factor

QCE: quantum confinement effects

DOS: density of states

Bi: Bismuth

$\mu$: carrier mobility

$m^*_{\text{e}}$: electron effective mass

$m_0$: free electron mass

$m^*_{\text{e}}$: electron effective mass

$m^*_{\text{h}}$: hole effective mass

$\Delta T$: temperature difference

$T_H$: temperature (hot end)

$T_C$: temperature (cold end)

$T$: temperature
Glossary (Continued)

Π: Peltier coefficient

I: current

ε: thermoelectric efficiency

ε_c: Carnot efficiency

E_F: Fermi level

ΔE: band gap

L-point: electron pockets

T-point: hole pockets

E_{gL}: band gap between the L-points

E_{gT}: band gap between the T-points

E_g^{bulk}: bulk band gap

E_g*: band gap energy between the top of the valence band at the L-point to the top of the valence band at the T-point

E_{T,0}: energy at the T-point valence-band edge

M_h^{-1}: inverse of the T-point hole effective mass tensor

m_p*: in-plane effective mass

ΔE_L: change in the L-point due to quantum confinement

ΔE_T: change in the T-point due to quantum confinement

d: diameter

h: Planck’s constant

E_A*: absorption threshold

T(w): infrared transmission
Glossary (Continued)

IR: infrared

FTIR: Fourier-transform infrared

UV-Vis: Ultra-Violet

\( r \): particle radius

\( e \): charge of an electron

\( \varepsilon_0 \): permittivity of free space

\( \alpha_{01} \): first-order of the zeroth-order Bessel function (2.405)

PLV: pulsed laser vaporization

HR-TEM: high-resolution transmission electron microscopy

NiS: nickel sulfide

CdS: cadmium sulfide

NLO: nonlinear optics

\( \pi \): 3.14

FWHM: full width half maximum

KBr: potassium bromide

ARPES: angle-resolved photoemission spectroscopy

\( n_2 \): intensity-dependent refractive index

\( I_0 \): peak intensity at the focal point

\( z \): sample position at the focal point

\( \alpha_0 \): linear absorption coefficient

\( \alpha_2 \): total nonlinear extinction coefficient
Glossary (Continued)

\( \alpha_{2.4} : \)  nonlinear absorption coefficient

\( \alpha_{2.5} : \)  nonlinear scattering coefficient

\( \lambda : \)  wavelength

\( t : \)  time

\( \omega_0 : \)  beam waist radius at the focal point

\( T(z) : \)  normalized transmission energy

NLA:  nonlinear absorption

NLS:  nonlinear scattering

\( \Delta n : \)  thermal refractive index gradient

\( F_0 : \)  fluence

\( \frac{dn}{dT} : \)  thermo-optic coefficient

\( C_v : \)  specific heat

DMG:  dimethylglyoxime

XRD:  x-ray diffraction

PAS:  photoacoustic spectroscopy

PL:  photoluminescence

\( I_s : \)  saturation intensity

2PA:  two-photon absorption

3PA:  three-photon absorption
CHAPTER 1

INTRODUCTION

A worldwide over-dependence on fossil fuels for energy needs has led to an urgent need for alternative energy and novel energy conversion technologies. Thermoelectric (TE) processes which can convert wasted heat into useful electrical energy (Seebeck effect), [1] or transport the heat away to do refrigeration (Peltier effect) [2] for better power generation devices are mechanisms proving to be plausible solutions to our energy needs. These devices have several unique features, such as their all solid-state assembly without movement parts, ease of switching between power generation mode and refrigeration mode, low maintenance cost and ease of coupling to other energy conversion devices [3]. This idea of the conversion of wasted heat into electrical power is already finding its way into industry. One of the largest emerging markets is the incorporation of TE power generation for recovery of the large amount of waste heat (≈ 2/3 of generated power) from an automobile’s exhaust or engine, and harvesting this into usable electrical energy. Meanwhile, TE refrigeration finds its wide application in cooling microelectronics (e.g. central processing unit chips) and optoelectronics (infrared detectors and laser diodes).

The potential of a material for TE applications is determined by the materials’ figure-of-merit, $ZT$, defined in Eq. (1.1),

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_L} = \frac{S^2 T}{\rho (\kappa_e + \kappa_L)} \quad (1.1)$$
where \( S \) is the Seebeck coefficient, \( \sigma \) the electrical conductivity, \( \rho \) the electrical resistivity and \( \kappa \) the total thermal conductivity \((\kappa = \kappa_L + \kappa_E \) the lattice and electronic contributions, respectively\)). The power factor, \( S^2\sigma T \), (or \( S^2T/\rho \)) is usually optimized as a function of carrier concentration (typically around \( 10^{19} \) carriers/cm\(^3\)) [4], through doping in order to attain the largest \( ZT \).

Enhanced TE performance is expected in nano-scaled structures in which the electronic properties can be drastically different from those found in the corresponding bulk material. This direction of nano-scaled research has been motivated by several recent theoretical [5, 6] and experimental investigations [7-9]. Low dimensional materials like ultra-thin films, nanotubes and nanowires can significantly improve the \( ZT \) as compared to their bulk counterparts. For example, the theoretical framework for the possible enhancement of \( ZT \) in nanowire systems due to quantum confinement effects (QCE) has been discussed in Ref. 5. As one of the dimensions of a bulk material is decreased to a scale that is comparable with the wavelength of the electrons, the motion of the charge carriers (electrons or holes) becomes confined along that direction [10]. Thus, a material begins to exhibit electronic properties that are different from the bulk and can start to exhibit 1D (or 2D) properties if it attains nano-scaled dimension along one (or two) dimensions. This quantum confinement phenomenon leads to a dramatic change in the electronic density of states (DOS), which will be discussed in further detail later in this chapter.

On the experimental side, recently, Hsu et al. [11] showed that developing high-performance bulk TE materials that incorporate low-dimensional (nanostructured)
materials (Fig. 1.1) into a bulk matrix, e.g. AgPb\textsubscript{18}SbTe\textsubscript{20}, one lead to a $ZT \sim 2.2$ (where $\sigma = 230 \text{ S/cm}$, $S = -335 \text{ \mu V/K}$, thus resulting in $S^2\sigma T = 28.0 \text{ \mu W/(cm\cdot K)}$ at 800 K. The negative value for the thermopower indicates an $n$-type semiconductor. This power factor value $S^2\sigma T$ is larger than that of other candidate materials such as K\textsubscript{2}Bi\textsubscript{8}Se\textsubscript{13}, which has a $S^2\sigma T = 10.0 \text{ \mu W/(cm\cdot K)}$ [12]. Recently, skutterudite materials have sparked

Figure 1.1: A TEM image of a AgPb\textsubscript{18}SbTe\textsubscript{20} sample showing a nano-sized region (a “nanodot” shown in the red area) of the crystal that is Ag-Sb-rich in composition [11].

the interest of researchers in search of new thermoelectric materials. Sales et al. [13] prepared filled skutterudite antimonides (CeFe\textsubscript{4-x}Co\textsubscript{x}Sb\textsubscript{12} and LaFe\textsubscript{4-x}Co\textsubscript{x}Sb\textsubscript{12}) and showed that they exhibit extremely low lattice conductivity, $\kappa_L$ due to the effectiveness of the rattling rare-earth ions in scattering phonons. Hicks et al. [8] showed that PbTe quantum dot structures exhibit a good $ZT$ because of its high carrier mobility and low thermal conductivity. Making an important development in this area,
Venkatasubramanian et al. [9] showed that Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattice materials exhibit a $ZT \sim 2.5$ at 300 K (Fig. 1.2). In addition to the nanostructured Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattice thin films that have shown a great deal of promise, other nanomaterials have also shown potential in improving thermoelectric materials. One example involving PbTe/PbSeTe quantum dot superlattices was shown to provide an enhanced $ZT \sim 1.5$ at room temperature that was a great deal higher than the bulk $ZT$ value for either PbTe or PbSeTe $\sim 0.5$ [14, 15]. By layering these two compounds together, they greatly enhanced the carrier mobility, and equally importantly, decreased the thermal conductivity. Recently, Poudel et al. showed that a $ZT$ value of 1.4 at 100°C can be achieved in a $p$-type nanocrystalline BiSbTe alloy. More recently, two research groups [16, 17] have shown that individual silicon nanowires can act as efficient TE materials. Each group found the

Figure 1.2: Temperature dependence of $ZT$ of 10Å/50Å $p$-type Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattice compared to those of several recently reported materials [9].
$ZT \sim 0.6$ for their structures, even though bulk silicon is known to be a poor TE material (approximately $ZT \sim 0.01$ at room temperature) because of its low $\kappa_L$ due to boundary scattering of phonons. The message is clear: low dimensional structures of TE materials can exhibit higher $ZT$ values than their bulk counterparts (i.e. $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ at 300 K).

Semimetallic bulk Bi is a poor TE material since the electron and the hole contributions to the thermopower approximately cancel each other [18]. Bi has the smallest effective mass (~0.001$m_0$) of all known materials. The small effective mass of Bi makes it easy to observe QCE. This topic will be discussed in more detail in Chapter 2. Bi also has a very long mean free path in the bulk (~0.4 mm at 4 K and ~100 nm at 300 K) [19], which makes it a suitable material for studying transport properties. The mean free path is defined as the average distance a particle travels before colliding with other particles.

As theoretical work predicts [5], it is possible that nanostructured Bi or Bi-Sb may have exceptionally high $ZT$. The power factor, $S^2\sigma T$, depends on the quantity $\mu(m^*/m_0)^{3/2}$, where $\mu$ is the carrier mobility and $m^*/m_0$ is the ratio of the effective mass to the free electron mass (see Table 1.1 for effective mass components along different crystallographic directions). Bismuth has the best known value of $\mu(m^*/m_0)^{3/2}$ for any material, 0.075 m$^2$V$^{-1}$s$^{-1}$ for its electrons.

Lastly, the calculation by Lin et al. [5], state that these changes (in effective and free electron masses) are due to the band structure changing as the diameter of the wires is reduced. This change will be discussed in more detail in Chapter 2. They then calculated the Seebeck coefficient as a function of carrier density at 77 K and yielded $ZT \sim 2$ for $n$-type Bi nanowires along the trigonal direction with a diameter of 10 nm.
Table 1.1: Calculated effective mass components of each carrier pocket for determining the band structure in Bi nanowires at 77 K along the indicated crystallographic directions, based on the effective mass parameters of bulk Bi [19, 20]. The $z'$ direction is chosen along the wire axis and all mass values are in units of the free electron mass, $m_0$ [21].

(Fig. 1.3). Bi nanowires with diameters < 50 nm have been predicted to be an excellent TE material based on these unique properties [22]. Bi has a low carrier concentration of $\sim 10^{18}$ cm$^{-3}$ which make it favorable material for doping. Such dopants include Te ($n$-type), and Pb or Sn ($p$-type). Lin et al. [5] have shown that the Seebeck coefficient is about $-400$ $\mu$V/K, which is much greater that the value for crystalline Bi. The high power factor comes from an electrical conductivity of $\sim 3.4 \times 10^6$ $\Omega^{-1}$m$^{-1}$, which is attributed to a high density of states (to be discussed later in this chapter).

<table>
<thead>
<tr>
<th>Mass component</th>
<th>Trigonal</th>
<th>Binary</th>
<th>Bisectrix</th>
<th>[0112]</th>
<th>[1011]</th>
</tr>
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<tr>
<td>$e^-$ pocket $L(A)$</td>
<td>$m_{1z'}$</td>
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<td>0.0023</td>
<td>0.0029</td>
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<tr>
<td></td>
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<td>0.0012</td>
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<td>0.0023</td>
<td>0.0016</td>
</tr>
<tr>
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<td>0.0016</td>
<td>0.0048</td>
<td>0.0125</td>
</tr>
<tr>
<td></td>
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<td>0.0666</td>
<td>0.0352</td>
</tr>
<tr>
<td></td>
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<td>0.0023</td>
<td>0.0023</td>
<td>0.0016</td>
</tr>
<tr>
<td></td>
<td>$\bar{m}_{2z'}$</td>
<td>0.0012</td>
<td>0.0016</td>
<td>0.0048</td>
<td>0.0125</td>
</tr>
<tr>
<td>$e^-$ pocket $L(C)$</td>
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<td>0.0666</td>
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<tr>
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<td>0.6340</td>
<td>0.6340</td>
<td>0.1593</td>
</tr>
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<td>0.0590</td>
<td>0.0590</td>
<td>0.0590</td>
</tr>
<tr>
<td></td>
<td>$m_{2z'}$</td>
<td>0.6340</td>
<td>0.0590</td>
<td>0.0590</td>
<td>0.2349</td>
</tr>
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</table>
Figure 1.3: Predicted $ZT$ of Bi thin films (2D) and nanowires (1D). As the nanowire diameter decrease, the $ZT$ increases. When diameter reaches ~10 nm, the $ZT$ is predicted to be ~1 (2D) and ~2 (1D) [22].

Using the values given by Lin et al. [5] for the electrical conductivity and the Seebeck coefficient, a power factor of 41.9 W/m·K at 77 K is obtained. Combining the power factor and the lattice conductivity (2.9 W/m·K), one can achieve a $ZT \sim 6$ for a 5 nm diameter wire. By changing the lattice conductivity to 0.1 W/m·K, the lowest limit for phonon conductivity as calculated by Cahill et al. [23] the $ZT$ becomes considerably greater as seen in Fig. 1.4.
The easiest way to think about thermoelectricity is to realize that electrical and thermal currents are coupled. The particles that carry electric charge in a material also carry heat. Discussed below are some of the fundamental ideas around how to achieve the best possible TE material, and why nano-structured forms of bulk TE materials warrant further study.

1.1 Seebeck Effect

To start this discussion, we will look at the Seebeck coefficient, also known as thermopower. In a TE material there are free electrons or holes which carry both charge and heat. The effect is that a voltage is created in the presence of a temperature difference ($\Delta T$) between two different metals or semiconductors. This effect causes a continuous current to flow in the conductors when they form a complete loop. The $\Delta T$
across the material leads to an unequal distribution of charge carriers. Free carriers will have more energy at the “hot” end of the material than the “cold” end and electrons (or holes) will thermally diffuse from the hot end ($T_H$) to the cold end ($T_C$), carrying their charge with them. As seen in Fig. 1.5, the charge is built up on the cold end and creates an electric field inside the sample. When the current generated by this electric field cancels the flow due to the thermal diffusion, equilibrium is reached. Measuring the Seebeck coefficient is one way to determine the dominant charge carriers.

Figure 1.5: Schematic of a conductor showing electrons (or holes) diffusing from the hot end ($T_H$) to the cold end ($T_C$).

1.2 Peltier Effect

An effect very similar to the Seebeck effect is the Peltier effect. The Peltier effect is the reversible exchange of heat from a junction of dissimilar materials in the presence of a current passing through the junction, which is held at a constant temperature. The Peltier coefficient, $\Pi$, is the ratio of the rate of heating (or cooling) to the electrical
current passing through the junction and can be defined as \( \Pi = \frac{1}{I} \frac{dQ}{dt} \), where \( I \) is the current and \( \frac{dQ}{dt} \) is the heat flow per unit of time. An electric current flowing through this system causes a change in the energy level of charge carriers, thus providing heat that is being absorbed at one junction and being evolved at the other (see Fig. 1.6). Imagine that on the bottom is a material of type A and the one on the top is a material of type B. Both of the materials will be carrying heat towards the junction and thus, some heat will be absorbed.

Figure 1.6: Schematic of the Peltier effect showing a current flowing through two different materials. At the junction, heat is produced which can be used as energy.
1.3 Thomson Effect

The last of the TE effects is the Thomson effect. Let us consider a material with a current flowing through it and a temperature gradient is applied to it (see Fig. 1.7). Due to the change in temperature, $\Delta T$, thermal energy is generated along the length of the material. This idea is very similar to the Peltier effect and thus it can be thought of as a series of many small Peltier junctions, each of which generates heat. If the temperature difference is small enough, $q = \frac{\Pi}{\Delta T}$, where $\Pi$ is the Peltier effect [3].

