

“Synthesis and Characterization of PbSe and PbTe Nanostructures for Thermoelectric applications”

A dissertation

Submitted in Partial Fulfilment for the requirements of the award of the Degree of

MASTER OF TECHNOLOGY

in

Nanoscience and Technology

By

Sandeep Kumar Prajapati

(Roll. No. 13/NST/2K11)

Under the Supervision of

Dr. Amrish K. Panwar

(Assistant Professor)

Department of Applied Physics

Delhi Technological University, Delhi



Department of Applied Physics

Delhi Technological University, Delhi.

2011-2013



CERTIFICATE

This is to certify that the project entitled "**Synthesis and Characterization of PbSe and PbTe Nanostructures for Thermoelectric applications**" completed by Mr. Sandeep Kr. Prajapati student of M.Tech., Nanoscience and Technology in Applied Physics Department at Delhi Technological University, New Delhi embodies the original work carried out by him under my supervision and guidance. His work has been found very well for the partial fulfilment of the requirement of the degree of M.Tech.

It is further certified that, the student has developed the project during the period starting from 2nd January, 2013 to 30th June, 2013. This report has not been submitted in part or full in any other University for award of any other degree or diploma.

Mr. Sandeep Kr. Prajapati is student of good moral character. We wish him success in future.

Date.....

Dr. Amrish K. Panwar

Assistant Professor

Department of Applied Physics

Delhi Technological University

Prof. S. C. Sharma

Head of the Department

Department of Applied Physics

Delhi Technological University

DECLARATION

I hereby declare that the work which is being presented in this thesis entitled **“Synthesis and Characterization of PbSe and PbTe Nanostructures for Thermoelectric applications”** my own work carried out under the guidance of **Dr. Amrish K. Panwar**, Assistant Professor, Delhi Technological University, New Delhi. I further declare that the matter embodied in this thesis has not been submitted for the award of any other degree or diploma.

Date.....

Sandeep Kumar Prajapati

Roll No- 13/NST/2K11

M.Tech Nanoscience and Technology

Delhi Technological University

New Delhi

ACKNOWLEDGEMENT

Now the final report is in my hands. It is not a one night venture; it requires firm determination, dedication, warmth bliss and grace of the Formless one that equips me to perform this task. A formal statement of acknowledgement will hardly meet the end of justice while writing these words, I feel obliged to all of them who extended their inconceivable co-operation towards the achievement of whatever we have achieved.

I also express my gratitude towards **Prof. S.C Sharma**, Head of the Dept, Dept. of Applied Physics, Delhi Technological University, for extending her support & valuable guidance.

First of all I would like to express deep sense of gratitude and sincere thanks to my supervisor **Dr. Amrish K. Panwar, Assistant Professor, Delhi Technological University, New Delhi** for his continuous encouragement and thoughtful discussion during the course of present work. I am very grateful to him for giving me the opportunity to work on thermoelectric material, appreciating my ideas and allowing me the freedom to take on the tasks independently. Constant supervision of my guide throughout the project, learned guidance and invaluable suggestions helped me to complete the project well in stipulated time.

I am highly indebted to **Dr. Pawan K. Tyagi**, for providing me necessary experimental arrangements at DTU and making available other facility.

With due regards, I express sincere thanks to **Mr. Aman & Mr. Sandeep** for helping me a lot in my characterization work. I would like to express my special gratitude and thanks to our research scholars **Mr. Vinay Kumar, Miss Lucky Krishnia** and **Mrs. Reetu Sharma** for giving me such attention and time.

Also I express deep sense of gratitude and sincere thanks to all the faculty members **Dr. Mohan S. Mehata, Dr. Rishu Chaujur, Dr. Yogita Kalra, Dr. Ajeet Kumar, Dr. Nitin K. Puri, Dr. M. Jayasimhadri, Dr. Amrish K. Panwar** who has been part of my M.Tech program at Delhi Technological University during course work and has helped me in my research.

Finally I would like to thank my parents and other family members who were always anxious to help me & contributed a major driving force behind the completion of this project.

Date.....

Sandeep Kumar Prajapati

Place.....

Roll No- 13/NST/2K11

M.Tech Nanoscience and Technology

Delhi Technological University

New Delhi

CONTENTS

Title Name	Page No.
List of Figures	viii
List of Tables	x
List of Abbreviations	xi
Abstract	xii
Chapter 1 Introduction	1
1.1 Nanotechnology	2
1.2 History	3
1.3 Basic concepts	4
1.4 Energy Related Technologies	4
Chapter 2 Literature Review	8
Chapter 3 Thermoelectricity	12
3.1 Waste Heat Harvesting	12
3.2 History	13
3.3 Thermoelectric Effect	17
3.3.1 Seebeck Effect	17
3.3.2 Peltier Effect	18
3.3.3 Thomson Effect	19
3.4 Thermoelectric Power Generation	20
3.4.1 Working	21
3.4.2 Figure of Merit	22
3.5 Thermoelectric Refrigeration Systems	23
3.6 Design of Thermoelectric System	25
3.7 Module Selection	25
3.8 Thermoelectric Materials	27
3.9 Improvement of Performance of Thermoelectric Elements	28
Chapter 4 Synthesis and Characterization Techniques	29
4.1 Synthesis of Lead Selenide	29
4.2 Synthesis of Lead Telluride	30

Title Name	Page No.
4.3 Characterization Techniques	31
4.3.1 X-ray Diffraction	32
4.3.1.1 Utility of XRD for Nanomaterials	34
4.3.1.2 Crystal Identification	34
4.3.1.3 Crystallite Size	34
4.3.2 Scanning Electron Microscopy	35
4.3.3 Transmission electron microscopy	39
4.3.4 UV-visible Spectroscopy	43
4.3.5 Raman Spectroscopy	45
4.3.5.1 Origin of Raman Effect	46
4.3.5.2 Instrumentation	48
4.3.6 FTIR spectroscopy	49
4.2.3 Photoluminescence	50
Chapter 5 Results and Discussion	53
5.1 Characterization of Lead Selenide	53
5.1.1 Scanning Electron Microscope Analysis	53
5.1.2 XRD analysis	57
5.1.3 EDX analysis	58
5.1.4 Fourier Transform Infra-red Spectroscopy	59
5.1.5 Transmission Electron Microscopy	60
5.2 Characterization of Lead Telluride	63
5.2.1 Scanning Electron Microscope	63
5.2.2 Fourier Transform Infra-red Spectroscopy	66
5.2.3 Transmission Electron Microscopy	67
Conclusion	70
References	71

LIST OF FIGURES

Sr.No	Figure Title	Page No.
1.	Figure 3.1 Schematic diagram of partisan's canteen	15
2.	Figure 3.2 Schematic diagram of 500w portable generator using liquid fuel Lead telluride thermoelement	16
3.	Figure 3.3 Schematic diagram of candle radio	16
4.	Figure 3.4 Schematic diagram of experimental set up for measurement of seebeck coefficient S	18
5.	Figure 3.5 Schematic diagram of Peliter effect	19
6.	Figure 3.6 Schematic diagram of Thermoelectric generator	21
7.	Figure 3.7 Schematic diagram of a thermoelectric refrigeration System	24
8.	Figure 3.8 Schematic diagram of Module components	25
9.	Figure 3.9 Schematic diagram of Construction of a thermo element	27
10.	Figure 4.1 Photograph of XRD Bruker D8 Advance at DTU	32
11.	Figure 4.2 Schematic diagram showing Bragg diffraction from a set of planes	34
12.	Figure 4.3 Schematic diagram of Interaction of high energy electrons with solid	37
13.	Figure 4.4 Schematic diagram of Working of SEM	38
14.	Figure 4.5 Picture of Hitachi S-3700 SEM at DTU	39
15.	Figure 4.6 Working of Transmission Electron Microscope	41
16.	Figure 4.7 Photograph of TEM	42
17.	Figure 4.8 Photograph of UV-5704	44
18.	Figure 4.9 UV-visible Spectrometer	45
19.	Figure 4.10 Schematic diagram of Different type of scattering	47
20.	Figure 4.11 Photograph of Nicolet-380 FTIR	50
21.	Figure 4.12 Photograph of Photoluminescence Instrument	51
22.	Figure 5.1(a) SEM micrograph of sample PbSe at 4h	53
23.	Figure 5.1(b)SEM micrograph of sample PbSe at 4h	54

24.	Figure 5.1(c) SEM micrograph of sample PbSe at 4h	54
25.	Figure 5.1(d) SEM micrograph of sample PbSe at 8h	55
26.	Figure5.1(e) SEM micrograph of sample PbSe at 8h	55
27.	Figure 5.1(f) SEM micrograph of sample PbSe at 8h	56
28.	Figure 5.1(g) SEM micrograph of sample PbSe at 8h	56
29.	Figure5.1.2 XRD pattern of PbSe sample	57
30.	Figure5.1.3 EDX analysis of PbSe sample	58
31.	Figure5.1.4 FTIR spectra of Sample of PbSe	59
32.	Figure5.1.5 (a): TEM micrograph of PbSe at 4h	60
33.	Figure5.1.5 (b): TEM micrograph of PbSe at 4h	61
34.	Figure5.1.5(c): TEM micrograph of PbSe at 4h	61
35.	Figure5.1.5 (d): TEM micrograph of PbSe at 8h	62
36.	Figure5.1.5 (e): Electron diffraction (ED) of PbSe at 8h	62
37.	Figure5.2 (a): SEM micrograph of PbTe sample at 4h	63
38.	Figure5.2 (b): SEM micrograph of PbTe sample at 4h	64
39.	Figure5.2(c): SEM micrograph of PbTe sample at 4h	64
40.	Figure 5.2(d): SEM micrograph of sample PbTe at 8h	65
41.	Figure5.2 (e): SEM micrograph of sample PbTe at 8h	65
42.	Figure 5.2.2: FTIR analysis of PbSe	66
43.	Figure5.2.3 (a): TEM micrograph of PbTe at 8h	67
44.	Figure 5.2.3(b): TEM micrograph of PbTe at 8h	68
45.	Figure 5.2.3(c): TEM micrograph of PbTe at 8h	68
46.	Figure5.2.3 (d): Electron diffraction (ED) of figure 5.2.3(b)	69

LIST OF TABLES

Sr.No.	Table Title	Page No.
1.	Physical Properties of PbSe	9
2.	Physical Properties of PbTe	11
3.	Characteristics of different thermoelectric materials	27
4.	Spectral Region	43

LIST OF ABBREVIATIONS

1. nm	Nanometer
2. XRD	X-ray Diffraction
3. SEM	Scanning Electron Microscope
4. TEM	Tunnelling Electron Microscope
5. DSC	Differential Scanning Calorimetry
6. TGA	Thermal Gravimetry
7. FTIR	Fourier Transform Infrared Spectroscopy
8. UV-Vis	Ultraviolet-visible Spectroscopy
9. PVD	Physical Vapour Deposition
10. CVD	Chemical Vapour Deposition
11. TE	Thermoelectricity

ABSTRACT

Lead telluride (PbTe) and Lead selenide (PbSe) and its alloys are currently best known thermoelectric (TE) materials for the application of thermoelectric generators. Lead telluride is an intermediate thermoelectric power generator. Lead selenide is widely used in LED's, photovoltaic cells, sensing applications, biology (as biological markers) [1] and as again media in very special types of micro-lasers. Lead selenide and Lead telluride nanostructures such as nanoparticles, nanorods have been successfully synthesized by Organic precursor method, Co-precipitation approach in organic solvent and hydrothermal method and so on. Hydrothermal method is the one of the simplest method by which we can synthesize the nanoparticles of the size ranging 18nm to 23nm. Hydrothermal reaction of selenium and tellurium with lead acetate in sodium hydroxide solution in presence hydrazine hydrate as a reductive was investigated to prepare lead chalcogenides, PbE (E=Se,Te). Nanocrystals with different morphology could be obtained under mild conditions. The formation of Lead chalcogenides in our process is based on the direct elemental combination pathway. The product was characterized by XRD, SEM and TEM. Further characterization was done using FTIR, UV- visible spectroscopy. The cubic structure of PbTe and PbSe was confirmed by XRD spectra. The optical properties of the samples were studied by UV-visible spectroscopy. The primary goal of this thesis is to dig up the thermoelectric properties of Lead selenide and Lead telluride and to learn the synthesis techniques and characterization of nanostructure TE materials for better energy conversion.

Chapter 1

Introduction

Energy has the most important role in our life. The energy consumption around the world is order of 10^{13} watts per annum [2] and mostly come from fossil-fuel [3]. The demand of energy is growing day by day as we are growing infrastructure and society, which means that the energy sources will deplete even sooner. Electrical energy is prior necessity of the human kind in today's world. Conventional sources of energy are going to finish someday so we have to find alternative energy sources and develop such techniques that are nonconventional. We have many sources for this type of power generation like solar energy, wind energy, hydropower. These produces power at larger scale and need big investments. Now we have to develop an efficient and low cost power generator as well. Thermoelectric materials can be used for power generation with the phenomenon of Seebeck Effect. Electricity can be produced directly by heat in thermoelectric power generation but due to less efficiency of thermoelectric materials it has not been utilized for power generation. Now this method is receiving more attentions due to the breakthroughs in the field of thermoelectric materials recently. In recent years, nanometer sized materials started to emerge as new building blocks of better energy conversion devices, which may help us to meet with the energy demands in the next few decades. The experimental proof on the effectiveness of nanostructures over the TE figure of merit was reported in the nanostructure super lattice thin films and in quantum dot TE super lattices by researchers [4-8].

1.1 Nanotechnology

Nanotechnology is the study of manipulating matter on an atomic and molecular scale. Generally, it deals with developing materials, devices, or other structures possessing at least one dimension sized from 1 to 100 nanometres. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly. It is valuable in developing new materials with dimensions on the nanoscale to investigating whether we can directly control matter on the atomic scale. Nanotechnology evokes the application of fields of science as diverse as surface

science, organic chemistry, molecular biology, semiconductor physics, micro-fabrication, etc. [9]. Generally nanotechnology can be understood as a technology, which allows in the controllable way not only create nanomaterials but also operate them, i.e. to influence them or to use them according to their intended purpose. Accordingly nanomaterials can be understood as the materials, which are characterized at least in one of the three measurements by nanometre scale concerning both sample of a material as a whole and its structural elements. In 1959 Richard Feynman at Cal Tech spoke of “Plenty of Room at the bottom” to highlight the tremendous scientific and technological potential of materials and device at atomic/molecular dimensions. Eric Drexler in the early 1980’s coined the word “Nanotechnology”. Nanotechnology may be able to create many new materials and devices with a massive range of applications, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterials [10] and their potential effects on global economics, as well as belief about various doomsday scenarios. These concerns have led to a debate among advocacy groups and governments on whether special regulation of nanotechnology is warranted.

1.2 History

Although nanotechnology is a relatively recent development in scientific research, the development of its central concepts happened over a longer period of time. In 1974, Norio Taniguchi introduced the term “nanotechnology” to represent extra-high precision and ultra-fine dimensions, and also predicted improvements in integrated circuits, optoelectronic devices, mechanical devices and computer memory devices [11]. This is the so called ‘top-down approach’ of carving small things from large structures. K. Eric Drexler developed and popularized the concept of nanotechnology and founded the field of molecular nanotechnology. In 1979, Drexler encountered Richard Feynman's 1959 talk "There's Plenty of Room at the Bottom" [12]. In 1986, K. Eric Drexler in his book “*Engine of Creation: The Coming Era of Nanotechnology*” discussed the future of nanotechnology, particularly the creation of larger objects from their atomic and molecular components, the so called ‘bottom-up approach’ [13]. Drexler's vision of nanotechnology is often called "Molecular

Nanotechnology" (MNT) or "molecular manufacturing," and Drexler at one point proposed the term "zettatech" which never became popular. The emergence of nanotechnology in the 1980s was caused by the convergence of experimental advances such as the invention of the scanning tunnelling microscope in 1981 and the discovery of fullerenes in 1985. The scanning tunnelling microscope, an instrument for imaging surfaces at the atomic level, was developed in 1981 by Gerd Binnig and Heinrich Rohrer at IBM Zurich Research Laboratory, for which they received the Nobel Prize in Physics in 1986. Fullerenes were discovered in 1985 by Harry Kroto, Richard Smalley, and Robert Curl, who together won the 1996 Nobel Prize in Chemistry.

In the early 2000s, the field was subject to growing public awareness and controversy, with prominent debates about both its potential implications, exemplified by the Royal Society's report on nanotechnology, as well as the feasibility of the applications envisioned by advocates of molecular nanotechnology, which culminated in the public debate between Eric Drexler and Richard Smalley in 2001 and 2003. Many nations moved to promote and fund research into nanotechnology with programs such as National Nanotechnology Initiative, Centre for Nanotechnology. The early 2000s also saw the beginnings of commercial applications of nanotechnology, although these were limited to bulk applications of nonmaterial's, such as the Silver, nano platform for using silver nanoparticles as an antibacterial agent, nanoparticle-based transparent sunscreens, and carbon nanotubes for stain-resistant textiles [14].

1.3 Basic Concepts

One nanometer is equal to one billionth of a meter. The nanometer is the level of atoms and molecules. By convention, nanotechnology is taken as the scale range 1 to 100 nm following the definition used by the National Nanotechnology Initiative in the US. The lower limit of the above range is set by the size of atoms since nanotechnology must build its devices from atoms and molecules. The upper limit is more or less arbitrary but is around the size that phenomena not observed in larger structures start to become apparent and can be made use of in the nano device. Nanotechnology is technology to control and manipulate a substance at the nanometre level, and create new devices and materials with fascinating functions making the best use of the special properties of nanosized substances. When the size of the matter is at

the level of several molecules or atoms, certain properties (quantum effect or the surface effect) are clarified, which are not particularly noticeable when a substance is large mass. Quantum size effect results in unique mechanical, electronic, photonic, and magnetic properties of nanoscale materials. Chemical reaction of nanomaterials is different from more macroscopic form. As the dimensions minimise to the nanolevel the following changes come into the picture:

- Quantum Confinement
- Large Surface to Volume Ratio
- Quantized Energy State

According to Dr. K. Eric there are many things which became practical with nanotechnology [15]:

- Faster pc's than today
- Safe space travel
- Virtual end of illness
- End of famine and starvation

There are so many devices which appear to be physically possible and practically realizable with nanotechnology. Faster computers, cooling systems, nanomechanical systems, biosensors, nanomedical devices and strong, tensile material are the fine outcome of nanotechnology. Logic gates of very low dimension of 10^{-26} m³ volume, operating speed as high as 0.1 ns, power consumption of 10^{-21} joules can be fabricated. The discovery of novel materials, processes, and phenomena at the nanoscale, as well as the development of new experimental and theoretical techniques for research provide fresh opportunities for the development of innovative nanosystems and nanostructured materials.

1.4 Energy Related Technologies

Nanotechnologies provide the potential to enhance energy efficiency across all branches of industry. It provides essential improvement potentials for the development of both conventional energy sources (fossil and nuclear fuels) and renewable energy sources like geothermal energy, wind, sun, water, tides or biomass. There are various energy related technologies in which nanotechnology play a role these include the following:

1.4.1 Thermoelectricity

For thermoelectric cooler and power generator to be practical and competitive with more traditional forms of technology, the thermoelectric devices must reach a comparable level of efficiency a converting between thermal and electric energy. The efficiency of thermoelectric devices is generally depending upon the factor, known as figure of merit of the material used for the fabrication of the thermoelectric device. The best available thermoelectric material should exhibit figure of merit nearly unity at their operating temperature. PbTe and PbSe is an intermediate thermoelectric power generator [16]. The specialized application of thermoelectric generators is very successful and has motivated a search for materials with an improved figure of merit Z , and also for materials which operate at elevated temperature. PbTe thermoelectric generators are widely have been widely used by the US army, in space craft's to provide onboard power, and in pacemaker's batteries.

1.4.2 Photovoltaic cell

The growing energy demand and the depletion of conventional energy sources along with global warming threats has motivated researchers to design the most efficient photovoltaic cells. In order to improve conversion efficiency major research in photovoltaic cells is directed towards absorbing more sunlight using nanotechnology, for example 'nanotube', 'quantum dots' (QDs), and 'hot carrier' solar cell [16].

1.4.3 Energy Storage

The remarkable properties of CNTs could enable CNT-based electrodes in batteries to generate increased electricity output as compared to traditional electrodes. The new battery offers to vastly faster discharge and charge rates, meaning that the time to recharge the battery can be measured in minutes rather than in hours. Researchers have covered capacitor electrodes with millions of nanotubes to increase electrode surface area and thus the amount of energy that they can hold. The nanostructure materials also increase the useful lifetime of the battery by 10 to 20 times over current lithium batteries and provide battery performance over a broader range of temperatures than currently achievable [16].

1.4.4 Lighting

High-brightness light-emitting diodes (LEDs) are the most promising light source, as these offer better efficiency, longer life and higher mechanical strength. Semiconductors used in the preparation of LEDs for lighting are increasingly being built at nanoscale dimensions, and projections indicate that nanotechnology-based lighting advances have the potential to reduce worldwide consumption of energy by more than 10%. Nanocrystals which are also known as quantum dots are known primarily for their ability to produce distinct colours of light as the size of the individual crystals is varied. Nanomaterials play big role in the heat dissipation in LEDs. PbSe nanocrystals are widely used in LED's, photovoltaic cells, sensing applications, biology [as biological markers] and as gain media in very special types of micro-lasers [16].

