Measurement of Thermal & Optical properties of Metal Oxide nanoparticles

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Dear Sir,

I submit this thesis entitled “Measurement of Thermal & Optical properties of Metal Oxide nanoparticles”, based on MCEN4005 Mechanical Engineering Research Project 1 and MCEN4006 Mechanical Engineering Research Project 2, undertaken by me as part-requirement for the degree of B.Eng. in Mechanical Engineering.

Yours faithfully,

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Pages 1 to 8 of this thesis includes material previously submitted as part of the Progress Report assessment for the MCEN4005 Mechanical Engineering Research Project 1 unit (Chandrabahu, 2019).

Abstract

Nanoparticles are known to show different properties when compared to their bulk equivalents. Metal oxides are a crucial technological material group that exhibits unique properties. This research paper will measure and/or document the methods used to find several important thermal & optical properties of metal oxide nanoparticles. A total of about 2g of Tin Oxide (SnO_2) nanoparticles were produced using a chemical co-precipitation method and thermal properties such as Heat Capacity, melting point and optical properties such as Infrared reflectance and photoluminescence were to be measured by performing various nanoparticle characterization techniques such as Scanning Electron Microscope (SEM), Energy dispersive X ray (EDX), Differential Scanning Calorimeter (DSC), IR spectroscopy and Photoluminescence (PL) spectroscopy. DSC which can be used to measure heat capacity and PL spectroscopy were not performed and their methods were documented only. The size of the nanoparticles produced were found to be 50nm whereas the chemical composition and purity of the sample were confirmed using EDX. IR spectroscopy was performed on the samples and it was observed that the percentage of IR radiation of wavelengths 2.8-10 micrometers reflected was between 2.5% to 3.6%. Due to the inability to perform DSC, no thermal properties were measured, however the methods to measure critical thermal & optical properties have been shown.

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1. Introduction

1.1 General Overview

Engineers make use of many skills as they work in the world around them. One such vital skill is the ability to take measurements, a measurement may be simply an observation such as a color or texture of an object. Without the ability to measure, it would be challenging for scientists to conduct experiments and form theories. Measurements are important not only in engineering but also numerous other occupations and activities such as farming, construction, manufacturing and commerce, etc. Measurements are made using tools and provide us with a quantity or value from which a property can be derived. The measurements made in this project deal with nanoparticle metal oxide thermal and optical properties

The term 'nanoparticle' is used to represent particles with their rough diameters measured in the nanoscale. Fine nanoparticles may cover a range of sizes between 100-2500 nm, whereas ultrafine nanoparticles may cover a range of sizes between 1-100 nm. When a certain material made of nanoparticles is compared to another sample of the same material consisting of larger particles, for e.g. microparticles, different properties are exhibited between the two materials. This difference in properties is often a positive difference which makes nanoparticles more desirable & useful for engineering applications. A significant part of the effort that scientists spend on using nanoparticles for engineering applications include efforts to measure and compare required properties with alterative nanoparticle materials in order to choose the best material for the job. More detailed information on why and how nanoparticles show unique properties is included in the literature review section of this thesis.

Metal elements are capable of forming a large variety of oxide compounds, also known as metal oxides which is a material group that show properties associated with metallic, semiconductive or insulative materials. A metal oxide is formed when one or more oxygen atom combines with a metal atom to form a compound. Common examples of metal oxides include Iron oxide, Titanium oxide which is the most common nanoparticle used in applications, Zinc oxide and Tin Oxide. In addition, oxides formed with the same metal may have multiple forms (oxidation states), for example iron forms three main types of oxides; a) Iron (II) Oxide (FeO) also known as ferrous oxide or Iron monoxide, is a rare form of iron oxide, b) Iron (III) Oxide (Fe_2O_3) or

ferric oxide occurs naturally in the mineral known as hematite and c) Iron (II,III) Oxide (Fe_3O_4) which also occurs naturally in the mineral known as magnetite and has properties such as permanent magnetism, and generally better electrical conductivity than ferric oxide. Ferric oxide when hydrated through reaction with water or acidic substances is also known as rust. For this project, Tin (Sn) was the metallic element used to form the metal oxide nanoparticle. Similar to Iron, Tin may also exist in the following major forms; a) Tin (II) Oxide also known as Stannous Oxide (SnO) and b) Tin (IV) oxide also known as Tin Dioxide or Stannic Oxide (SnO_2) which is found mainly occurring in the nature with the mineral called cassiterite that has been used historically and is the main source of Tin today.

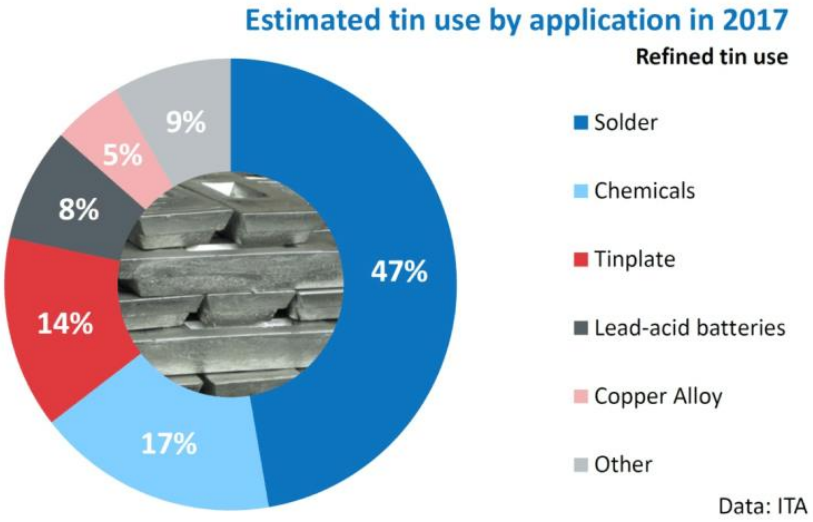

Figure 1. Applications of Tin in 2017 (Elementos Limited, 2019)

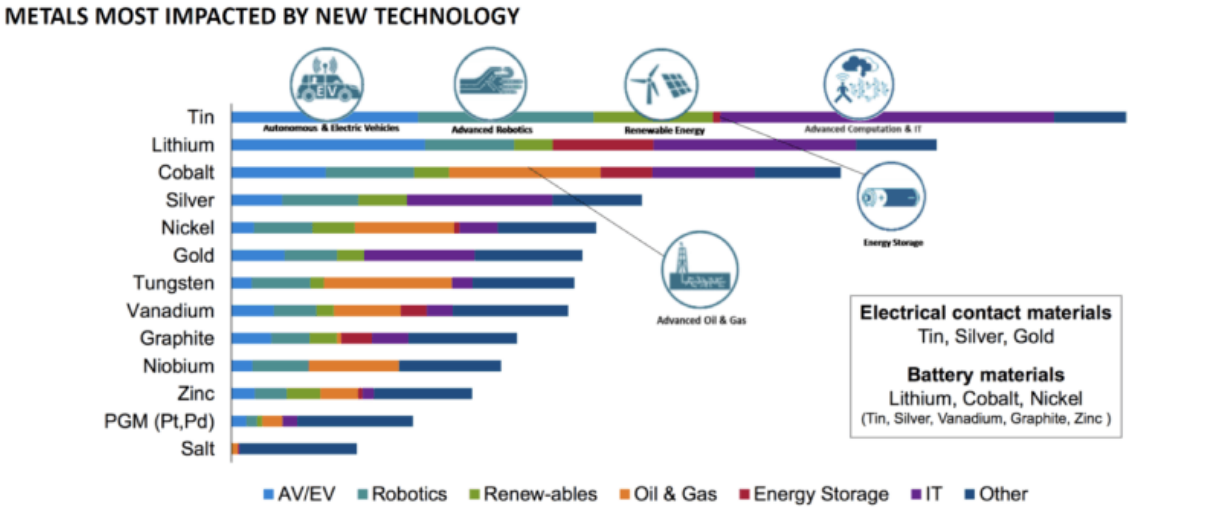

Figure 2. Impact of New technology on metals (Elementos Limited, 2019)

Shown in figures 1 and 2 above are applications of tin for the year 2017 and the metal usage/impact for applications in new technologies, respectively (Elementos Limited, 2019*).* Some technological applications of metal oxides nanoparticles include the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for protection against corrosion and also as catalysts (Fernández-Garcia and A. Rodriguez, 2007). Tin oxide nanoparticles exhibit unique physical and chemical properties which make them suitable for the above applications.

Thermal and optical properties are important to measure, analyze and compare for nanoparticles as they are able to prove the suitability of a certain substance for a given application. Thermal properties such as Heat Capacity, thermal conductivity, and thermal expansion coefficient of a substance need to be measured to determine the suitability of the material as an insulator/conductor, whereas optical properties such as color, refractive index, photoluminescence, Ultra Violet (UV),Light and Infra-red (IR) reflection and transmission need to be measured to determine the suitability of the material optically. Usually a choice of material is made by choosing materials with all or most of the desired properties. For example, a material with good thermal conductivity and high IR reflectivity may be chosen as a pigment for a paint/coating

Therefore, In the field of nanotechnology, in order to develop robust products, we need discrete analytical methodologies to determine critical properties that affect the performance of a product. The purpose of this project is to act as a quick guide for some of the important property measurements of metal oxide nanoparticles.

1.2 Objectives

The main goal of this project is to simply show the methods that can be used to measure certain significant thermal and optical properties of metal oxide nanoparticles. Research was made into the methods available to perform such property measurements and the calculations required to determine the properties were also noted. In order to achieve this objective, the project was divided into the following sub tasks:

- Studying nanoparticles
- Synthesizing nanoparticles
- Achieving uniform nanoparticle size
- Finding out available measurement methods
- Performing experiments & find out procedure

1.3 Project Outline

The first semester of this project was focused on synthesizing several nanoparticle samples. For synthesis, a co-precipitation method was used, and the goal of synthesis was to be able to repeatedly form the same sized nanoparticles with a uniform and crystalline structure.