Figure 1.7: Schematic of the Thomson effect. A current flows through the material and a temperature gradient is applied to it, thus thermal energy is created.
1.4 Thermoelectric Generation and Figure-of-Merit

The figure-of-merit ($ZT$) is often used for gauging the potential of a particular TE material for realistic applications. As mentioned earlier, $ZT$ is defined as

$$ZT = \frac{S^2 \sigma T}{\kappa} \quad (1.2)$$

where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the temperature and $\kappa$ is the total thermal conductivity. In addition, the thermoelectric efficiency, $\varepsilon$, is proportional to $ZT$ and is given by [25]

$$\varepsilon = \varepsilon_C \left( \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_C}{T_H}} \right) \quad (1.3)$$

where $\varepsilon_C$ is the Carnot efficiency, $\varepsilon_C = (T_H-T_C)/T_H$ and $T_H$ and $T_C$ are the hot and cold temperature, respectively. Equation (1.3) shows that increasing the efficiency requires both having high $ZT$ values and maximizing the $T$ gradient across the TE materials. A significant difference in $T$ is needed to generate sufficient electrical energy.

Currently, the best TE materials ($\text{Bi}_2\text{Te}_3$) used in devices have $ZT \approx 1$. The goal for our ongoing research is to find new materials that can potentially reach a desired $ZT \approx 2-3$. Figure 1.8 shows the $ZT$ as a function of temperature for several bulk TE materials. There are, however several hurdles which have to be overcome before higher $ZT$ values
can be achieved. As seen through Eq. (1.2), $ZT$ may be increased by increasing the thermopower and increasing the electrical conductivity. $ZT$ may also be increased by decreasing the thermal conductivity. The current materials exhibit conversion efficiencies of 7-8% depending on the specific materials and the temperature differences involved. For example, a TE power conversion device with $ZT = 3$ operating between 773 K and 300 K would yield about 40% of the Carnot efficiency (Eq. (1.3)). A value of $ZT > 4$ however, does not significantly increase the conversion efficiency (from 42% at $ZT = 3$ compared to 46% at $ZT = 4$) over that of materials having a $ZT \approx 2-3$ (Fig. 9) [25].

Up to this point in time, the best room temperature TE materials are based on compounds such as Bi$_2$Te$_3$ and Si$_{1-x}$Ge$_x$ [26]. So far, the best known bulk material is Bi$_{0.5}$Sb$_{1.5}$Te$_3$ which has a $ZT \approx 1$ at 300 K [22].
Figure 1.8: The figure of merit as a function of temperature for a variety of bulk TE materials [26].
Figure 1.9: Ratio of the thermoelectric efficiency to the Carnot efficiency ($\varepsilon/\varepsilon_C$) as a function of the figure-of-merit ($ZT$) [25].

1.5 Density of States

As noted previously, there are several theories which suggest enhanced TE properties in low dimensional systems. As the characteristic length of the material is decreased toward the wavelength of the electrons, the motion of the electrons (or holes) is confined in one direction, leading to a change in the shape of the electronic density of states (DOS). Figure 1.10 shows the DOS as a function of the energy for a 3D bulk material, 2D quantum well, 1D quantum wire and 0D quantum dot.
Figure 1.10: Electronic density of states for 3D bulk materials, 2D quantum well, 1D quantum wire and 0D quantum dot [27].

The parabolic shape of the DOS for bulk materials implies that the electron density surrounding the Fermi level $E_f$ is small. The spike-like shape of the DOS for quantum wires implies that the electronic states are enhanced near the Fermi level, thus resulting in an increased thermal power factor. Dresselhaus et al. [22] proposed that: (i) the Seebeck coefficient being directly related to the slope of the DOS at the Fermi surface and (ii) boundary scattering at the interface reducing the thermal conductivity much more than the electronic conductivity can lead to superior TE properties in nanostructured materials.

In the following chapters, the foundation for this thesis is laid out through discussion of QCE and optical properties (linear and nonlinear) in Bi nanorods, CdS nanowires and NiS$_2$ nanoparticles.
CHAPTER 2

BACKGROUND

2.1 Bismuth Band Structure

In Bi, the small band overlap (~38 meV), with tiny ellipses of electrons at the L-point and of holes at the T-point, is predicted to change to a small indirect band gap ($\Delta E$) when the diameter of Bi nanowires decreases below 50 nm [28, 29]. The location of the electron (L-point) and hole (T-point) carrier pockets in the Brillouin zone [30] of Bi is shown in Fig. 2.1. In bulk Bi, electron carrier pockets are three ellipsoids centered at the L-points, and the hole carrier pocket is an ellipsoid of revolution centered at the T-point whose axes coincide with the high-symmetry crystal axes as seen in Fig. 2.1. A very interesting feature about Bi is its highly anisotropic Fermi surface and non-parabolic L-point energy bands.

At low temperatures (77 K) the electronic band structure of bulk Bi at the L-points reveals highly non-parabolic electronic energy bands. These bands are mirror images of each other and are separated by a small energy gap, $E_{gl} = 13.6$ meV. [31]. Figure 2.2 shows a schematic diagrams of the Bi band structure at the L-points and T-point near the Fermi energy level, showing the band overlap, $E_0 = 38$ meV, of the L-point conduction band and the T-point valence band.
Figure 2.1: Brillouin zone for bismuth showing the location of the three electron carrier (L-point) pockets (A, B, C) and of the hole carrier pocket at the T-point [32]. The size of the electron and hole pockets are actually much smaller than shown on the diagram and the length and width ratio are greater than shown.
2.2 Semimetal-to-Semiconductor Transition

As the bismuth nanowire diameter decreases, the lowest conduction subband increases in energy and correspondingly the highest valence subband decreases in energy, so that the $L$-point band gap, $E_{gL}$, effectively increases. At the same time, as the nanowire diameter decreases, the highest $T$-point subband decreases in energy, lowering the band overlap. But because the $L$-point effective mass is smaller than that of the $T$-point, the $L$-point valence band decreases faster than that of the $T$-point, so that the indirect $L$ to $T$-point transition energy increases with decreasing wire diameter.
This indirect energy band gap can be measured experimentally in the mid-infrared spectral regime. This energy feature is assigned as the indirect transition from electronic states in the \(L\)-point valence band to unoccupied states above the Fermi energy in the \(T\)-point valence band. This \(\Delta E\) can be observed as an absorption band using infrared spectroscopy and may be tracked as a function of wire diameter, \(d\). This increase in \(\Delta E\) is related to the nanowires diameter \(d\) by,

\[
\Delta E \approx \frac{\hbar^2 \pi^2}{m^* d^2}
\]  

(2.1)

where \(m^*\) is the electron effective mass (0.001\(m_o\) - 0.26\(m_o\), depending on the crystalline direction) [19], \(m_o\) is the free electron mass and \(\hbar\) is the Planck’s constant. Cornelius \textit{et al.} [31] have observed this \(1/d^2\) dependence in their infrared absorption threshold data obtained from individual Bi nanowires with diameters between 30 and 400 nm. They ascribed the blue-shift of the absorption threshold \((E_A)\) with decreasing \(d\), to the \(d\)-dependent splitting of the valence and conduction bands (discussed later in this thesis), and consequently to the resulting energy gaps. In their study, the \(d\)-dependent absorption threshold was evident from their plots of \(A(\omega)\) vs. \(\omega\), where \(A(\omega) \approx 1 - T(\omega)\), \(\omega\) ranged between 800 – 5500 cm\(^{-1}\), and \(T(\omega)\) is the infrared transmission spectrum for each nanowire. Black \textit{et al.} [21, 30] studied the behavior of similar Bi nanowires although with a predominantly <012> orientation rather than the predominantly <110> orientation of Cornelius \textit{et al} [31]. Therefore, for a small enough diameter wire, the lowest conduction subband will no longer overlap with the highest valence subband in energy,
thus making the nanowire semiconducting [24, 33]. This transition is shown schematically in Fig. 2.3 and is known as a semimetal-to-semiconductor transition. The diameter at which this transition takes place is called the critical diameter. Figure 2.4 shows the highest valence subband energy and the lowest conduction subband energy plotted as a function of the nanowire diameter along the trigonal direction, <012>, for a Bi nanowire at 77 K [5]. Figure 2.4 was derived from the square wire model approximation which will be described in more detail in Section 3.1.3. As seen from Fig. 2.4, the critical wire diameter at which this semimetal-to-semiconductor transition

![Figure 2.3: Schematic diagram of the energy bands in a Bi nanowire undergoing a semimetal-to-semiconductor transition. The lowest conduction subband (L-point) moves up in energy and the highest valence subband (T-point) moves down in energy [24, 33].](image)

Figure 2.3: Schematic diagram of the energy bands in a Bi nanowire undergoing a semimetal-to-semiconductor transition. The lowest conduction subband (L-point) moves up in energy and the highest valence subband (T-point) moves down in energy [24, 33].
occurs is calculated to be 54.2 nm. This is where the lowest conduction subband edge formed by the $L$-point electrons crosses the Fermi level at the highest $T$-point valence subband edge and a semimetal-to-semiconductor transition occurs.

Several groups have confirmed this transition in Bi nanowires through measurements of temperature and magnetic field dependencies of the electrical resistance [6, 34] and room temperature infrared (IR) absorption spectroscopy [21, 30, 31]. Recently, Wang et al. [35] have also confirmed the semimetal-to-semiconducting transition in 5-500 nm diameter Bi nanoparticles prepared by reducing Bi$^{3+}$ with sodium borohydride in the presence of poly(vinylpyrroldone). However, Huber et al. [36] recently reported the lack of semiconducting nature in their 30 nm diameter Bi nanowire arrays and have interpreted their experimental results (using Shubnikov-de Hass
magnetoresistance measurements) in terms of surface-induced charge carriers in a spherical Fermi surface pocket. It should also be noted that a semimetal-to-semiconductor transition has been observed for Bi thin films. Rogacheva et al. [37] measured the temperature dependences of the Hall coefficient of Bi thin films and established that a film thickness smaller than ~25 – 30 nm yielded no semimetallic conductivity.

2.3 Quantum Confinement

Low dimensional materials continue to attract much interest due to their promising potential use for applications. The potential advantages of these materials arise from the spatial confinement of the carrier charges and corresponding modification of their DOS [33]. In recent years, Bi has been the focus of quantum wires for studying the modification of its DOS at lower dimensions [38]. Due to their semimetal-to-semiconducting transition, Bi nanowires have been suggested to be good TE materials [39]. This prediction is due to some of their unique properties, such as their long mean free path and high carrier concentrations. QCE in Bi nanostructures can be experimentally quantified through Fourier-transform infrared (FTIR) and UV-visible (UV-Vis) spectroscopy.

The equation for the band gap energy ($E_g$) in nanoparticles, using the effective mass model, can be expressed as [40, 41]
\[ E_g = E_{g}^{bulk} + \frac{\hbar^2 \pi^2}{2e r^2} \left( \frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right) - \frac{1.8e}{4\pi \varepsilon \varepsilon_0 r} - \frac{0.124 e^3}{\hbar^2 (4\pi \varepsilon \varepsilon_0)^{3/2}} \left( \frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right)^{-1} \]  

(2.2)

where \( E_{g}^{bulk} \) is the bulk band energy, \( \hbar \) is Plank’s constant, \( r \) is the particle radius, \( m_e^* \) is the electron effective mass, \( m_h^* \) is the hole effective mass, \( m_o \) is the free electron mass, \( e \) is the charge on the electron, \( \varepsilon \) is the relative permittivity, and \( \varepsilon_0 \) is the permittivity of free space. This formula is possible because of the correlation between electron and hole positions, induced by the Coulomb interaction, is not strong. The major effect is additive, independent confinement energies for the electrons and holes [41]. The above calculation is for a 0D quantum dot. What happens when the 1D quantum wire system is studied? Gudiksen et al. [42] recently explored these size-dependent effects on the photoluminescence in InP nanowires. The effective mass model was modified by using radially symmetric wave functions for both electrons and holes. The calculated energy shift, relative to the bulk band gap, can be expressed as a function of the nanowire radius, \( R \). This new wave function can be written as

\[ \Delta E = \frac{\hbar^2}{2m} \left( \frac{\alpha_{01}}{R} \right)^2 + \left( \frac{\pi}{L} \right)^2 - \left| \Psi(x_e) \Psi(x_h) \right| e \frac{e^2}{\varepsilon |x_e - x_h|} \Psi(x_h) \Psi(x_e) \]  

(2.3)

where \( m^* \) is the reduced effective exciton mass \((m_e m_h/(m_e + m_h))\), \( \varepsilon \) is the dielectric constant of InP, \( L \) is the length of the cylinder, and \( \alpha_{01} \) is the first zero of the zeroth-order Bessel function (2.405) [43]. The first term of the above equation is dependent on the sum of the inverse radius and inverse length of the nanowire. The second term is the
attractive Coulomb interaction between the electron and the hole. As seen from the above expression, the only term which strongly influences the band gap energy is the inverse sum of the first term.

It has already been discussed in Fig. 2.4 that Bi exhibits a semimetal-to-semiconducting transition at ~54 nm. The above equation (Eq. (2.3)) can tell us at what critical value $d$, the Bi nanorods will exhibit QCE. Figure 2.5 shows the predicted band gap energy versus the nanorods diameter using the modified effective mass model for Bi nanorods. For Bi nanorods, the following conditions were applied to Eq. (2.3). The electron effective mass, $m_e^*$ is 0.001$m_o$, $m_h^*$ is 0.059$m_o$, $\epsilon$ is ~100 and the bulk band gap, $E_{g}^{\text{bulk}}$ is 38 meV. As can be seen from Fig. 2.5, Bi nanorods are not predicted to show appreciable QCE until a nanorod diameter of ~35 nm is reached.
Figure 2.5: Plot of the predicted band gap energy as a function of nanorod diameter based on the modified effective mass model for Bi nanorods [44].

2.4 Experimental Results

Bismuth nanorods (~10 nm in diameter) were successfully prepared using the pulsed laser vaporization (PLV, please see Chapter 3 for more details) technique [44]. The morphology of the as-prepared nanomaterials obtained from the PLV method of an Au-impregnated Bi target was analyzed via high-resolution transmission electron microscopy (HR-TEM). In addition to TEM, the crystal structure of the 1D structures was determined by using electron diffraction. Figure 2.6(a) shows a TEM image of the as-produced deposit collected on the cold finger. The deposit predominantly contains filamentous nanostructures which were dispersed amongst spherical Bi nanoparticles and flat Bi$_2$O$_3$ sheets. When viewed under a HR-TEM (Fig. 2.6(b)), the filamentous objects
resemble nanorods (short 1D structures) as opposed to nanowires. The nanorods contain a crystalline core of Bi encapsulated in a thin (< 2 nm) Bi$_2$O$_3$ layer (Fig. 2.6(c)). From the analysis of the electron diffraction pattern (inset Fig. 2.6(c)), the nanorod growth direction was found to be <012>. Furthermore, the lattice spacing of the planes oriented along the length of the Bi nanorods was found to be 0.328 nm, which is consistent with the <012> growth direction in the trigonal Bi crystal structure. The dominant nanorod diameter was ~10 nm with an average length of ~200 nm.

Figure 2.6: (a) TEM image of the as-prepared Bi deposit obtained from a pulsed laser vaporization of an Au-impregnated bismuth target. (b) HR-TEM image of an isolated Bi nanorod with a diameter of ~10 nm wrapped in a thin Bi$_2$O$_3$ sheath. (c) HR-TEM image of a Bi nanorod showing the excellent ordering of the lattice planes. Inset shows the corresponding selected area diffraction pattern for the Bi nanorods [45].