1.4.5 Energy Storage

Many sustainable energy sources like wind and solar power deliver significant power only part of the time. Strategies to store the energy are needed. Nanotechnology may play a role in distributed generation through the development of cost-effective energy storage in batteries, capacitors, and fuel cells Nanotechnology will make novel type of energy stores, including electrical stores such as batteries and chemical stores such as hydrogen, more competitive. Also the remarkable properties of carbon nanotubes could enable CNTS based electrodes in batteries to generate increased electricity output as compared to traditional electrodes. Researchers have covered capacitor electrodes with millions of nanotubes to increase electrode surface area and thus the amount of energy that they can hold [16]. The nanostructure materials also increase the useful lifetime of the battery by 10 to 20 times over current lithium batteries and provide battery performance over a broader range of temperatures than currently achievable.

1.4.6 Heating

Nanotechnology may help accelerate the development of energy-efficient central heating. When added to water, CNTs disperse to form a nanofluid. Researchers have developed nanofluids whose rates of forced convective heat transfer are four times better than the norm by using CNTs.

1.4.7 Transportation

Nanotechnology may enable more efficient transportation via catalysts in fuels; lighter, stronger materials; and more efficient batteries. The fuel additive uses nanoscale (10 nm across) particles of cerium oxide to catalyze the combustion reactions between diesel fuel and air. Nanoparticle-reinforced materials that are as strong as or stronger than today's materials but weigh less will help provide better fuel economy. Nanotechnology is being used in lithium-ion and other batteries that are expected to increase the efficiencies of hybrid and electric vehicles. Nanoscale capacitors made from multiwall CNTs dramatically boost the amount of surface area, and thus the electrical charge, that each metal electrode in the capacitor can possess. Nanoadditives, including nanoparticles and nanopowders, could be used to enhance the transfer of heat from solar collectors to storage tanks. When added to heat-transfer fluids, the solid nanoparticles conduct heat better than the fluid alone, and they stay suspended longer than larger particles and they have a much greater surface area, which is where heat transfer takes place.

1.4.8 Power chips

Power Chips are nanotechnology devices that use thermionic to convert heat directly into electricity. Thermionic is the science that deals with the phenomenon (also known as the Edison effect) in which the flow of electrons from a metal or metal oxide surface, caused by thermal energy, overcomes the electrostatic forces holding electrons to the surface. Power chips contain no moving parts or motors and can be either miniaturized or scaled to very large sizes for use in a variety of applications.

CHAPTER-2

Literature Review

The synthesis of semiconductor nanocrystals and the synthesis of PbTe, PbSe nanocrystals in a particular is a cross-disciplinary science. Since it addresses the making of a chemical (binary) compound, one might infer that the nanocrystal production is chemistry related discipline. This is partly true, because the motivation that drives the nano-technology people resides in the need for novel optical devices that can be used, for example in optics and biology. Moreover the interdisciplinary character of this science is better emphasized by the need for characterization of these NCs. This is related to the experimental method used in Applied Physics and signal recording and processing methods that are mostly used in Electrical Engineering. There are many enabling technologies that are currently used in this field. However, a distinction must be made between the technologies that help produce PbSe and PbTe nanocrystals that are responsible with the NCs characterization. Due to their small sizes, starting from a few to tens of nanometers, semi-conductive PbSe and PbTe NCs are generally searched by means of electron microscopy. It is good to emphasize the fact that each synthesis method can produce different type of nano-crystals, hence the need for various characterization methods. Transmission Electron Microscopy (TEM) was used to get the approximate size of the particles. The NCs that have been obtained using the methods that were presented in the main section of the thesis was also characterized by XRD in order to get good description of type of crystalline structure NCs. Energy Dispersive Analysis (EDX) can be easily done to get the compositional analysis of the compound. Other diagnostic method that is widely used to search the optical properties of the PbSe NCs is absorption spectroscopy.

Lead selenide is a semiconductor material. It forms cubical crystal of NaCl structure. The cubic semiconductor PbSe has been attracting scientific attention for more than seven decades mainly because of its optical properties. For example, the infra-red behaviour of PbSe has been appreciated since the 1940's [17] and eventually found applications in photo detectors and thermal imaging [18]. More recently, the advent of nanoscience raised interest in photovoltaic applications based on excitonic effect in PbSe nanocrystals [19-21]. PbSe melts at a relatively high temperature (1080°C), is a

composed of earth abundant elements, is easy to scale up, and performs better than PbTe at 900K, one of the choice thermoelectric materials in the temperature range 600-900K. Lead selenide nanocrystals embedded into various materials can be used as quantum dots, for example in nanocrystal solar cells. There are various method used for the preparation of PbSe nano-particles such as solvothermal process, organic precursor method, electron beam radiation, hydrothermal process. In order to alleviate the reaction conditions and decrease the economic cost, the synthesis of this kind of materials through hydrothermal process would be prior to other process if the properties of them could be retained. Lead-salt quantum dots (QDs) are among the few materials that can provide size-quantized electronic transitions at technologically-important infrared wavelengths. Structures containing these QDs may find use in optoelectronic applications as well as in biophysical applications such as fluorescence microscopy

Some Physical properties of Lead selenide mentioned in the given table below:

Table 1: Physical Properties of PbSe

Property	Value
Band gap	0.27eV
Work function	4.5eV
Melting point	1351K
Density	8270kgm ⁻³
Lattice constant	0.565nm
Molar mass	286.16g/ml

PbTe and the solid solutions based on it are promising materials for use in thermoelectric generation [22, 23], laser industry and microelectronics [24–30]. PbTe is a semiconductor with an energy gap of 0.3 eV. Its crystal structure is FCC The melting point of undoped PbTe is 1190K for 50 at% Te and has a density of 8.15×10^3 kgm⁻³. Thermoelectric materials exhibit a dimensionless figure of merit (ZT) on the order of unity (ZT=1).[31,32].An enhancement of ZT by a factor of at least 2–3 for the existing thermoelectric materials is necessary in order for thermoelectric applications to compete with other more standard techniques in routine refrigeration

or power generation applications. Over a decade ago it was predicted that nanoscaled thermoelectric materials might have superior properties to their bulk counterparts [33]. Subsequently, a significant increase in ZT ($ZT > 2$) has been reported on the nanoscaled systems constitutively based on those commonly used bulk TE materials (e.g., Bi_2Te_3 , PbTe) and theoretically interpreted in terms of the quantum confinement effect and size-dependent electronic structure change [34,35]. In fact, it was known in the 1980s that the ZT for highly disordered alloys of PbTe with a mean grain size of $1\mu\text{m}$ could be $\approx 10\%$ higher than the equivalent single-crystal value.⁶ From these results and for the purpose of practical applications, one promising route to enhanced ZT materials is to incorporate nanoparticles into a bulk PbTe phase matrix, in hopes that the phonon scattering at grain boundaries could significantly reduce the lattice thermal conductivity while the electrical properties could be largely preserved.

Lead Telluride has a rock salt structure (face centered cubic). PbTe can be n- or p-type material as a result of departure from stoichiometry, (Pb - rich PbTe is n- type and Te - rich PbTe is p- type). The electrical properties of PbTe are greatly affected by adding foreign atoms to the PbTe lattice. Halogens may be used via PbCl_2 , PbBr_2 or PbI_2 to produce donor centres. Other n-type doping agents such as Bi_2Te_3 , TaTe_2 , MnTe_2 , are added to PbTe , they substitute for Pb and thus create uncharged vacant Pb -sites. These vacant sites are subsequently filled by atoms from the lead excess. Because the valence electrons of these vacant atoms are not involved in chemical bonding, they diffuse through the crystal. The donor concentration induced by the foreign species is found to be independent of heat treatment. Alkali acceptor agents in lead telluride are discussed by Kovalchik et al. [23], Borisova [36] and Rustamov et al.[37]. P-Type doping agents such as Na_2Te , K_2Te , and Ag_2Te substitute for Te and create vacant uncharged Te sites. These sites are filled by Te atoms which are ionized to create additional positive holes. The free electron (n-type) or hole concentration (p-type) in PbTe is the sum of the electrons or holes originating from Pb or Te in solution plus the electrons or holes introduced by the donor or acceptor species. Some physical properties of lead telluride are given in the table [38]:

Table 2: Physical Properties of PbTe

Property	Value
Band gap	0.22eV
Work function	4.1eV
Melting Pointing	1190K
Lattice constant	0.644nm
Density	8150kgm ⁻³
Molar mass	334.80gm/mol

CHAPTER-3

Thermoelectricity

Thermoelectricity deals in the conversion of thermal energy into electrical energy or vice versa. The phenomenon is called "Thermoelectric Effect. The term thermoelectricity" refers to the phenomenon of interconnected transport of electrical charge and thermal energy, i.e., the transport of charge carriers under a temperature gradient, and the transport of thermal energy under a potential gradient. It collectively refers to the three effects: Seebeck effect, Peltier effect and Thomson effect." With the growing public interest in solving environmental problems during recent years, the importance of thermoelectric power generation, an energy conversion technology, is being re-recognized.

Thermoelectric generators are all solid-state devices that convert heat into electricity. Unlike traditional dynamic heat engines, thermoelectric generators contain no moving parts and are completely silent. Such generators have been used reliably for over 30 years of maintenance-free operation in deep space probes such as the Voyager missions of NASA. Compared to large, traditional heat engines, thermoelectric generators have lower efficiency. But for small applications, thermoelectric can become competitive because they are compact, simple (inexpensive) and scalable. Thermoelectric systems can be easily designed to operate with small heat sources and small temperature differences. Such small generators could be mass produced for use in automotive waste heat recovery or home co-generation of heat and electricity. Thermoelectric have even been miniaturized to harvest body heat for powering a wristwatch.

3.1 Waste Heat Harvesting

One of the major social problems for the 21st century is going to be making available a sustainable supply of energy to the world's population since world demand increases while fossil-fuel supplies decrease. As a measure against global warming, recovering waste heat and converting it into electrical energy is very effective. While there are various methods of recovering waste heat, many expectations are being entertained of the thermoelectric module that has no moving parts and that is capable

of converting waste heat directly into electrical energy. Thermoelectric energy converters are a solid-state device that is able to convert waste heat into electricity, with no moving components, is silent, totally scalable and extremely reliable. For all these reasons, they are expected to play an increasingly important role in meeting the energy challenge of the future.

3.2 History

Economic growth and consistent industrial development of economically developed countries in XXI century will depend on the effective use of natural-resource potential and increased proportion of electrical power generation from renewable sources. It raises great interest in thermoelectric method of thermal into electric energy conversion and makes us to analyze the path covered in this field of science and technology [39]. It is possible to consider the studies of Petersburg academician F. Aepinus, carried out in Russia in 1762, the first research in the field of thermoelectricity presented in the work “Memoirs comprising precise description of tests with tourmaline” [40]. In thermoelectric pendulum proposed by the author a cork ball performed swing motions under the influence of electric potential of heated tourmaline used as a thermoelectric material. A natural tourmaline single crystal possesses specific thermal EMF considerably larger than that of the best semiconductor materials near the room temperature. Therefore, application of this material in thermoelectric voltage source for F. Aepinus's pendulum is an optimal solution.

The above-mentioned investigations in the history of the world science of obtaining electricity by means of a direct thermal energy conversion are the first attempt which was undertaken 60 years prior to the well-known studies of German physicist Seebeck [41] who established that electric current appeared in electrical circuit consisting of different conductors, when one junction was heated and the other - cooled. This phenomenon, related by the researcher to the appearance of free magnetism, was afterwards referred to as the Seebeck thermoelectric effect in science and technology. The first thermoelectric generators (TEG) operated in accordance with the Seebeck effect, were produced abroad at the end of XIX century and were used as the sources of electrical energy for everyday and technical purposes. The illumination of exhibition pavilion in London in 1879 is an example of a successful application of

thermoelectricity. TEG developed by Klimon and demonstrated at the exhibition was used for illuminating the exhibition hall providing power supply for 100 incandescent lamps. Thermoelectric power generation is mainly based on Seebeck Effect given by Thomas Johann Seebeck in 1821 A.D. Since the discovery of the Seebeck effect, thermoelectric modules have been studied for more than 180 years. Nevertheless, the thermoelectric module has not become widespread yet. The major reasons for these are the low efficiencies of conventional thermoelectric modules. In recent years, however, the characteristics of thermoelectric modules have improved so much that the prospect of thermoelectric power generation has rapidly become very bright.

By virtue of certain circumstances, academician A.F. Ioffe left Physics and Technical Institute and in 1952 he organized Laboratory of Semiconductors of the Academy of Sciences of the USSR, and 2 years later – Institute of Semiconductors of the USSR Academy of Sciences where a team of young talented scientists carried out a revolution in thermoelectric power engineering. As a result of basic research in the field of physics of semiconductors conducted by A.F. Ioffe and his colleagues, the fundamentals for thermoelectric materials science, new thermoelectric semiconductor materials, the technology of production of thermocouples and electro-generating and cooling devices were developed and created [42, 43, 44].

The development of practical device and equipment for thermoelectric generation was mainly carried out in Soviet Union since A.I.Ioffe, a Russian physicist, for the first time, theoretically explained in a book in 1929 that semiconductor thermoelectric material has high thermoelectric performance. The book, "Semiconductor Thermoelectric Cooling" is called "The Bible of Thermoelectric Semiconductor"[45]. Even if you used semiconductor materials Dr. Ioffe indicated, you could only get efficiency of 2 to 4 %, however, compared to the conventional metallic material's efficiency of below 0.1%, the theory was epoch-making! See Figure 3.1, the equipment besides a fire cooking something with an odd-shaped pot is a wireless communication gear. At the bottom of the pot, thermoelectric element couples made of zinc antimony composite semiconductor and constantan are installed. The pot was called "Partisan's canteen" that were used at the World War II in Soviet Union at around 1940. The pot in the illustration is much like home cooking one, a bit different

from a typical curved canteen. The temperature at the bottom of the pot scorched by fire could have reached to several hundred degrees centigrade, while the temperature of the content of the pot should have been around 100°C; the temperature difference possibly was kept above 200°C. To call this system "a thermoelectric generation" sounds a bit exaggerated, it rather appropriately be called "a campfire electric generation." Anyway, this can truly be admitted the very first practical beginning of thermoelectric generation.

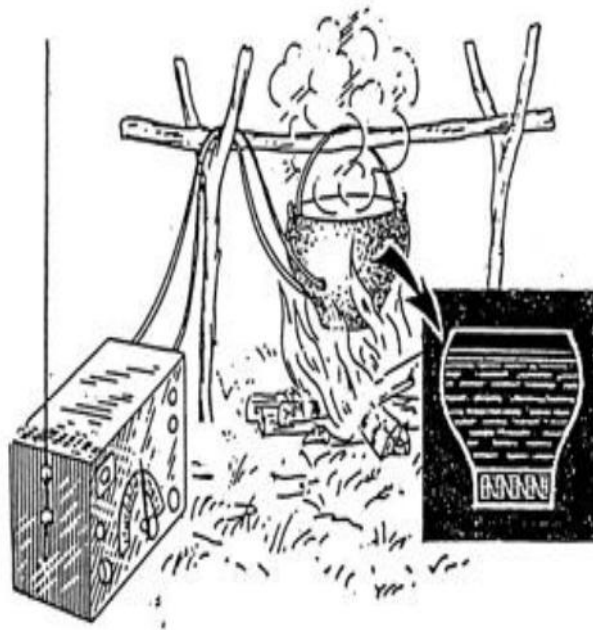


Figure 3.1: Partisan's Canteen: Thermoelectric generation by a campfire

In 1970s, about 30years later since the practical use of thermo-electric generation in Soviet Union, a thermo-electric generator such as shown in Fig. 3.2 was deployed as a battery charger for the United States Army. This generator, could be operated with gasoline, jet fuel and diesel fuel, had an efficiency of 3%. In the structure of the generator in Fig. 3.2, there were a lot of ideas in fuel injector, fan and burner mantle to efficiently burn fuel and effectively transmit heat to the thermo-elements. As a result, it relatively had a high efficiency. This generator obviously had advantages with the noise level of one fifth of a gasoline engine generator and with no maintenance for 1500 hours.

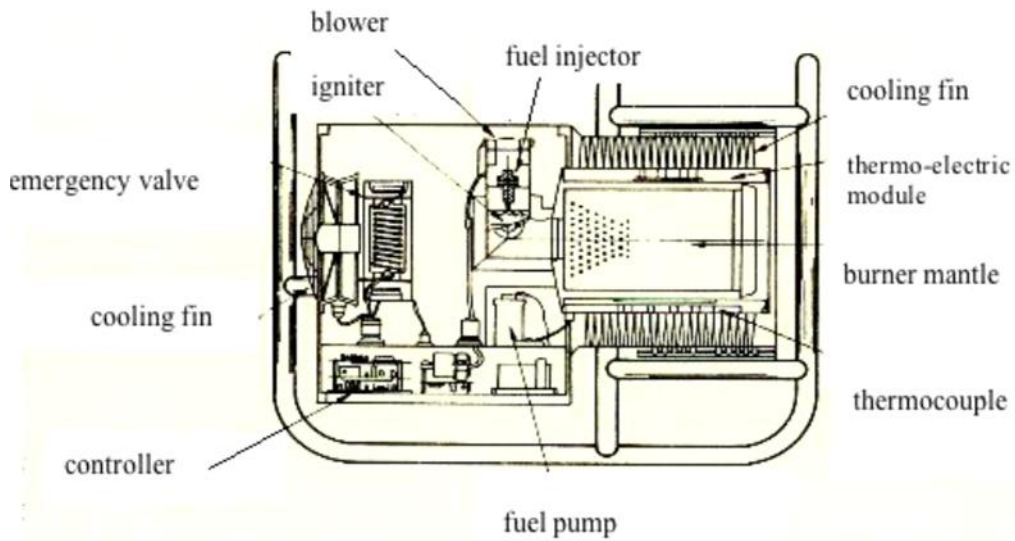


Figure 3.2: 500W portable generator using liquid fuel Lead telluride (PbTe) thermo-element

Fig. 3.3 shows "candle radio" sold around 1990, using iron silicide (FeSi_2) thermo-elements produced at KELK Ltd. [46].

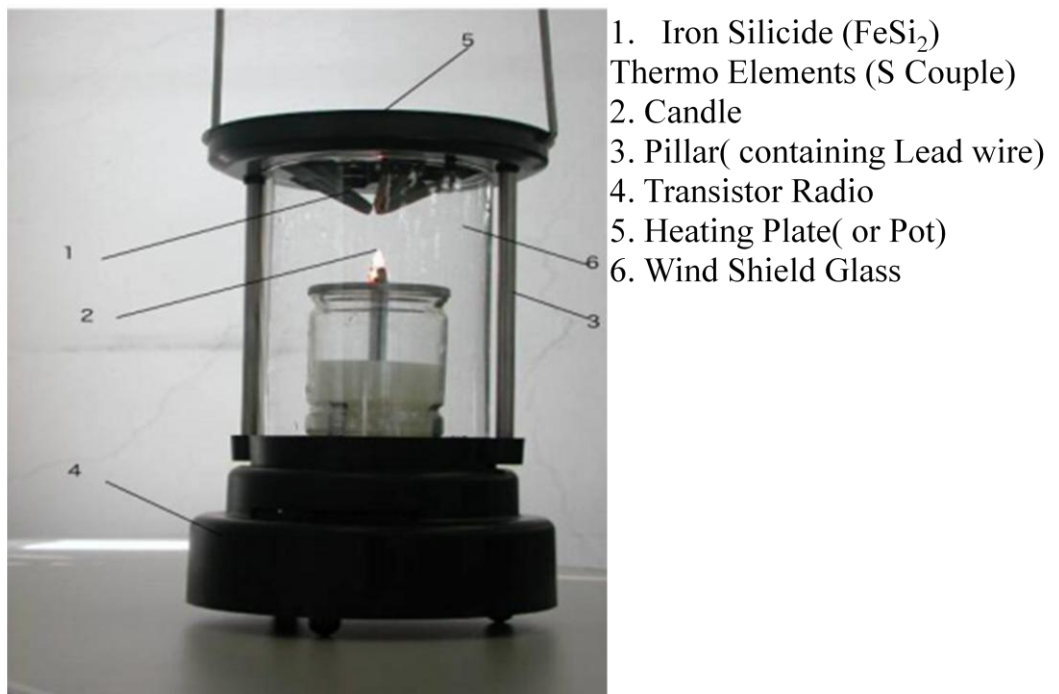


Figure 3.3: Candle Radio

This product is undoubtedly an application of thermoelectric generation, but it features a kind of amusement rather than usefulness. Compared to the previously mentioned "lamp generator," a difference of the necessity of the two products, which come from the background of the era and the technological infrastructure, can be clearly found.

3.3 Thermoelectric Effects

The three basic thermoelectric effects are the Seebeck effect, the Peltier effect, and the Thomson effect. These effects underlie the conversion of heat energy into electric energy or vice versa. The basics of these effects are described below:

3.3.1 Seebeck Effect

When a temperature gradient is introduced along the length of a metal wire, electrons start to diffuse from one end to the other end of the wire (Chambers, 1977). The direction of electron diffusion depends on the electrical properties of the metal wire. By convention, if electrons diffuse from the hot end towards the cool end of the wire, a negative thermoelectric emf is generated in the wire with respect to the hot end. Similarly, if electrons diffuse from the cool end towards the hot end of the wire, a positive thermoelectric emf is generated in the wire with respect to the hot end. This phenomenon in metals, known as the Seebeck effect.

The Seebeck effect is the conversion of temperature differences directly into electricity and is named after German physicist Thomas Johann Seebeck, who, in 1821 discovered that a compass needle would be deflected by a closed loop formed by two metals joined in two places, with a temperature difference between the junctions. This was because the metals responded differently to the temperature difference, creating a current loop and a magnetic field. Seebeck did not recognize there was an electric current involved, so he called the phenomenon the thermo magnetic effect. Danish physicist Hans Christian Orsted rectified the mistake and coined the term "thermoelectricity." The voltage created by this effect is on the order of several micro volts per Kelvin difference. One such combination, copper-constantan, has a Seebeck coefficient of 41 micro volts per Kelvin at room temperature [47].