First, research into the subject & literature of nanoparticles was carried out since it was a new and interesting subject for which detailed knowledge was lacking. The goal of this literature search was to find out methods of synthesis of metal oxide nanoparticles as well as characterization techniques available and how they may be used to either measure or calculate thermal and optical properties.

Synthesis of nanoparticles was performed in conjunction with another project performed by Mr. Siyaratne Peiris introduced to me by my supervisor, Dr. Samantha Wijewardana. The main objective of this project was to prepare a transparent pigment which would be an ingredient for a paint that is capable of reflecting Infra-red (IR) radiation which would ideally result in much of the heat rejected (and prevent heat gain) through the painted walls of the building. The transparent features of this pigment towards visible frequencies would allow the paint to maintain its natural color and texture. Since thermal and optical properties are dependent on particle size, the current goal of this project was to synthesize tin oxide nanoparticles with the size being maintained between 400-500nm. Tin oxide was chosen as it showed the most relevant properties to the above-mentioned requirements.

Several samples of Tin Oxide were produced, and the resulting particle sizes were measured using Scanning Electron Microscope (SEM) analysis. The samples were then tested for purity by conducting Energy Dispersive X-Ray spectroscopy (XRD) which confirmed the presence of Tin and Oxygen in the sample composition. Infra-red (IR) spectroscopy was also conducted and a graph of reflected radiation intensity vs wavenumber of the IR wave for each sample was obtained.

A total of 8 samples, each weighing about 0.5g were produced for the purposes of this research. The methods that were to be used for the characterization and measurement of metal oxide nanoparticle properties have been included in the results section of this thesis.

2. Literature Review

In today's rapidly developing technological world, nanotechnology appears to be at the forefront of new scientific discoveries. The word 'Nano' indicates dimensions of the scale $10^{-9}\,m$. Some examples of Nanotechnology applications include uses in medicine such as for cancer treatment, electronics also known as nanoelectronics, Energy applications, defence/military applications as well as in materials and manufacturing fields (Understandingnano.com, 2019).

Figure 3 below can be used to effectively illustrate the scale of nanoparticles and make scale comparisons to various micro and nano sized entities.

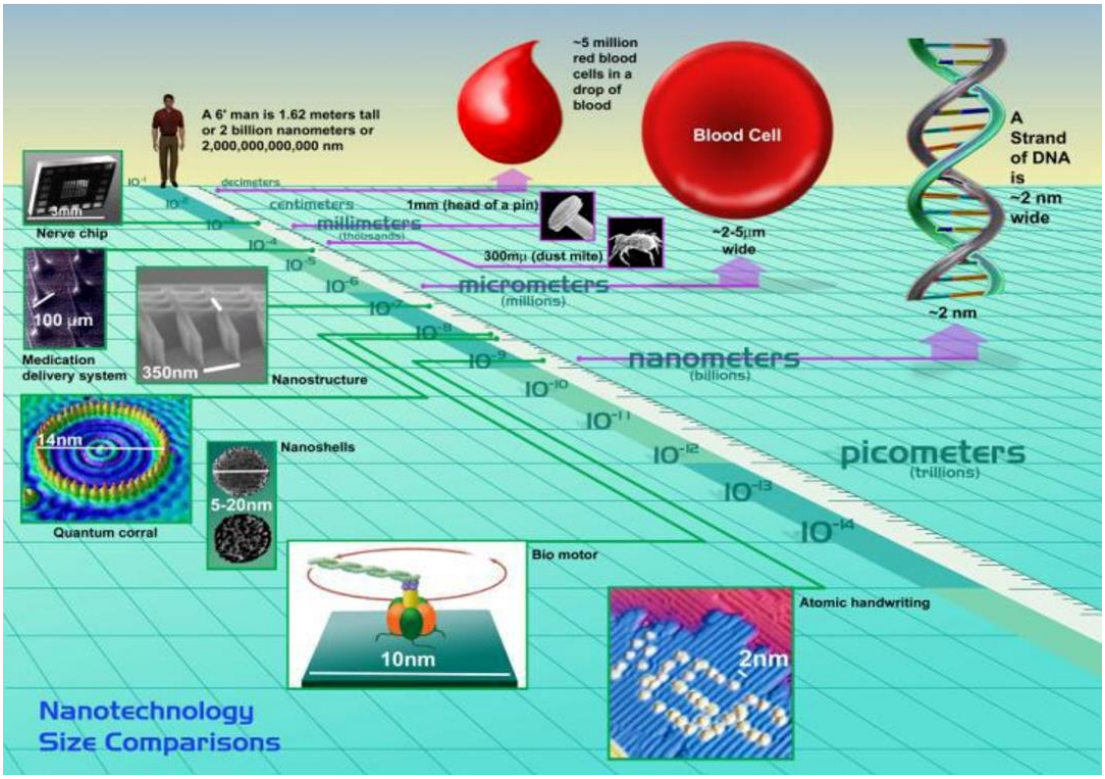

Figure 3. Nanotechnology Size Comparisons (Koçak and Karasu, 2018)

Investigating the properties of nanomaterials is perhaps the most important aspect of studying nanomaterials. As by understanding how to manipulate matter in its smallest form to obtain desired material properties, the path may be paved lots of new discoveries in various fields. Therefore, the primary purpose of this research project is to investigate the different methods available to measure various nanomaterial properties in thermal and optical categories.

Nanoscience, Nanoengineering or Nanotechnology often interchangeably used, in simple terms is the science, engineering and technology conducted where the atoms

and molecules involved are usually in the range of 1 to 100 nanometres or a billionth of a meter ("What Is Nanotechnology?", 2019). Nanotechnology involves the capability to observe and control individual nanoparticles to meet the requirements of its application. Nanotechnology is a very broad field and includes fields such as surface science, organic chemistry, molecular biology, semiconductor physics, energy storage, microfabrication, molecular engineering, etc. Nanotechnology may be able to create many new materials and devices with a wider range of applications such as nanomedicine, nanoelectronics, biomaterials, energy production and consumer products. While the majority of advantages are beneficial there are also some issues to be handled with such as toxicity and the environmental impact of nanomaterials.

With the decreased size of nanoparticle compared to microparticles, phenomena such as statistical and quantum mechanical effects such as the 'quantum size effect' where electronic properties of solids are changed with the reduce particle size have become more important than ever. The properties of nanomaterials will change proportionally to the nanoparticle size as quantum effects dominate the material properties in the nanoscale range. A larger surface area is available for nanomaterials compared to materials with larger particles due to the much smaller in size, but larger in number nanoparticles, a larger surface area leads to higher reactivity as more material can come in to contact with the nanoparticles thus affecting the nanomaterial properties. Simply put, the properties change with size due to the increased surface area to volume available for interaction as shown in Figure 4 below.

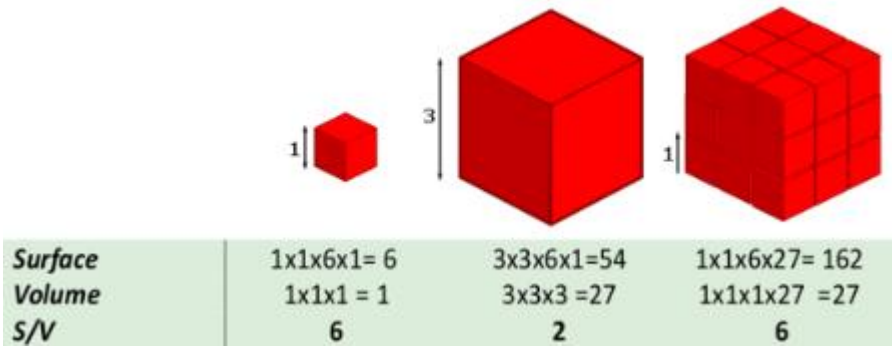

Figure 4. Surface area to volume ratio (S/V) for small (left) and larger (center) particles and bulk (right)

2.1 History of nanotechnology

Nanomaterials have always existed in the nature, the earliest and most premodern example of such nanomaterials in recorded history was in the 4th century, Rome where the 'Lycurgus cup' ("Nanotechnology Timeline", 2019) made of dichroic glass containing gold and silver nanoparticles glows in red colour when light passes through it (or lit from inside) but looks opaque green when lit from outside. Figure 5 shown below is an example of a naturally occurring nanomaterial where the unique mixture of color of the gem stone is caused by the interference and diffraction of light between silica sphere particles of the gem stone which are nanosized with diameters in the range of 150-300nm (Red Carpet Opals, 2019).

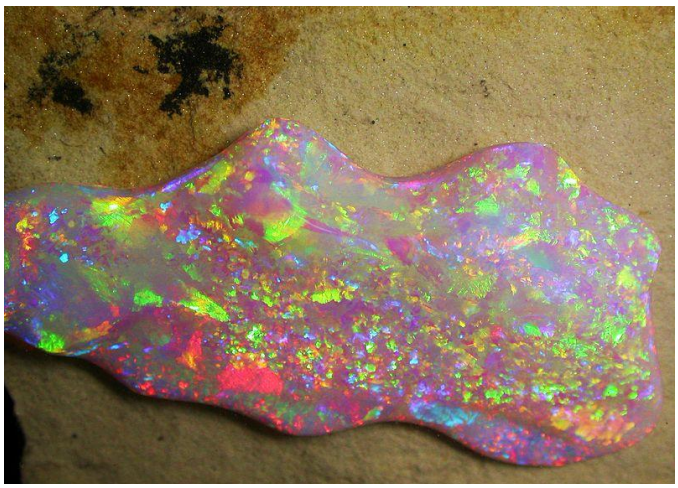

Figure 5. Brazilian Crystal Opal (Red Carpet Opals, 2019).