Recently, Black et al. [30] made IR absorption measurements on their ~45 nm Bi nanowires grown inside an alumina template. Figure 2.7 (inset) shows the previously reported IR absorption band at ~965 cm$^{-1}$ for 200 nm diameter nanowires [21]. This band was found to be blue-shifted in energy to ~1090 cm$^{-1}$ in the IR spectrum for a 45 nm diameter Bi nanowires. Interestingly, a further blue-shift in energy to ~1393 cm$^{-1}$ was observed for our ~10 nm Bi nanorods. In an independent infrared experiment, we
confirmed that the IR band featured in Fig. 2.7 was not due to the presence of the residual Bi\textsubscript{2}O\textsubscript{3} present in the as-obtained deposit (Fig. 2.8). It is known that Bi\textsubscript{2}O\textsubscript{3} has very little optical absorption in the spectral range depicted in Fig. 2.7 [30]. Under identical synthesis conditions used in this study, the PLV of a rotating Bi target without the gold catalyst yields a cold-finger deposit which do not contain the nanorods, and the 1393 cm\textsuperscript{-1} feature is absent in the IR spectrum.

Figure 2.7: FTIR absorption spectrum for \textasciitilde 10 nm Bi nanorods. The inset absorption spectra reveals the presence of broad absorption bands at 965 cm\textsuperscript{-1} and 1090 cm\textsuperscript{-1} in 200 and 45 nm diameter wires, respectively Black \textit{et al}. [21].
Figure 2.8: Room temperature IR absorption spectra of Bi nanorods annealed in air for 5 hrs. As annealing time increases, the 1393 cm$^{-1}$ peak intensity decreases.

Figure 2.9 shows a plot of the band gap energy $\Delta E$ (left $y$-axis) vs. inverse $d$-dependence (bottom $x$-axis) for nanowires studied by Black et al. (▲) [21] and our ~10 nm diameter nanorods (■), and the inverse $d$-dependence (top $x$-axis) for the absorption threshold $E_A$ (right $y$-axis) reported by Cornelius et al. (○) [31]. As seen from Fig. 2.9, the frequency shift was consistent with a $1/d^2$ behavior as predicted by quantum confinement.
Figure 2.9: Dependence of the band gap energy ($\Delta E$) and absorption threshold energy ($E_A$) on the diameter of Bi nanorods and nanowires. The ○ represent $E_A$ values (right y-axis) reported by Cornelius et al. [31] for their nanowire diameters (top x-axis). The ▲ and ■ data points represent the diameter-dependence (bottom x-axis) for $\Delta E$ (left y-axis) reported by Black et al. [21] and this study, respectively. The solid line represents the best fit line showing a $1/d^2$ dependence [45]. Inset show the $1/d^2$ dependence of Black et al. and our ~10 nm Bi nanowires which have the same growth direction <012>.

In our UV-visible absorption studies, a UV-visible (model PerkinElmer Lambda 950) spectrometer was used to study the as-prepared Bi nanorods. As a further confirmation of the QCE, we suspended our as-prepared deposit (~3 mg) in ethanol (~10 ml) and measured its UV-visible absorption spectrum. Wang et al. [46] reported observing a surface plasmon absorption peak at 281 nm (4.4 eV) in 6.5 nm Bi nanoparticles. Surface plasmons are coherent electron oscillations that exist at the interface between any two materials where the real part of the dielectric function changes
sign across the interface (e.g. a metal-dielectric interface, such as a metal sheet in air). Surface plasmons have lower energy than bulk plasmons which quantize the longitudinal electron oscillations about positive ion cores within the bulk plasma. They can also propagate along the surface of a metal until energy is lost either via absorption in the metal or radiation into free-space. We observed a broad peak present at 302 nm (4.1 eV) that was due to the surface plasmon absorption (Fig. 2.10). The observation of a surface plasmon in our Bi nanorods is suggestive of carriers which produce a collective mode near the surface of the nanorod. Consistent with the QCE, the surface plasmon peak in the nanorod spectrum was red-shifted relative to the corresponding peak reported for the Bi nanoparticles.

Figure 2.10: UV-visible absorption spectrum shows the as-prepared Bi nanorods suspended in ethanol referenced against bulk Bi powder. An absorption peak is observed at 302 nm or 4.1 eV [45].
2.5 Other Nanostructures with Interesting TE Properties

2.5.1 Nickel Sulfide

Nickel Sulfide (NiS) was selected due to its narrow band gap and simultaneously unusual magnetic properties [47]. The hexagonal phase (see Fig. 2.11) of NiS undergoes a metal-to-insulator transition between 150 and 260 K depending on the sulfur content [48]. Below this temperature a small band gap (~100 meV) opens up due to electron correlation. Above the transition temperature NiS shows paramagnetism, and below NiS is anti-ferromagnetic. Kloc et al. [47] recently grew single crystals of NiS via the Bridgman method and performed resistivity and Seebeck measurements on them (Fig. 2.12). The resistivity measurements revealed a magnetic phase transition while the Seebeck coefficient of the anti-ferromagnetic phase was only slightly larger than that of the paramagnetic phase. Photonic nanoparticles systems have attracted considerable

![Hexagonal crystal structure of nickel sulfide.](image)
attention due to a wide variety of nonlinear optical (NLO) applications such as optical limiting, saturable absorption, second harmonic generation and two-photon absorption [49-52]. In our present study, we will show that a new synthesis technique of NiS nanoparticles (~5 – 10 nm in diameter) can be engineered to deliver systems displaying more complex behavior involving the interplay of two nonlinear phenomena or more.

![Figure 2.12: Resistivity and thermopower of NiS near antiferrmagnetic and paramagnetic transition [47].](image)

2.5.2 Cadmium Sulfide

As a direct wide band gap (~2.42 eV) semiconductor in the visible range, with a cubic structure (see Fig. 2.13), cadmium sulfide (CdS) is an excellent material used for a host of applications in optoelectronics, such as nonlinear optics and light-emitting diodes [53, 54]. The increased interest in such materials arises mainly from their band gap tunability; the band gap increases upon decreasing the size as a result of quantum
confinement. Synthesis of such materials with confined dimensions and desired optical and electronic properties is always a challenging issue in nanoscale device technology.

Several synthetic routes have been followed in an attempt to develop nanomaterials with specific composition, size and crystallinity [55]. Xiong et al. [56] used an *in situ* micelle-template-interface reaction route to prepare CdS nanowires of ~5 nm diameter through a rolling-broken-growth process. Highly aligned nanowires (50 – 200 nm in diameter) have been prepared using the physical evaporation of CdS powder. Recently, Khabibullaev et al. [57] used an electrochemical deposition method to fill pores of an Al2O3 matrix. Measurements of the heat capacity and thermal conductivity of the porous Al2O3 films and CdS/Al2O3 nanostructures were preformed. For the porous Al2O3, the effective thermal conductivity was measured long the pore length and was found to be 1.47 W/(m·K) [58] at 293 K and decreases to ~100 W/(m·K) at 90 K, which makes this structure an attractive matrix for the creation of various TE energy converters. Figure 2.14(a) shows a SEM image of the CdS nanowires imbedded inside the porous Al2O3 matrix. Figure 2.14(b) shows a comparison of the temperature dependence of the thermal conductivity of the CdS nanostructures with the experimental data for bulk CdS. Most of these methods described above require several catalyst or high temperatures. We will report on (Chapter 5) a new synthesis technique for CdS nanowires (50 – 100 nm in diameter) and their unique optical properties.
Figure 2.13: Cubic crystal structure of cadmium sulfide.

Figure 2.14: (a) SEM image of the porous Al₂O₃ matrix with CdS nanowires grown in the pores. (b) Temperature dependences of the thermal conductivity of bulk and nanostructured CdS embedded in Al₂O₃ [39].
Pulsed laser vaporization (PLV) was one of the first methods developed for synthesizing nanowires. Morales et al. [59] at Harvard University first used the principle of the vapor-liquid-solid growth process in their PLV apparatus to grow small diameter Si and Ge nanowires. Figure 3.1 shows a schematic of our PLV system. In our PLV process, a Nd:YAG laser (Yttrium-aluminum-garnet, 1064 nm excitation, 650 mJ/pulse, 10 Hz) was used to ablate a rotating target with the elemental composition desired in the nanowire forms. For example, for preparing Bi nanorods, a target was first prepared by compacting Bi powder which contains one atomic percent Au catalyst particles. Next, the target was placed on a rotating rod which resides inside a quartz tube reactor maintained at 200°C. The quartz tube was sealed at both ends and a continuous flow of argon (flow rate ~150 sccm) and hydrogen (flow rate ~15 sccm) assisted in transporting the ablated material downstream to the water-cooled copper cold finger placed inside the quartz tube. As the target is ablated, the vaporized material and catalyst particles flow downstream and condense on the cold finger [45]. During the reaction, the catalyst particles serve as the seed for the nanowire growth. After the reaction, the reactor is cooled to room temperature and the ablated material is collected from the cold finger. The low-temperature FTIR and nonlinear optical properties (NLO) will be discussed in further detail in this section.
3.1 Low-Temperature Infrared Absorption

3.1.1 Two Band Model

Since Bi has 3-fold trigonal symmetry (Fig. 3.1); there are three equivalent \(L\)-points and one \(T\)-point. The constant energy hole ellipsoid at the \(T\)-point may be characterized by the effective mass tensor at the valence band edge and may be written in Cartesian coordinates as the following:

\[
M_h = \begin{bmatrix} m_{h1}^* & 0 & 0 \\ 0 & m_{h2}^* & 0 \\ 0 & 0 & m_{h3}^* \end{bmatrix} \quad (3.1)
\]

where \(x\), \(y\), and \(z\) coordinates correspond to the binary, bisectrix, and trigonal axes (Fig. 2.1), respectively. \(m_{h1}^* = m_{h2}^*\) due to symmetry and \(m_{h3}^* >> m_{h1}^*\), indicating a large anisotropy in the \(T\)-point hole Fermi surface. At 0 K, the effective mass components (derived from Shudnikov-de Hass measurements) are \(m_{h1}^* = m_{h2}^* = 0.059\) and \(m_{h3}^* = 0.634\) [19]. All of the effective masses are given as a function of the free electron mass \(m_0\). The \(T\)-point effective mass values are not expected to have a strong temperature dependence. The valence band at the \(T\)-point is well approximated by a parabolic dispersion relation [60]:

\[
E_T(\vec{k}) = E_{T,0} - \frac{\hbar^2}{2m_0} \vec{k} \cdot M_h^{-1} \cdot \vec{k} \quad (3.2)
\]
Figure 3.1: (a) Bismuth crystal structure showing 4 unit cells. Z-axis is pointing upward. (b) Hexagonal pattern created by the trigonal (3-fold) symmetry of Bi. Z-axis is pointing out of the page.

where $E_{T,0}$ is the energy at the $T$-point valance-band edge, and $M_h^{-1}$ is the inverse of the $T$-point hole effective mass tensor in Eq. (3.1); where $M_h^{-1}$ is:

$$M_h^{-1} = \begin{bmatrix} \frac{1}{m_{h1}} & 0 & 0 \\ 0 & \frac{1}{m_{h2}} & 0 \\ 0 & 0 & \frac{1}{m_{h3}} \end{bmatrix}$$

(3.3)

and

$$\vec{k} = \begin{bmatrix} k_x \\ k_y \\ k_z \end{bmatrix}$$

(3.4)
By expanding Eq. (3.2),

\[
E_T(\vec{k}) - E_{T,0} = -\frac{\hbar^2}{2m_0} \left( \frac{k_x^2}{m_{h1}^*} + \frac{k_y^2}{m_{h2}^*} + \frac{k_z^2}{m_{h3}^*} \right)
\]

(3.5)

we can see that the constant energy surfaces are indeed ellipsoids centered at the \( T \)-point and having their major axes in the trigonal (\( z \)) direction. The two minor axes are equal and can therefore be aligned with the binary and bisectrix axes [61].

The dispersion relation for the \( L \)-point carriers is much more complex. The principal axes of the \( L \)-point ellipsoids are not aligned with the trigonal, bisectrix, and binary axes, thus making the effective mass tensor not diagonal in our Cartesian coordinates. The generalization of noncubic materials uses a Lax two-band model [60] and in the case of Bi, the electron pocket at the \( L \)-point can be approximated by its effective mass tensor

\[
M_e = \begin{bmatrix}
  m_{e1}^* & 0 & 0 \\
  0 & m_{e2}^* & m_{e4}^* \\
  0 & m_{e4}^* & m_{e3}^*
\end{bmatrix}
\]

(3.6)

Where \( m_{e2}^* > m_{e1}^*, m_{e3}^* \) and the \( x \) axis is the binary axis perpendicular to the mirror plane in Bi and the matrix elements have four independent components, while the major axis and the other minor axis lie in the trigonal-bisectrix plane. At 0 K, the effective mass components (derived from Shudnikov-de Hass measurements) in units of \( m_0 \) are
$m^*_{e_1} = 0.00113$, $m^*_{e_2} = 0.26$, $m^*_{e_3} = 0.00443$, and $m^*_{e_4} = 0.0195$ [19, 62]. Unlike the $T$-point, the $L$-point band structure has a strong temperature dependence for temperatures above 80 K [63, 64], and the $L$-point effective mass components vary with temperature approximately according to the empirical relation given by Vecchi and Dresselhaus [64], obtained from magneto-reflection studies is

$$m^*(T) = \frac{m^*(0)}{1 - 2.94 \times 10^{-3} T + 5.56 \times 10^{-7} T^2}.$$  (3.7)

Equation (3.7), for $T = 300$ K, becomes $m^*(300) = 5.951 \times m^*(0)$, so the $L$-point effective mass components at 300 K become $m^*_{e_1} = 0.00672$, $m^*_{e_2} = 1.547$, $m^*_{e_3} = 0.02636$, and $m^*_{e_4} = 0.116$. The other two $L$-point pockets are obtained by 120° rotations of $M_e$ about the trigonal ($z$) axis. As we can see from Fig. 2.1 and from the effective mass tensor in Eq. (3.6), one of the minor ellipsoids axes is along the binary axis.

The $L$-point band structure can be best described by using the Lax model [60], which makes use of $k \cdot p$ perturbation theory [65] for a strongly coupled two-band model ($L$-point valence and conduction bands).

Taking the energy at the band edge of the $L$-point conduction band to be zero, the Lax model [60] gives the following non-parabolic dispersion relations:

$$E_L(k) = -\frac{E_{gl}}{2} \left( 1 \pm \sqrt{1 + \frac{2\hbar^2}{m_0E_{gl}} k \cdot M_e^{-1} \cdot k} \right)$$  (3.8)
where

\[
M_e^{-1} = \begin{bmatrix}
\frac{1}{m_{e1}^*} & 0 & 0 \\
0 & \frac{m_{e3}^*}{m_{e2}^* m_{e3}^* - m_{e4}^*} & \frac{m_{e4}^*}{m_{e2}^* m_{e3}^* + m_{e4}^*} \\
0 & \frac{m_{e4}^*}{-m_{e2}^* m_{e3}^* + m_{e4}^*} & \frac{m_{e2}^*}{m_{e2}^* m_{e3}^* - m_{e4}^*}
\end{bmatrix}
\]

The + and – signs describe the dispersion relations of the $L$-point valence and conduction bands, respectively, which are mirror images of each other due to their strong coupling. The magnitude of the $k$ vector or energy dependence of the effective mass is very important in narrow gap materials such as Bi. At the band edge, the effective mass parameter for electrons in Bi is $\sim 0.001 m_0$ whereas at the Fermi level $m^* \sim 0.008 m_0$ [19]. The number of electron carriers in Bi is only $10^{17} \text{ cm}^{-3}$. The density of states for simple bands in a 3D crystal has a dependence $\sim m^{3/2} E^{1/2}$, but we can expect a large increase in the density of states with increasing energy in a non-parabolic band with a small effective mass at the band edge. This basic model can be used to handle the corresponding dispersion relations in the nanowires, which maintain the same crystal structure as bulk Bi, with the same lattice constants down to $\sim 7 \text{ nm}$ in diameter [33].
3.1.2 Indirect $L$–$T$ Transition

In bulk Bi, optical absorption is dominated by the direct $L$-point valence band to conduction band transitions [66]. At low temperatures, the threshold energy for this transition is $E_{gl} + 2E_f$ (Fig. 3.2), assuming mirror bands for the conduction and valence bands at the $L$-point as in the Lax two-band model [60].