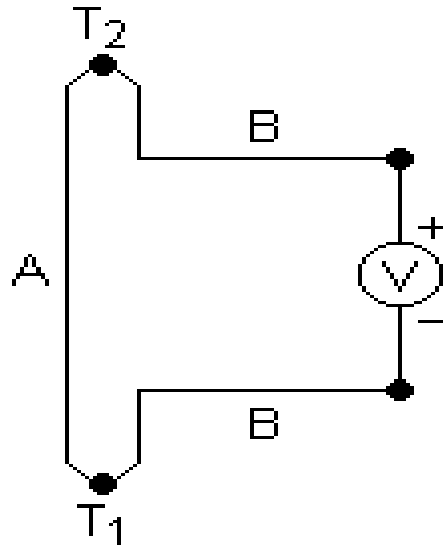


Figure 3.4: Experimental setup for measuring the Seebeck coefficient S

The voltage V developed can be derived from:

$$V = (S_B - S_A) (T_2 - T_1) \dots \dots \dots (1)$$

Where, S_A and S_B are Seebeck coefficient of material A and B respectively.

3.3.2 Peltier Effect

The Peltier effect is the conversion of electricity into heat transfer. This effect was first observed in 1834 by Jean Peltier. The Peltier effect can be regarded as the reverse of the Seebeck effect. The Peltier effect is the underlying foundation for thermoelectric refrigeration. When an electric current passes through two dissimilar materials such as metals or semiconductors that are connected at two junctions, heat will be absorbed at one junction and liberated at the other junction. As a result, one junction cools off while the other heats up, depending on the direction of the current. Cooling of one junction and the heating of the other when electric current is maintained in a circuit of material consisting of two dissimilar conductors; the effect is even stronger in circuits containing dissimilar semiconductors.

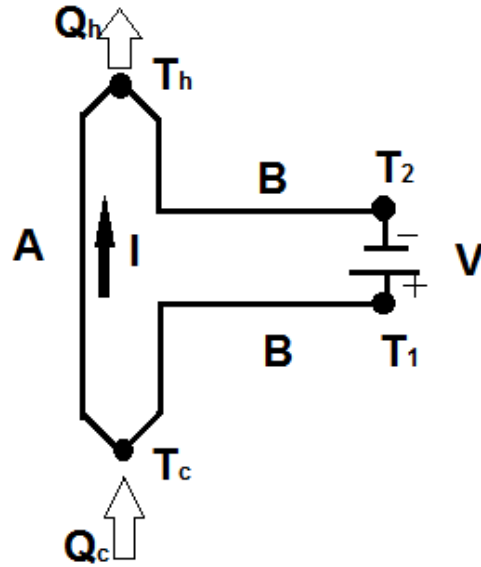


Figure 3.5: Peliter effect

The Peltier heat Q absorbed by the lower junction per unit time is equal to:

$$Q = (\Pi_A - \Pi_B) I \dots\dots\dots (2)$$

Where Π_A and Π_B are Peltier coefficient of material A and B respectively. I is the electric current flow in amperes. Q is the rate of heating or cooling in watts, depending upon the chosen junction respectively.

3.3.3 Thomson Effect

The Thomson effect was predicted and subsequently observed by Lord Kelvin in 1851. It describes the heating or cooling of a current-carrying conductor with a temperature gradient. Any current-carrying conductor (except for a superconductor) with a temperature difference between two points either absorbs or emits heat, depending on the material. If a current density J is passed through a homogeneous conductor.

The heat production q per unit volume is:

$$q = \rho J^2 - \mu J dT/dx \dots\dots\dots (3)$$

Where ρ is the resistivity of the material, dT/dx is the temperature gradient along the wire and μ is the Thomson coefficient. The first term is the Joule heating, which does

not change in sign; the second term is the Thomson heating, which follows J changing sign.

In metals such as zinc and copper, whose temperature is directly proportional to their potential, when current moves from the hotter end to the colder end, there is a generation of heat and the positive Thomson effect occurs. Conversely, in metals such as cobalt, nickel, and iron, whose temperature is inversely proportional to their potential, when current moves from the hotter end to the colder end, there is absorption of heat and the negative Thomson effect occurs.

If the Thomson coefficient of a material is measured over a wide temperature range, it can be integrated using the Thomson relations to determine the absolute values for the Peltier and Seebeck coefficients. This needs to be done only for one material; since the other values can be determined by measuring pair wise Seebeck coefficients in thermocouples containing the reference material and then adding back the absolute thermo-power of the reference material. Lead is commonly stated to have a Thomson coefficient of zero; in fact, it is non-zero, being very small. In contrast, the thermoelectric coefficients of all known superconductors are zero.

In 1854, Lord Kelvin found relationships between the three coefficients, implying that only one could be considered unique.

The first Thomson relation is:

$$\mu = T ds/dT \dots\dots\dots (4)$$

Where T is the absolute temperature, μ is the Thomson coefficient and S is the Seebeck coefficient. The second Thomson relation is:

$$\Pi = S.T \dots\dots\dots (5)$$

Where Π is the Peltier coefficient. It predicted the Thomson effect before it was formalized.

3.4 Thermoelectric Power Generation

In 1821, the German physicist T.J. Seebeck reported that when two junctions of dissimilar metals are kept at two different temperatures, an electro motive force (emf) is developed, resulting in flow of electric current. The emf produced is found to

be proportional to temperature difference. The seebeck effect is utilized to generate electrical power with thermo Electric Generator (TEG), which is the combination of thermoelectric modules that converts thermal energy into electrical energy. Thermoelectric in general are of strong scientific and technological interest. Alternatively, thermoelectric generators could be a better solution for today’s energy challenge, especially for rural development. Waste heat from sources such as solar radiation, automotive exhaust and industrial processes can be converted into electricity through the thermoelectric route without producing greenhouse-gas emissions. Moreover, thermoelectric coolers can be used to make refrigerators and other cooling systems. In this thesis, the structures and physical properties of thermoelectric materials will be discussed for their possible applications in clean and sustainable technology. Skutterudites have excellent thermoelectric properties [48] at high temperature and mimics the opportunity for building thermoelectric devices that are operational at room temperature.

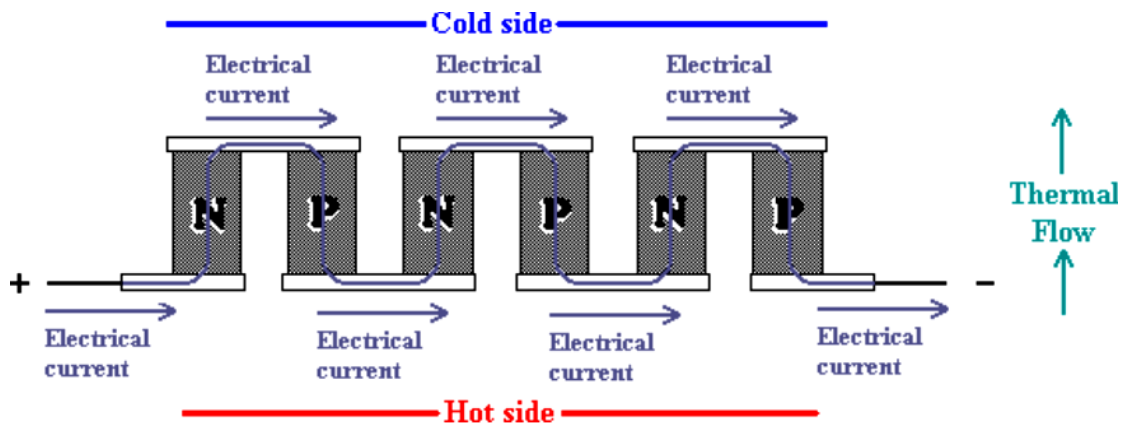


Figure 3.6: Thermoelectric Generator

3.4.1 Working

Electrons on the hot side of a material are more energized than on the cold side. These electrons will flow from the hot side to the cold side. If a complete circuit can be made, electricity will flow continuously.

Semiconductor materials are the most efficient, and are combined in pairs of “p type and “n type.” The electrons flow from hot to cold in the “n type,” While the electron holes flow from hot to cold in the “p type”. This allows them to be combined

electrically in series. Thermoelectric generators are devices, which convert heat directly into electrical energy. Their typical efficiencies are around 5-10%. Older Seebeck-based devices used bimetallic junctions and were bulky while more recent devices use Bismuth Telluride (Bi₂Te₃), Lead Telluride semiconductor p-n junctions [49] and can have thicknesses within the millimetre range. These are solid-state devices and unlike dynamos have no moving parts, with the occasional exception of a fan. Thermal quantities are stated:

Thermoelectric power

$$P = I^2 R_L = (\alpha_n - \alpha_p)^2 (T_h - T_c)^2 R_L / (R + R_L)^2 \dots\dots\dots(6)$$

Where I be the current flowing; α_n and α_p are thermo power of n and p type leg; T_h , T_c are temperature of hot and cold side; R, R_L is equivalent resistance of circuit and load resistance.

Thermal efficiency

$$\eta = \frac{P}{Q} = \frac{I^2 R_L}{[(\alpha_n - \alpha_p)^2 I^2 T^{\frac{1}{2}} + K(T_h - T_c)]} \dots\dots\dots(7)$$

3.4.2 Figure of Merit

A thermoelectric generator works between two different temperatures, and is some- what like a heat engine, converting heat into electrical energy. The conversion efficiency of the device (ratio of electrical power generated to the heat absorbed at the hot junction) can be expressed in terms of the Carnot efficiency and the specific material parameter corresponding to the thermoelement. The potential of a material for thermoelectric applications is determined in large part to a measure of the material's dimensionless figure of merit,

$$Z = \frac{\sigma S^2}{K} \dots\dots\dots(8)$$

Where S is Seebeck Coefficient, σ is Electrical Conductivity, κ is Thermal Conductivity.

The thermoelectric power or Seebeck coefficient (S) can be thought of as the heat per carrier over a temperature range or more simply the entropy per carrier, $S=C/q$ where C is the specific heat and q is the charge of the carrier [50]. For the case of a classical gas, each particle has an energy of $3/2 k_B T$, where k_B is the Boltzmann constant. The thermo power is thus approximately k_B/e , where e is the charge of the electron. Let us estimate an expected magnitude for the thermo power of metals and semiconductors. For metals, the heat per carrier is essentially a product of the electronic specific heat (C_e) and the temperature divided by the number of carriers (N), i.e., ($S=C_e T/N$) and then is approximately:

$$S = \frac{C_e T}{N e} = \left(\frac{k_B}{e}\right) \frac{k_B T}{E_F} \dots\dots\dots(9)$$

Where E_F is the Fermi energy (related to the chemical potential of the material) which is basically the energy, such that at $T=0$, all states above this energy are vacant, and all the states below are occupied. The quantity, $k_B/e=87\text{mV/K}$, is a constant, which represents the thermo power of a classical electron gas [51].

3.5 Thermoelectric Refrigeration Systems

In 1834, a Frenchman, J. Peltier observed the reverse effect of Seebeck effect, i.e., cooling and heating of two junctions of dissimilar materials when direct current is passed through them, the heat transfer rate being proportional to the current. In 1857, William Thomson (Lord Kelvin) proved by thermodynamic analysis that Seebeck effect and Peltier effect are related and he discovered another effect called Thomson effect after his name. According to this when a current flow through a conductor of a thermocouple that has an initial temperature gradient in it, then heat transfer rate per unit length is proportional to the product of current and the temperature. As the current flow through thermoelectric material it gets heated due to its electrical resistance. This is called Joule effect, further, conduction heat transfer from the hot junction to the cold junction transfers heat [52]. Both these heat transfer rates have to be compensated by the Peltier Effect for some useful cooling to be produced. For a long time, thermoelectric cooling based on the Peltier effect remained a laboratory curiosity as the temperature difference that could be obtained using pure metals was too small to be of any practical use. Insulating materials give poor thermoelectric

performance because of their small electrical conductivity while metals are not good because of their large thermal conductivity. However, with the discovery of semiconductor materials in 1949-50, the available temperature drop could be increased considerably, giving rise to commercialization of thermoelectric refrigeration systems. Figure 3.7 shows the schematic of the thermoelectric refrigeration system based on semiconductor materials.

The Russian scientist, A. F. Ioffe is one of the pioneers in the area of thermoelectric refrigeration systems using semiconductors. Several domestic refrigerators based on thermoelectric effect were made in USSR as early as 1949. However, since 1960s these systems are used mainly used for storing medicines, vaccines etc and in electronic cooling. Development also took place in many other countries.

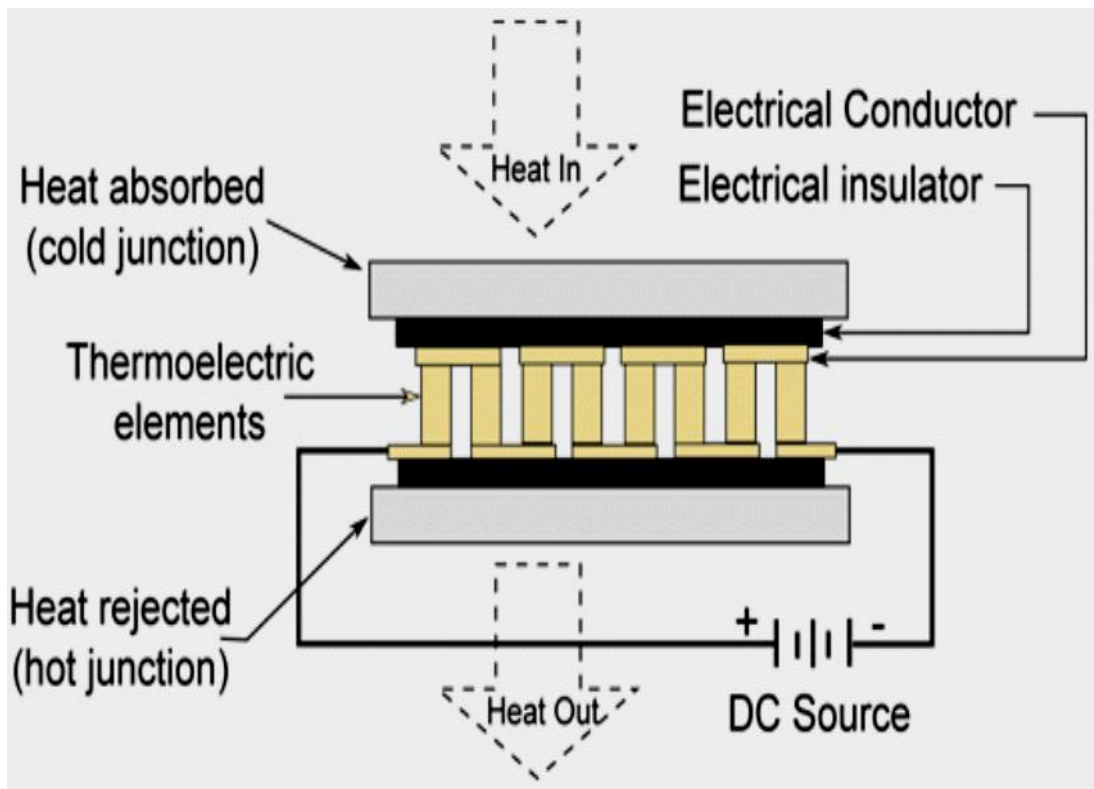


Figure 3.7: Schematic of a thermoelectric refrigeration system

In USA domestic refrigerators, air conditioners, water coolers, air conditioned diving suits etc. were made using these effects. System capacities were typically small due to poor efficiency. However some large refrigeration capacity systems such as a 3000 kcal/h air conditioner and 6 tonne capacity cold storage were also developed. By using multistage temperatures as low as -145°C were obtained. These systems due to

their limited performance (limited by the materials) are now used only in certain niche applications such as electronic cooling, mobile coolers etc. Efforts have also been made to club thermoelectric systems with photovoltaic cells with a view to develop solar thermoelectric refrigerators.

3.6 Design of Thermoelectric System

In designing a thermoelectric generator, there are many complexities that must be considered. Each component must be evaluated on how it will perform with the rest of the system, rather than individually. The components of the system are the thermoelectric module, the heat exchangers, the cooling fan, the power electronics, and the load. This is a very dynamic system that requires a thorough effort in design to maximize performance. The various generator components (fan, cold sink, module, hot sink) of the system are shown in the Figure 3.8 [53].

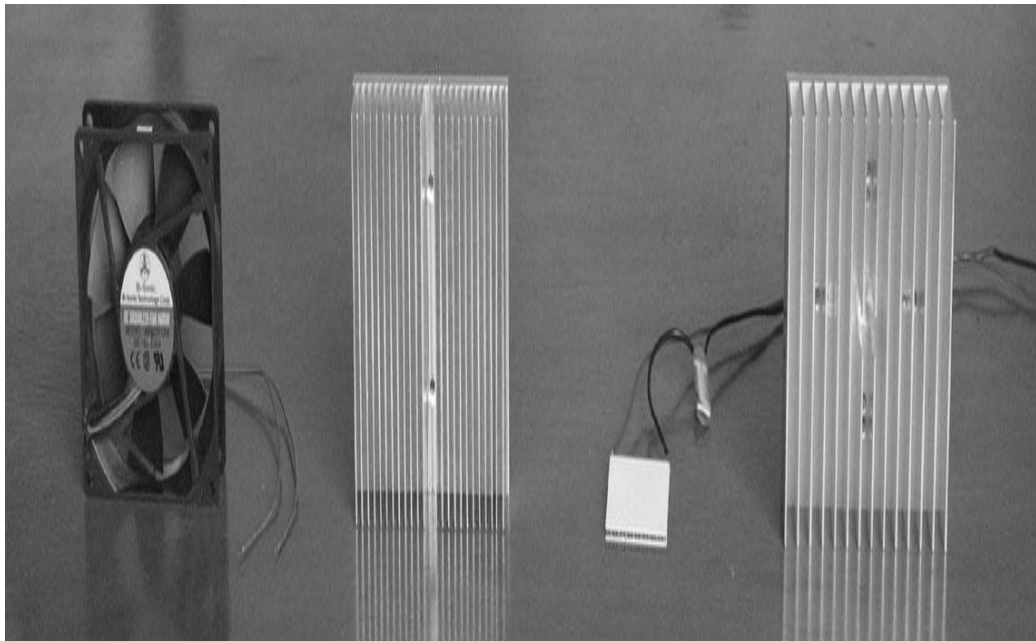


Figure 3.8: Module components

3.7 Module Selection

There are several considerations in selecting the appropriate module. The most important are the material and module construction. There are many materials capable of producing power from a temperature difference. These materials vary in cost,

efficiency, and operation temperature. Module construction also affects these three categories, as well as the maximum power of a module, and the voltage/current characteristics of the system. In selecting a module it is important to evaluate each one as it will perform in the entire system. In many cases, especially when using air for cooling, the power output listed by the manufacturer is very difficult to achieve. Initially, it was believed that a low cost, low efficiency material may be the best solution for this application since the heat source is abundant and could be considered free. However, this is not necessarily the case. In general, thermoelectric materials have very low efficiencies, typically less than 10%. A very cheap material may have an efficiency of around 1%. This means to generate 5 watts of power, 500 watts must be moved through the system. This would require a very large heat exchanger, including a powerful cooling fan. These components have additional monetary and power costs, negating any advantage of using a low cost material. Lead telluride is the material with the higher efficiency in the range of temperatures. Lead telluride is also the most common material used in Peltier coolers, making it relatively cheap. High temperature Lead telluride modules achieve around 4% efficiency at max power. For these reasons, a PbTe module was selected for this application. There are also many decisions to be made in module construction. The module construction consists of the number and geometry of the thermo-elements, as well as the method for connecting the elements. Figure shows the construction of a thermo element. Modules are typically composed of around a hundred elements. Modules can be constructed as Peltier coolers or as high temperature generators. Both of these use the same materials and can be used to produce power, but they differ in how the thermo elements are soldered to the conducting strip. The solder on a Peltier cooler is typically PbSn, which melts at approximately 138°C. Most high temperature generator modules can withstand intermittent temperatures up to 400°C. This increased performance comes at a cost though, typically twice as much as a low temperature Peltier module, but is compensated by a dramatic increase in power.