There have been further recorded instances where nanomaterials were used before developments in nanotechnology in the Modern era began and only some of them have been described here. Stained glass windows present in European cathedrals during the period of 6th-15th century were very colourful as they were made by mixing with gold chloride, silver nitrate and other metal oxide nanoparticles. Middle eastern metal workers in the 12th century used steel ingots imported from India to forge damascene blades sharper and more durable than other blades and through modern investigating done in 2006 material scientists found traces of carbon nanotubes and nanowires in the blades.

Nanotechnology in the modern era leading to the high-tech research performed in the 21st century began in 1857, when Michael Faraday discovered nanostructured 'ruby' gold when lit under specific lighting conditions produced different coloured solutions. This was also the case with the Lycurgus cup in the 4th century, but where the reason

was unknown. In 1936, Erwin Müller invented the field emission microscope and later also invented the field ion microscope in 1951 allowing the ability to observe in an atomic level resolution. Jack Kilby in 1958 invented the first Integrated circuit (IC), where in 1965 Gordon Moore, who is also the co-founder of Intel corporation, then came up with the 'Moore's law' stating how the density of transistors in IC's would double every two years. This has been true for the next 50 years where the semiconductor manufacturer's growing reliance on nanotechnology has been evident. In 1974, Tokyo science university professor Norio Taniguchi came up with the word "nanotechnology" for the first time to describe accurate machining of materials to within atomic scale dimensional tolerances. The atomic force microscope invented in 1986 by Gerd Binnig, Calvin Quate, and Christopher Gerber provided the capability to view, measure and manipulate materials in a scale of nanometres where forces intrinsic to nanoparticles could be measured. This discovery led to IBM researchers manipulating 35 individual xenon atoms to spell out the IBM logo in the year 1989. Moungi Bawendi of MIT in the year 1993 found a method for controlled synthesis of nanocrystals otherwise known as quantum dots.

There have been many more discoveries since the beginning of the 21st century that has helped technology progress rapidly, such as in 2003 when Naomi Halas, Jennifer West, Rebekah Drezek and Renata Pasqualin at Rice university tuned the size of gold nanoshells to absorb near-infrared light and this served as the platform to discover chemotherapy in cancer treatments. More recently in 2010, IBM used a silicon tip with a minimum tip width of a few nanometers to chisel away material from organic molecular glass to make a 3D pattern of the world the size of 1/1000th of a grain of salt in only 143 seconds. This process showed the powerful (due to the reduced time required, cost and complexity) nanoparticle patterning method for structures as small as 15 nanometers which has paved the way for further discoveries in fields such as electronics and nanobiology. Figure 1 below shows a rendered image of the process undertaken by IBM in 2010 where the part of map visible is the Mediterranean Sea and Europe ("Nanotechnology Timeline" 2019).

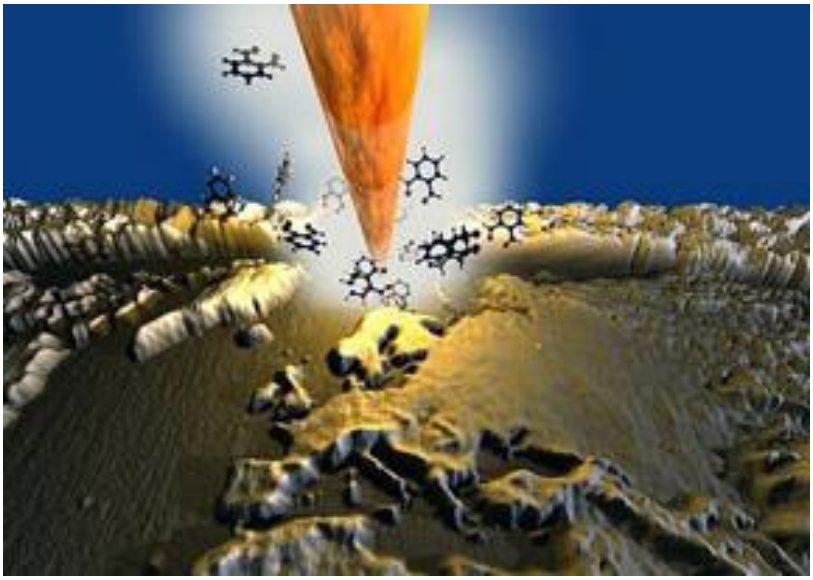

Figure 3: IBM's nanopatterning process drawing a 3D world map using a silicon tip (National nanotechnology initiative, 2019)

The most modern advancements in nanotechnology include the formation of stronger materials with high strength composite materials such as carbon fiber used in automobiles and carbon nanotube pre-impregnated materials offering better conduction which is not present in traditional carbon fiber. The scalability of production of nanoparticles is important as they are required to be produced in extremely large quantities depending on the application and is thus expensive to be manufactured in large scale. This further highlights the need to properly find out the proper method of nanoparticle synthesis with its properties measured and found to be within the requirements before being mass scale manufacturing can progress. The next few years will without doubt see more nanotechnology related discoveries specially in terms of structure and purity as well as reducing costs for mass manufacturing in order to achieve more commercialization.

2.2 Metal oxide nanoparticles

Nanoparticles can be categorized according to their size, morphology, physical and chemical properties. A few of the main categories of nanoparticles in use today include: Polymeric nanoparticles, Ceramic nanoparticles, Lipid-based nanoparticles, Carbon-based nanoparticles as well as metallic nanoparticles (Literature Review on Metal Oxide Nanoparticles and Its Applications in Organic Transformations, 2019).

Metal oxide nanoparticles have been chosen as the type of nanoparticles for which property measurements will be investigated in this research project as they are widely used in numerous applications in materials science and as there are several metals that form oxides in nanoparticle form. Metal oxide nanoparticles are used in various applications such as in material sciences, medicine, optoelectronics, fabrication of microelectronics, sensors, fuel cells and piezo-electric devices. These nanoparticles exhibit unique chemical and physical properties due to their high density and limited size of corner/edge on site. Table 1 below lists applications of various types of metal oxide nanoparticles (Literature Review on Metal Oxide Nanoparticles and Its Applications in Organic Transformations, 2019

Type of Metals forming Oxide nanoparticles	Applications
Copper	CuO nanoparticles are used in microwave irradiation processes and as a catalyst in oxidation processes also used in photoconductive and photothermal applications.
Tin	SnO_2 has been used as catalysts, energy saving coatings and as transparent and electrically conductive coatings on glass as well as in magnetic storage devices due to its magnetic properties.
Zinc	ZnO is used as a catalysts in organic reactions and as ‘UV blockers’ in various applications such as solar cells.

Magnesium	MgO is used in chemical industries as a remover of air pollutant gases such as CO_2, NO_x and SO_x
Zirconium	ZrO_2 used as a catalyst and gas sensors.
Cerium	CeO_2 nanoparticles are used as catalysts, electrochemistry and material chemistry.
Titanium	TiO_2 absorbs UV light and reflects all colors in the visible light spectrum and can be used as white pigment in paint. Also used as photocatalyst.
Aluminium	Al_2O_3 nanoparticles are extremely hard and thermally stable therefore it can be used in abrasive materials, bone substitutes, also used in small amounts in antacid medications for heartburn.

Table 1. Applications of various types of metal oxide nanoparticles

2.3 Synthesizing nanoparticles

Naturally occurring nanoparticles can be found in volcanic ash, ocean spray, fine sand/dust and in biological organisms such as viruses/bacteria. However, these natural nanoparticles usually are not useful at all for engineering applications as they come in all sizes, shapes and compositions. Therefore, it is important to 'engineer' or more commonly known as 'synthesize' nanoparticles of the required kind. Nanoparticles are synthesized in chemical laboratories with a lot more control over its physical properties such as size, shape and composition. Nanoparticles can be engineered very simply through chemical reactions alone and this would mean that nanoparticles were engineered throughout history but without knowledge of its particle size.

However, the more advanced methods of nanoparticle synthesis allow fine tuning the numerous required physical properties. This is especially useful to obtain the required properties of nanomaterials for mass manufacturing. Listed below are some of these methods. (Dhand et al. 2015)

Bottom-up methods:

Bottom up methods refers to methods of nanoparticle synthesis where the material is built up atom by atom or molecule by molecule starting from its raw materials leading to self-assembly of the nanoparticles.

- Co-precipitation
- Chemical vapour deposition
- Physical vapour deposition
- Electrolytic deposition
- Sol-gel method
- Microemulsion
- Pyrolysis
- Sputtering
- Plasma arcing

Top-down methods:

Top-down methods indicate that nanoparticles are formed by techniques such as slicing/cutting a larger bulk material into smaller parts until nanoparticles are achieved.

- Photo Lithography
- Electron beam lithography
- Cutting
- Etching
- Grinding

All methods have their own advantages and disadvantages and the most suitable method should be chosen depending on the application, cost requirements and complexity involved. For example, while synthesizing Tin oxide nanoparticles as later described in the report none of the above methods were used, but a simple chemical co-precipitation method and an annealing process was used to produce the SnO_2 nanoparticles.