In a nanowire, assuming parabolic bands, the subbands split apart in energy proportionally to $\frac{\hbar^2}{(m_p^*d^2)}$, where $m_p^*$ is the in-plane effective mass of the nanowire and depends on crystalline orientation. Note that the highest $L$-point valence band subband decreases in energy faster than the highest $T$-point valence subband since the $L$-point effective mass components (~0.001$m_o$) are smaller than the $T$-point effective mass (~0.26$m_o$) components. Although this indirect valence band transition may occur in bulk Bi ($L$-$T$ transition), it is not easily observed because optical absorption in bulk Bi is dominated by the direct $L$-point transition and free carrier absorption processes [61].

Figure 3.2 again shows a schematic view of the electronic band structure of bulk Bi near the Fermi surface (notice this schematic is without the $T$-point conduction band,
Figure 3.2: A schematic of the bismuth band structure near the Fermi level, indicating the direct band at the $L$-point ($E_{gL}$), as well as the band overlap $E_0$ from the $T$-point valence band edge to the $L$-point point conduction band edge.

which does not play a role in the $L$-$T$ transition). Also notice that the energy difference between the $L$ and $T$-point band edges can be expressed as $E_{gL} + E_0$ in bulk Bi. The situation remains the same for a nanowire, except the highest valence subbands decrease in energy due to quantum confinement. We will call this energy difference, $\Delta E_L(d)$, the difference between the band edges at the $L$-point of the valence band in bulk Bi and the highest $L$-point valence subband of a nanowire of diameter $d$. The corresponding term at the $T$-point is $\Delta E_T(d)$. We obtain the formula for the energy of the $L$-$T$ transition (see Fig. 3.3) in nanowires to be

$$E_{L-T}(d) = E_{gL} + E_0 - \Delta E_L(d) + \Delta E_T(d).$$

(3.10)

Note that $E_{gL}$ and $E_0$ are bulk quantities. When diameter $d$ becomes small enough (~50 nm), the nanowire undergoes a transition from semimetal-to-semiconductor (as discussed
in Chapter 2). For this value of $d$, the highest valence subband at the $T$-point will fall below the Fermi energy, so that there are no longer any holes at the $T$-point and there will no longer be states to accept $L$-point valence electrons, thus quenching the $L$-$T$ transition.

3.1.3 Square Wire Model for $L$-$T$ Transition

In the simplest model [60], but one that still explains several of the keys features in of the $L$-$T$ transition, we assume that the $L$- and $T$-point carrier pockets each have an isotropic effective mass, which we call $m^*_e$ and $m^*_h$ respectively. For the isotropic effective mass, the carrier pockets are assumed to be spherical in nature for both the
electrons and holes. Let \( m^*_e \) and \( m^*_h \) be the effective mass values at the \( L \)- and \( T \)-points of the Bi Brillion zone, respectively.

Long square wires of side length \( d \) were calculated treating the nanowire as an infinite potential well. The square wire model [67] is easy to implement and the infinite potential assumption is generally quite accurate. Let \( z' \) be the direction of the nanowire axis and let \( x' \) and \( y' \) be oriented along the sides of the square wires, in the plane of the nanowire cross section. Since the mass is assumed to be isotopic, it does not matter how we choose of axes \( x' \) and \( y' \), as the in-plane mass is always the same in this simplified model. The vector \( \vec{k} \) in Eqs. (3.2) and (3.8) consist of components \( k_{x'} \), \( k_{y'} \), and \( k_z \). Due to quantum confinement, the values of \( k_{x'} \) and \( k_{y'} \) will be quantized:

\[
k_{x'} = k_{y'} = \frac{n\pi}{d}
\]  

(3.11)

For the highest valence subband, as we are considering, we have \( n = 1 \). To find \( \Delta E_T (d) \), we use Eq. (3.2):

\[
\Delta E_T (d) = E_T (d) - E_{T,0} = -\frac{\hbar^2}{2m_0} \vec{k} \cdot M_\text{h}^{-1} \cdot \vec{k} = -\frac{\hbar^2}{2m_{h,p} m_0} \left( k^2_{x'} + k^2_{y'} + k^2_z \right) 
\]  

(3.12)

Substituting Eq. (3.11) into Eq. (3.12), and noting that \( k_z = 0 \) at the band edge:
\[
\Delta E_t(d) = -\frac{\hbar^2}{2m_{h,p}m_0} \left(2\pi^2\right) = -\frac{\hbar^2}{4m_{h,p}m_0d^2} .
\]  

(3.13)

Similarly, we use Eq. (3.8) to obtain \( \Delta E_L(d) \)

\[
\Delta E_L(d) = \frac{E_{gl}}{2} \left(1 - \sqrt{1 + \frac{2\hbar^2}{m_0E_{gl}}} \cdot \frac{\mathbf{k} \cdot M_e^{-1} \cdot \mathbf{k}}{E_{gl}} \right) = \frac{E_{gl}}{2} \left(1 - \sqrt{1 + \frac{1}{E_{gl}m_{e,p}m_0d^2}} \right)\hbar^2 .
\]  

(3.14)

The expressions \( \Delta E_t(d) \) and \( \Delta E_L(d) \) in Eqs. (3.13) and (3.14) can be inserted into Eq. (3.10), along with the bulk values \( E_{gl} \) and \( E_0 \) (see Table 3.1), to find the transition energy \( E_{L-T}(d) \)

\[
E_{L-T}(d) = E_{gl} + E_0 - \frac{E_{gl}}{2} \left(1 - \sqrt{1 + \frac{1}{E_{gl}m_{e,p}m_0d^2}} \right) - \frac{\hbar^2}{4m_{h,p}m_0d^2} .
\]  

(3.15)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Temperature Dependence</th>
</tr>
</thead>
</table>
| Band overlap (meV): \( E_0 \) | \( -38 \)  
| \( -38 - 0.044(T - 80) + 4.58 \times 10^{-4}(T - 80)^3 - 7.39 \times 10^{-6}(T - 80)^3 \) \((T < 80K)\)  
| \( -38 - 0.044(T - 80) + 4.58 \times 10^{-4}(T - 80)^3 - 7.39 \times 10^{-6}(T - 80)^3 \) \((T > 80K)\)  
| L-point direct band gap (meV): \( E_{gl} \) | \( 13.6 + 2.1 \times 10^{-3}T + 2.5 \times 10^{-4}T^2 \)  
| L-point electron: \( m_{e,p}^* \) | \( \frac{m^*(0)}{1 - 2.94 \times 10^{-3}T + 5.56 \times 10^{-7}T^2} \)  

Table 3.1: Temperature dependence values for \( m_{e,p}^* \), \( E_0 \) and \( E_{gl} \) for bulk Bi.
3.1.4 Energy of the $L$-$T$ Transition

One difficulty in implementing this model (Eq. (3.15)) is the fact that the bulk Bi band parameters are not accurately known at room temperature. The $L$-point band gap and the $L$-$T$ band overlap have be estimated to be $E_{gL} = 38$ meV and $E_0 = 98$ meV, respectively, but since only one study measures these values, it is not clear how accurate there values are. We will use the published value of $E_{gL} = 38$ meV and calculate $E_0$ using Eq. (3.15).

There are three experimental data points available to us that have been identified as an $L$-$T$ transition. Black et al. [30] measured absorption peaks at 965 cm$^{-1}$ (119.6 meV) and 1090 cm$^{-1}$ (135.1 meV) for nanowires with diameters of 200 and 45 nm, receptivity, while our 10 nm diameter nanorods observed an absorption peak at 1393 cm$^{-1}$ (172.7 meV). Levin et al. [61] recently used these values to obtain the band overlap $E_0$. They used values obtained from calculating the in-plane effective mass (Table 3.2) such that $E_{gL} = 38$ meV, $m^*_h,p = 0.0835$, and $m^*_e,p = 0.014$ and inserted them into Eq. (3.15), for $d = 200$ nm. This gave them a value of $E_0 = 82.5$ meV. Note that the cross-sectional area of a cylindrical wire of diameter $d$ is smaller by a factor $\pi/4$ than the cross-sectional area of a square wire with side length $d$. Therefore, in Fig. 3.4, $d^2$ has been multiplied by $\pi/4$ in Eq. (3.15) in order to account for the cross-sectional area. Levin et al. [61] plotted the parameters of the non-parabolic model (Eq. (3.15)) as a function of $E_{L-T}$ vs. $1/d^2$ for
Table 3.2: Values of the $m_p^*$ components for each carrier pocket (in units of $m_0$), calculated for nanowires oriented in the [012] direction.

<table>
<thead>
<tr>
<th>Pocket</th>
<th>$m_p^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>0.0835</td>
</tr>
<tr>
<td>$L(A)$</td>
<td>0.020</td>
</tr>
<tr>
<td>$L(B)$</td>
<td>0.011</td>
</tr>
<tr>
<td>$L(C)$</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Figure 3.4: A plot of $E_{L-T}$ vs. $1/d^2$ for the non-parabolic model, with $d$ ranging from 300 to 10 nm. The blue trace (top) uses a value of $m_{e,p}^* = 0.011$, the green trace (middle) uses $m_{h,p}^* = 0.014$, and the red trace (bottom) uses $m_{e,p}^* = 0.020$. The three experimental data points ($d = 300, 45, 10$ nm) are indicated by arrows and their respective energy peaks are plotted as blue circles, and they best fit to $L(B)$ [61].
each of the three in-plane $L$-point masses in Table 3.2. Levin et al. [61] included all three experimental data points (Black et al. [30] and our 10 nm dia. nanorods [45]) as reference, and use the values $E_0 = 82.5$ meV and $E_{gl} = 38$ meV. They concluded that the energy of the transition has a strong dependence of the value of $m_{e,p}^*$ [61]. One can see from Fig. 3.4 the non-parabolic model agrees well with the experimental data and especially well when the calculated value of the $L(B)$-point in-plane effective mass, $m_{e,p}^* = 0.011$, is used.

By looking at Fig. 3.4 it can be found that the $L(B)$-point in-plane effective mass best fits to the non-parabolic model, hence we decided to take a closer look at the $L(B)$-point.

Using the empirical relationships determined for these values as a function of temperature $T$ [64], we have expanded on the non-parabolic model presented by Levin et al. [61] and predict the energy of the $L-T$ transition for a range of temperatures from room temperature down to 80 K, for transitions from any of the three $L$-points, as three distinct peaks have been observed at room temperature and attributed to this indirect transition. This model of the $L-T$ transition also implies a $T$ dependence. The $L$-point band structure, in contrast to the $T$-point, has a strong $T$ dependence above 80 K due to the coupling between the non-parabolic $L$-point valence and conduction bands. Using Mathematica, we can generate the $E_{L-T}$ transition, using the $L(B)$ effective mass components, as a function of $T$. As seen in Fig. 3.5, for the $L(B)$-$T$ transition, we expect to observe a downshift of the transition frequency on the order of $\sim 140$ cm$^{-1}$ (in the IR absorption spectrum) for nanowires with diameter $\sim 10$ nm as $T$ decreases from 300 K to 100 K. We also expect a narrowing of the peaks, as the lower temperatures should reduce dissipation. Although the values used for the bulk band parameters are not known with high accuracy at these temperatures, empirically derived formulas have been used to
Figure 3.5: A plot of $E_{L-T}$ vs. $1/d^2$ for the non-parabolic model. Using $m^*_{e,p} = 0.011$ for the $L(B)$-$T$ transition and plotted as a function of temperature.

approximate the shift as a function of $T$, and the shift in frequency should still be significant compared to the resolution of the instrument, and easily observed over the temperature range used. The $L(A)$-$T$ and $L(C)$-$T$ transitions, Fig. 3.6 and 3.7, respectively, were also calculated (using the $m^*_{p}$ values found in Table 3.2) to determine if they too had strong temperature dependence. It was found that the $L(A)$-$T$ transition (Fig. 3.6) should shift by $\sim$30 meV ($\sim$245 cm$^{-1}$) and that the $L(C)$-$T$ transition (Fig. 3.7) should shift by $\sim$35 meV ($\sim$290 cm$^{-1}$) with decreasing $T$. 

50
Figure 3.6: A plot of $E_{L,T}$ vs. $1/d^2$ for the non-parabolic model. Using $m^*_{e,p} = 0.020$ for the $L(A)-T$ transition as a function of temperature.

Figure 3.7: A plot of $E_{L,T}$ vs. $1/d^2$ for the non-parabolic model. Using $m^*_{e,p} = 0.014$ for the $L(C)-T$ transition as a function of temperature.
Recently, we measured the absorption spectrum of Bi nanorods with \( d \approx 10 \text{ nm} \) (Fig. 2.7). Briefly, a modified Bruker FTIR spectrometer (model IFS 66v/s) equipped with a deuterated triglycine sulfate detector was used to measure the infrared absorption spectrum of the as-prepared Bi nanorods in the range of 400 – 4000 cm\(^{-1}\). A potassium bromide (KBr) beamsplitter was used in the interferometer. About \( \sim 3 \text{ mg} \) of the as-prepared deposit was mixed with \( \sim 50 \text{ mg} \) of KBr powder (Thermo Spectra-Tech, FT-IR Grade 99+\%) and pressed into a 5 mm diameter pellet [45]. The sample chamber was cooled to 77 K (see Appendix A for details) and evacuated to 2 \( \mu \text{bar} \) in order to eliminate the interfering infrared (IR) absorption by the water vapor and \( \text{CO}_2 \) present in the ambient atmosphere. A platinum resister (OMEGA Engineering, 2PT100KN3026) was used to measure the temperature at the sample. Figure 3.8(b) shows the 293 K and 83 K IR spectra for our Bi nanorods as well as the change in the full width half maximum (FWHM) of the 1393 cm\(^{-1}\) absorption peak (inset Fig. 3.8(b)). The FWHM change follows \( e^{-\hbar \omega / kT} \) nicely. As seen from Fig. 3.8(a) and (b), the absorption peak of our Bi nanorods does not change position as \( T \) changes. However, the FWHM does decrease with decreasing \( T \).
Figure 3.8: (a) Infrared absorption spectrum of 10 nm Bi nanorods as a function of temperature. The main peak at 1393 cm\textsuperscript{-1} is due to the $L$ to $T$-point transition. (b) Infrared absorption spectrum of Bi nanorods at 300K and 83K. The inset shows the linear trend of the FWHW 1393 cm\textsuperscript{-1} peak.
We can clearly resolve the IR band into a main absorption peak centered at around 1393 cm\(^{-1}\), as well as a second smaller peak around 1460 cm\(^{-1}\). This second peak can be identified with an indirect process in the scheme of Black et al. [21, 30] in which the incident photon energy is used to create a phonon spanning the \(L\) and \(T\)-points in the Brillouin zone providing for momentum conservation, as well as a photon of energy of 1393 cm\(^{-1}\) to excite an electron from the \(L\)-point valence band to the \(T\)-point valence band. An additional third absorption peak is seen as a weak shoulder around 1360 cm\(^{-1}\) and is identified with the absorption of a phonon spanning the \(L\) and \(T\)-points and the excitation of an electron from the \(L\) to \(T\)-points in the Brillouin zone. This feature is expected to be weak due to the low probability of having a \(\sim 70\) cm\(^{-1}\) phonon thermally excited at 300 K [66].

Finally, it is important to raise questions about the point that the IR absorption peaks in our \(\sim 10\) nm nanorods do not exhibit a red-shift (downshift) with decreasing \(T\). We know that below the semimetal-to-semiconductor transition, the \(L-T\) transition is quenched, as there are no more empty states in the highest \(T\)-point valence subband to accept electrons. Lin et al. [5] predicted this transition to occur at \(\sim 14.0\) nm for nanowires oriented in the [012] direction.

Although the theory described above in Eq. (3.15) agrees well with room temperature data, it severely lacks in predicting / understanding the \(E_{L-T}\) transition at low temperatures. Several groups [68-70] have used angle-resolved photoemission spectroscopy (ARPES) and first-principles calculations to help predict when the lowest
quantized subband of the electron pocket is raised to an energy higher than the highest hole subband in thin films (~13 nm thickness) of Bi.