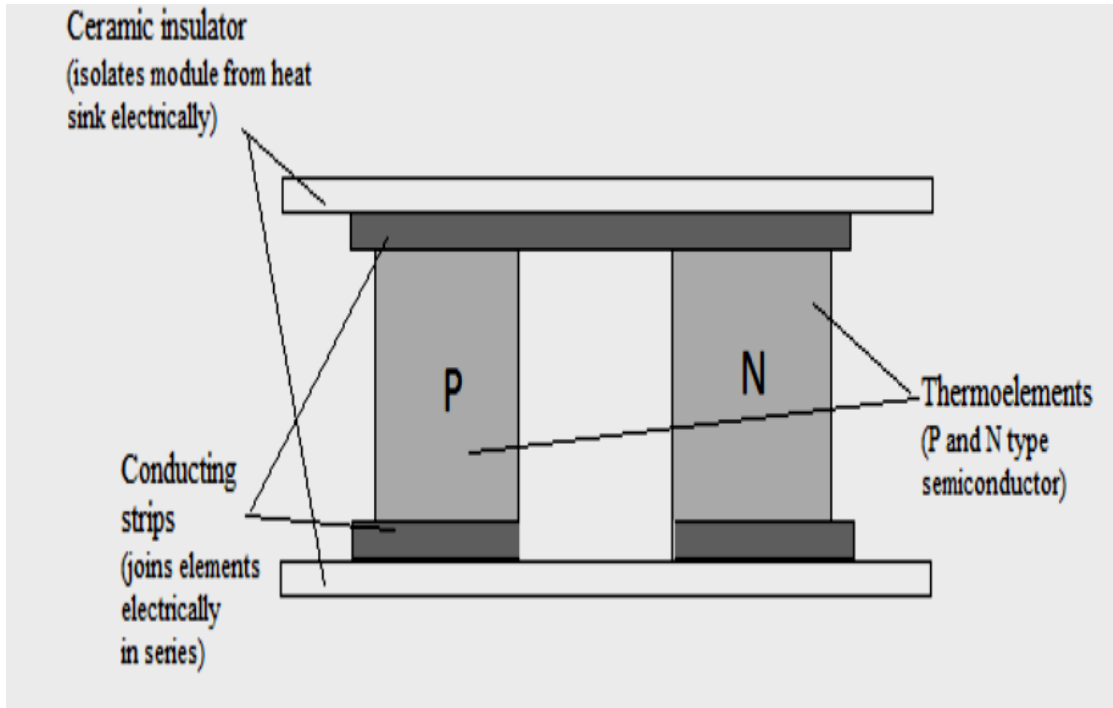


Figure 3.9: Construction of a thermo element

3.8 Thermoelectric Materials

The characteristics of different thermoelectric material are shown in table 3 [54]:

Table.3: Characteristics of different thermoelectric materials

Material	Component	Conduction type	Optimum temperature	Production process	Figure of merit
Silicides	Mn-si	P	300-600	Melting and Refining	0.80
Si-Ge based	Si _{0.8} Ge _{0.2}	N	730	Hot press	1.00
Oxide based	NaCo ₂ O ₄	P	300-500	Flux	1.20
PbTe based	PbTe	N	230-577	Hot press	0.70
Bi-Sb-Te-Se	Bi-Sb-Te-Se	n and p	-180-250	Hot press	0.3-1.01

3.9 Improvement of Performance of Thermoelectric Elements

Thermoelectric elements have been used mainly as Peltier modules for cooling and temperature control. The representative products that apply thermoelectric elements are room temperature controls, communication laser coolers, and refrigerators. Because of their major applications, thermoelectric elements have been so designed that their characteristics become optimum at or near room temperature. However, when a thermoelectric module is used for power generation, the optimum temperature becomes higher than room temperature. Therefore, a thermoelectric element/module suitable for power generation is such that the value of Z is large and that the optimum temperature is on the higher side. Researchers have found that to improve the performance of a thermoelectric element/module for power generation by taking the following two approaches:

(A) Improving the basic characteristic (Z) of thermoelectric element (Improve the characteristics of the element at room temperature and thereby improve them at higher temperatures.)

(B) Shifting the peak of Z toward the high temperature side (Even if the value of Z in the low temperature region decreases, the overall efficiency of the element improves as the value of Z in the high temperature region increases.)

It is necessary that the thermoelectric element should have high figure of merit Z in its working temperature range. Therefore, thermoelectric elements which display high performance at room temperature have been called for. Although the figure of merit at room temperature decreases, the average performance index on the high temperature side increases. As the methods for shifting the peak value of Z of a thermoelectric element toward the high temperature side, the following two are considered:

1. Adjusting the carrier concentration to improve the high temperature characteristic
2. Changing the composition to control the energy band gap.

CHAPTER-4

SYNTHESIS AND CHARACTERIZATION

TECHNIQUES

Hydrothermal reaction of selenium and tellurium with lead acetate in sodium hydroxide solution in the presence of hydrazine hydrate as a reductive was investigated to prepare PbE (E=Te,Se). Nanocrystals with different morphology could be obtained under different mild conditions. The source material and the temperature condition play an important role in preparation of Lead Chalcogenides.

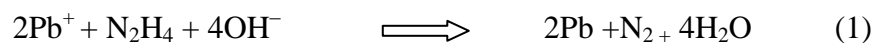
4.1 Synthesis of Lead Selenide

- **Hydrothermal process**

The precursor in the synthesis of lead selenide nanoparticles by the hydrothermal process are Selenium (99.95%) with molecular weight 78.96 gm, lead acetate solution (99% conc.) with molecular weight 325.29 gm, sodium hydroxide solution (1mol/l), hydrazine hydrate(50% > v/v).

Steps involve in the synthesis of lead selenide nanoparticles are as:

- Firstly in a 30 ml capacity of Teflon lined stainless steel autoclave Se (99.95% conc.) 8.28 gm and lead acetate (99% conc.) 13 gm were added.
- It is filled with 30 ml aqueous solution of sodium hydroxide.
- 2-3 ml of hydrazine hydrate added.
- The solution was neither shaken nor stir during heating period.
- The system maintained at temperature 100-160°C for 18-72 hours and then allows cooling at room temperature.
- Black precipitate were collected and washed with distilled water and dried for 4 hours.



The final product was analysed with XRD. The shape and morphology of particles were studied by SEM picture obtained. Optical properties were studied by PL.

Alkaline medium is a complementary condition for this hydrothermal process. It was observed that the alkaline medium could make the selenium disperse in the liquid

medium, which is beneficial for the formation of nanosized products. In an acid or neutral solvent and keeping the other reaction conditions constant, the reaction cannot be initiated or the output is low as the reductive potential of hydrazine hydrate is significantly affected by the concentration of OH⁻ ion in the solution. For example, when pH is 7, the calculated reductive potential of hydrazine hydrate would be -0.32. Further increase of the concentration of H⁺ ion will cause hydrazine hydrate to be an oxygenate and retard the reactions.

4.2 Synthesis of Lead Telluride:

The precursor in the synthesis of lead Telluride nanoparticles by the hydrothermal process are Tellurium (99.95%) with molecular weight 78.96 gm, lead acetate solution (99% conc.) with molecular weight 325.29 gm, sodium hydroxide solution (1mol/l), hydrazine hydrate(50% > v/v).

Steps involve in the synthesis of lead telluride nanoparticles are as:

- Firstly in a 30 ml capacity of Teflon lined stainless steel autoclave Se (99.95% conc.) 8.28 gm and lead acetate (99% conc.) 13 gm were added.
- It is filled with 30 ml aqueous solution of sodium hydroxide.
- 2-3 ml of hydrazine hydrate added.
- The solution was neither shaken nor stir during heating period.
- The system maintained at temperature 100-160°C for 18-72 hours and then allows cooling at room temperature.
- Black precipitate were collected and washed with distilled water and dried for 4 hours.



The final product was analysed with XRD. The shape and morphology of particles were studied by SEM picture obtained. Optical properties were studied by PL.

The synthesis of the above two compounds were systematically investigated in the range of 80- 180°C for various reaction times. If the temperature was low, the reaction time should be prolonged to ensure the full transfer of source materials to final products. For PbSe, the grain size would grow with the elevation of temperature. For PbTe, nanorod could be obtained at 100°C for 72 hours.

4.3 Characterization Techniques

The synthesized materials were characterized using different characterisation techniques. The important characterisation techniques used for the investigation of the synthesized material are X-Ray diffraction (XRD), Scanning electron microscope (SEM), Transmission electron microscope (TEM), Fourier transform Infra red Spectroscopy (FTIR), UV visible spectroscopy, Photoluminescence. The working principle and basic theory of these techniques are explained below:

4.3.1 X-ray Diffraction

X-ray diffraction (XRD) is a versatile, non-destructive analytical technique for identification and quantitative determination of the various crystalline forms, known as “phases” of compounds present in powdered and solid samples. The result of an XRD measurement is called a XRD pattern or diffractogram, showing phases present, phase concentrations, amorphous content and crystallite size; which are analysed from peak positions, peak heights, background bump and peak widths respectively. Identification is achieved by comparing the diffractogram obtained from an unknown sample with an internationally recognized database containing reference patterns called JCPDS.

XRD diffraction has applications in many fields because of the flexibility in its requirements for a sample. While other test required large amount of sample, XRD require small amount of sample. This is partially because XRD is non-destructive to the sample, meaning that after being tested, that sample is unchanged and can be used again for other tests. X-rays are used because their wavelengths are similar in size to atoms and their bonds. This characteristic makes X-rays an excellent tool for investigating the arrangements of atoms and molecules inside the sample.

A crystal lattice is a regular 3-dimensional distribution of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance d , which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations, each with its own specific d -spacing.

When a monochromatic X-ray beam with wavelength λ is incident on lattice planes in a crystal at an angle θ , diffraction occurs only when the distance travelled by the rays

reflected from successive planes differ by a complete number n of wavelengths. By varying the angle θ , the Bragg's law ($n\lambda = 2d\sin\theta$), conditions are satisfied by different d -spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffraction peaks produces a pattern which is characteristic of the sample. Where a mixture of different phases is present, the diffractogram is formed by addition of the individual patterns.

The characteristic of the sample can be determined by plotting the angular positions and intensities of the resultant diffracted peaks of radiation. XRD is used to determine the structure of sample, i.e. how the atoms pack together in the crystalline state and what the interatomic distances and angle are.

The figure below shows the X-Ray diffractometer Bruker D8 advance available in DTU.



Figure 4.1: Photograph of XRD Bruker D8 Advance at DTU

The main components of XRD are an X-ray tube, a sampler holder, an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons towards a target by applying a voltage, and bombarding the target material with electrons. When electron has sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_{α} and K_{β} . K_{α} consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ is sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with Cu K_{α} radiation = 1.5418Å [55]. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotate at an angle of 2θ . The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data is collected at 2θ from $\sim 5^{\circ}$ to 70° .

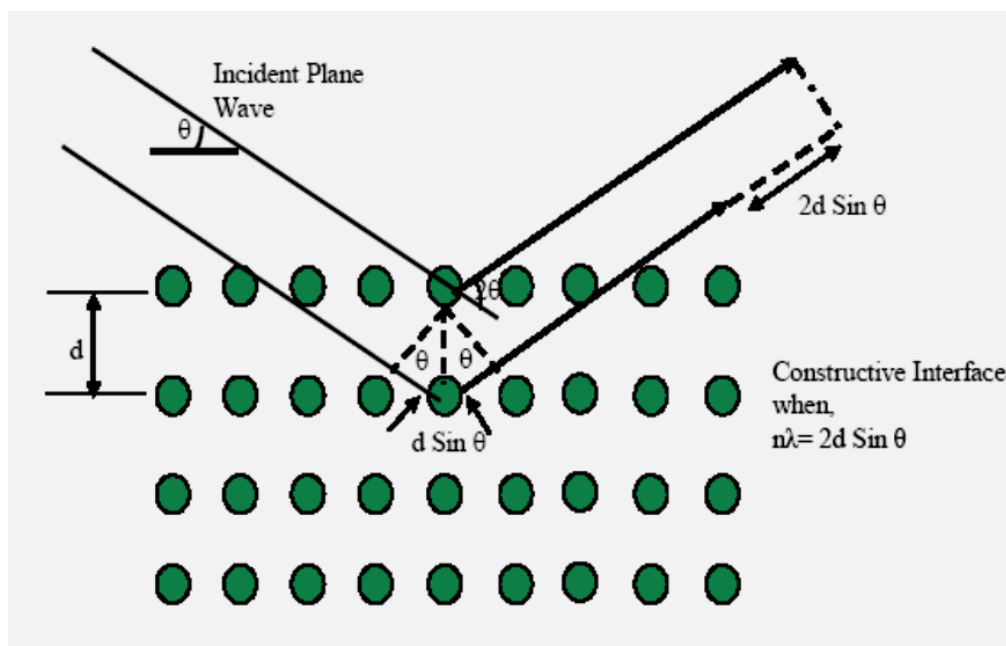


Figure 4.2: Schematic diagram showing Bragg diffraction from a set of planes

4.3.1.1 Utility of XRD for Nanomaterials

Many structural properties of the nanostructures such as crystalline phase, particle size and structure evolution in Bragg planes, macroscopic stress/strain etc. can be revealed with the help of XRD. But here we shall mention few aspects directly relevant to our work.

4.3.1.2 Crystal Identification

A new method have been attempted to prepare nanomaterials. Therefore, it is important to identify these materials with the help of XRD data; we can check the amorphous or crystalline nature of the newly formed material. We can determine if the prepared material is crystalline and its basic lattice structure (e.g. cubic or hexagonal, etc.) by indexing its lattice planes. One can also determine the changes in various lattice parameters of a particular bulk and nanosized material.

4.3.1.3 Crystallite Size

A perfect crystal would extend in all directions to infinity, so we can say that no crystal is perfect due to its finite size. This deviation from perfect crystalline leads to a broadening of the diffraction peaks. However, above a certain size (100-500 nm) this type of broadening is negligible. Scherrer (1918) first observed that small

crystallite size could give rise to line broadening. He derived a well-known equation for relating the crystallite size to the broadening, which is called Debye-Scherrer Formula is given by:

$$Dv = k\lambda/\beta \cos\theta \dots\dots\dots (10)$$

Where, Dv = Volume weighted crystallite size. D is the “average” dimension of the crystallites normal to the reflecting planes. We call it “average” because the x-ray beam irradiates a large number of crystallites, so that the value of D obtained represents the mean value of the actual size distribution present, λ = wavelength of the radiation, k = Scherrer constant. k varies from 0.89 to 1, but for most cases, is close to 1, β = the integral breadth of a reflection (in radians 2θ) located at 2θ commonly considered as the full width at half maxima (FWHM) in radians for a certain peak position 2θ .

Crystallite size is a measure of the size of a coherently diffracting domain. Due to the presence of polycrystalline aggregates, crystallite size is not generally the same thing as particle size. When crystallites are less than approximately 100 nm in size, appreciable broadening in the x-ray diffraction lines will occur. These regions may, in fact, correspond to the actual size of the particles. At other times, however, these regions form “domains” in a larger particle and may be a distinguishing and important feature. In either case, the observed line broadening can be used to estimate the average size. In the simplest case where the particles are stress-free, the size is estimated from a single diffraction peak. However, in cases where stress may be present, a more robust method involving several diffraction peaks is required.

4.3.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a powerful and popular technique for imaging the surfaces of almost any material with a resolution down to about 1 nm. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. It utilizes the secondary electrons (SEs) and backscattered electrons (BSEs) being emitted from different areas of the specimen (as shown in Fig. 4.3) as well as the trajectories they take in relation to the location of the detector. The signals that derive from electron sample interactions reveal information about the sample including its size, shape,

external morphology (texture), of the three dimensional samples. The SEM is also capable of performing analyses of selected point locations on the sample, this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD). The design and function of the SEM is very similar to the EPMA, and considerable overlap in capabilities exists between the two instruments.

The image resolution offered by SEM depends not only on the property of the electron probe, but also on the interaction of the electron probe with the specimen. Interaction of an incident electron beam with the specimen produces secondary electrons, with energies typically smaller than 50eV, the emission efficiency of which sensitively depends on surface geometry, surface chemical characteristics and bulk chemical composition. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time and produces an image that is a good representation of the three-dimensional sample.

The image that is produced by the SEM is usually viewed on CRTs located on the electronic console but, instead with FEI the image can be seen on the computer monitor. Images that are captured can be saved in digital format or printed directly. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm) [56].

The combination of higher magnification, larger depth of field, greater resolution, compositional and crystallographic information makes the SEM one of the most heavily used instruments in education institutions and laboratory research areas and industry.

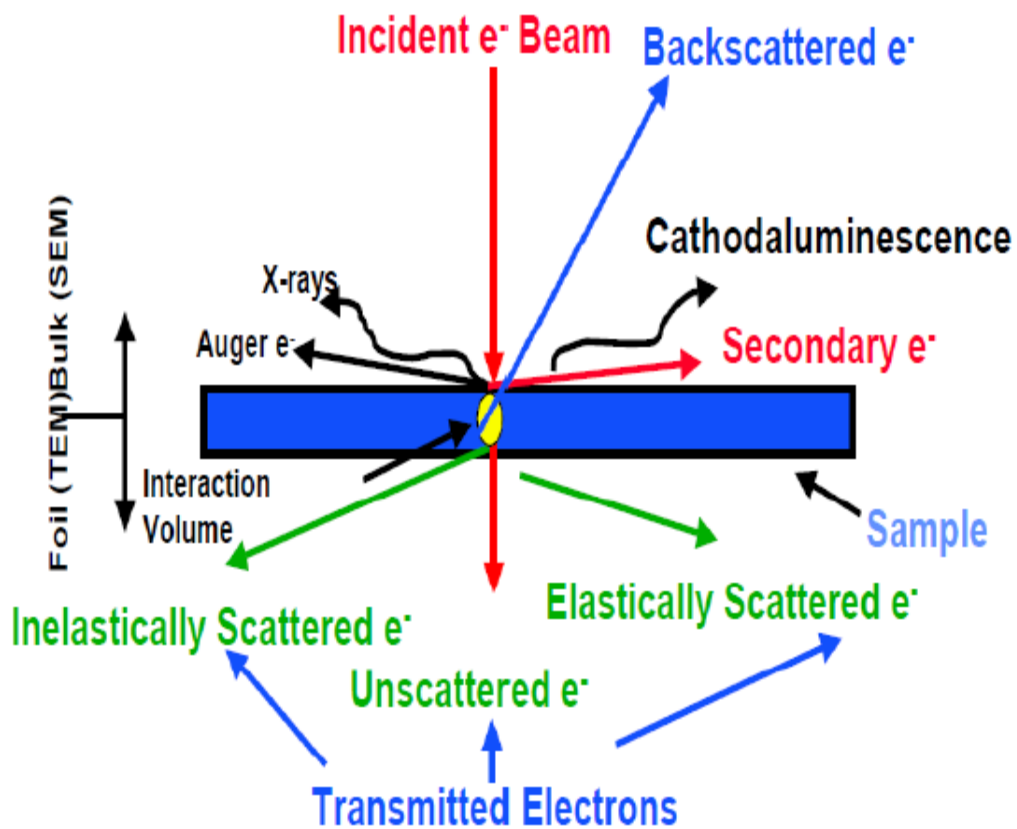


Figure 4.3: Interaction of high energy electrons with solid

The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample.

Because the SEM utilizes vacuum conditions and uses electrons to form an image, special preparations must be done to the sample. All water must be removed from the samples because the water would vaporize in the vacuum. All metals are conductive and require no preparation before being used. All non-metals need to be made conductive by covering the sample with a thin layer of conductive material. This is done by using a device called a "sputter coater."

The figure below shows the typical SEM working:

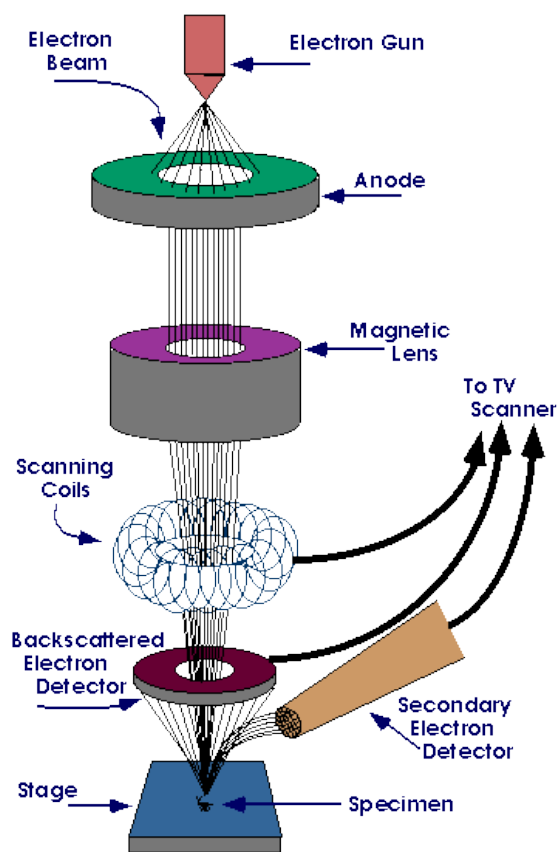


Figure.4.4: Working principle of Scanning Electron Microscope [57]

The sputter coater uses an electric field and argon gas. The sample is placed in a small chamber that is at a vacuum. Argon gas and an electric field cause an electron to be removed from the argon, making the atoms positively charged. The argon ions then become attracted to a negatively charged gold foil. The argon ions knock gold atoms from the surface of the gold foil. These gold atoms fall and settle onto the surface of the sample producing a thin gold coating.

The semiconducting nanoparticles were imaged using Hitachi S-3700 variable pressure SEM, of resolution 3nm with accelerating voltage of 0.3 to 3 kV, showing in figure 4.5:



Figure 4.5: Picture of Hitachi S-3700 SEM at DTU

4.3.3 Transmission electron microscopy

The Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. At smaller magnifications TEM image contrast is due to absorption of electrons in the

material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging. The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939.

The TEM is composed of several components, which include a vacuum system in which the electrons travel an electron emission source for generation of the electron stream, a series of electromagnetic lenses, as well as electrostatic plates.

The latter two allow the operator to guide and manipulate the beam as required. Also required is a device to allow the insertion into, motion within, and removal of specimens from the beam path. Imaging devices are subsequently used to create an image from the electrons that exit the system.