2.4 Characterization of nanoparticles

Once the nanoparticles are synthesized, it is important to characterize the produced nanoparticles and various techniques exists for this process. Characterization is performed to assess the physical and chemical properties of the nanoparticles and check if they fit the requirements. Since we are interested in measuring thermal and optical properties of nanoparticles, the methods listed below (Mourdikoudis, Pallares and Thanh 2018) are applicable for these purposes:

2.4.1 Scanning Electron Microscope (SEM)

The SEM method is a surface imaging method that is very often used when characterizing nanoparticles as the primary objective is to determine the shape, rough magnified image of a sample and the particle size of the sample. Since particle size can affect thermal/optical properties it is essential to be included as one of the primary characterization techniques. Energy Dispersive X ray method (EDX) can also be used in conjunction with SEM so that the composition and the areas of the sample where the element is present can be accurately found. Both these forms of characterization were done, and more details are shown in the results and discussion section of this report.

In a typical scanning electron microscope, electrons are shot at high speed towards the sample with huge amounts of kinetic energy. The electron beams are focused on a position on the sample using electromagnets. Once these electrons strike the solid sample, the retardation of the electrons results in a signal that is picked up by the SEM that produces the SEM images (SLINTEC, 2016). The produced SEM images will not contain any color due to being formed through electron information, but the images may be artificially colored. SEM images produced are 2 Dimensional, although there is a depth of field effect that may seem to indicate the produced image is 3D although it is not (Microscopy Australia, 2019).

SEM imaging typically makes use of computer software from which different levels of focus and zoom may be achieved so that the morphology and size of the sample can be conveniently observed. The apparatus used in SEM is described in detail later on in this report.

2.4.2 UV-Visible (UV-vis) spectroscopy

A sample is irradiated with electromagnetic waves in ultra-violet and visible ranges and the absorbed light is analyzed. Graphs of either uv-vis absorption or reflection vs wavenumber can be obtained for analysis. It can be used to find the compositions of the sample. Size dependent properties such as peak broadening, shifts in the energy absorption wavelength and band gap energies can be determined from this technique.

2.4.3 Photoluminescence (PL) spectroscopy

In simple terms, a photon is defined as a bundle of electromagnetic energy and are referred to as an elementary particle. Photons are the basic unit which makes up light rays. Some properties of a photon include: zero mass, stable, no electric charge, carry energy and momentum which is dependent on the light frequency, interacts with electrons, are created and destroyed by natural processes, and travel with the speed of light inside a vacuum like medium. Photons are the basic unit that makes up all electromagnetic energy such as microwaves, radio waves, x rays, etc. (Ducksters, 2019).

This characterization technique concerns measuring the light emitted from nanoparticles after they absorb photons. Characterization is performed depending on the parameters such as intensity, wavelength, bandwidth and stability of the emitted light. Again, PL properties may change with the size of nanoparticles further highlighting the importance of SEM in order to make comparisons.

2.4.4 Infrared (FT-IR) spectroscopy

There are several types of Infrared spectroscopy such as Fourier Transform Infrared Spectroscopy (FT-IR), Reflectance infrared spectroscopy, Infrared spectrophotometer and Near Infra-red spectroscopy (NIR) (labcompare, 2019)

The FT-IR equipment emits infrared radiation through a sample where some of the IR waves are absorbed and some transmitted through the sample. The absorbed radiation is converted into rotational and/or vibrational energy by the sample molecules. The produced signal is picked up by a detector and the instrument is able to provide a spectrum representing a molecular fingerprint of the sample. Therefore, FTIR is commonly used as a chemical identification tool (RTI Laboratories, 2019).

FTIR and Reflectance spectroscopy essentially work the same way, however, Reflectance IR spectroscopy is focused on making absorption/reflectance measurements, two common methods exists when measuring reflectance properties

which include measuring specular reflectance and Diffuse reflectance. Table 2 draws comparisons and between specular reflectance and diffuse reflectance (Khoshhesab, 2019).

Specular Reflectance	Diffuse Reflectance
• Incident angle of infrared ray is the same as reflection angle • Occurs when surface is perfectly smooth or polished • External reflection • Spectroscopy of this form is used to evaluate surface coatings, thin films or contaminated metal surfaces	• Infrared rays are scattered upon reflection • Occurs when the incident surface is rough or jagged • External reflection • Spectroscopy of this form is used to evaluate powders and solid samples (as they have rough surfaces)

Table 2. Specular vs Diffuse reflectance

Figure 4 (The Physics Classroom Tutorial, 2019) below illustrates the difference between specular reflection and diffuse reflection. This is important as for the purposes of this research, diffuse reflectance spectroscopy is used as the samples are in powder which have rough surfaces.

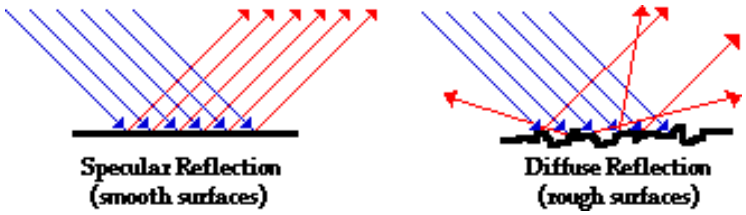

Figure 4. Illustration of Specular and Diffuse reflectance

Waves incident on a solid sample may have both partial specular reflection but majority of the reflection is through diffuse reflectance therefore Diffuse reflectance spectroscopy must be used. When diffuse reflectance spectroscopy is performed using FTIR, the resulting spectra can be described using the 'Kubelka-Munk' function (Khoshhesab, 2019).

2.4.5 Differential scanning calorimetry (DSC)

DSC is a thermal analysis technique where the amount of heat energy required to increase the temperature of a sample can be used to obtain various thermal properties

such as thermal conductivity, melting point, solidification point, and latent heat. A differential scanning calorimeter works by measuring the difference in heat flow rate between a sample and inert reference as a function of time and temperature.

The ‘inert reference’ used in DSC can be simply an empty pan where the sample is placed on a different pan and compared with this reference pan. The pan’s contribution to heat absorption or release is cancelled out as both pans are designed to have identical properties. An Endothermic response occurs when the sample absorbs heat whereas an Exothermic response occurs when the sample releases heat. Examples of Endothermic processes include: Glass transition, Melting, Evaporation/Volatilization, Enthalpic recovery, Polymorphic transitions, and some other thermal decompositions. Various examples of Exothermic processes include: Crystallization, Cure reactions, Polymorphic transitions, Oxidation and decomposition. (TA Instruments, 2019)

The DSC equipment is capable of producing a graph of Heat flow vs Temperature and certain property points at temperatures can be determined by observing the position of peaks on this graph. Endothermic properties/processes are shown by downward peaks on this graph whereas Exothermic properties/processes are shown by upward peaks on the same graph. This effect is shown in figure 4 below.

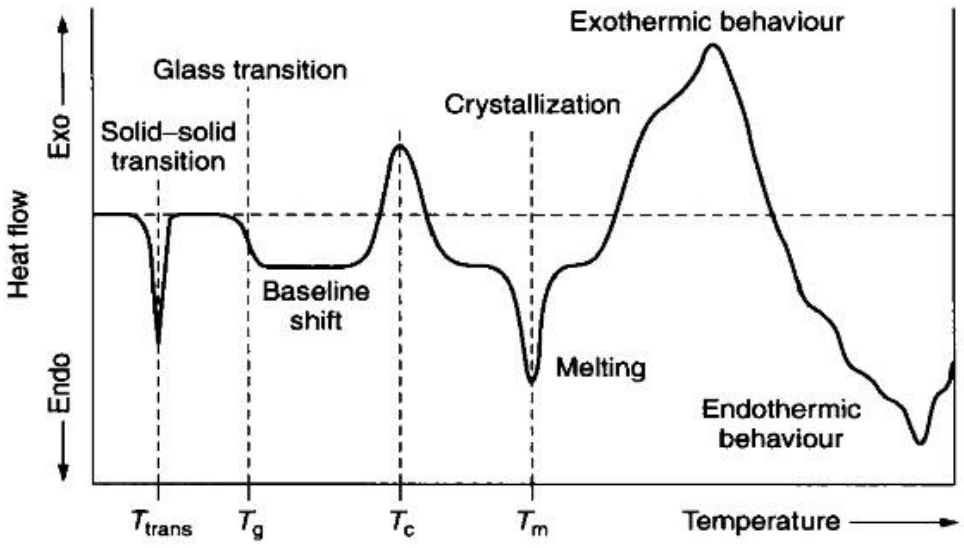

Figure 5. Thermal properties shown by DSC (Pashaie, 2014)

The baseline shift shown in Figure 4 are usually caused by changes in sample weight, heating rate or the Specific heat after undergoing a transition such as curing, crystallization or melting. The sample weight may change during volatilization (vaporization of sample), or decomposition. A good practice to avoid errors caused due to baseline shifts is to weigh the sample before and after running the experiment to determine if weight loss had occurred (TA Instruments, 2014).

While there are several forms of DSC in terms of component arrangement, such as Heat flux DSC, Power Compensated DSC, and Temperature modulated DSC, figure 5 shows the basic arrangement of the major components as used in a Heat Flux DSC.