Angle-resolved photoemission spectroscopy makes use of the photoelectric effect to study the electron structure of solids. First, a lamp outputs photons to a small, thin sample. The phonons then bombard electrons out of the substance, and a sensor collects these electrons. The sensor measures the number of electrons, their momentum (measured by the angles) and their kinetic energy. The data collected by the APRES sensor provides information about electrons’ energy after the photons bombard them on the sample.

A band gap develops when the film thickness ~50 nm (known as the semimetal-to-semiconductor transition). Such the prediction is based on the bulk band structure, but when the system downsizes to the nanometer scale, significant contributions from the surface effects are predicted [69, 71]. In remarkable contrast to the predicted semimetal-to-semiconductor transition, it is found that film (≥ 7 bilayers) are highly metallic and their Fermi surfaces have little thickness and temperature dependence, and thus the dominant conduction electrons are associated with surface states rather than bulk states formed by surface states [72].

One way surface states can alter the optical properties of a material is by inducing band bending to the material near the surface. Bismuth nanowires differ from bulk Bi insofar as nanowires are expected to have a high surface-to-volume ratio. Depending on the method of preparation of nanowires, surface states may be formed resulting in a tube of charge at the nanowire surface. An example of such surface states is found in Bi nanowires prepared by the Ulatovski method, whereby the wires are drawn in a glass tube
and are very rapidly cooled. Such surface states were first reported by Brandt et al. [73] in Bi wires of 800 nm in diameter, where magneto-oscillatory effects periodic in magnetic field were observed. The carrier density of the surface states far exceed the intrinsic carrier density and dominate the transport properties, so that for Bi nanowires in the 50 nm diameter range prepared by the Ulatovski method, the semimetal-to-semiconductor transition is masked by surface state carriers [36].

Figure 3.9(a) shows a schematic drawing of the Fermi surface of the Bi films in the <111> surface Brillouin zone. There is a hexagonal electron pocket around the $\Gamma$ point and six hole lobes along the $\Gamma - M$ direction. It is evident that these features are quite different from the projected bulk Fermi surface (Fig. 3.9(b)) and show strong metallicity, in contrast to the prediction of the semimetal-to-semiconductor transition for the bulk states [68].

Figure 3.9: (a) A schematic drawing of the Fermi surface of Bi films in the surface Brillouin zone. (b) The Fermi surface of bulk Bi depicted in bulk (orange) and its projection to the surface (red) Brillouin zone [68].
Recently, Rogacheva et al. [37] studied the temperature dependences of the Hall coefficient of Bi thin films with thicknesses $d = 8$ to 200 nm prepared by thermal evaporation in vacuum on mica substrates. It was established that at thicknesses smaller than $\sim 30$ nm no semimetallic conductivity is observed (Fig. 3.10). Using this assumption and taking into account the existence of surface states, it was shown that the gap between the valence and conduction bands in the semiconductor region increases with decreasing $d$.

![Figure 3.10: Temperature dependences of the Hall coefficient $R_H$ with different film thickness $d$ vs. $1/T$ [37].](image)
3.2 Nonlinear Optical Properties

The field of nonlinear optics (NLO) emerged into prominence three decades ago with the development of the lasers and the demonstration of the frequency doubling phenomena. These milestone discoveries not only generated much interest in laser science, but also set the stage for future work on NLO. In recent years, the field has progressed towards technological applications and the main focus has been on the discovery of materials with high performance NLO properties. For example, there is a growing need for materials which can serve as optical limiters for high power lasers over a wide range of frequencies and pulse durations for protection of sensors and eyes of the user. Apart from this crucial application for eye and sensor protection, optical limiters are used for laser pulse shaping, passive mode locking, and photo-thermal spectroscopy.

For optical limiting applications it is necessary that the sample possesses slow linear losses and high nonlinear losses. Nonlinear losses can be due to multi-photon absorption, reverse saturable absorption, nonlinear scattering, and self-action of laser radiation (Kerr and thermal self-focusing and self-defocusing). Collective excitation of electrons in nanostructured materials under illumination, so-called surface plasma resonance (SPR), which results in highly linear absorption [74] can also stimulate NLO effects in the same spectral region. Such a plasmonic resonance peak was observed in our Bi nanorod samples at 302 nm. It is also known [75, 76] that materials doped with high concentrations of metallic nanostructures, exhibiting surface plasmonic resonance, demonstrate large nonlinear optical Kerr coefficients (see Appendix B). Moreover, a number of organic and inorganic materials, including fullerenes, carbon nanotubes
(CNTs) [77] and various inorganic nanoparticles [78, 79] have been found to show a strong nonlinear extinction effect at high-intensity light. For a certain material, the optical response may be a result of various mechanisms at work rather than one mechanism alone. For example, absorption band, particle size, morphology, etc., can simultaneously play a role in influencing the optical limiting performance. Moreover, various nanomaterials exhibit distinct nonlinear responses for laser sources with different parameters, including wavelength, pulse duration, and repetition rate. In nanostructures quantum confinement effects in tandem with surface plasmon resonance (SPR) can lead to interesting changes in nonlinear properties.

In case of Bi nanorods a semimetal-to-semiconductor transition, due to confinement of carries, can lead to radical changes in its physical and photophysical properties. In order to employ nanomaterials as optical limiters one first needs to understand, especially in the case of Bi nanostructures, the effect of quantum confinement on NLO properties in detail.

3.3 Z-Scan Technique

The Z-scan technique [80] is a sensitive, single beam technique to measure the real and imaginary part of the nonlinear refractive index. There are two basic versions of the Z-scan technique, the open-aperture and the closed-aperture technique; the closed-aperture is a method of extracting phase information from power measurements, while the open-aperture technique (used in this thesis) is a refinement of transmittance measurements.
In the open-aperture Z-scan technique (Fig. 3.11) one measures the transmittance of a sample through an aperture placed in the far-field as the sample is translated across the focus of a Gaussian beam. If a sample with positive intensity-dependent refractive index ($n_2$) is placed in a Gaussian beam, the beam acquires a positive amount of phase in addition to the phase given by linear propagation while traveling through the sample. This additional “nonlinear” phase is a function of intensity and therefore of transverse position across the beam, larger at the center of the beam and smaller at the edges [82].

In the open-aperture technique, one of the apertures is large enough to capture all of the energy of the beam. In this technique the only effect that can contribute to a
variation in transmission, with a change in intensity is nonlinear absorption. This is the configuration that has been used in this thesis.

The theoretical treatment suggested by Sheik-Bahae et al. [80] for this experimental configuration goes beyond the thin-sample approximation by taking into account that the intensity change as the light travels through the sample is given not only by linear absorption, but also by nonlinear absorption. It still ignores diffraction on the length scale of the sample. The amplitude $\sqrt{I}$ and the phase of the light as governed by the equations

$$\frac{d\Delta \phi}{dz} = kn_2 I$$  \hspace{1cm} (3.16)$$

and

$$\frac{dI}{dz} = -\alpha_0 I - \alpha_2 I^2$$  \hspace{1cm} (3.17)$$

where $\Delta \phi = kn_2 I_0$, $n_2$ is the intensity-dependent refractive index, $I_0$ is the peak intensity at the focal point, $z$ is the sample position with respect to the focus, $\alpha_0$ is the linear absorption coefficient and $\alpha_2$ is the total nonlinear extinction coefficient (see Appendix C for the full derivation). The coefficient $\alpha_2$ is a sum of contributions from both nonlinear absorption $\alpha_{2, a}$ and nonlinear scattering $\alpha_{2, s}$: $\alpha_2 = \alpha_{2, a} + \alpha_{2, s}$. The beam phase and intensity as the light exits the sample are given by
\[ \Delta \phi = \frac{kn_2}{\alpha_z} \ln[1 + q(z)] \tag{3.18} \]

and

\[ I_e = \frac{I e^{-\alpha_0 L}}{1 + q(z)} \tag{3.19} \]

where \( L \) is the effective length of the sample given by \([1 - \exp(\alpha_0 l)/\alpha_0]\), and \( l \) is the sample length. The complex field pattern at the far-field aperture can be expressed again by a superposition of Gaussian beams, but since we are interested only in the total transmitted energy, we only need to integrate Eq. (3.19). The results of the integration is the transmitted power

\[ P(z, t) = \int_0^L I e^{-\alpha_0 L} \ln[1 + q_0(z, t)] \frac{dz}{1 + q(z)} e^{-\alpha t} \ln[1 + q_0(z, t)] \tag{3.20} \]

where \( q_0 = \alpha_2 I_0 L/[1 + (z/ z_0)^2] \) and \( z_0 = \pi \omega_0^2 / \lambda \) is the Rayleigh range, \( \omega_0 \) is the beam waist radius at focus, \( t \) is time and \( \lambda \) is the wavelength of the incident light [80].

If we assume a temporally Gaussian pulse and integrate Eq. (3.20) over time we obtain the normalized energy transmission
This position dependent transmittance (Eq. (3.21)) is referred to as the “Z-scan curve” [80, 83]. A typical curve obtained from an open-aperture experiment is shown in Fig. 3.12 [84].

\[ T(z) = \frac{1}{\pi q_0(z)} \left[ \ln \left[ 1 + q_0(z) e^{-2} \right] \right]^{+\infty}_{-\infty} \]

\[ \text{Eq. (3.21)} \]

Figure 3.12: The curve resulting from an open-aperture Z-scan experiment on an optical limiter [84].

We used visible and IR laser pulses from a Nd:YAG laser (Quanta system, 7 ns, 10 Hz at both 532 and 1064 nm) to measure the optical limiting performance of Bi nanorod suspensions by the Z-scan technique at room temperature (~300 K) [80]. To separate the contributions of nonlinear absorption (NLA) and nonlinear scattering (NLS), we used a Z-scan setup following Jourdier et al [85] (see Fig. 3.11). Scattering involves the spatial redistribution of beam intensity over a cross-sectional area larger than that of
the incident beam leading to two components in the beam transmitted through the sample; the \textit{unscattered} part ("dark green-filled" central region) and the \textit{scattered} part ("faded green" region). The beam is split 50:50 (BS2 in Fig. 3.11) to reach two detectors D2 and D3 to measure the transmittance $T$ of the sample with detector D1 as a reference. A 2 inch wide lens (L4) collects light both from the scattered and unscattered parts making D2 insensitive to transmittance $T$ changes due to spatial redistribution. This ensures that our collection efficiency is >90%. Thus, D2 records changes in transmittance solely due to absorptive effects and the nonlinear extinction coefficient measured by the $Z$-scan curve is only due to contribution from nonlinear absorption. On the other hand, D3 detects only the unscattered part since aperture (A) can be adjusted to prevent the scattered part from reaching D3. Therefore, D3 records a reduced transmittance due to nonlinear scattering and nonlinear absorption unlike the case of D2 [81]. Venkatram \textit{et al.} [86] recently used a similar configuration for quantitative studies on CdS nanocrystals (to be discussed later in Chapter 5).

The intensity variation along the beam propagation direction ($z$) in a medium having a third order nonlinearity is described in Eq. (3.17). The value for $\alpha_z$ is obtained by fitting the $T(z)$ equation (Eq. (3.21)) to the experimental data. In the context of our experiment, the $Z$-scan curve of D3 gives $\alpha_z$ and the D2 curve are fit with $\alpha_{2A}$ thus, $\alpha_{2A}$ can be extracted.

The $Z$-scan curves for the Bi nanorod suspension (optical transmittance of 60%) in a 1 mm cuvette (made of fused silica) under a 55 $\mu$J, 532 nm (7 ns) excitation, are shown in Fig. 3.13. The suspension remained stable for ~6 hours which permitted us to collect reliable data from the $Z$-scans that lasted ~10 min. each. Figure 3.13 shows the $Z$-
Figure 3.13: Z-scan curves for Bi nanorods suspension in chloroform having linear transmittance of 60% at 532 nm excitation recorded by D2 and D3 for an input energy of 55 μJ. Solid lines show the corresponding $I^2$ dependent fits while the broken line shows an $I^3$ dependent fit for the D3 case [81].

scan curves recorded by detectors D2 (NLA alone) and D3 (NLA and NLS). The depth of the valley in the Z-scan curve is a direct measure of the extent of optical limiting and is different in the D2 and D3 curves with dips of ~0.65 and ~0.25, respectively. Since D2 records the contribution due to NLA alone and the D3 curve has contributions of NLS added to this, it is clear that NLS induced by NLA makes a significant contribution to the total extinction. In fact, the contribution of NLS to optical limiting is greater than that due to NLA. Interestingly, in the case of 1064 nm excitation (55 μJ, 7 ns) the D2 and D3 curves overlap (Fig. 3.14) and the minimum transmittance in both the cases is ~0.75.
Figure 3.14: Same as in Fig. 3.13 but instead using the 1064 nm excitation rather than the 532 nm excitation for an input energy of 55 μJ. The overlapping curves confirm that nonlinear scattering is absent when excited with 1064 nm in contrast to the 532 nm case. Inset shows the “flat” Z-scan curves of the bulk Bi (●) and Bi$_2$O$_3$ (○) suspensions in CHCl$_3$ [81].

Thus, NLS is absent at 1064 nm, and only NLA makes a contribution to the total extinction observed at this wavelength. At 532 nm, however, both NLA and NLS are responsible for the observed optical limiting unlike the 1064 nm case. This is very unlike the behavior of carbon black and single and multi-walled carbon nanotubes in suspension, where NLS dominates at both 532 and 1064 nm excitations [87, 88]. Lastly, it should be mentioned that we also performed measurements on bulk Bi (●) and Bi$_2$O$_3$ (○) powders suspended in chloroform (CHCl$_3$) (inset Fig. 3.14). These additional experiments, as were also seen in Fig. 2.8, were needed to unambiguously rule out contribution from residual Bi and Bi$_2$O$_3$ to the features described in Figs. 3.13 and 3.14.
These observations can be explained using the following phenomenology. A small band overlap (~38 meV) makes bulk Bi a semimetal with a small electron mass in the range of $0.001m_0 - 0.26m_0$, depending on the crystalline direction [19]. When irradiated by the 532 nm laser pulses, the sample absorbs energy via interband and intraband transitions, free carrier absorption, and two-photon excitation. The presence of the surface plasmon peak (see Fig. 2.10) makes the absorption a “near-resonant” process. The absorbed energy is transferred to the surrounding medium through nonradiative de-excitation, resulting in localized heating. Optically induced thermal effects and heating using the surface plasmon resonance in nanoparticles are well-established and have been exploited in various applications [89]. Several other mechanisms can be invoked to explain this large effective Kerr nonlinearity (see Appendix B for details). Local change in temperature causes local refractive index gradients ($\Delta n$) depending on the fluence ($F_0$), thermo-optic coefficient ($dn/dT$), absorption coefficient ($\alpha$), density ($\rho$), and specific heat ($C_v$) of the medium since [80, 89]

$$\Delta n = \left(\frac{dn}{dt}\right) \left(\frac{F_0\alpha}{2\rho C_v}\right).$$

(3.22)

The refractive index gradients centered at the nanorod sites act as scattering centers. The leading part of the pulse creates these scattering centers and the remaining part of the pulse gets scattered, hence the nonlinear intensity dependent scattering. This mechanism has been used to explain the optical limiting behavior of carbon nanotubes as well [88].
Although NLA is significant at 1064 nm excitation, it is much weaker than that at 532 nm where the 302 nm surface plasmon peak makes the interaction near resonant. The NLA at 1064 nm is not large enough to create sufficiently strong thermal refractive index gradients (since $\Delta n$ is proportional to $\alpha$), at the nanorod sites which can act as scattering centers. The propensity of scattering at 1064 nm is further diminished by a factor of 16 when compared to 532 nm, considering the simple case of Rayleigh scattering (scattering cross section is proportional to $\lambda^{-4}$). Nonetheless, the nonlinear intensity dependent absorption at 1064 nm is sufficient for an appreciate optical limiting performance [81].