Theoretically, the maximum resolution, d , that one can obtain with a light microscope has been limited by the wavelength of the photons that are being used to probe the sample, λ and the numerical aperture of the system, NA [58].

$$d = \frac{\lambda}{2n \sin \alpha} \approx \frac{\lambda}{2NA}$$

Applications

The instrument allows performing the Morphological analysis, Electronic diffraction, X-EDS qualitative and semi-quantitative analysis, either in Spot or in Semi Stem mode. The instrumentation is particularly suitable for the study and characterization of material from a morphological, chemical and structural point of view, especially in the field of polymeric, metallic, and ceramic technology. On the basis of available techniques, some specific applications in which the instrument plays

an important role are:

- Nano-structured materials study
- Defects from the manufacturing process in semi-conductors
- Ceramic systems
- Plastic Deformations
- The study of layers and structures
- Phase transformations
- Nanometric systems
- Ordered alloy structures
- The study of cellular structures

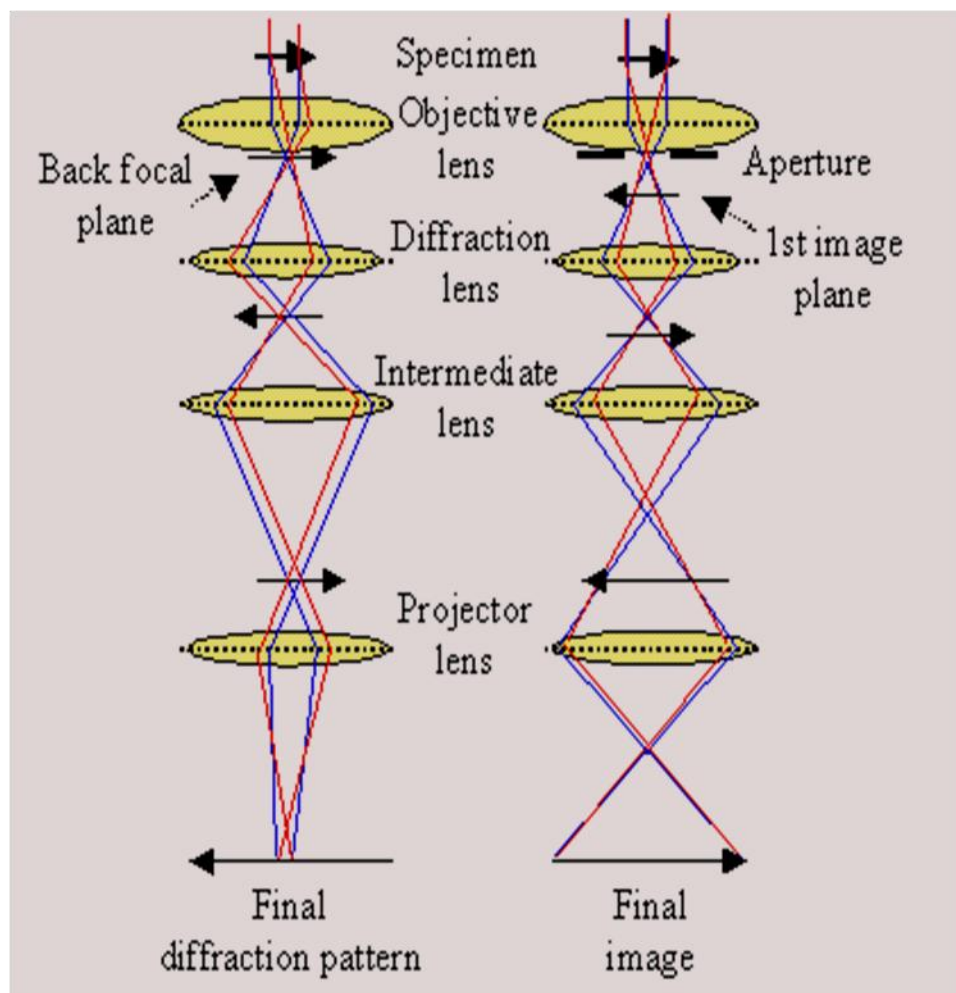


Figure.4.6: Working of Transmission Electron Microscope



Figure.4.7 Photograph of Transmission Electron Microscope

Samples Used and Their Preparation

For viewing the morphology of the nanoparticles formed, nanoparticles were washed several times in methanol to remove the extra groups. Very dilute solutions of these washed nanoparticles in methanol were dropped on carbon coated meshed TEM grids and the solvent was allowed to evaporate leaving the nanoparticles on the grid. These grids were then loaded in the vacuum chamber of the microscope for viewing.

4.3.4 UV-visible Spectroscopy

Ultraviolet and visible spectrometers have been in general use for the last 35 years and over this period have become the most important analytical instrument in the modern day laboratory. In many applications other techniques could be employed but none rival UV-Visible spectrometry for its simplicity, versatility, speed, accuracy and cost-effectiveness. This description outlines the basic principles for those new to UV-Visible spectrometry. It is intended purely as a brief introduction to the technique and it is Thermo Spectronic's policy to continually add to this range of documentation for further details, as they become available. For convenience of reference, definitions of the various spectral regions have been set by the Joint Committee on Nomenclature in Applied Spectroscopy:

Table 4.1 Spectral Region

Region	Wavelength (nm)
Far ultraviolet	10-200
Near ultraviolet	200-380
Visible	380-780
Near infrared	780-3000
Middle infrared	3000-30,000
Far infrared	30,000-300,000
Microwave	300,000-1000,000,000

Molecules containing π -electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb.

Ultraviolet-visible spectroscopy or ultraviolet-visible spectroscopy photometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR) ranges. The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. In

this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_0). The ratio I/I_0 is called the transmittance. Absorption may be presented as Transmittance ($T=I/I_0$) or Absorbance ($A=\log I_0/I$). Absorbance is directly proportional to the path length, b , and the concentration, c , of the absorbing species.

Beer's Law states that:

$$A = \epsilon bc \dots \dots \dots (11)$$

Where ϵ is a constant of proportionality known as the molar absorptivity or extinction coefficient, called the absorptivity in Absorbance units (AU).

If no absorption has occurred, $T = 1.0$ and $A = 0$. Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance) [59]. The wavelength of maximum absorbance is a characteristic value, designated as λ_{\max} .

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

The figure below shows the UV 5704 instrument:



Fig.4.8: Photograph of UV-5704

The function of UV-visible Spectrometer is shown in the figure 4.9:

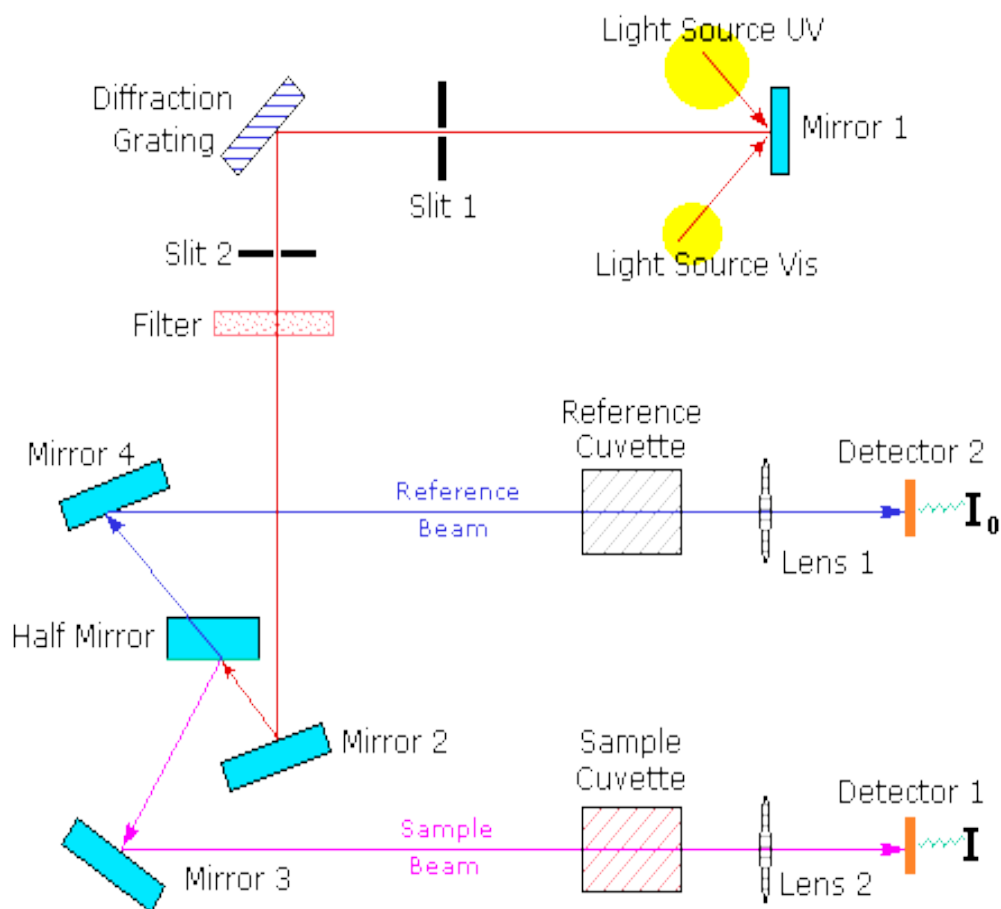


Fig.4.9: UV-visible Spectrometer

4.3.5 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman Effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples.

4.3.5.1 Origin of Raman Effect

The Raman effect is based on molecular deformations in electric field E determined by molecular polarizability α . The laser beam can be considered as an oscillating electromagnetic wave with electrical vector E . Upon interaction with the sample it induces electric dipole moment $P = \alpha E$ which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency ν_m . Amplitude of vibration is called a nuclear displacement. In other words, monochromatic laser light with frequency ν_0 excites molecules and transforms them into oscillating dipoles. Such oscillating dipoles emit light of three different frequencies (Fig.4.10).

1. A molecule with no Raman-active modes absorbs a photon with the frequency ν_0 . The excited molecule returns back to the same basic vibrational state and emits light with the same frequency ν_0 as an excitation source. This type of interaction is called an elastic Rayleigh scattering.

2. A photon with frequency ν_0 is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon's energy is transferred to the Raman-active mode with frequency ν_m and the resulting frequency of scattered light is reduced to $\nu_0 - \nu_m$. This Raman frequency is called Stokes frequency, or just "Stokes".

3. A photon with frequency ν_0 is absorbed by a Raman-active molecule, which, at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $\nu_0 + \nu_m$. This Raman frequency is called Anti-Stokes frequency, or just "Anti-Stokes".

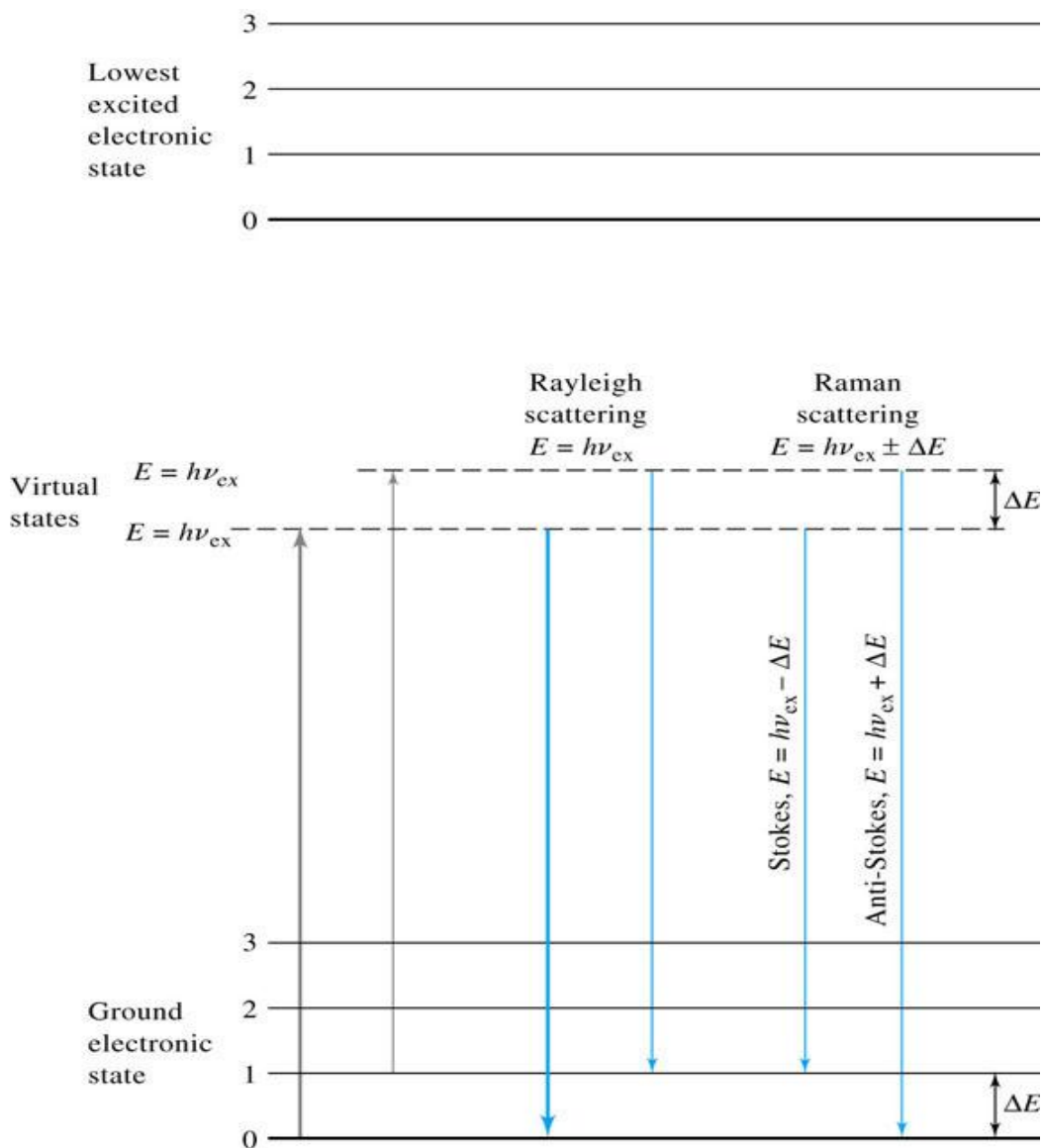


Fig. 4.10: Different type of scattering

About 99.999% of all incident photons in spontaneous Raman undergo elastic Rayleigh scattering. This type of signal is useless for practical purposes of molecular characterization. Only about 0.001% of the incident light produces inelastic Raman signal with frequencies $\nu_0 \pm \nu_m$. Spontaneous Raman scattering is very weak and special measures should be taken to distinguish it from the predominant Rayleigh scattering. Instruments such as notch filters, tunable filters, laser stop apertures, double and triple spectrometric systems are used to reduce Rayleigh scattering and obtain high-quality Raman spectra.

4.3.5.2 Instrumentation

A Raman system typically consists of four major components:

1. Excitation source (Laser).
2. Sample illumination system and light collection optics.
3. Wavelength selector (Filter or Spectrophotometer).
4. Detector (Photodiode array, CCD or PMT).

A sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample. Since spontaneous Raman scattering is very weak, the main difficulty of Raman spectroscopy is separating it from the intense Rayleigh scattering. The major problem here is not the Rayleigh scattering itself, but the fact that the intensity of stray light from the Rayleigh scattering may greatly exceed the intensity of the useful Raman signal in the close proximity to the laser wavelength. In many cases the problem is resolved by simply cutting off the spectral range close to the laser line where the stray light has the most prominent effect. Researchers use commercially available interference (notch) filters which cut-off spectral range of $\pm 80\text{-}120\text{ cm}^{-1}$ from the laser line. This method is efficient in stray light elimination but it does not allow detection of low-frequency Raman modes in the range below 100 cm^{-1} . Stray light is generated in the spectrometer mainly upon light dispersion on gratings and strongly depends on grating quality. Raman spectrometers typically use holographic gratings which normally have much less manufacturing defects in their structure than the ruled one. Stray light produced by holographic gratings is about an order of magnitude less intense than from ruled gratings of the same groove density. Using multiple dispersion stages is another way of stray light reduction. Double and triple spectrometers allow taking Raman spectra without use of notch filters. In such systems Raman-active modes with frequencies as low as $3\text{-}5\text{ cm}^{-1}$ can be efficiently detected. In earlier times people primarily used single-point detectors such as photon-counting Photomultiplier Tubes (PMT). However, a single Raman spectrum obtained with a PMT detector in wave number scanning mode was taking substantial period of time, slowing down any research or industrial activity based on Raman analytical technique. Nowadays, more and more often researchers use multi-channel detectors like Photodiode Arrays (PDA) or, more commonly, a Charge-Coupled Devices (CCD)

to detect the Raman scattered light. Sensitivity and performance of modern CCD detectors are rapidly improving. In many cases CCD is becoming the detector of choice for Raman spectroscopy.

4.3.6 FTIR spectroscopy

FTIR (Fourier Transform Infrared) or simply FTIR Analysis, is most useful technique for identifying chemicals that are either organic or inorganic. It can be utilized to quantities some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. FTIR spectroscopy is a multiplexing technique, where all optical frequencies from the source are observed simultaneously over a period of time known as scan time. In this technique whole data is collected and converted from an interference pattern to a spectrum.

By interpreting the infrared absorption spectrum, the chemical bonds (functional groups) in a molecule or molecular structure of materials, whether organic or inorganic can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule i.e. those frequencies where the infrared light affects the dipolar moment of the molecule. Thus monatomic (He, Ne, Ar, etc) and homopolar diatomic (H_2 , N_2 , O_2 , etc) molecules do not absorb infrared light. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analyzed and matched with known signatures of identified materials in the FTIR library. IR absorption information is generally presented in the form of a spectrum with wavelength or wave number as the x-axis and absorption intensity or percent transmittance as the y-axis. Transmittance, T , is the ratio of radiant power transmitted by the sample (I) to the radiant power incident on the sample (I_0). Absorbance (A) is the logarithm to the base 10 of the reciprocal of the transmittance (T).

$$A = \log_{10} 1/T = -\log_{10} T = -\log_{10} I/I_0 \dots\dots\dots (12)$$

The transmittance spectra provide better contrast between intensities of strong and weak bands because transmittance ranges from 0 to 100% T whereas absorbance ranges from infinity to zero.

FTIR analysis can give not only qualitative (identification) analysis of materials, but with relevant standards, can be used for quantitative (amount) analysis. FTIR can be used to analyze samples up to ~11 millimetres in diameter, and either measure in bulk or the top ~1 micrometer layer.

The goal of any absorption spectroscopy (FTIR, ultraviolet-visible ("UV-Vis") spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength. The most straightforward way to do this, the "dispersive spectroscopy" technique, is to shine a monochromatic light beam at a sample, measure how much of the light is absorbed, and repeat for each different wavelength.

Figure below shows the FTIR available in DTU:



Fig.4.11: Photograph of Nicolet-380 FTIR

The normal operation mode of this spectrometer is temperature stabilized. The spectrometer utilizes continuous dynamic alignment to ensure exceptional high-resolution line shapes. Its compact optical path minimizes beam path length and

improves spectral performance by limiting the number of beam reflections, which translates into extremely reproducible results with no instrument drift. Before measurement the instrument is properly sealed and desiccated. The desiccant protects the beam splitter and other optical components by reducing the amount of water vapour inside the spectrometer.

4.2.3 Photoluminescence

Photoluminescence (abbreviated as PL) describes the phenomenon of light emission from any form of matter after the absorption of photons (electromagnetic radiation). Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. Features of the emission spectrum can be used to identify surface, interface, and impurity levels and to gauge alloy disorder and interface roughness. The intensity of the PL signal provides information on the quality of surfaces and interfaces [60].



Figure4.12: Photograph of Photoluminescence Instrument

In a typical PL experiment, a semiconductor is excited with a light-source that provides photons with energy larger than the band-gap energy. The incoming light excites a polarization that can be described with the semiconductor Bloch equations.

Once the photons are absorbed, electrons and holes are formed with finite momentum k in the conduction and valence bands, respectively. The excitations then undergo energy and momentum relaxation towards the band gap minimum. Typical mechanisms are Coulomb scattering and the interaction with phonons. Finally, the electrons recombine with holes under emission of photons.

Ideal, defect-free semiconductors are many-body systems where the interactions of charge-carriers and lattice vibrations have to be considered in addition to the light-matter coupling. In general, the PL properties are also extremely sensitive to internal electric fields and to the dielectric environment (such as in photonic crystals) which impose further degrees of complexity.

CHAPTER 5

RESULTS AND DISCUSSION

The synthesised sample was characterized using various characterization techniques such as Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). Although the characterization has been done at different places in order to get the best possible results.

Characterization of Lead Selenide

5.1.1 Scanning Electron Microscope Analysis:

SEM images for analysis of morphology and structural shape of synthesised powder has been taken with Hitachi S-3700 SEM at 15 kV with appropriate magnification. Hydrazine hydrate not only plays as the reducing agent but also play an important role for the nucleation of PbSe.