Heat flux DSC:

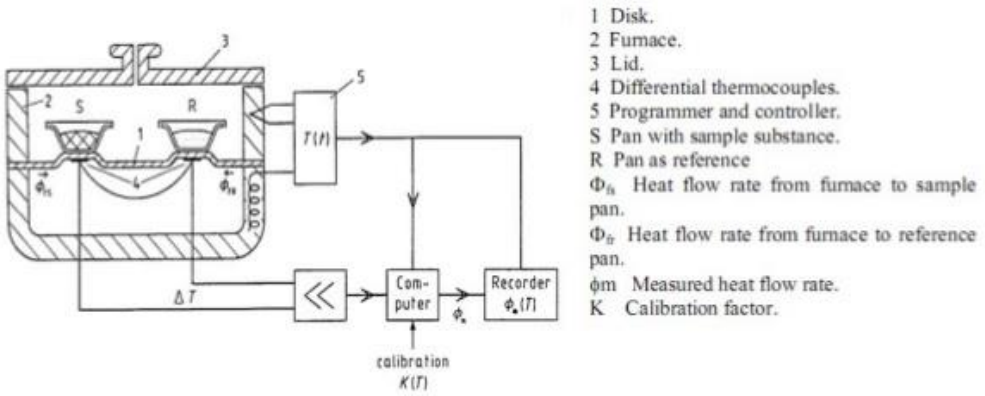

Figure 6. Heat Flux DSC component arrangement (Pashaie,

It can be seen from Figure 5 the arrangement of important components such as the furnace, differential thermocouples, the reference pan and sample pan as well as the thermoelectric disk surrounded by the furnace that helps heating both pans. (Gill, Moghadam and Ranjbar, 2010)

In power-compensated DSC, the sample and reference are maintained at the same temperature heated by two separate furnaces. The thermal power required to maintain the two pans at the same temperature is then plotted as a function of temperature or time.

Temperature-Modulated (TM) DSC is a combination of standard (heat flux DSC) with another form of DSC known as AC calorimetry, a technique that measures the oscillating temperature of a sample that is periodically heated and is thus represented

in an expression using a sinusoid form (Hitachi High-tech, 1993). TM DSC is often preferred for low-temperature field and is used for example to make analysis in the areas of polymers and pharmaceuticals (AZO Materials, 2009). Benefits of this technique include: Ability to better separate and distinguish between superimposed effects at a single frequency as well as accurate Specific heat determination using aluminum as a reference (Mettler-Toledo reserved, 2019).

The following assumptions are needed when performing Heat flux (conventional) DSC experiments:

- The heat flow rate in an empty and perfectly symmetrical twin calorimeter is zero.
- Thermal resistances between sample pan sensor and furnace is the same as the resistance between reference pan sensor and furnace.
- The heat capacity of the pan and sensor for both sample and reference is ignored.
- Measured temperature is taken as the sample temperature
- Negligible heat gain/loss with surroundings.

We may already see from figure 5 that DSC is able to provide scientists with some of the most important thermal properties that need to be measured. The following sections covers detailed descriptions of some of these thermal properties including optical properties of interest in this project.

2.5 Optical properties of interest

This section covers the optical properties that can be measured/calculated from the metal oxide nanoparticle characterization techniques listed in the previous sections. Optical properties of interest for this project are color, photoluminescence and infrared reflectance.

2.5.1 Color

Color measurement of samples is necessary for accurate color determination and communication. Color measurement is required because visual evaluation is subjective for each person and may depend on external factors such as viewing conditions. Spectrophotometers and Colorimeters can be used to accurately state the color of a sample. Measurements made from such devices may consist of color information beyond what is observable by the human eye. Spectrophotometers are more accurate

and more versatile in color measurement compared to colorimeters however are also more expensive, and more complex to operate. Colorimeters cannot be used for complex color analysis and should be used only for comparing similar colors under constant conditions. An example of application for calorimeters is monitor calibration which makes use of a colorimeter (Navigator, 2019).

2.5.2 Photoluminescence

Photoluminescence (PL) is the sudden and random emission of photons (or light) from a material after being excited by incident radiation. PL measurements include the PL emission spectrum showing the intensity of PL emission and is also able to provide information such as crystal defects of semiconductors due to oxygen vacancies.

Simply put, the emission spectrum of a PL experiment would be a graph of PL emission intensity vs wavelength of emitted light. The wavelength of peak photon emission intensity can correspond to a photon energy value which can be used to confirm sample composition. Photon energy values are usually known and the results of PL spectrum can be compared with the known values to identify the sample contents (University of Warwickshire, 2011).

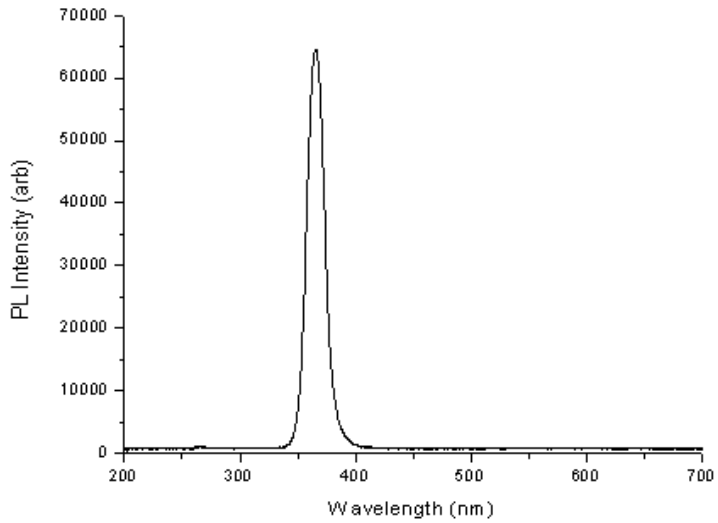

Figure 7. PL spectrum for wurtzite (University of Warwickshire, 2011)

Shown above in Figure 7 is the PL emission spectrum for a sample of wurtzite, a zinc, iron sulfide mineral. The peak intensity occurs at a wavelength of 365nm which corresponds to a photon energy of 3.4 eV (University of Warwickshire, 2011).

The unit eV stands for electron-volt and one eV is equivalent to 1.602 x 10^{-19} joules (Units Wiki, 2019). The conversion between wavelength is performed using the following equation (equation 1) used in quantum mechanics: (UNL, 2019)

$$E = h.c/\lambda \quad (1)$$

Where E is the photon/light energy, h is the Planck constant which is equal to 6.626 × 10^{-34} J·s, c is the speed of light and λ is the wavelength of the photon/light radiation. The value of the speed of light is known to be 3 x 10^{8} m/s. The speed of light is also related to the wavelength and frequency of light through equation 2 shown below, where f is the frequency of light radiation (UNL, 2019).

$$c = \lambda.\, f \quad (2)$$

2.5.3 Infrared reflectance

Infrared reflectance is similar to PL, except the radiation being measured is within a certain wavelength range. The wavelength range for radiation between 700nm to 1mm (between visible red light and microwaves) is considered to be Infra-red radiation.

Infrared reflection spectrum can be used to measure the intensity of infrared waves being reflected for each wavenumber. It can also be used for the identification of organic compounds in the chemical composition of the sample. This is done by comparing the position & shape of peaks (both ups and downs) with previously known data. Known organic compounds usually have IR reflective spectra peaks at known wavelengths (wavenumber, in spectra).

In IR spectrum, the downward peaks (troughs) which are caused by the absorption of IR radiation by chemical bonds can lead to identification of the presence of functional groups or chemical bonds. For example, Figure 8 shows an example IR spectrum obtained for a sample. The bond labelled 3358 (leftmost trough) can be identified as an O-H bond. The spectrum also shows several other bonds that have been identified (Interest, 2019).

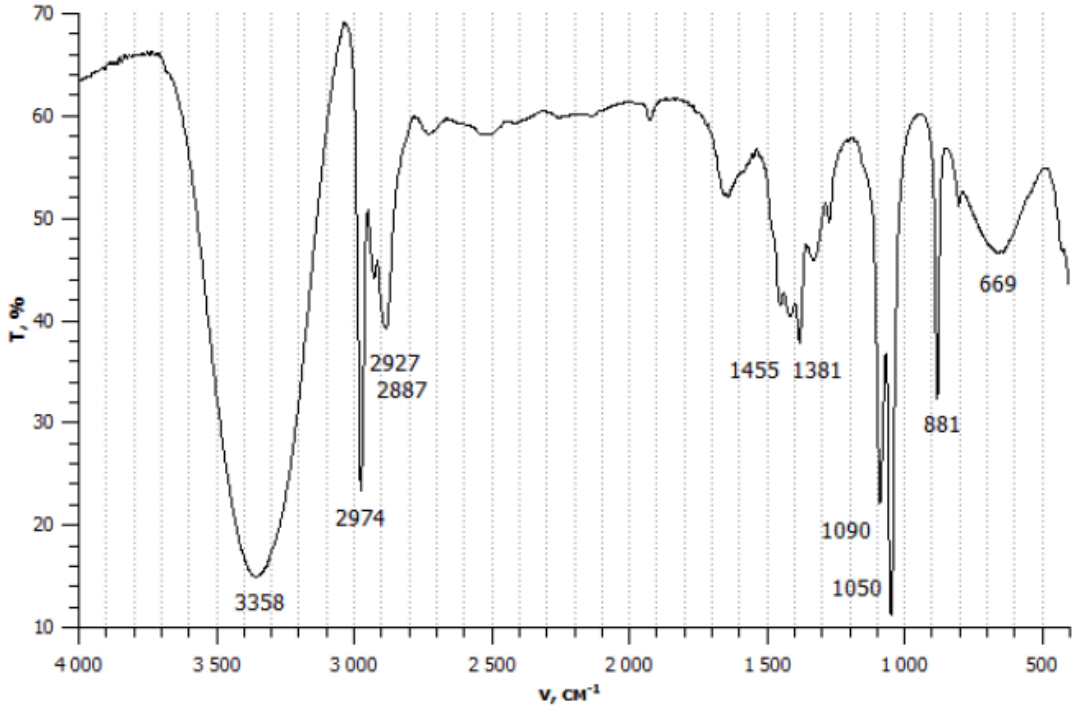

Figure 8. IR spectra with identified bonds (Interest, 2019)

2.6 Thermal properties of interest

This section covers the thermal properties that can be measured/calculated from the metal oxide nanoparticle characterization techniques listed in the previous sections. Thermal properties of interest for this project are Heat Capacity, Thermal Conductivity, Solid Transition temperature, Crystallization temperature, and Melting temperature.