We obtain a value for the total extinction coefficient $\alpha_2$ of 5.3 cm/GW for input pulses of 55 $\mu$J at 532 nm by fitting the $T(z)$ equation (Eq. (3.21)) in the D3 curve of Fig. 3.13. This value does not change significantly for other input optical energies of 10, 20, and 40 $\mu$J. In Fig. 3.13 the dashed line shows a fitting for an $I^3$ dependence of the total extinction. Clearly the $I^2$ curve fits the data better than the $I^3$ curve. Thus, higher-order contributions to the nonlinear processes are negligible. However, our value for the total extinction coefficient $\alpha_2$ differs in sign and magnitude from the value of -3.97 cm/W reported by Liu et al. [90] for Bi thin films (~7 nm). Liu et al. [90] postulated localized melting as the mechanism responsible for an observed giant nonlinear response under quasi-continuous wave (25 ms pulses) 532 nm excitation. The differences in the magnitude and the sign of the nonlinear coefficient are primarily due to the widely different excitation regimes and nature of the media of interest, viz., short 7 ns pulses and two-component medium (this work) and quasi-continuous wave 25 ms pulses and a single component medium (Liu et al.). The quasi-continuous wave and the single-
component medium in the latter case aid accumulative effects that result in large nonlinearities in the film.

To complete this study, we also recorded the nonlinear transmittance at various incident energies for both 532 and 1064 nm excitations. Figures 3.15 and 3.16 show the Z-scan curves recorded by detector D3 at 532 and 1064 nm respectively, and the guide to the eye for each curve. Fitting the $T(z)$ equation (Eq. (3.21)) to the Z-scan curve of Fig. 3.16, the total extinction coefficient $\alpha_z$ at 1064 nm for an input optical energy of 50 $\mu$J was determined to be 2.4 cm/GW. Collectivity, they show that the extent of optical limiting increases with an increase in the input energy of incident optical pulse. Notwithstanding the difference in mechanism of optical limiting at 532 and 1064 nm, Bi nanorods suspensions display excellent optical limiting properties and are potential candidates for application as broadband optical limiters [81].

The ability to control light intensity in a predetermined manner is crucial for many photonic devices, as might be found in all-optical communication systems. An important requirement in many optical systems is the protection of the photonic systems from optical inputs that exceed the damage threshold of their detectors. Providing this protection requires the exploitation of NLO response in materials. While the linear
response of materials, which give rise to refraction, dispersion, scattering and birefringence among others, does not depend on the intensity or the electric field strength of the light incident on the medium, the nonlinear response by definition depends on the light intensity and/or the electric field strength. Optical limiting is a nonlinear optical process in which the transmittance of a material decreases with increasing incident light intensity. Optical limiters are one of the most important types of devices used to control the amplitude of high intensity optical pulses. Ideal optical limiters have a linear transmittance at low input intensities. Above the threshold intensity the transmittance becomes constant. Figure 3.17 shows a typical ideal optical limiting curve [91]. Figure 3.18 shows the optical transmittance as a function of input fluence incident on the sample. The decrease in transmittance with increasing incident fluence constitutes optical limiting. The optical limiting curve in Fig. 3.16 is obtained from the Z-scan curve in Fig. 3.15. Clearly, Bi nanorods in chloroform show optical limiting while bulk Bi
Figure 3.16: Z-scan curve for a Bi nanorod suspension in chloroform having linear transmittance of 60% at 1064 nm excitation recorded by D3, with contributions from both nonlinear absorption and scattering at optical input energies of 30 and 50 μJ [81].

 powder dispersed in the same solvent does not. As explained above, the mechanism for optical limiting involves the absorption of the leading part of the laser pulse by the nanorods, the nonradiative decay which transfers energy to the surrounding host medium, resulting in the formation of local thermal refractive gradients which act as scattering centers for the incoming light. This scattering increases with an increase in the incident intensity, since larger refractive index gradients are then formed by the increased incident light intensity [66].
Figure 3.17: Schematic of a typical optical limiting curve [91].

Figure 3.18: Comparison of the optical limiting properties at 532 nm for 10 nm diameter bismuth nanorods in comparison with bulk bismuth [66].
CHAPTER 4

NICKEL SULFIDE NANOPARTICLES

Photonic nanoparticles systems have attached considerable attention due to a wide variety of NLO applications such as optical limiting, saturable absorption, second harmonic generation and two-photon absorption [49-52]. Typically, such systems are designed with a view of enhancing one of the nonlinear optical properties over their bulk counterparts. Our present study shows that nanomaterials can be engineered to deliver systems displaying more complex behavior involving the interplay of two nonlinear phenomena or more. In such systems, however, if two competing mechanisms operate simultaneously, the stronger dominates the weaker. We present a case of complete quantitative characterization, in a single experiment, of two simultaneous but contrary optical transmission phenomena (i) optical limiting and (ii) saturable absorption in surface-modified nickel sulfide nanoparticle suspensions by employing a modified Z-scan method (as described for Bi nanorod suspension in Chapter 3).

4.1 Synthesis and Characterization

Among the many synthetic routes in vogue, the one-step solid phase reaction method is attractive because of the ease, scalability, and large yield of products. Further, these dry processes can be carried out at room temperature in a relatively short reaction
time. Wang et al. [92] reported the synthesis of CuS nanorods by a one-step process reaction. In our synthesis of NiS nanoparticles, we exploited the well-known affinity of Ni to dimethylglyoxime \((C_4H_8N_2O_2)\) (DMG) which is commonly used in the detection and estimation of Ni in inorganic analysis [93]. Roughly 3.8 g of nickel chloride \((NiCl_2 \cdot 6H_2O)\) was thoroughly ground for 10 min. in a mortar and pestle. Then, 2.32 g of DMG, which acts as chelating or capping agent, was added to the mortar and the mixture was further crushed for 30 min. Next, the mixture was left unattended for 2 hr. following which 2.41 g of sodium sulfide \((Na_2S \cdot 9H_2O)\) was added for an additional 30 min. Finally, the product was washed with water several times to remove the residual ions. The washed product was dried at 60 °C for 6 hr. in air. The rationale of this synthetic route is summarized in the following reaction sequence which leads to the formation of nanometer-sized NiS:

\[
NiCl_2 \cdot 6H_2O + DMG \rightarrow [Ni-DMG] + Na_2S \cdot 9H_2O
\]

\[
\rightarrow NiS_2(nano) + DMG + NaCl + 15H_20
\]

In the initial grinding process, the presence of defects in the hydrated metal salt leads to the energetically favored formation of the Ni-DMG complex. The exchange of coordinated water further increases the number of defects, interfacial diffusion and opening of the coordination sites which further lowers the activation energy of the reaction. As a consequence, the reaction temperatures are lowered and the reaction rates are increased leading to easy formation of the bulk complex. The bulk complex is broken down by the addition of sodium sulfide with grinding. The size of the nanoparticles and
the possibility of nucleation are largely determined by the nature of bonding between the capping agent and the metal ion.

In this study [94], DMG was found to be very suitable for the formation of NiS nanoparticles of an average diameter of 5 nm. The high-resolution transmission electron microscope (TEM) images (Fig. 4.1) reveals lattice planes with a spacing of the (211) planes of NiS₂. We note that this method is suitable for a scalable synthesis by methods like ball-milling and has the added advantage of being a completely dry synthesis unlike others reported in the literature [95]. Figure 4.2 shows the X-ray diffraction (XRD) of the NiS₂ nanoparticles. The XRD of the NiS₂ nanoparticles was carried out using a Rigaku MiniFlex diffractometer. The reflection peaks in Fig.4.2 can be indexed as a mixture of NiS₂ (JCPDS 011-0099) and S (JCPDS 023-0562). The XRD patterns indicate that the cubic structure remains the same as that of bulk NiS₂, while the TEM

Figure 4.1: TEM images of nickel sulfide nanoparticles with an average diameter of 5 nm. Panel (a) shows a uniform size distribution of the nanoparticles while panel (b) shows a crystalline nanoparticle with a lattice plane spacing of 0.241 nm [94].
Figure 4.2: X-ray diffraction pattern of the nickel sulfide nanoparticles obtained from the starting materials NiCl$_2$ · 6H$_2$O and dimethylglyoxime (DMG) [94].
and XRD confirm the existence of the nanoparticles and their composition, the presence of the Ni-DMG bond, which is confirmed by the peak at 1572 cm\(^{-1}\) in the FTIR spectrum (see Fig. 4.3). In pure DMG, intramolecular hydrogen bonding inhibits the appearance of the 1572 cm\(^{-1}\) peak which is due to the C=N stretching mode [93]. The UV-Visible absorption spectrum (Fig. 4.4) reveals a broad peak centered at 554 nm. All of the other peaks at 416 nm, 342 nm, and 375 nm are well separated from this, and are a part of an excited state manifold. The 416 nm peak is due to the metal-ligand charge transfer in the Ni-DMG complex which is a \(d\pi - \pi^*\) transition, and the 554 nm peak is due to the \(3d_{z^2} - 4p_z\) transition in the Ni\(^{2+}\) ion [96]. In contrast, the NiS nanoparticles prepared without DMG as a capping agent do not possess this absorption peak at 554 nm [95].
The significance of this peak will be discussed in the context of NLO transmission in the following section. The FTIR

![Figure 4.4: UV-Visible spectrum of NiS$_2$ nanoparticles in 2-propanol. Inset shows a schematic of the excited manifold [94].](image)

spectrum of DMG and Ni-DMG further corroborates the bonding between Ni and DMG [94]. The absorption peak at 554 nm is a result of surface modification and could make DMG-capped NiS nanoparticles important in solar cell applications.

### 4.2 Nonlinear Optical Transmission

The intensity-dependent nonlinear transmission study of NiS$_2$ nanoparticles suspended in 2-propanol (C$_3$H$_7$OH) was carried out using the single beam open-aperture Z-scan technique [80] (as was used in Chapter 3 for the Bi nanorods). Briefly, in a
typical Z-scan, the sample is translated across the focus of a converging lens and the area of the incident beam on the sample varies while the energy and pulse-width remains constant. Thus, the intensity varies as the sample is scanned on either side of the focus along the propagation axis (Z-axis) of the beam. The transmittance of the incident pulse at each Z-position of the sample is recorded using a reference detector and another which captures the pulse transmitted through the sample (see Fig. 3.11 for reference). NiS$_2$ nanoparticles were suspended in an appropriate amount of 2-propanol so that the sample held in a 1 mm cuvette had a linear transmittance of 80% at 532 nm. The second harmonic of a Q-switched Nd:YAG laser (532 nm) of pulse width 7 ns at 10 Hz repetition are used in the Z-scan studies employing a converging lens with a focal length of 20 cm. The sample was translated across the focus (Z-axis) using a motorized stage. The transmittance was recorded as a function of translation distance giving the Z-scan curve (Fig. 4.5(a)) and transmittance as a function of input fluence is shown in Fig. 4.5(b). It is apparent that the optical transmittance falls as intensity increases exhibiting an optical limiting behavior. The Z-scan curves were recorded at two energies: 30 $\mu$J (□) and 50 $\mu$J (●). The corresponding intensities at the incident on the sample are 274 MW/cm$^2$ and 456 MW/cm$^2$, respectively. It is apparent from Fig. 4.5(b) that the optical transmittance falls as intensity increases exhibiting an optical limiting behavior. A transmission of 50% is reached at 300 $\mu$J/cm$^2$ which is the threshold fluence for optical limiting.
Figure 4.5: (a) Z-scan curves for nickel sulfide nanoparticles in 2-propanal and (b) the corresponding plot of optical transmission as a function of input fluence [94].

The observed optical limiting is due to the intensity-dependent scattering visible to the naked eye. Figure 4.6 shows the transverse image of the beam before incidence (panel (a)) and after traversing through the sample (panel (b)) [94]. The effect of scattering on the transverse profile of the beam is evident. As Figs. 3.11 and 4.6 suggest,

Figure 4.6: Panel (a) shows the transverse profile of the incident beam and panel (b) presents the scattered beam profile after traversing through the sample [94].
scattering involves the spatial redistribution of the beam intensity over a cross-sectional area larger than that of the incident beam (as discussed in detail in Section 3.1). A collection efficiency greater than 90% was insured in this case. Thus, D2 (collects light both from scattered and unscattered parts) records changes in transmittance solely due to absorptive effects, and the nonlinear extinction coefficient measured by the Z-scan curve is only due to the contributions from nonlinear absorption. On the other hand, D3 detects only the unscattered part since aperture $A$ was adjusted to deter the scattered part from reaching D3. Any intensity-dependent transmittance change recorded by D3 is due to changes in absorption, scattering, or both as a function of intensity. Therefore, D3 records the transmittance as a function of sample position due to nonlinear scattering and nonlinear absorption unlike the case of D2. It is worth mentioning that the conventional Z-scan is equivalent to the measurement with D3 alone with the role of the aperture being equivalent to the limited spatial extent of the detector. Efficient collection of scattered light into detector D2 plays a crucial role in our experiment.

Figure 4.7 shows the Z-scan curves from detectors D2 (●) and D3 (□) for NiS$_2$ nanoparticles suspended in 2-propanol. Nonlinear scattering is found to be the dominant mechanism for NLO extinction in multi-walled carbon nanotubes and carbon black suspensions [97]. The Z-scan curve due to detector D2 (●) shows an upward peak indicative of the saturation of absorption. The transmittance of the sample increases as it is brought close to the focus of the Z-scan lens. This is in sharp contrast to the recent study on our Bi nanorods [81] and CdS nanocrystals [86] where the corresponding curve is a valley indicating that nonlinear absorption increases with intensity and transmission.
falls with intensity. Saturable absorption observed in this case is similar to the behavior of rhodamine B under similar experimental conditions [98].

Further, in Fig. 4.7, the Z-scan curve of detector D3 (□) which records intensity dependence transmittance due to both absorption and scattering shows a typical optical limiting valley. A closer observation reveals that both the fall in transmittance due to optical limiting (□) and the rise in transmittance (●) due to saturable absorption is at a Z-position of 1.75 cm, with respect to the focal point (Z = 0). Thus, the two effects begin simultaneously, and are not sequential as has been observed in other experiments on nanoparticles systems [99]. The sequential occurrence of saturable absorption followed by an optical limiting behavior is indicative of excited state absorption. The occurrence and observation of two contrary, but concomitant, processes are indeed peculiar. We rationalize this observation in the following paragraphs.

For the purposes of this experiment, which involves a narrow laser excitation at 532 nm, the absorption peak at 554 nm in the UV-Visible spectrum (Fig. 4.4) alone needs to be considered. There are no other peaks close to this peak which covers the spectral range of 525 – 572 nm. To explain the intensity dependence of absorption we use a two-level model (inset Fig. 4.4). Similarities of small nanoparticle systems to molecules in
Figure 4.7: Z-scan curves of detector D3 (□) and D2 (●). While D3 measures the contribution of both nonlinear scattering and nonlinear absorption, D2 gives a measure of intensity-dependent absorption alone [94].

The context of similar experiments have been pointed out by Thomas et al. [100]. Under the 532 nm excitation the nanoparticles are excited from the ground state (labeled “0”) to the higher state (labeled “1”) as shown in the inset in Fig. 4.4. As the intensity of the exciting laser pulse is increased to a maximum of 200 MW/cm², nearly half of the nanoparticles occupy the excited state. As the ground state is bleached, the system becomes increasingly transparent to the incident laser pulse at 532 nm resulting in a saturation of absorption and the consequent Z-scan curve. The intensity-dependent absorption coefficient for a two-level system is give by [101]:

\[
\alpha_{SA}(I) = \frac{\alpha_0}{1 + I/I_s}
\]  

(4.1)
where $\alpha_0$ is the absorption coefficient, $I$ is the intensity of the laser beam, and $I_S$ is the saturation intensity. This helps explain the upper curve in Fig. 4.4.

The simultaneous occurrence of nonlinear intensity-dependent scattering with saturable absorption can be explained as follows. Following the excitation of nanoparticles from the ground to the excited state, the system de-excites by a nonradiative path transferring energy to the surrounding medium. This leads to local heating and the formation of thermal refractive index gradients ($\Delta n$) according to Eq. (3.7). The nanoparticles sites, which are thus centers of refractive index gradients, act as scattering centers [94]. The leading part of the pulse gets absorbed and leads to the formation of the scattering centers and the trailing part of the pulse gets scattered thereafter. As the incident intensity increases, the scattering also increases. The optical limiting observed in the case of carbon nanotubes and carbon black is explained on similar grounds [87].