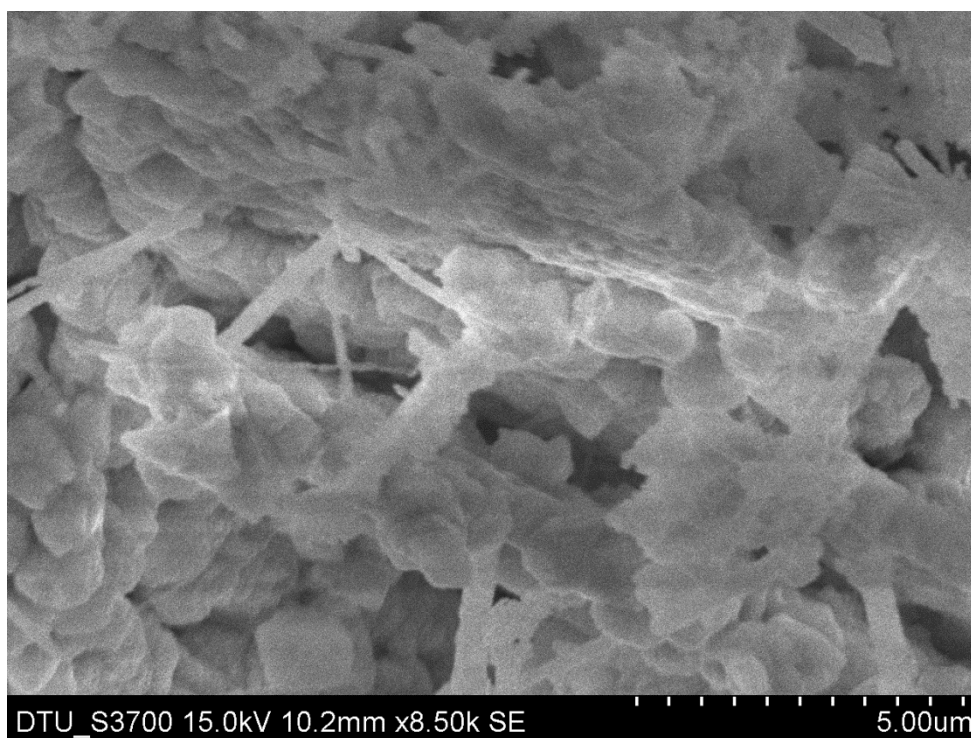


Figure 5.1(a): SEM micrograph of sample PbSe at 4h

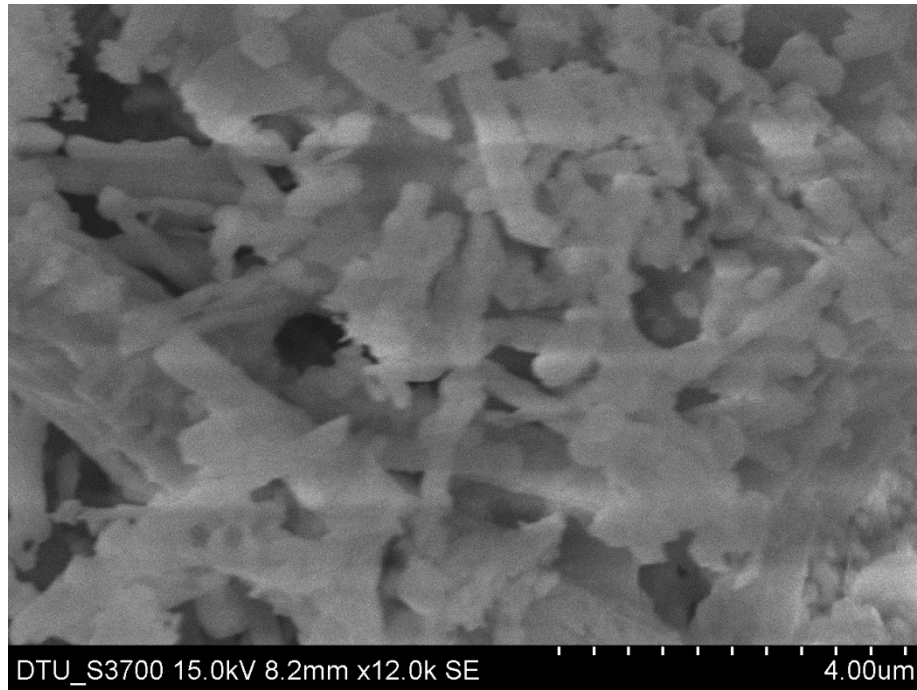


Figure 5.1(b): SEM micrograph of PbSe at 4h



Figure 5.1(c): SEM micrograph of sample PbSe at 4h

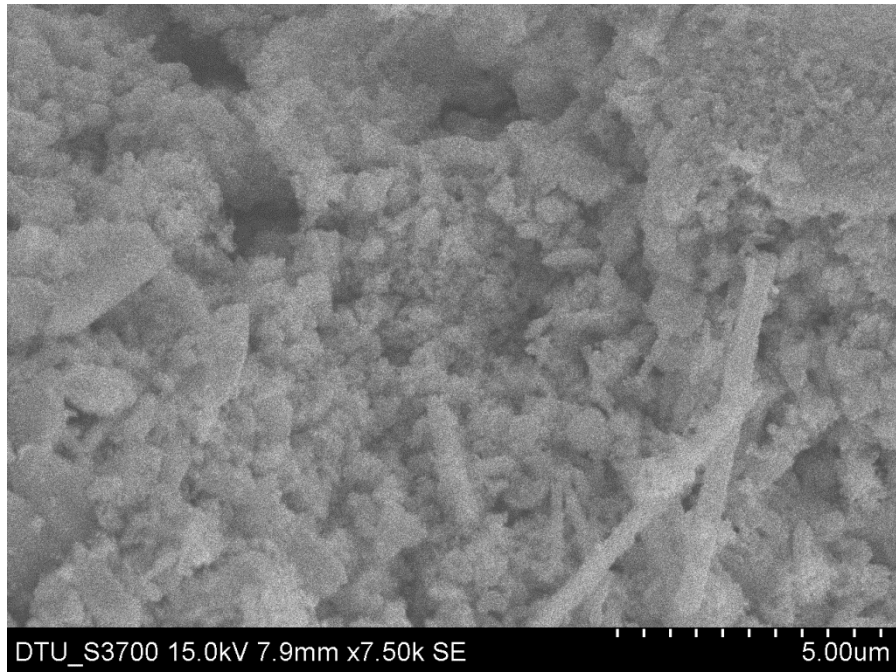


Figure5.1 (d): SEM micrograph of sample PbSe at 8h

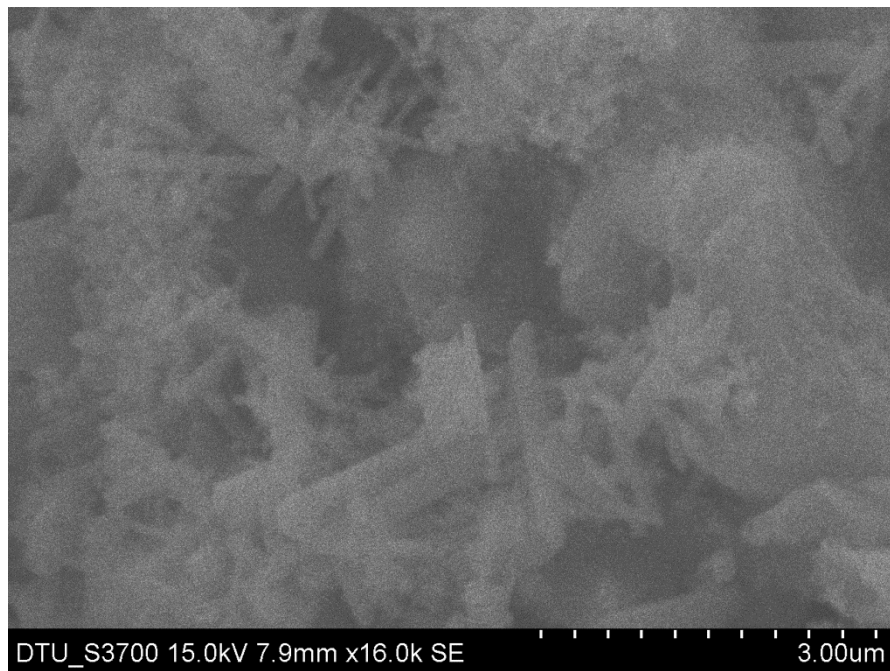


Figure5.1 (e): SEM micrograph of sample PbSe at 8h

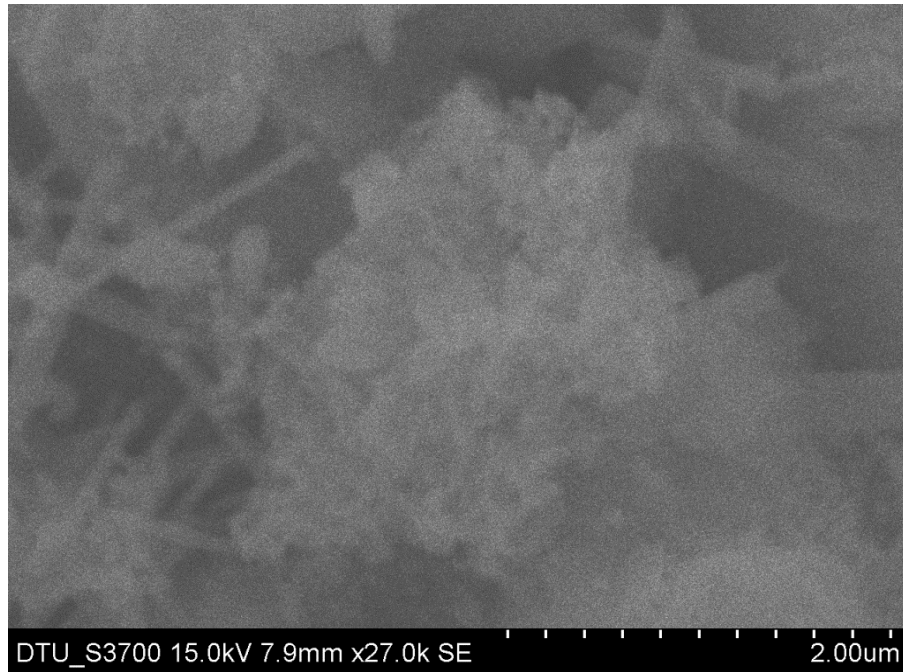


Figure5.1 (f): SEM micrograph of sample PbSe at 8h

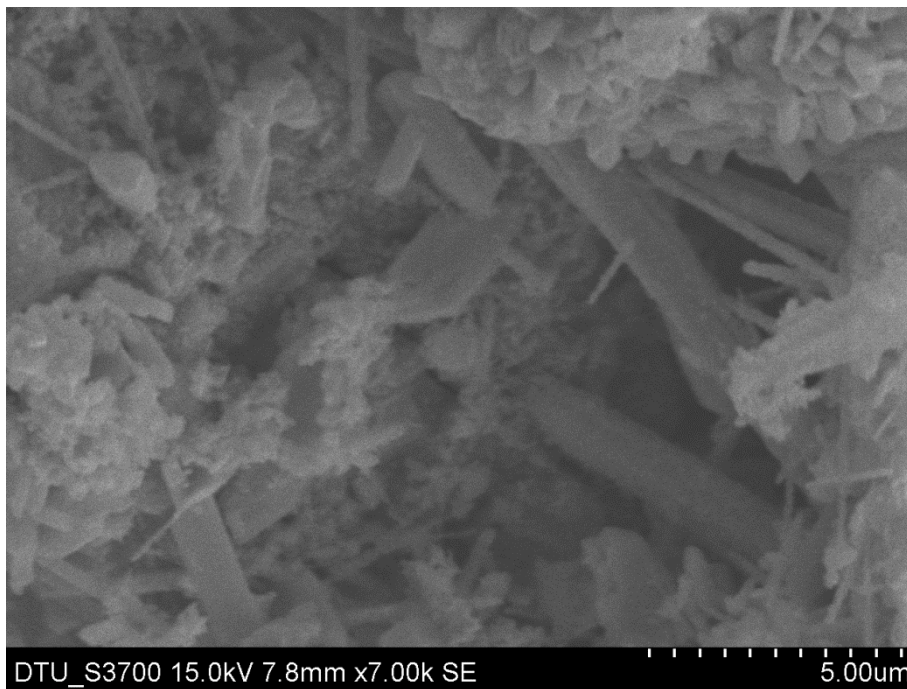


Figure5.1 (g): SEM micrograph of sample PbSe at 8h

SEM image of sample of PbSe are shown in the figure above. Samples of PbSe were heated at 70°C at different time period. As the heating period of sample is increased

rods of nano diameter and few micrometers were formed. Different picture of sample were taken at different resolution. From the above figure it is clear that nanorod type structure have been found in high magnification.

5.1.2 XRD analysis of PbSe sample:

The figure below shows the XRD pattern obtained of the sample at room temperature.

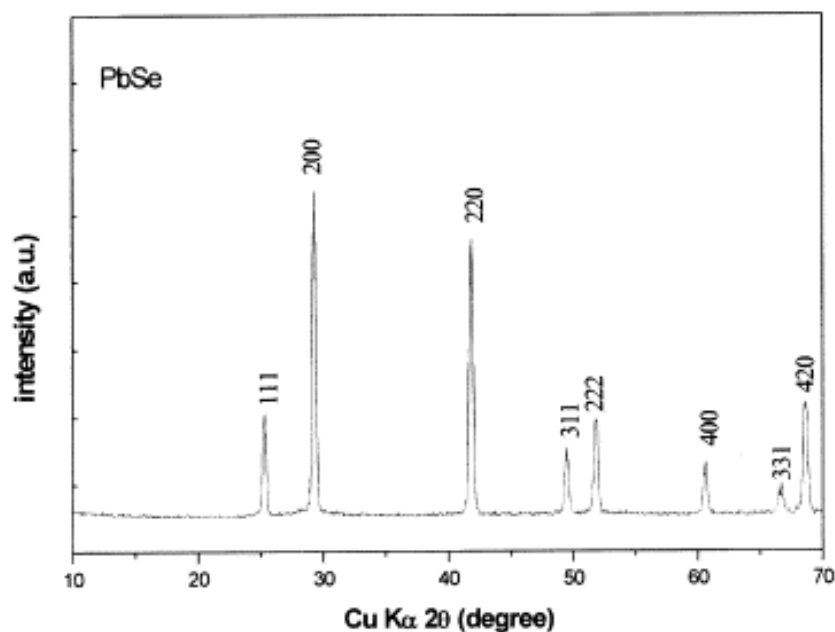


Figure5.1.2: XRD pattern of PbSe

The as synthesized PbSe semiconductor nanocrystals are generally spherical dots; the size distribution is very narrow. The X-ray diffraction pattern of the nanocrystals is a perfect rock salt crystal structure. The size calculated from the Scherrer equation is in the range of 60 nm to 90 nm. The obtained samples are all cubic phase confirm by the study of JCPDS cad file:PbSe No.6-354.The XRD pattern reveals that the intense peak at (110), (200), (220) plane corresponding to the cubic structure. The peaks are obtained at the 2θ value are 24° (111), and 30° (200) and 42° (220).

5.1.3 EDX analysis:

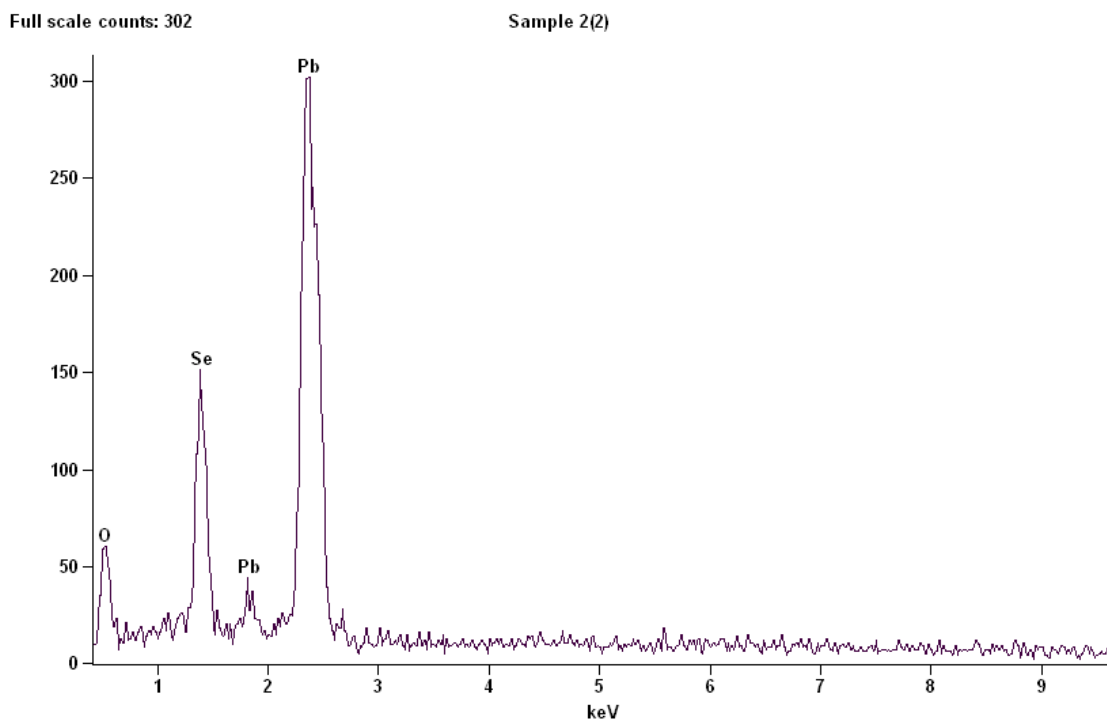


Figure 5.1.3: EDX analysis of PbSe sample

Acc. Voltage: 15.0 kV Take Off Angle: 76.9 deg.

Quantitative Results for Sample of PbSe

Element	Net Counts	Int. Cps/nA	Weight %	Weight % Error	Atom %	Atom % Error	Formula	Standard Name
O K	439	0.000	8.05	+/- 0.50	47.15	+/- 2.90	O	
Se K	87	0.000	---	---	---	---		
Se L	1465	0.000	15.35	+/- 0.66	18.21	+/- 0.78	Se	
Pb L	123	0.000	---	---	---	---		
Pb M	6024	0.001	76.60	+/- 1.96	34.64	+/- 0.89	Pb	
Total			100.00		100.00			

EDX is an analytical technique used for the elemental analysis of a sample. EDX analysis indicated the presence of respective element in the stoichiometric ratio.

The peak at 1.5eV corresponds to Se L of PbSe and peak at 2.4eV correspond to Pb M of PbSe.

5.1.4 Fourier Transform Infra-red Spectroscopy:

FTIR spectroscopy is used to identify the functional group in a sample. FTIR spectrum of PbSe nanoparticles synthesized by hydrothermal process which was acquired in the range 500-4000 cm^{-1} .

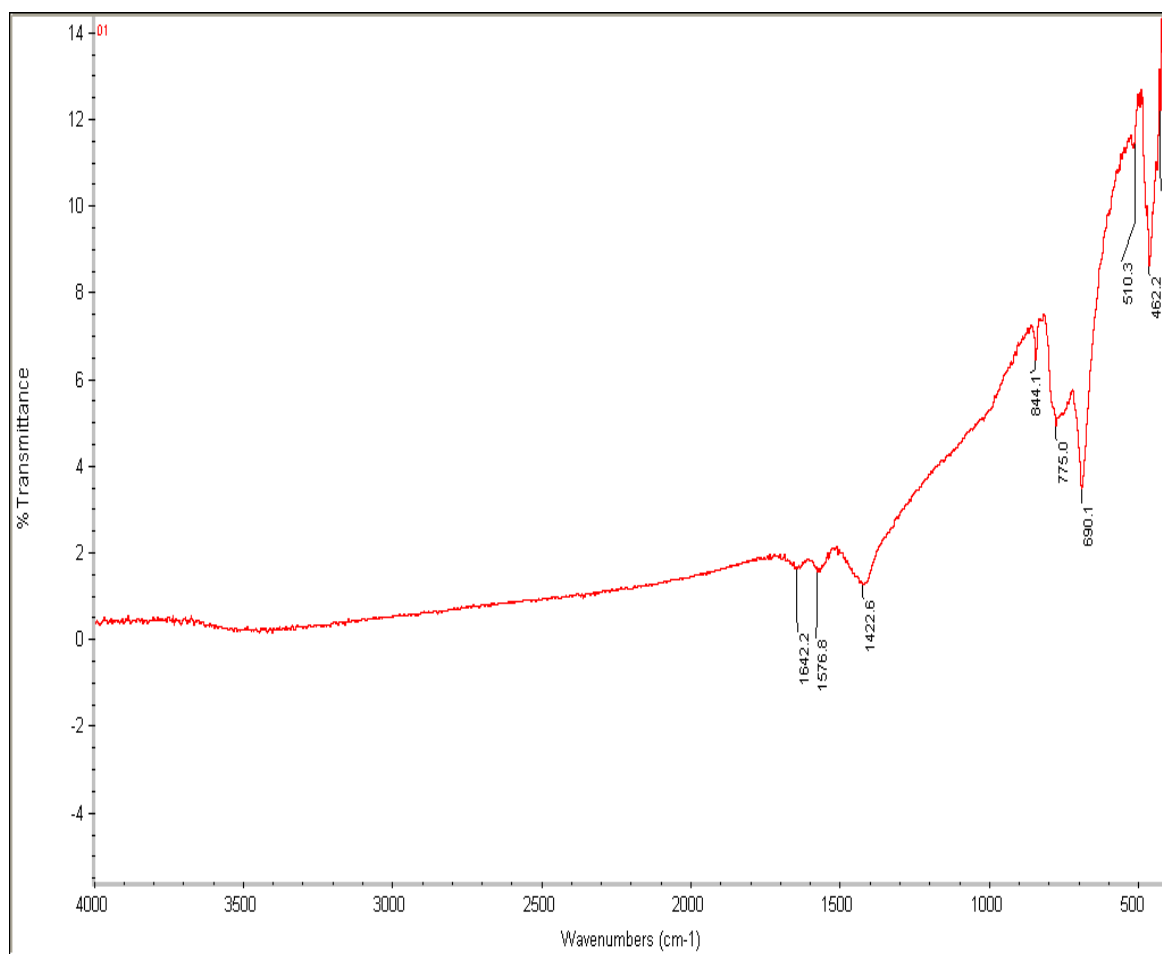


Figure 5.1.4: FTIR spectra of Sample of PbSe

In order to quickly establish the presence or absence of the various vibrational modes present in PbTe nanoparticle, we performed FTIR spectroscopy of PbTe nanoparticles. Two small intensity absorption peaks of C-O stretches are found in the spectra corresponding to the wave numbers 462.2 and 510.3 cm^{-1} . The stretching vibration of C=O at 1642.2 and 1576.8 cm^{-1} .