2.6.2 Heat Capacity

Heat capacity is a measurement of the response of a substance to heat addition/rejection. The reason that water is commonly used as a coolant for machinery is because of its high specific heat capacity which translates to being able to absorb high amounts of heat and thus take away larger amounts of heat away from the system (LibreTexts, 2019) Heat capacity is important for nanoparticles also as when used in various applications, the ability to absorb heat without too much temperature rise (high heat capacity) is important for applications such as paint coatings, or surface applications.

The basic unit of heat capacity is J K^{-1} (Joules per kilogram kelvin) and is defined as the heat energy required to increase the temperature of a substance by 1 Kelvin (Difference, 2019).

The following equation 3 can be used to calculate the heat capacity for constant pressure measurements taken by the DSC.

$$C_p = \left(\frac{\Delta H}{\Delta T}\right)_p \quad (3)$$

Where C_p is the constant pressure heat capacity, ΔH is the heat flow, and ΔT is the temperature change in the range for which the above calculated heat capacity is valid. It should be noted that this method in reality is not accurate as the heat capacity changes with temperature as there are elements such as enthalpy and entropy of the sample to consider.

However, for simplicity, it can be seen that the output produced by a DSC experiment provides a graph of Heat flow vs Temperature, and the gradient of this graph can be taken as the Heat Capacity of the sample (O'Neill, 2019)

2.6.3 Thermal Conductivity

The thermal conductivity, k of a material is a measure of a material's ability to transfer or conduct heat. Heat Conduction occurs through molecular excitation and contact with surrounding molecules, there is no bulk movement of particles however. Heat moves from an area of high energy to an area of low thermal energy, or in simpler terms, from an area of high temperature to low temperature. Heat transfer continues until thermal equilibrium is reached between the two points.

Thermal conductivity is calculated through the following equation 4:

$$k = \frac{QL}{A(T_1 - T_2)} \quad (4)$$

Where Q is the heat flow (in watts), L is the length /thickness of the material, A is the surface area of the material, and T_1 and T_2 are two temperature points used to determine the temperature gradient for the portion of the object for which thermal conductivity is measured (Instruments, 2019). The basic units of thermal conductivity are W/m.K (watts per meter kelvin)

A thin film of the nanoparticle sample is needed to be produced in order to measure thermal conductivity and it has been confirmed that Thermal Conductivity cannot be measured through DSC experiments.

2.6.4 Solid Transition temperature

It is the temperature at which crystalline structures of a material changes while still in the solid phase, for example austenitic transition. The transition occurs as the atoms in the solid are not locked in place and can move. It is important to know the solid transition temperature for alloys as several different crystalline structures can be made for various applications. (Rennie, 2014)

2.6.5 Crystallization temperature

Crystallization temperature, T_c is the temperature point at which the molecules of a material transforms into a crystalline structure. It is directly measured through DSC experiments and is observed by an upward peak since it is an exothermic process (Direct, 2019).

2.6.6 Melting temperature

It is simply the temperature at which a substance transitions phase from solid to liquid (or vice-versa). The melting temperature can be identified as a single temperature point from the curve obtained through a DSC experiment, provided the sample indeed melts (Direct, 2019)

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3. Experimental Procedure

The procedure used for Nanoparticle synthesis, SEM, XRD and IR reflectance measurements have been outlined in this section.

3.1 Nanoparticle synthesis

Nanoparticle synthesis was conducted using the following chemicals mixed using chemical co-precipitation.

Stannous Chloride Dihydrate ($SnCl_2.2H_2O$).

Butanol (C_3H_9OH)

Ammonia Hydroxide (NH_4OH)

The exact procedure used for synthesis has been outlined in the procedure section.

3.1.1 Apparatus

The following apparatus was used for nanoparticle synthesis.

- Cylinders
- Beakers
- Muzzle furnace
- Centrifuge
- Magnetic stirrers

Apparatus images are shown below.

Figure 9. Muzzle Furnace

Figure 9. Centrifuge

Figure 10. Rotating part of Centrifuge

Figure 11. Magnetic Stirrer (Sci-Supply, 2019)

3.1.2 Procedure

As mentioned before Co-precipitation method was used for nanoparticle synthesis. Shown below are the steps involved in nanoparticle synthesis.

- 0.503 g of $SnCl_2.2H_2O$ was placed into a clean beaker
- 50ml of butanol was measured and poured into a cylinder
- Butanol and $SnCl_2.2H_2O$ were mixed together
- Performed magnetic stirring
- Poured Ammonia hydroxide into a burette.
- A volume of 5.3ml of Ammonia hydroxide was poured slowly into the solution of $SnCl_2.2H_2O$ and butanol.
- The time taken for ammonia hydroxide addition was measured in order to calculate the flow rate
- Samples were centrifuged, washed dried using distilled water for 3 minutes at 3000 RPM.
- Resulting wet powder was dried at 60℃ for 3 hours.
- Annealing was performed at for 4 hours using the muzzle furnace.
- The sample was stored in Eppendorf tubes

The following conditions were changed in order to affect nanoparticle size and to achieve uniform crystalline structure: Annealing temperature and Flowrate of Ammonia Hydroxide.

The annealing temperature was varied between 400℃ and 700℃ while keeping all other factors constant.

The flowrate of Ammonia Hydroxide was varied by allowing the flow of ammonia hydroxide.

3.2 Scanning Electron Microscope (SEM)

SEM analysis was conducted on each sample in order to determine particle morphology and size.

3.2.1 Apparatus Design

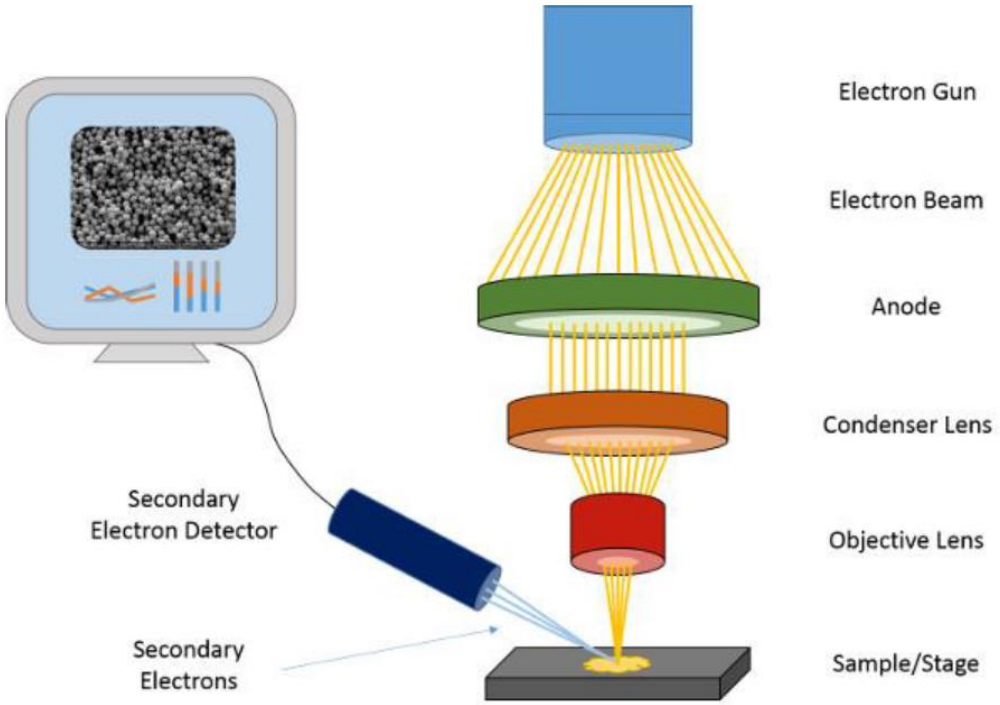

Figure 12. SEM Apparatus (Steckl, 2019)

3.2.2 Procedure

The following procedure was used during SEM analysis:

- Samples were prepared on circular disk films (4 samples on one plate)
- Samples were sputtered with gold nanoparticles (5nm in size) for 15 minutes
- Sample plate was placed and fit inside SEM instrument
- Electron beam was focused on plate
- Zoom level was varied to desired level using computer
- Images were captured using the computer
- The electron beam was focused on the next sample (on the same plate) until all sample images were taken

The sputtering of gold nanoparticles is required in order for the electron beam to interact with a gold nanoparticle to illuminate the sample and obtain clear SEM images (Bhattacharyya, 2018).

3.3 Energy Dispersive X-ray spectroscopy

Performed in conjunction using the SEM equipment

3.4 Infra-red reflectance spectroscopy

Thin films were used to place the sample inside the spectrometer and IR spectra were obtained.