A complete description of the Z-scan experiment requires that both the saturable absorption and optical extinction due to nonlinear scattering be taken into account. We use the following equation describing the two concomitant processes similar to Venkatram et al. [86] and Eq. (3.17) previously:

$$\frac{dI}{dz} = -\left[ \alpha_0 + \alpha_2 I + \alpha_0 \frac{I}{1 + I/I_S} \right] I,$$

(4.2)

where $\alpha_2$ is the nonlinear scattering coefficient. The value of $I_S$ and $\alpha_2$ can be extracted from numerical fitting of the data to this propagation. As mentioned earlier, the Z-scan
curve of D2 is restricted to absorptive effects, hence if the equation is first solved by setting $\alpha_2 = 0$ so then a value for $I_S$ is obtained, which in our case is 64 MW/cm$^2$. This value of $I_S$ is much smaller than the incident intensity at the focus (at both 30 $\mu$J and 50 $\mu$J), eventually favoring the domination of nonlinear scattering following the absorption of a fraction of the leading part of the incident pulse. Thereafter, the value of $\alpha_2$ was obtained by using this value of $I_S$ in the complete equation and finding the best fit to the Z-scan curve from detector D3. The nonlinear scattering coefficient, $\alpha_2$, was found to be 63 cm/GW [94].

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CHAPTER 5

CADMIUM SULFIDE NANOWIRES

In recent years, nanostructured semiconducting materials have gained wide interest due to their inherently novel optical and electronic properties [53, 102, 103]. Future applications of these nanomaterials in optical switching and optical limiting warrant a better understanding of their size-dependent nonlinear optical switching properties. In addition, with the advent of high power lasers over a range of wavelengths and pulse widths, the search for novel nonlinear optical materials with superior optical limiting properties for protection of human eyes and sensing elements has increased dramatically [77].

Nanostructured sulphides and selenides (e.g. CdSe, ZnSe, CdS and ZnS) have been extensively studied with a view to establish a relationship between structure, size and optical properties [104, 105]. Among these, the II-VI semiconductor cadmium sulfide (CdS) has shown strong nonlinear nonlinearities in the band gap region. Studies hitherto on nanostructured CdS have been performed mainly in the regime of strong quantum confinement wherein the dimensions of the nanoparticles are smaller than the excitonic Bohr radius [76, 106]. We present a detailed investigation of the synthesis, optical properties and intensity-dependent nonlinear optical transmission studies in CdS nanowires.
5.1 Synthesis and Characterization

Crystalline CdS nanowires were prepared using the pulsed laser vaporization technique described in Chapter 3 for the preparation of Bi nanorods. A Nd: YAG laser was used to ablate a rotating target prepared from CdS powder. The rotating target was placed inside a quartz tube reactor that was maintained at ~650 °C. A gentle flow of hydrogen (~100 sccm) causes the ablated material to flow downstream and collect on a water-cooled copper cold finger. The morphology of the as-prepared nanomaterials obtained from the CdS target were analyzed by SEM and TEM microscopy. The average diameters of the nanowires were found to be between 50 and 100 nm and were tens of micrometers in length. Figure 5.1(a) shows an SEM image of the as-prepared CdS nanowires [107]. When viewed under TEM (Fig. 5.1(b)), the as-prepared material revealed a wire like structure (1D structure) resembling a nanowire. Figure 5.1(c) revealed the crystalline structure of the CdS nanowire. From the analysis of the Fourier transform (inset Fig. 5.1(c)), the lattice spacing of the planes oriented along the length of the CdS nanowire was found to be 0.67 nm, which is consistent with the [108] planes in a hexagonal structure. This is in agreement with the interplanar distance of 0.67 nm observed in CdS nanowires prepared by the physical evaporation method using an Au catalyst [109]. Even though the lattice planes are tightly packed, we did not observe any dislocation or stacking faults for several observed nanowires. The nanowires produced are also free from an amorphous/polycrystalline CdS shell, as was observed in those formed by thermal evaporation [110].
5.2 Photoacoustic Spectroscopy

Photoacoustic spectroscopy (PAS) is a highly sensitive technique compared to the conventional absorption spectroscopy (i.e. infrared). The major advantage is that both transparent and opaque samples can be studied without any sample preparation [111, 112]. In PAS, the sample is excited to higher electronic excited states by intensity modulated light radiation. Nonradiative decay to the group state leads to heat generation modulated at the same frequency, which in turn leads to pressure oscillations in the gas that surrounds the sample. The pressure oscillations are sensed by a microphone, processed and plotted as a function of wavelength. The strength of the acoustic signal is proportional to the amount of light absorbed by the sample and there is a close correspondence between PA spectrum and the conventional optical absorption spectrum.
The resulting signal depends not only on the amount of heat generated in the sample (and, hence, on the optical absorption coefficient and the light-into-heat conversion efficiency of the sample) but also on how the heat diffuses through the sample [113].

In the PA spectrometer (Fig. 5.2), light from a 300 W xenon lamp is wavelength-selected using a monochromator. The wavelength-selected beam is intensity modulated using a mechanical chopper, whose frequency can be varied. The modulated beam is then focused onto the sample which is an airtight acoustically nonresonant cell. The PA cell is equipped with a microphone (3 Hz to 20 kHz). The spectra were recorded at 45 Hz. The signal generated as a result of the absorption is monitored by a microphone, which is then amplified and then acquired by a lock-in amplifier. The final data acquisition is done by a computer through the LabVIEW software.

Figure 5.2: Photoacoustic experimental set-up.
The photoacoustic spectra of bulk and CdS nanowires are shown in Fig. 5.3. The spectra are normalized with carbon-black spectra to remove the spectral structure resulting from the light source. The PA signal as compared to that from bulk (This is not obvious in Fig. 5.3 because the spectra are again normalized to a maximum intensity of 1 by dividing the carbon-black-normalized PA signal intensity with the maximum signal intensity for better comparison). This is expected because the PA signal is directly proportional to the surface area of the sample exposed to the light source. In the present case, the size of the CdS nanowire is considerably less than the bulk powder and, therefore, there will be a considerable increase in the surface-area-to-volume ratio leading to an increase in the PA signal. It is also possible that, as the size decreases, there will be strong overlapping of the wave functions of the confined charge carriers, which will lead to increased oscillator strength and hence the absorption signal. The optical absorption coefficient is directly proportional to the PA signal and from the PA amplitude-energy plot, shown in Fig. 5.3, the energy gap can be determined. As shown in Fig. 5.3(curve a), the band gap of bulk CdS powders occurs at 2.39 ± 0.04 eV, which agrees very well with the literature value of 2.42 eV [113]. The absorption edge of the CdS nanowires (curve b in Fig. 5.3) is much steeper and occurs at a slightly larger value of 2.49 ± 0.04 eV. The data does not show any significant quantum confinement effect. This is expected because the size of the wires (50 – 100 nm) is much larger than the exciton Bohr radius of ~3 nm for CdS [114]. The increased steepness for the CdS nanowires data might be attributed to the relatively well-ordered structure and size distribution.
Figure 5.3: Photoacoustic spectra of bulk CdS (curve a) and CdS nanowires (curve b). The inset shows the conventional optical absorption spectrum of CdS nanowires.

The optical absorption spectrum shown in the inset of Fig. 5.3 also shows similar observations; however, the background signal is significantly higher, probably due to scattered and reflected light. On the other hand, the PA spectra reveal a much better absorption profile with a steeper absorption edge. Since the PA signal produced as a result of pressure variations following nonradiative de-excitation in the sample and is measured using a microphone, scattered and/or reflected light does not contribute to the signal. Therefore, the PA technique measures the optical absorption, especially in highly light-scattering samples and samples with large optical densities, in a better way [115].

The photoluminescence (PL) spectrum of CdS nanowires is shown in Fig. 5.4. The PL peak at 491 nm (2.52 eV) agrees very well with the band gap (2.49 ± 0.04 eV) observed in the PA spectrum, which can be readily attributed to the band edge/exciton
transition. However, a very narrow (FWHM ~9 nm) peak shows a more excitonic nature for the transition. Generally, additional weak and broad PL peaks in the longer wavelength sides (above 500 nm) are observed if defects/impurities are present in the material. Therefore, the observation of a single PL peak clearly reveals the high quality of these nanowires [116].

Figure 5.4: Photoluminescence spectrum of CdS nanowires ($\lambda_{ex.} = 380$ nm) [107].

The micro-Raman spectrum of the as-prepared CdS nanowires is shown in Fig. 5.5. As shown in Fig. 5.5, the Raman peaks are found to be symmetric and narrow. The first-order Raman peak observed at 298 cm$^{-1}$ (FWHM ~$21$ cm$^{-1}$) is assigned to the LO phonon [109, 117] and the first overtone occurs at 567 cm$^{-1}$. It is well known that the quality of a crystalline material can be determined using Raman spectroscopy. A sharp
Raman peak with a relatively small FWHM has been reported to be an indicator of the overall quality of films [118] and nanowires [119].

![Raman spectra of CdS nanowires](image)

Figure 5.5: Raman spectra of the as-prepared CdS nanowires ($\lambda_{ex.} = 514.5$ nm) [107].

Recently, there has been some discussion on the relationship between the size of nanostructures and the extent of excitation-LO-phonon coupling in CdS nanostructures. It has been shown that the intensity ratio of the first overtone to the fundamental ($I_{2LO}/I_{1LO}$) increases with increasing the size of CdS quantum dots, revealing an increased exciton-LO-phonon coupling [120]. A recent study by Lee et al. [121] revealed that the 2LO-phonon response is much stronger in both the CdS nanobelts (50 nm thick and 0.5-1.5 μm wide) and nanosheets (50 nm thick and 5 μm wide) compared to the CdS nanowires (50 – 200 nm diameter), suggesting an increased exciton-LO-phonon coupling for larger-sized CdS nanostructures. Their studies are also in agreement with the theoretical results on
quantum dot structures [122]. On the other hand, Pan et al. [109] obtained the $I_{2LO}/I_{1LO}$ intensity ratios for the nanowires (50 – 200 nm dia.) and for the bulk material to be about 1.33 and 0.3, respectively. Their results suggest that the exciton-LO-phonon coupling strength in nanowires is much stronger than that in the bulk. In the present study [107], we obtained $I_{2LO}/I_{1LO}$ to be about 0.75, which is smaller than the value reported by Pan et al. [109] (average dia. ~125 nm). This supports the observation of increased exciton-LO-phonon coupling in larger-sized CdS nanostructures as observed by Lee et al. [121].

5.3 Nonlinear Optical Transmission

The intensity dependent nonlinear optical studies of our CdS nanowire suspensions were carried out using the open-aperture Z-scan technique (as was described in earlier in Chapters 3 and 4). The open-aperture Z-scan curve ($\circ$) of CdS nanowires shows a clear symmetric valley indicating the presence of nonlinear absorption (Fig. 5.6). Depending on the absorption mechanism, one obtains either a peak (maximum) or a valley (minimum) at the focal point ($z = 0$) where the input intensity or the fluence is maximum [80]. The intensity variation along the beam propagation direction ($z$) in a medium with multi-photon absorption can be described as in [101].

$$\frac{dI}{dz} = -(\alpha_0 + \gamma^{(n+1)} I^n) I$$  \hspace{1cm} (5.3)
Here, \( \alpha_0 \) is the linear absorption coefficient, \( \gamma^{(n+1)} \) is the \((n+1)\) photon absorption coefficient and \( I \) is the intensity. Equation (5.3) reduces to a two-photon absorption (2PA) process with \( n=1 \), while \( n=2 \) reduces to a three-photon absorption (3PA) process.

Figure 5.6: Open-aperture Z-scan transmission curve (○) recorded for an input energy of 40 \( \mu \)J with the theoretical fitting overlaid for both the effective three-photon (●) and two-photon (+) absorption processes. The effective nonlinear absorption coefficient was determined to be \( 4 \times 10^{-22} \text{ m}^3/\text{W}^2 \) from three-photon absorption process which is the best fit.

Involving third and fifth order nonlinear optical processes, respectively. It should be noted that Eq. (5.3) does not distinguish between direct and cascaded absorption, and therefore in the context of this study, both processes are treated identical. The strength of these nonlinearities is evaluated by the magnitude of “\( \gamma \)”, which in turn is estimated by numerically fitting the position dependent transmittance, \( T(z) \), of the Z-scan curve using the following relations representing 2PA and 3PA coefficients, respectively.
Here, $z$ is the sample position with respect to the focal point, $\alpha_0$ is the linear absorption coefficient, $R$ is the Fresnel reflection at the interface of the sample material with air, $L (= l)$ is the sample length, and $p_0^n = n!\gamma^{(n+1)}\left[\frac{1-\exp(-n\alpha_0 l)}{n\alpha_0}\right](1-R)^n I_0^n$, $I_0$ being the intensity at the focal point $p_0^n = q_0$ for a 2PA process with $n=1$. Theoretical fits to the experimental data have been made using the Eq. (5.4) and (5.5). The best fit was obtained by varying the value of $\gamma$. Figure 5.6 reveals that the 3PA fitting is more pertinent than the 2PA. Since a pure 3PA process is rather unlikely at the intensities available from nanosecond laser pulses, we attribute this effective 3PA process to free carrier absorption, induced by cascaded single-photon and two-photon absorption at the excitation wavelength. Figure 5.7 shows the difference between a 2PA process and a 3PA process. The value for the effective three-photon nonlinear absorption coefficient $\gamma^{(3)}$ is determined to be $4\times10^{-22}$ $\text{m}^3\text{/W}^2$. 

\[
T(z) = \frac{(1-R)^2\exp(-\alpha_0 L)}{\sqrt{\pi q_0}} \int_{-\infty}^{+\infty} \ln\left[1 + q_0 \exp(-x^2)\right]dx \quad (5.4)
\]

\[
T(z) = \frac{(1-R)^2\exp(-\alpha_0 L)}{\sqrt{\pi p_0}} \int_{-\infty}^{+\infty} \ln\left[\sqrt{1 + p_0^2 \exp(-2x^2)} + p_0 \exp(-x^2)\right]dx \quad (5.5)
\]
It is worthwhile to compare the optical nonlinearity of bulk CdS crystals which are transparent at 532 nm, to that of CdS nanoclusters which show exciton absorption at this wavelength. In bulk CdS the observed nonlinearity is attributed to genuine interband two-photon absorption and subsequent free carrier absorption [123, 124]. Furthermore, in bulk CdS, the contribution arising from two-photon excited free carrier absorption is more significant at higher irradiances (greater than 0.5 GW/cm²). On the other hand, CdS nanostructures excitonic absorption at this wavelength opens up the additional, more efficient path of cascaded single-photon absorption which induces free carrier absorption. Obviously, the difference in the origin of the nonlinear processes arises mainly from size-dependent changes in the optical properties of CdS.

Along with this nonlinear absorption, induced scattering also is identified as being responsible for the nonlinear response of CdS nanoclusters [106, 125, 126]. We could observe an increase in the scattered signal from the sample as it was translated closer to the focus ($z = 0$). This was experimentally confirmed by capturing the scattered signal with an additional detector placed at an angle of 45° with respect to the scan direction.
The detector was translated along with the sample during the scan. As the sample moved closer to the focus, the intensity of scattered signal (○) increased, and it gradually decreased as the sample moved away from the focus, as shown in Fig. 5.8. This confirms the presence of intensity dependent nonlinear scattering in the present samples in the nanosecond regime, following the absorption of nanosecond laser pulses. The nonlinear scattering arises from thermal effects. Similar observations were earlier reported for other nanostructured materials [81, 83, 88, 126-128] including CdS nanoparticles [77, 86, 129, 130]. We attribute nonlinear scattering to be the reason for minor deviations of the theoretical fit to the experimental data.