5.1.5 Transmission Electron Microscopy:

The HR-TEM images were recorded with JEOL JEM 2100. The TEM image of PbSe nanorods synthesized at 70°C were shown in the figure below. TEM images presented in the figure below indicate that PbSe nanostructures display rod-like morphology with diameters of 100-180 nm and lengths of up to 2 μm. Figure 5.1.5(c) shows a typical TEM image of a single PbSe nanorod. For PbSe, the grain size would grow with the elevation of temperature. The electron diffraction pattern shown in Fig. 5.1.5 (e) was obtained from a selected area of the PbSe nanorod shown in Fig. 5.1.5 (d) with a convergent beam and it revealed that the PbSe nanorod was a single crystal.

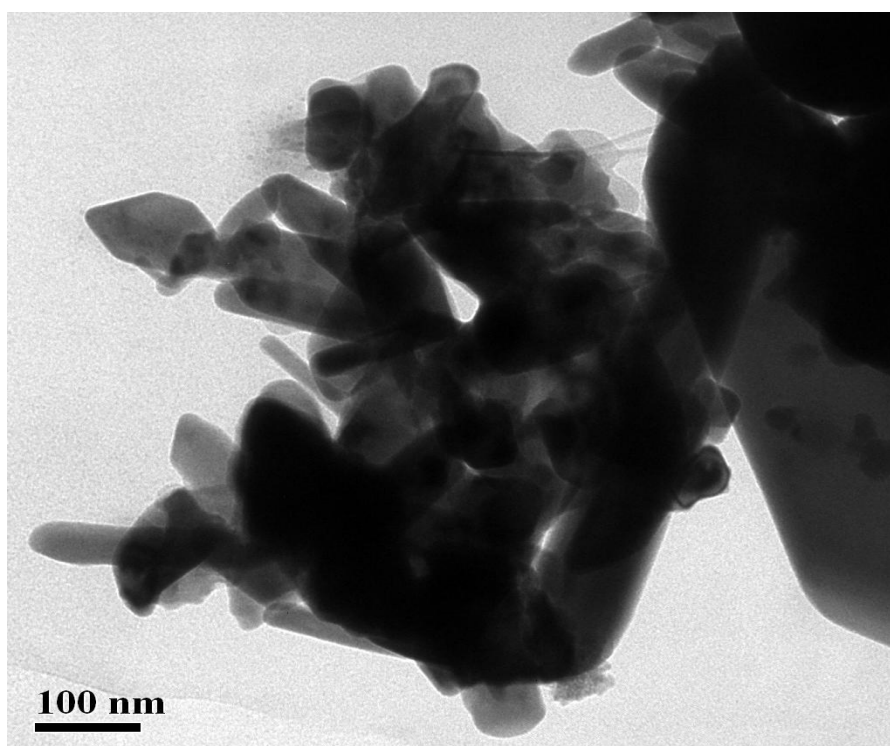


Figure 5.1.5 (a): TEM micrograph of PbSe at 4h

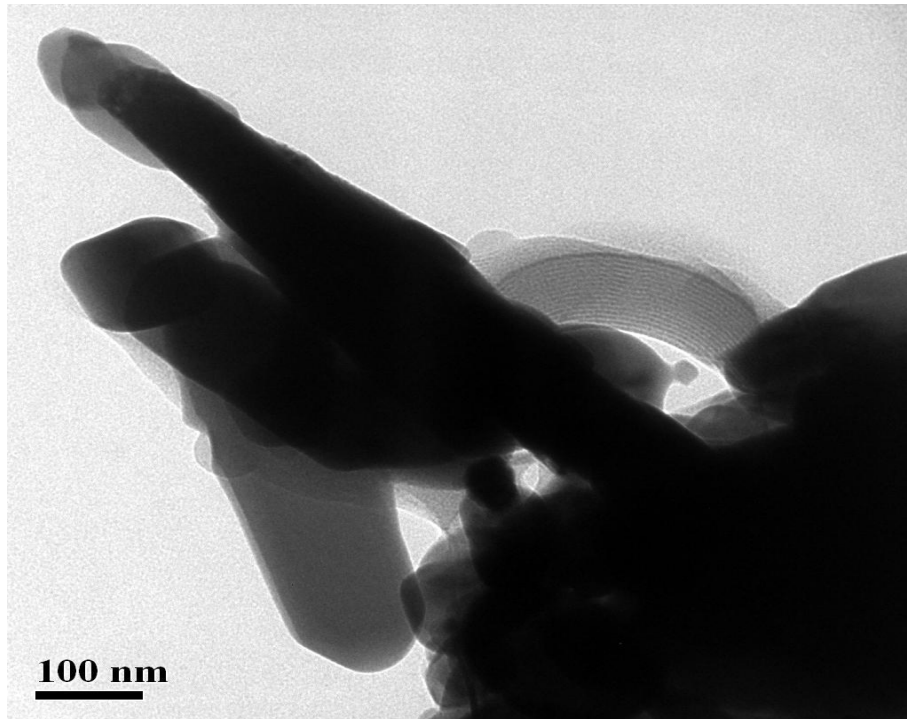


Figure5.1.5 (b): TEM micrograph of PbSe at 4h

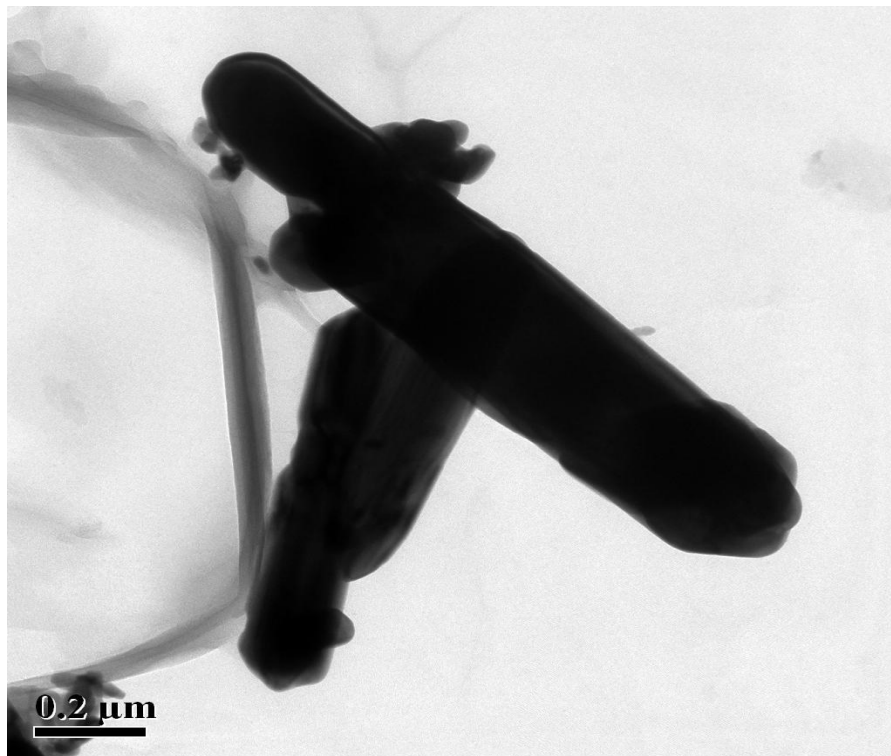


Figure5.1.5(c): TEM micrograph of PbSe at 4h

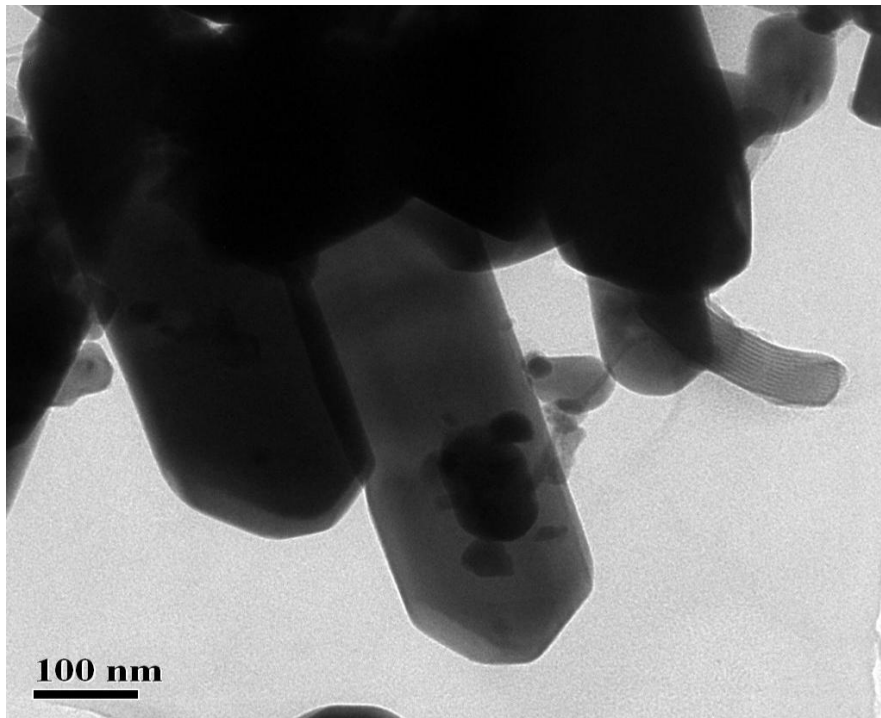


Figure5.1.5 (d): TEM micrograph of PbSe at 8h

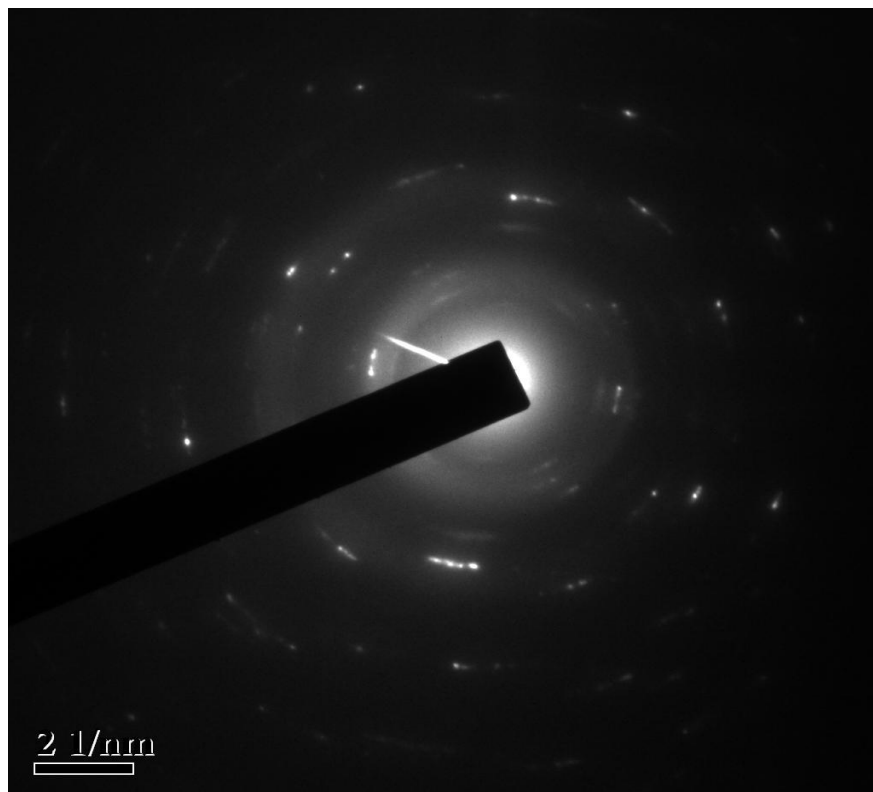


Figure5.1.5 (e): Electron diffraction (ED) of PbSe at 8h

5.2 Characterization of Lead Telluride

5.2.1 Scanning Electron Microscope:

SEM images for analysis of morphology and structural shape of synthesised powder has been taken with Hitachi S-3700 SEM at 15 kV with appropriate magnification.

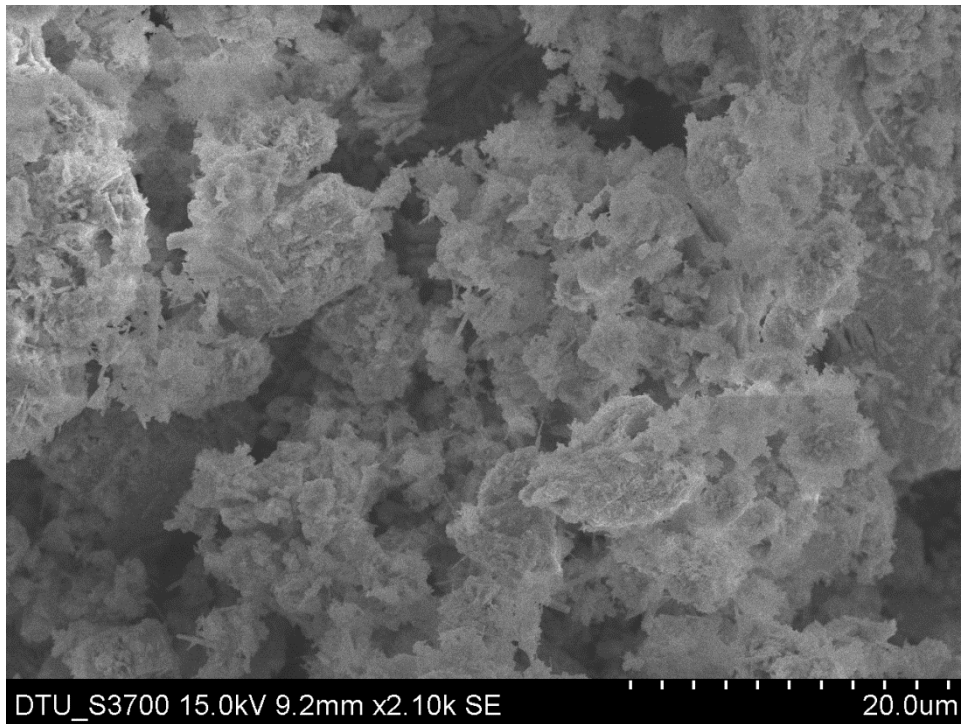


Figure5.2 (a): SEM micrograph of PbTe sample at 4h

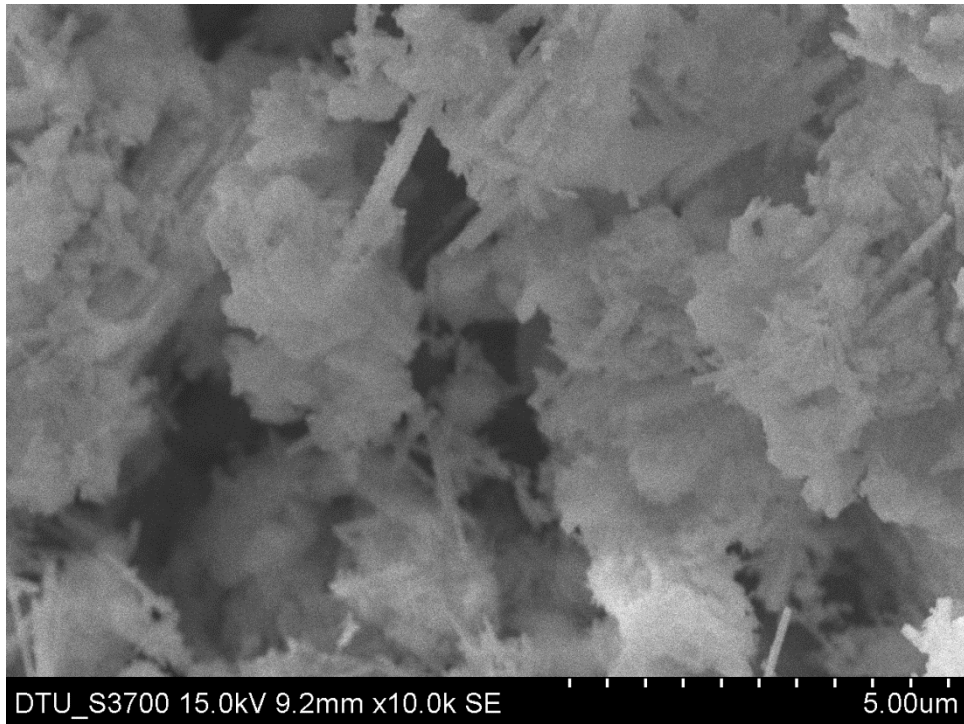


Figure5.2 (b): SEM micrograph of PbTe sample at 4h

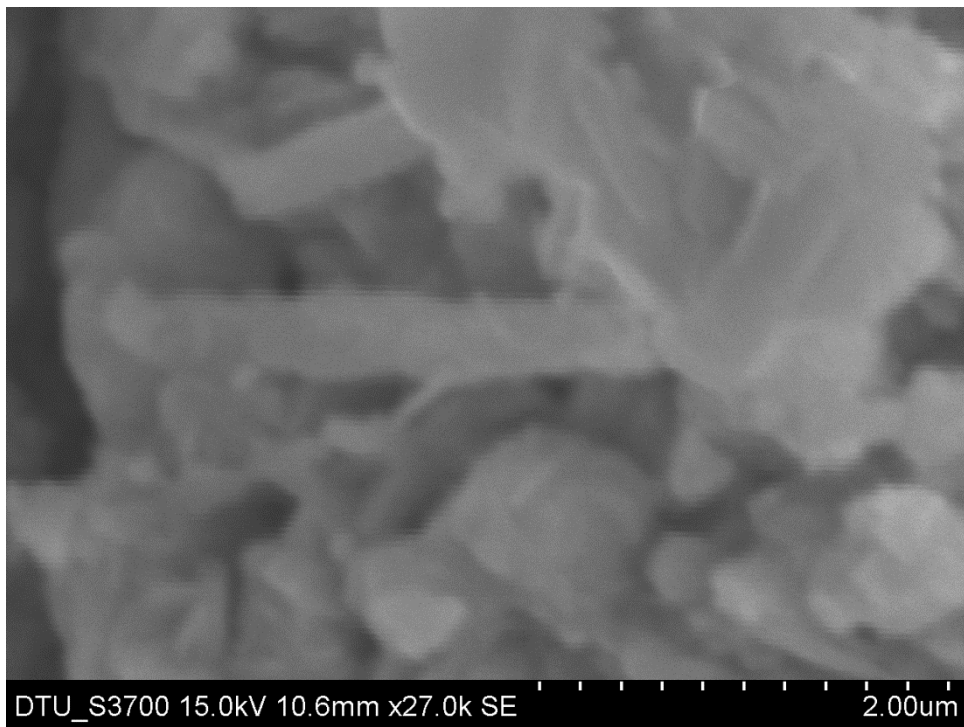


Figure5.2(c): SEM micrograph of PbTe sample at 4h

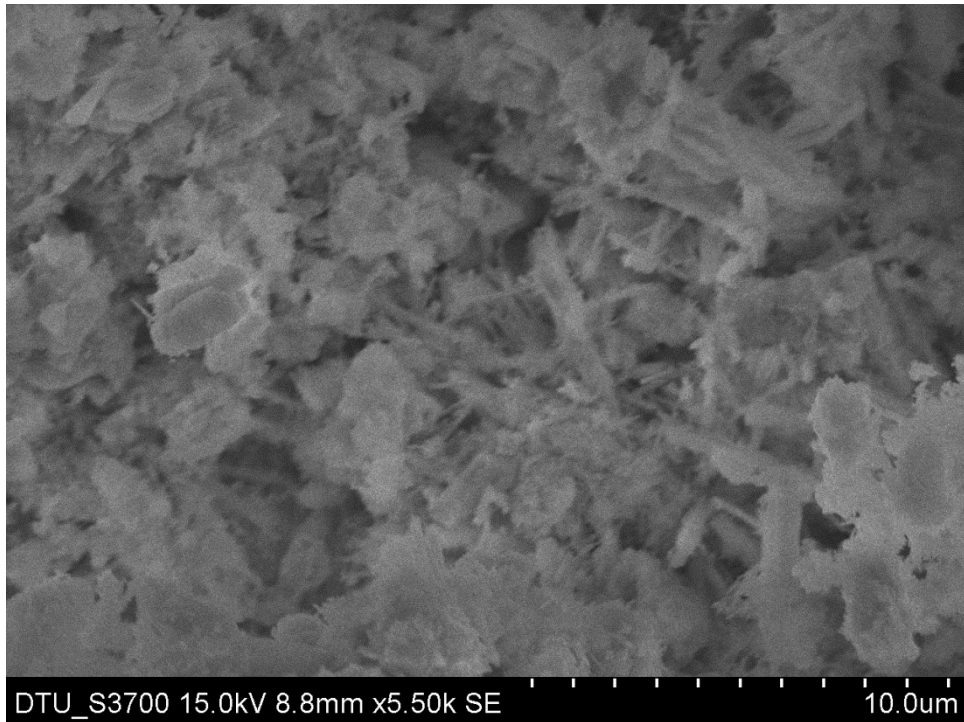


Figure 5.2(d): SEM micrograph of sample PbTe at 8h

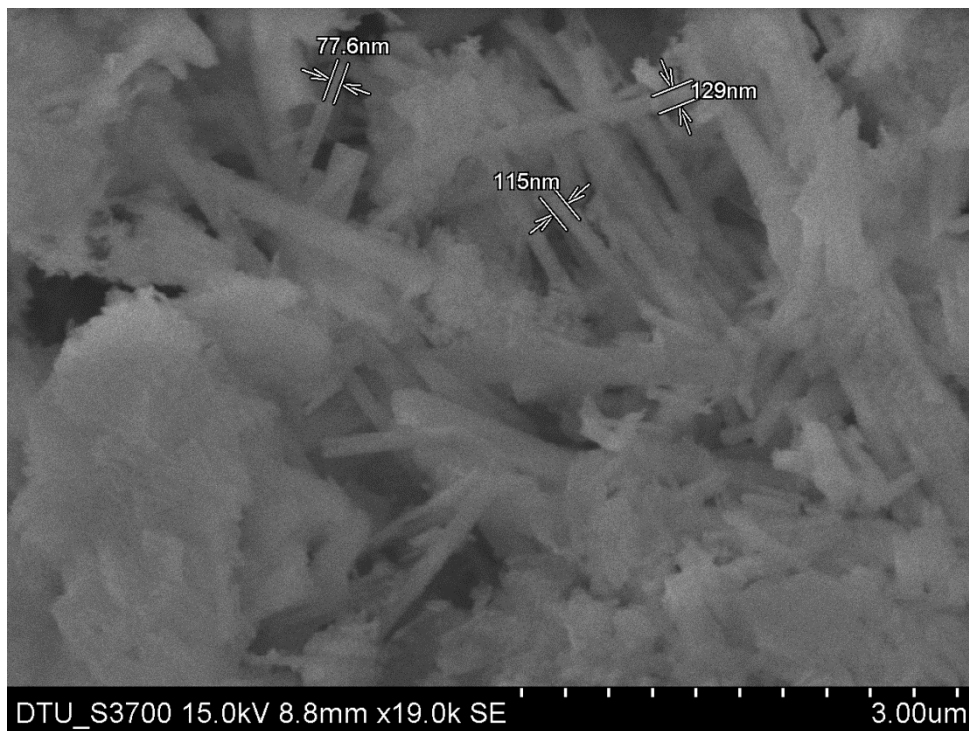


Figure 5.2 (e): SEM micrograph of sample PbTe at 8h

The synthesis of the compound was systematically investigated in the range of 70-180°C for various reaction times. If the temperature was low, the reaction time should

be prolonged to ensure the full transfer of source materials to final products. As the heating period of the sample is increases, some rod like nanocrystals with diameter ranging from 77.6nm to 129nm and length 2 μ m obtained. Figure 5.4(e) clearly shows the PbTe nanorod structure.