4. Results and Discussion

4.1 Samples

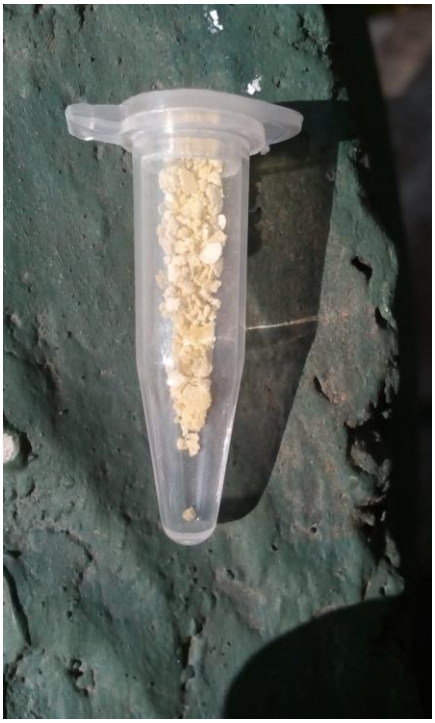

Figure 13. Picture of Sample 1

Figure 14. Picture of Sample 2

Figure 15. Picture of Sample 3

Figure 15. Picture of Samples 4 and 5

4.2 Particle Size

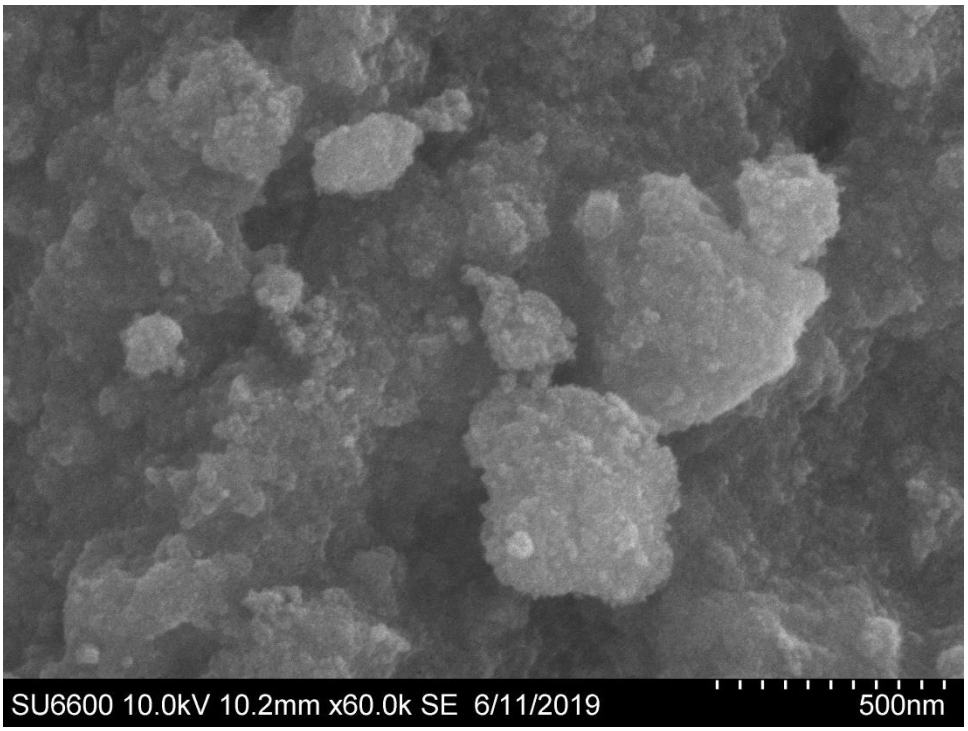

Figure 16. SEM image of Sample 1

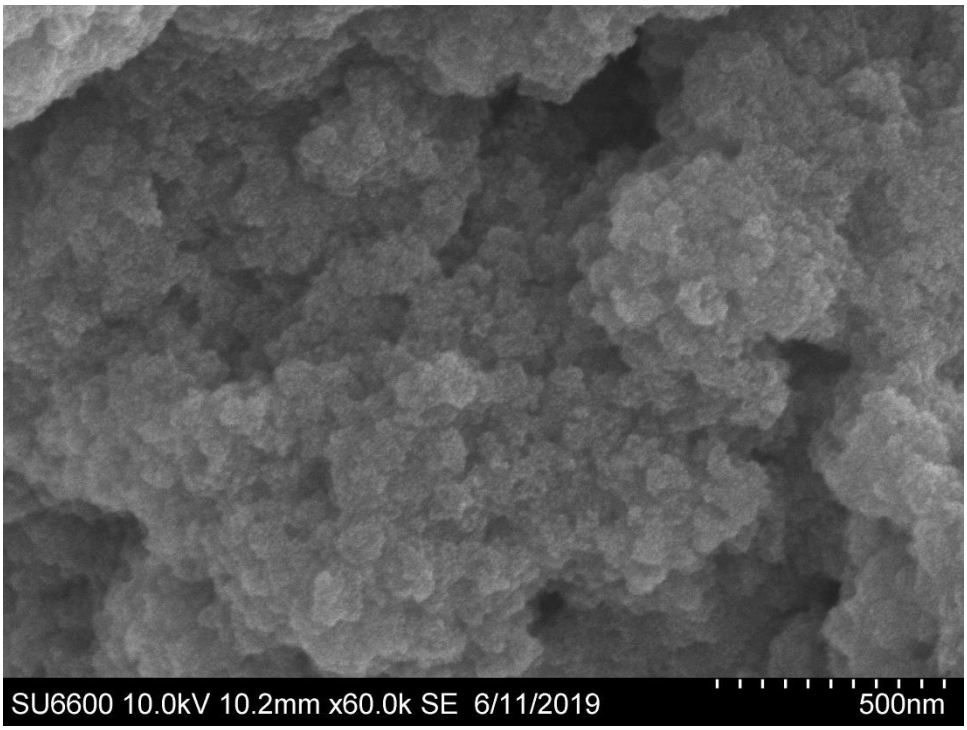

Figure 17. SEM image of Sample 2

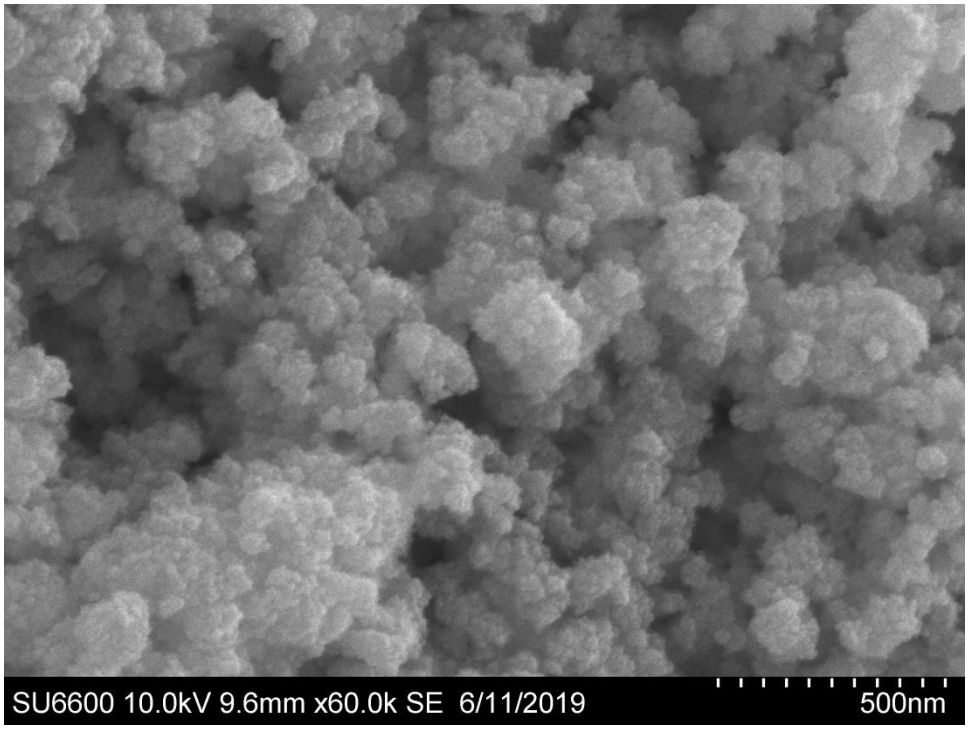