Figure 5.8: Variation of transmitted signal (□) and scattered signal (○) as a function of $z$. The scattered signal was recorded by keeping the detector at about 45°.
Figure 5.9 shows the normalized transmittance versus the input fluence data. We define the optical limiting threshold as the input fluence at which the output transmittance drops to 50% of its initial value. From Fig. 5.9, the optical limiting threshold value for the CdS nanowires is discerned to be 0.47 J/cm². Table 5.1 presents the comparison of the optical limiting thresholds for some popular one-dimensional nanostructured systems studied in the nanosecond regime to that of CdS nanowire suspensions in the present study. CdS nanowires showed a comparable optical limiting when evaluated against CdS nanoparticles reported earlier in literature.

![Figure 5.9](image_url)

*Figure 5.9: Optical limiting curve exhibiting a loss in transmission upon increasing the input fluence. The optical limiting threshold is determined to be 0.47 J/cm².*
<table>
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<tr>
<th>Nanostructures (diameter size)</th>
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<th>Linear Transmission (%)</th>
<th>Threshold Value (J/cm²)</th>
<th>Reference</th>
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<tr>
<td>CdS nanowires (50nm)</td>
<td>7 ns : 1 mm</td>
<td>70</td>
<td>0.47</td>
<td>Current work</td>
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<tr>
<td>C₆₀TPY-Pb nanowires (30-50 nm)</td>
<td>8 ns : 5 mm</td>
<td>75</td>
<td>0.5-1.3*</td>
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<td>Pd nanowires (50nm)</td>
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<td>2.5</td>
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<td>Ni nanowires (50nm)</td>
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<td>CdS nanoparticles (4.5 nm)</td>
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<td>1.42 to 0.42†</td>
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<td>CdS/Ag₂S nanoparticles (3.5 nm)</td>
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<td>68</td>
<td>0.5</td>
<td>Jia et al. (Ref. 129)</td>
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* solvent dependent; † concentration dependent

Table 5.1: Optical limiting threshold of popular one-dimensional nanostructures and nanoparticles in comparison with that of CdS nanowires (current work) suspension at 532 nm.
CHAPTER 6

SUMMARY

6.1 Conclusions

In my research I have developed a pulsed laser vaporization method to synthesize highly crystalline bismuth nanorods. This method yields grams quantities of ~10 nm diameter Bi nanorods with ~3 nm native oxide layer. A transition from semimetallic-to-semiconducting behavior was predicted in Bi nanowires as the nanowire diameter decreases to ~14 nm or less [5]. Prior research has identified this transition to the indirect transition from the valance band at the $L$-point to the valence band at the $T$-point as was observed in room temperature infrared absorption measurements and discussed in Chapter XX, section YY in this thesis. Furthermore, high electron mobilities and quantum confinement effects at the Fermi surface, and a softening of the $L$-$T$ transition energy were also predicted. As a further confirmation on the assignment of the infrared absorption peak to the $L$-$T$ transition, we have performed low temperature FTIR studies on ~10 nm Bi nanowires. The low temperature study was motivated primarily from prior magneto-resistance studies in which a theoretical model for the $E_{L-T}$ as a function of temperature was reported. Our FTIR spectrometer was modified in order to perform these measurements. We designed a low-temperature infrared cell with ZnSe windows and which hermetically coupled to the sample chamber of our IR spectrometer. We expected to observe a temperature dependence in the infrared absorption spectrum, as discussed in section ZZ in this thesis. However, the recorded low temperature infrared
spectra did not show the predicted down-shift in frequency for the $E_{L-T}$. This dichotomy in the infrared absorption measurements prompts us to revise the present theory and/or understanding for the origin of the infrared absorption band. Tentatively, we attribute the origin of the infrared band to the presence of surface states (as evidenced in superconductivity measurements and in angle-resolved photoemission spectroscopy in bismuth thin films), and not to the $L$ to $T$-point transition, as concluded previously in the literature.

Another surface phenomenon became evident in our nonlinear optical studies of Bi nanorods. As discussed in Chapter Z, we have conducted systematic studies to determine the optical limiting properties of bismuth nanorods suspended in chloroform using the Z-scan technique. We found that the bismuth nanorod suspension displayed excellent optical limiting properties for both 532 and 1064 nm excitations in the nanosecond laser pulse regime. At the 532 nm excitation, both nonlinear absorption and nonlinear scattering contribute to the limiting process, while nonlinear absorption alone is responsible for the observed optical extinction at 1064 nm excitation. We attribute the nonlinear absorption process to a two-photon absorption. This process couples the excitation energy to the surface plasmon peak present in Bi nanorods at 302 nm, and absent in bulk Bi. The presence of this surface plasmon in Bi nanorods is essential to the origin of the observed nonlinear response.

In addition to Bi nanorods whose optical properties abundantly display surface phenomena, we have synthesized other thermoelectric nanomaterials. Nickel sulfide nanoparticles with an average diameter of 5 nm were synthesized via a one-step solid phase reaction. The intensity-dependent nonlinear transmission study was carried out at
532 nm using the Z-scan technique, and nonlinear scattering was found to be the dominant mechanism for response. Importantly, the modified Z-scan technique allowed us to simultaneously measure two competing mechanisms: (i) optical limiting and (ii) saturable absorption in surface-modified nickel sulfide nanoparticle suspensions. The saturation intensity of the nanoparticle solution was extracted in spite of a strong nonlinear scattering of the nanoparticles. The nonlinearities observed in nanoparticles are attributed to the DMG-capping agent used in the synthesis of the nanoparticles. DMG was found to be very suitable for the formation of nickel sulfide nanoparticles with an average diameter of 5 nm. The 416 nm peak, found in the UV-Vis spectrum, is due to the metal–ligand charge transfer in the Ni–DMG complex, and the 554 nm peak is due to the transition in the Ni\(^{2+}\) ion as discussed in Chapter XX. In contrast, it was found that nickel sulfide nanoparticles prepared without the DMG capping agent do not possess this absorption peak at 554 nm.

Lastly, we have successfully synthesized single crystalline CdS nanowires by the pulsed laser vaporization method without the use of a catalyst and have explored the nonlinear optical transmission response of CdS nanowires using the open-aperture Z-scan technique. Although the quantum confinement is relatively weak in the nanowires used in this study, the optical limiting threshold of the CdS nanowire suspension was determined to be 0.47 J/cm\(^2\), which is relatively low when compared with those of metal nanowire suspensions reported in the literature. Intensity-dependent nonlinear absorption and scattering were the identified processes that lead to the nonlinear optical transmission. The observed nonlinear optical transmission data fits very well to a three-photon absorption model rather than the two-photon absorption model.
6.2 Future Work

One of our present goals is to prepare Bi nanowires with controlled mean diameters and investigate their temperature dependent infrared and UV absorption properties. Our recent experiments using the chemical vapor deposition synthesis method are proving successful, and we have synthesized bismuth nanowires with average diameter of ~1 μm. Besides controlling the synthesis parameters (i.e. temperature, gas flow rates, etc.), we find that the ratio of hydrogen to inert gas flow rates is critical for tuning the mean diameter of these nanowires. Furthermore, observation of superconductivity in bismuth nanowires has also been reported recently [131]. One of the interesting future projects is to correlate the superconducting transition temperature to the mean diameter of the bismuth nanowires [132].

Finally, we wish to leverage our capability of performing low temperature infrared absorption measurements at Clemson to probe the surface states akin to those reported by Hirahara et al. [68] using ARPES on Bi films. To this end, we plan to prepare Bi thin films with thickness ranging from x-y nm on specially cut KBr substrates so that the Clemson films have the same orientation as those used by Hirahara et al.
REFERENCES


Figure A1: Detailed drawing of the workings on the transfer line.
Figure A2: Detailed drawing of the inner workings on the low-temperature infrared cell.
Appendix B

Kerr Effect

The Kerr effect is a change in the refractive index of a material in response to an applied electric field. Two special cases of the Kerr effect are normally considered; the electro-optic Kerr effect and the optical Kerr effect. In the case for nonlinear optics, the latter of the two will be discussed. The optical Kerr effect is the case in which the electric field is due to the light itself. This causes a variation in index of refraction $\Delta n$ which is proportional to the local irradiance of the light. This refractive index variation is responsible for the nonlinear optical effects. This effect only becomes significant with very intense beams such as those from lasers.

In the optical Kerr effect, an intense beam of light in a medium can provide a modulating electric field, without the need for an external field to be applied; the electric field is then given by:

$$E = E_w \cos(\omega t)$$  \hspace{1cm} (B.1)

where $E_w$ is the vector amplitude of the wave. Combining Eq. (B.1) this with the equation for polarization Eq. (B.3) and taking only the linear terms and those in $\chi^{(3)} |E_w|^2$:

$$P \sqcap \varepsilon_0 \left( \chi^{(1)} + \frac{3}{4} \chi^{(3)} |E_w|^2 \right) E_w \cos(\omega t)$$ \hspace{1cm} (B.2)
where polarization $P$ is

$$P = \varepsilon_0 \chi^{(1)} : E + \varepsilon_0 \chi^{(2)} : EE + \varepsilon_0 \chi^{(3)}$$  \hspace{1cm} (B.3)$$

where $\varepsilon_0$ is the vacuum permittivity and $\chi^{(n)}$ is the $n$-th order component of the electric susceptibility of the medium. The "." symbol represents the scalar product between matrices. Equation (B.2) looks like a linear susceptibility with an additional non-linear term:

$$\chi = \chi_{Lin} + \chi_{NL} = \chi^{(1)} + \frac{3\chi^{(3)}}{4}|E_w|^2,$$  \hspace{1cm} (B.4)$$

and since:

$$n = (1 + \chi)^{1/2} = (1 + \chi_{Lin} + \chi_{NL})^{1/2} \equiv n_0 \left(1 + \frac{1}{2n_0^2} \chi_{NL} \right)$$  \hspace{1cm} (B.5)$$

where $n_0 = (1 + \chi_{Lin})^{1/2}$ is the linear refractive index. Using a Taylor expansion on Eq. (B.5) and since $\chi_{NL} \propto n_0^2$, this gives an intensity dependent refractive index of:

$$n = n_0 + \frac{3\chi^{(3)}}{8n_0} |E_w|^2 = n_0 + n_2 I$$  \hspace{1cm} (B.6)$$
where $n_0$ is the linear refractive index, $n_2$ is the second-order nonlinear refractive index, and $I$ is the intensity of the wave. The refractive index change is thus proportional to the intensity of the light travelling through the medium.
Appendix C

Theory of Nonlinear Optics

When one or more electromagnetic waves propagate in a material, the atoms and molecules oscillate not only at the frequencies of the electric field applied, but also at different combinations of those frequencies as a result of the nonlinear response of the medium. The particles in the medium are displaced from their equilibrium positions, so that positive charged particles move in the direction of the field, while the negative charged particles move in the direction opposite to the direction of the applied electric fields. Dipole moments are created because of the displacement between positive and negative charged particles, and the dipole moment per unit volume describes the induced polarization of the medium.

Nonlinear optics is a material phenomenon in which intense light induces a nonlinear response in the medium, and in return the medium modifies the optical fields in a nonlinear way. In fact, all media are nonlinear to a certain degree. When the applied electric fields are sufficiently small, the electric polarization, $P$ is approximately linearly proportional with the applied electric field $E$

$$P = \chi \cdot E \quad \text{(C.1)}$$

where $\chi$ is the electric susceptibility tensor. This is the case of linear optics. However, when the applied electric fields are high enough, the induced polarization has a nonlinear
dependence on these electric fields and can be expressed as a power series with respect to the electric field

\[ P = \chi^1 \cdot E + \chi^2 \cdot EE + \chi^3 \cdot EEE \] (C.2)

The first term \( \chi^1 \) is responsible for linear absorption and refraction, while the remaining terms are associated with light-induced nonlinear effects.

In nonlinear optics, the product of two or more oscillating fields generates oscillations at different combinations of the incident frequencies. In order to account for this and to have a complete description of the process, the following notation is used:

\[ P(w) = \chi^1 (-w; w) \cdot E(w) + \chi^2 (-w_3; w_1 w_2) \cdot E(w_1) E(w_2) + ... \] (C.3)

This notation also reflects the conservation of energy for each nonlinear process:

\[ w_3 = w = w_1 + w_2 \] (C.4)

for \( \chi^4 \). In order to find the wave equation for a beam that propagates through a nonlinear optical medium, one starts with Maxwell's equations (considering permittivity to be unity)

\[ \nabla \cdot D = \rho \] (C.5)
\[ \nabla \cdot B = 0 \quad (C.6) \]

\[ \nabla \cdot H = J + \frac{\partial D}{\partial t} \quad (C.7) \]

Assuming non-magnetic materials with no free charges or currents, i.e. \( \rho = 0 \) and \( J = 0 \), we get

\[ B = H \quad (C.8) \]

\[ D = P + \varepsilon E \quad (C.9) \]

Using the conditions above and Maxwell's equations, we can determine the wave equation:

\[ \nabla \times \nabla + E = -\left( \frac{\partial}{\partial t} \right) \nabla \times B = -\left( \frac{\partial}{\partial t} \right) \nabla \times H = -\mu \frac{\partial}{\partial t} \left[ \sigma E + \varepsilon \frac{\partial E}{\partial t} + \frac{\partial P^{NL}}{\partial t} \right] \quad (C.10) \]

Using the general vector notation \( \nabla \times \nabla \times E = \nabla (\nabla \cdot E) - \nabla^2 E \), we have for charge free medium,

\[ \nabla^2 E = \mu \sigma \left( \frac{\partial}{\partial t} \right) E + \mu \varepsilon \left( \frac{\partial^2}{\partial t^2} \right) E + \mu \left( \frac{\partial^2}{\partial t^2} \right) P^{NL} \quad (C.11) \]
Therefore, the **nonlinear wave equation** of which we will make use in becomes,

\[ \nabla^2 E - \mu \sigma \left( \frac{\partial}{\partial t} \right) E - \mu_e \left( \frac{\partial^2}{\partial t^2} \right) E = \mu \left( \frac{\partial^2}{\partial t^2} \right) P^{nl} \]  

(C.12)

\[ \nabla^2 E + \frac{1}{c^2} \left( \frac{\partial^2}{\partial t^2} \right) E = -\frac{1}{c^2 \epsilon} \left( \frac{\partial^2}{\partial t^2} \right) P^{nl} \]  

(C.13)

The second term in Eq. (C.13) is zero in current free regions. The equation is inhomogeneous, and the nonlinear response of the medium represents the source term, which is included as the right-hand term.

This means that \( P \) drives the electric field \( E \). This is responsible for many nonlinear optical phenomena like second harmonic and higher harmonic generation, sum and difference frequency generation etc.

In Eq. (C.2), the first term accounts for the linear absorption and refraction and the other higher order terms represent the nonlinear light-matter interaction processes such as sum and difference frequency mixing, optical rectification, and the electro-optic effect, electronic Kerr effect, nonlinear absorption, nonlinear refraction, etc. Further the magnitude and the response of these higher order effects can be compared only by evaluating their corresponding nonlinear coefficients \( \chi^2, \chi^3 \) etc.

The \( \chi^2 \) term is present only in non-centrosymmetric materials possessing inversion symmetry. Therefore materials that are isotropic, homogeneous such as a liquid, gases have the lowest nonlinear responses as third order nonlinear processes. Thus this third order becomes most widely applied one.
From the above discussions, one can invariably understand that the determination of the magnitude and response of third-order nonlinear susceptibility are vital parameters in characterizing and quantifying the applicability of any material as a nonlinear optical device. In general, the nonlinear index of refraction is defined as a variation of the index of refraction of the material caused by the intensity of light waves propagating through the medium. The third order nonlinear susceptibility is related to the nonlinear index of refraction, similar to the relationship of the linear susceptibility to the linear index of refraction.
Appendix D

List of Publications and Conferences During My PhD

Refereed Journal Publications


**Selected by “Virtual Journal of Nanotech. Environment, Health and Safety.” (March 5, 2009).**


**Selected by “Virtual Journal of Nanoscale Science and Tech.” (July 21, 2008).**


**Selected by “Virtual Journal of Nanoscale Science and Tech.” (Sept. 10, 2007).**


**“Highly Accessed”**


Conference Proceedings


Invited Review Articles


Book Chapters


Patents