5.2.2 Fourier Transform Infra-red Spectroscopy:

FTIR spectroscopy is used to identify the functional group in a sample. FTIR spectrum PbTe nanoparticles synthesized by hydrothermal process which was acquired in the range 500-4000 cm^{-1} .

The stretching vibration of C=O at 1574.8 and 1413.2 cm^{-1} . Two small intensity absorption peaks of C-O stretches are found in the spectra corresponding to the wave numbers 1051.1 and 994.0 cm^{-1} .

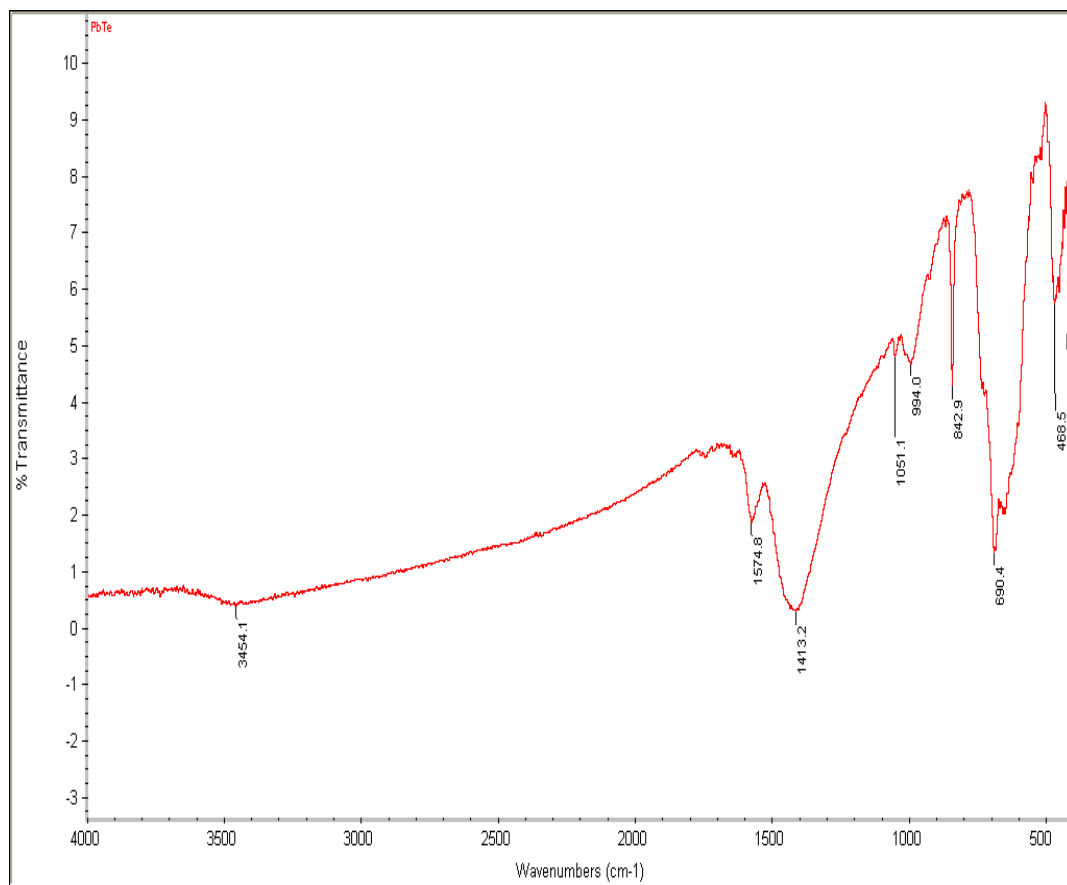


Figure 5.2.2: FTIR analysis of PbSe

5.2.3 Transmission Electron Microscopy:

The HR-TEM images were recorded with JEOL JEM 2100. The TEM image of PbTe nanorods synthesized at 70°C for different time periods (4h, 8h) are shown in the figure below. The TEM images presented in the figure below indicate that PbTe nanostructures display a rod-like morphology with diameters of 30-50 nm and lengths up to 1 μm . In figure 5.2.3(b) we investigated the rod-like structure. Figure 5.2.3(c) shows high magnification TEM showing high crystallinity.

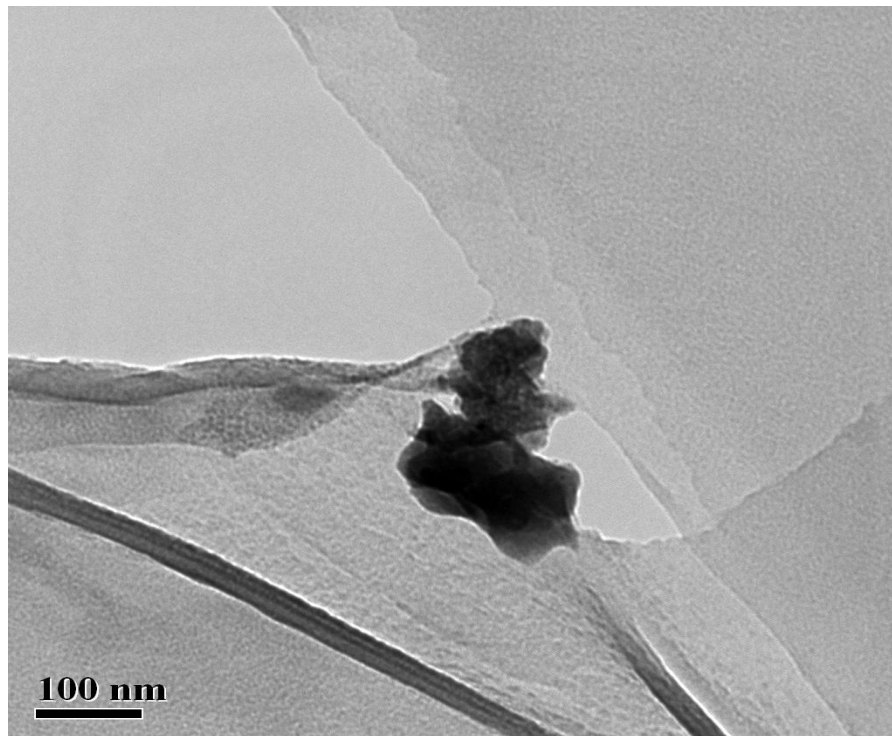


Figure 5.2.3 (a): TEM micrograph of PbTe at 8h

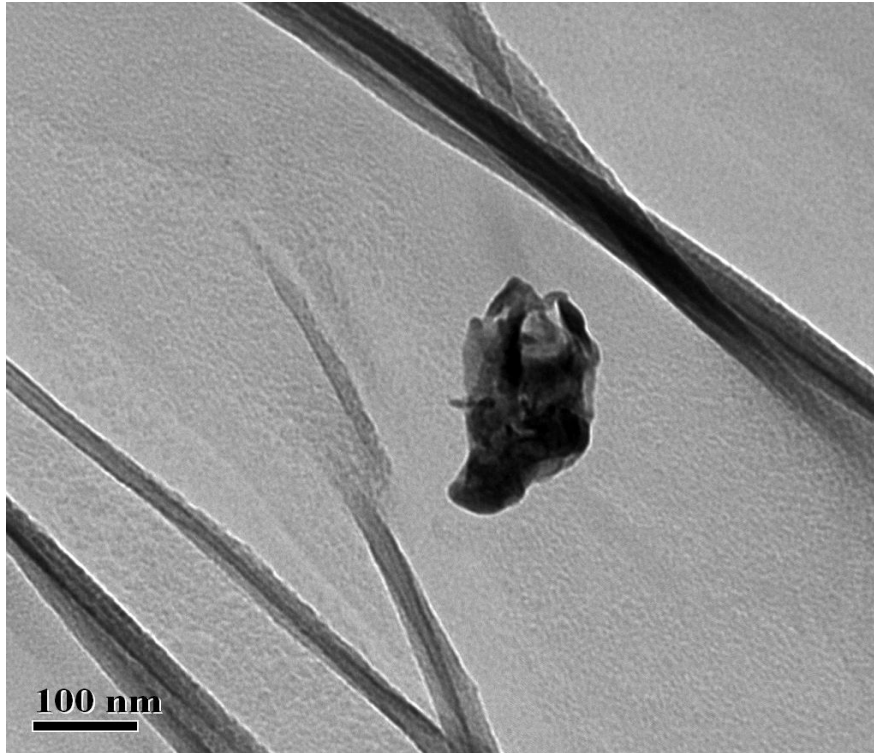


Figure 5.2.3(b): TEM micrograph of PbTe at 8h

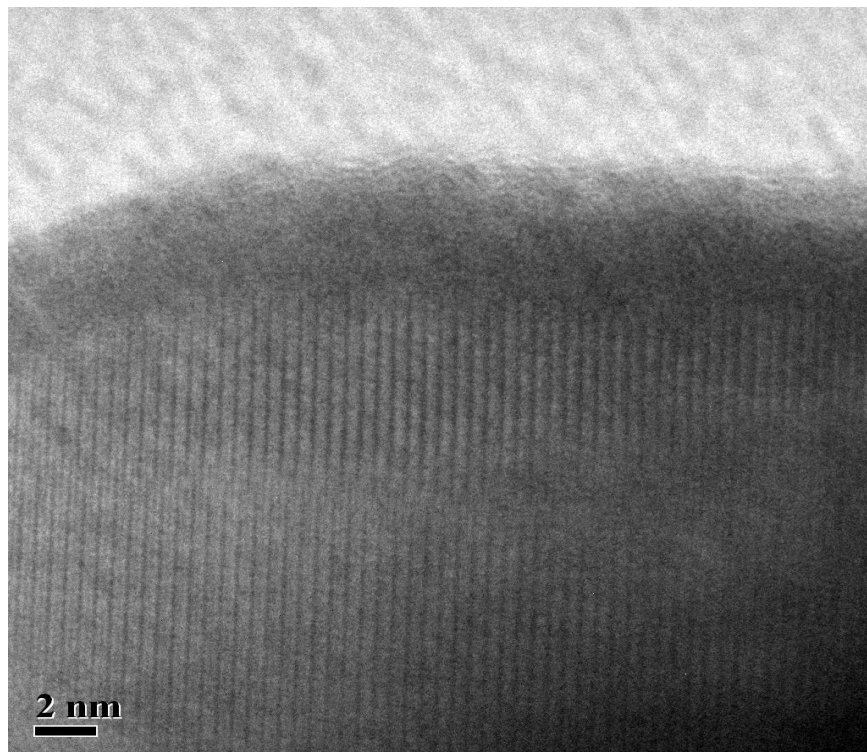


Figure 5.2.3(c): TEM micrograph of PbTe at 8h



Figure 5.2.3 (d): Electron diffraction (ED) of figure 5.2.3(b)

CONCLUSION

In conclusion, a new hydrothermal pathway to lead chalcogenides nanocrystal and nanorod by reaction of lead acetate with selenium or tellurium in sodium hydroxide in the presence of hydrazine hydrate as a reductive was successfully established. The reaction condition was mild. The possible mechanism, the effect of solvent alkalinity and temperature are discussed. PbSe and PbTe nanostructure were successfully synthesized by hydrothermal method. At small duration heating period small solid particles with cubic morphology were observed. HR-TEM investigation shows that all the nano and microstructures are single crystals with cubic symmetry.

REFERENCES

- [1] Smith, A.M., Gao, X. and Nile, S. *Photochemistry and Photobiology*, 2004, 80.
- [2] <http://www.indexmundi.com/g/g.aspx?c=xx&v=81>.
- [3] "U.S. EIA International Energy Statistics". Retrieved 2010-01-12
- [4] M. S. Dresselhaus, G. Chen, M. Y. Tang, R. G. Yang, H. Lee, D. Z. Wang, Z. F. Ren, J.P. Fleurial and P. Gogna, *Adv. Mater.*, 2007, 19(8), 1043–1053.
- [5] B.C.Sales, *Science*, 2002, 295(5558), 1248–1249.
- [6] R. Venkatasubramanian, E. Siivola, T. Colpitts and B. O'Quinn, *Nature*, 2001, 413(6856),597–602.
- [7] H. Bottner, G. Chen and R. Venkatasubramanian, *MRS Bull.*, 2006, 31(3), 211–217.
- [8] Y. G. Wang, X. F. Xu and R. Venkatasubramanian, *Appl. Phys. Lett.*, 2008, 93(11).
- [9] *Small Wonders, A survey of nanotechnology*, The Economist, 1 January 2005.
- [10] N. Taniguchi, *On the Basic Concept of 'NanoTechnology'*, Proc. Intl. Conf. Prod. Eng. Tokyo, Part II, Japan Society of Precision Engineering, 1974.
- [11] Cristina Buzea, Ivan Pacheco, and Kevin Robbie (2007) —*Nanomaterials and Nanoparticles: Sources and Toxicity*". *Biointerphases 2: MR17*.
- [12] Richard Feynman *There's Plenty of Room at the Bottom. An Invitation to Enter a New Field of Science*, lecture, annual meeting of the American Physical Society, California Institute of Technology, December 29, 1959.
- [13] K.E. Drexler, *Engines of Creation*, Anchor Press, New York, 1986.
- [14] European Commission *Nanotechnology Innovation for tomorrow's world* European Commission, Research DG, May 2004.
- [15] K.E. Drexler, *Engines of Creation*, Anchor Press, New York, 1986.
- [16] Potential Impacts of Nanotechnology on Energy Transmission Applications and Needs by Deborah Elcock, *Environmental Science Division, Argonne National Laboratory*.
- [17] R. F. Barrow, E.E. Vago, Proc. Phys. Soc. London 56, 76 (1944).
- [18] Y.I. Ravich, B.A. Efimova, I.A. Smirnov, *Semiconductor Lead Chalcogenides*, edited by L.S. Stil'bans (Plenum Press, New York-London, 1970).
- [19] R.D. Schaller, V.I. Klimov, Phys. Rev. Lett. 92, 186601(2004).

- [20] J. J. Choi, Y.-F. Lim, M.B. Santiago-Berrios, M. Oh., B.-R. Hyun, L. Sun, A.C. Bartnik, A. Goedhart, G.G. Malliaras, H.D. Abruna, F. W. Wise, T. Hanrath, *Nano Lett.* 9,3749 (2009).
- [21] W. Ma, J.M. Luther, H. Zheng, Y. Wu, A. P. Alivisatos, *Nano Lett.* 9, 1699 (2009).
- [22] A.F. Ioffe, *Semiconductor Thermo elements and Thermoelectric Cooling*, Info-search, London, 1956.
- [23] T.L. Kovalchik, I.U. P. Maslakovets, *Sov. Phys. Tech. Phys.* 1 (1957) 2337.
- [24] S.P. Yordanov, *Bulgar. J. Phys.* 17 (1990) 6.
- [25] S.P. Yordanov, *Bulgar. J. Phys.* 18 (1991) 15.
- [26] P.K. Parries, D. Mukherjee, C.A. Hogarth, *Phys. Stat. Sol. A* 152 (1995)461.
- [27] A.Y. Ueta, G. Springholz, F. Schinagl, G. Marschner, G. Beauer, *Thin Solid Films* 306 (1997) 321.
- [28] A.V. Wagner, R.J. Foreman, J.C. Farmer, T.W. Barbee Jr., *Material Research Society*, Philadelphia, PA, USA, 1997, p. 465.
- [29] L. Chen, T. YuGoto, R.Tu.T. Hirai, *IEEE*, USA, 1998, p. 539.
- [30] O. Ito, Seo Won-Son, K.Kounoto, *J. Mater. Res*14 (1999) 209.
- [31] G. S. Nolas, J. Sharp, and H. J. Goldsmid, *Thermoelectrics: Basic Principles And New Materials Development* (Springer, Berlin, 2001).
- [32] T. M. Tritt, *Thermoelectric Materials: Structure, Properties and Applications*, *Encyclopaedia of Materials: Science and Technology* Vol. 10, edited by K. H. J. Buschow (Elsevier, Oxford, 2002), pp. 1– 11.
- [33] L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B* 47, 12727 (1993).
- [34] R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O’Quinn, *Nature (London)* 413,597 (2001).
- [35] T. C. Harman, P. J. Taylor, M. P. Walsh, and B. E. LaForge, *Science* 297, 2229 (2002).
- [36] L.D. Borisova, *Phys. Stat. Sol. A* 53 (1979) K19.
- [37] P.G. Rustomov, M.A. Alidzhanor, C.H.I. Abilov, *Phys. Stat. Sol. A* 12 (1972) K103.
- [38] Z.H. Dughaish. *Physica B* 322 (2002) 205–223.
- [39] "Thermo-electric Semiconductors and Their Applications" written by Kin-ichi Uemura and Isao Nishida published from Nikkan Kogyo Shimbunsha in 1988.

- [40] Aepinus F.U. Theory of electricity and magnetism. – M.: The USSR Academy of Sciences Publ., 1951. – 448 p.
- [41] Ioffe A.F. Semiconductor thermo elements. – M-L.: The USSR Academy of Sciences Pub, 1960. – 37 p.
- [42] Shmelyov G.I. Materials for the thermo elements on the basis of three-component intermetallic compounds // FTT. – 1949. – V.1. – №1.
- [43] Stilbans L.S. Semiconductor thermoelectric coolers. – The USSR Academy of Science Publ., 1957.
- [44] Iordanishvili E.K. Thermoelectric power supply sources. – M.: Soviet Radio Publ., 1968.
- [45] A. F. Ioffe, “*semiconductor thermo elements and thermoelectric cooling*”, London, Info search Ltd., 1957.
- [46] <http://www.kelk.co.jp>
- [47] <http://www.bnl.gov/magnets/staff/gupta/cryogenic-datahandbook/Section13.pdf>.
- [48] Nolas G S, Kaeser M, Littleton IV R T, Tritt T M, 2000 a High figure of merit in ytterbium-filled skutterudite materials. Appl. Phys. Lett. 77, 1855–7.
- [49] Nolas G S, Sharp J, Goldsmid H J 2001a Thermoelectrics: Basic Principles and New/Materials Developments. Springer, New York.
- [50] Chaiken PM 1990 An introduction to thermopower, In: Kresin V Z, Little W A (eds.) Organic Superconductors. Plenum Press, New York, pp. 101–5.
- [51] Thermoelectric Materials: Principles, Structure, Properties, and Applications, Elsevier Science Ltd.
- [52] Luisa Consiglieri, —*The Joule-Thomson effect on the thermoelectric Conductors*”, Faculty of Sciences, University of Lisbon, 2007 .
- [53] Dan Mastbergen, Dr. Bryan Willson, Sachin Joshi, “*Producing Light from Stoves using a Thermoelectric Generator*”, Engines and Energy Conversion Laboratory, Department Of Mechanical Engineering, Colorado State University.
- [54] Seiji Sano, Hiroyuki Mizukami, Hiromasa Kaibe, —*Development of High-Efficiency Thermoelectric Power Generation System*”: Komatsu technical report, 2003 vol. 49 NO.152.
- [55] Geochemical Instrumentation and Analysis, Barbara L Dutrow, Louisiana State University ,Christine M. Clark, Eastern Michigan University.
- [56] Geochemical Instrumentation and Analysis, Susan Swapp, University of Wyoming.

- [57] Radiological and Environmental management, courtesy of Iowa State University.
- [58] Transmission electron microscopy and diffractometry of materials by James M. Howe, Brent Fultz.
- [59] <http://www2.chemistry.msu.edu>.
- [60] Photoluminescence in Analysis of Surfaces and Interfaces, Timothy H. Gfroerer in Encyclopaedia of Analytical Chemistry R.A. Meyers (Ed.) pp. 9209–9231 John Wiley & Sons Ltd, Chichester, 2000.