Figure 18. SEM image of Sample 3

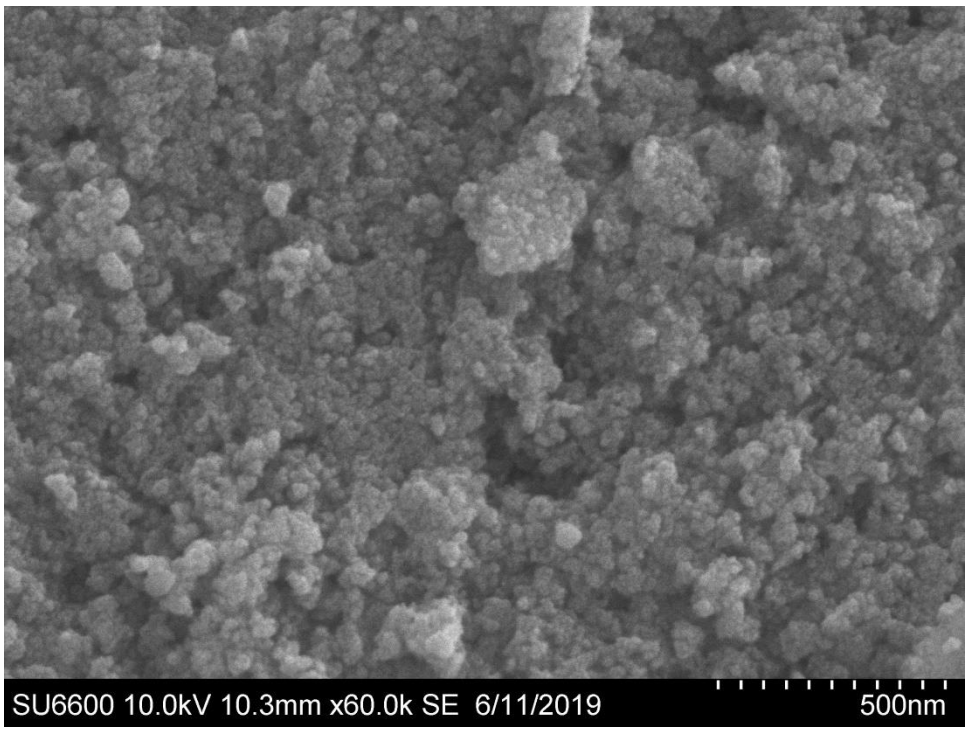

Figure 19. SEM image of Sample 4

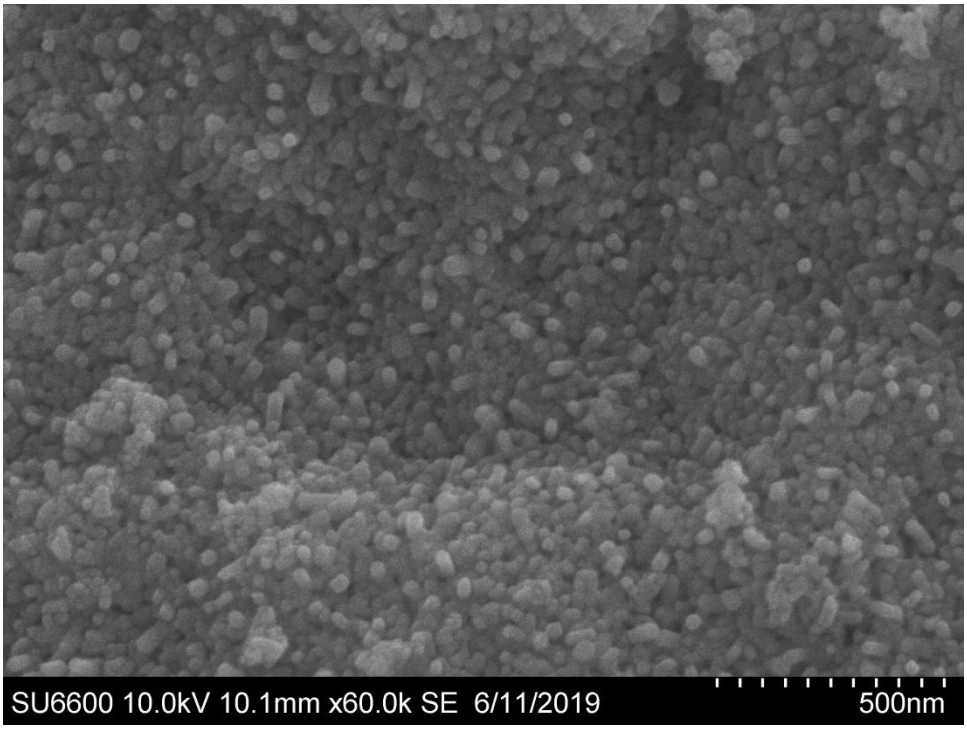

Figure 20. SEM image of Sample 5

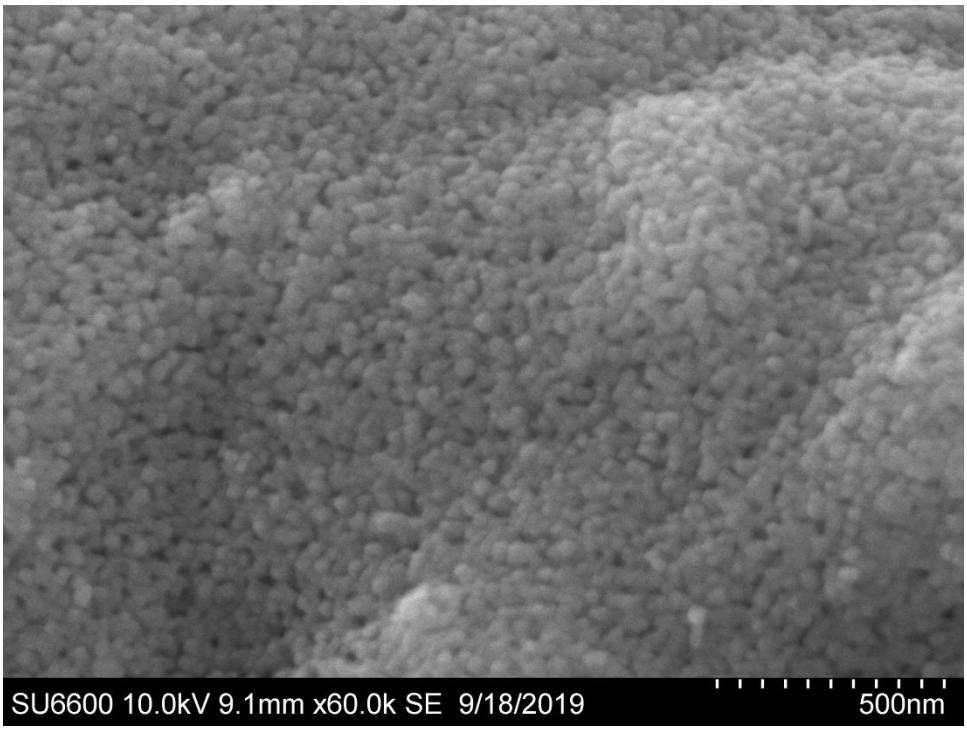

Figure 21. SEM image of Sample 6

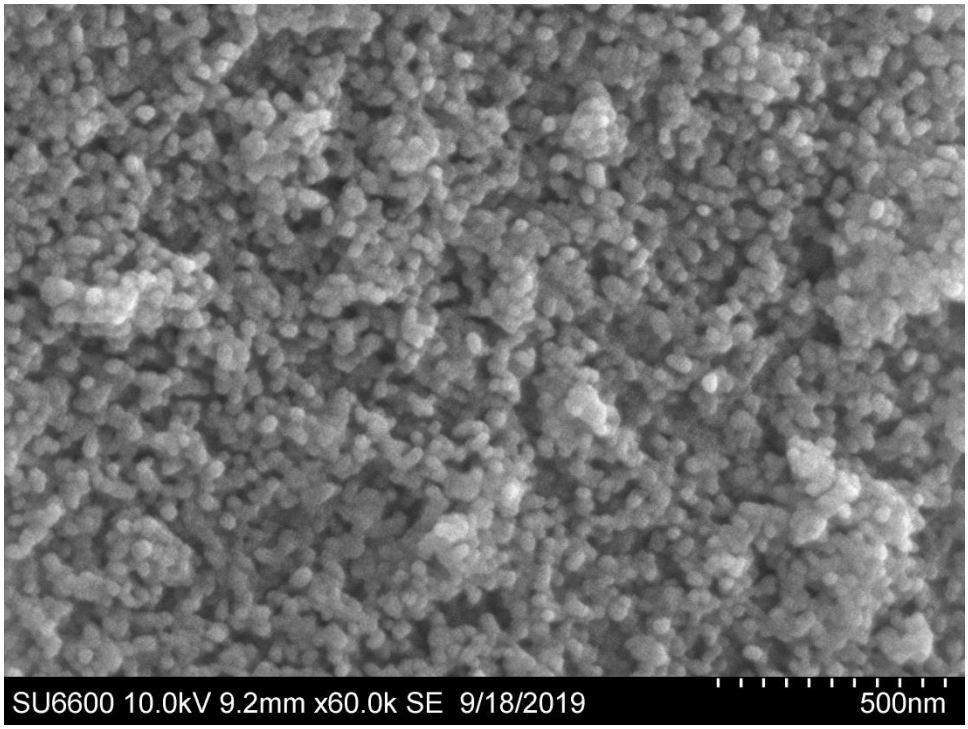

Figure 22. SEM image of Sample 7

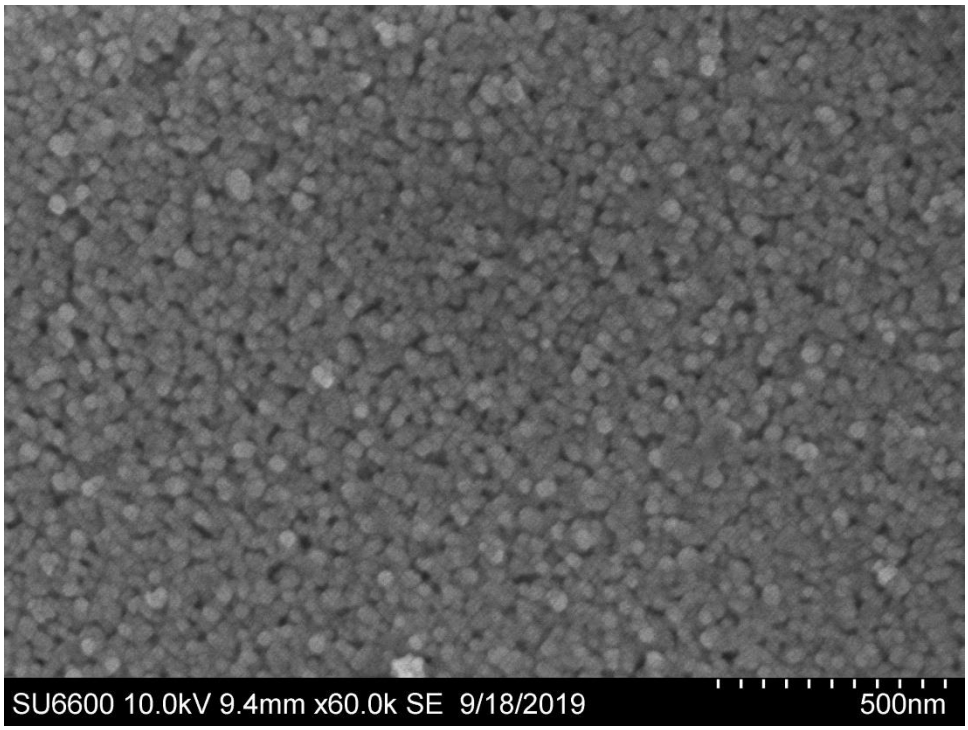

Figure 23. SEM image of Sample 8

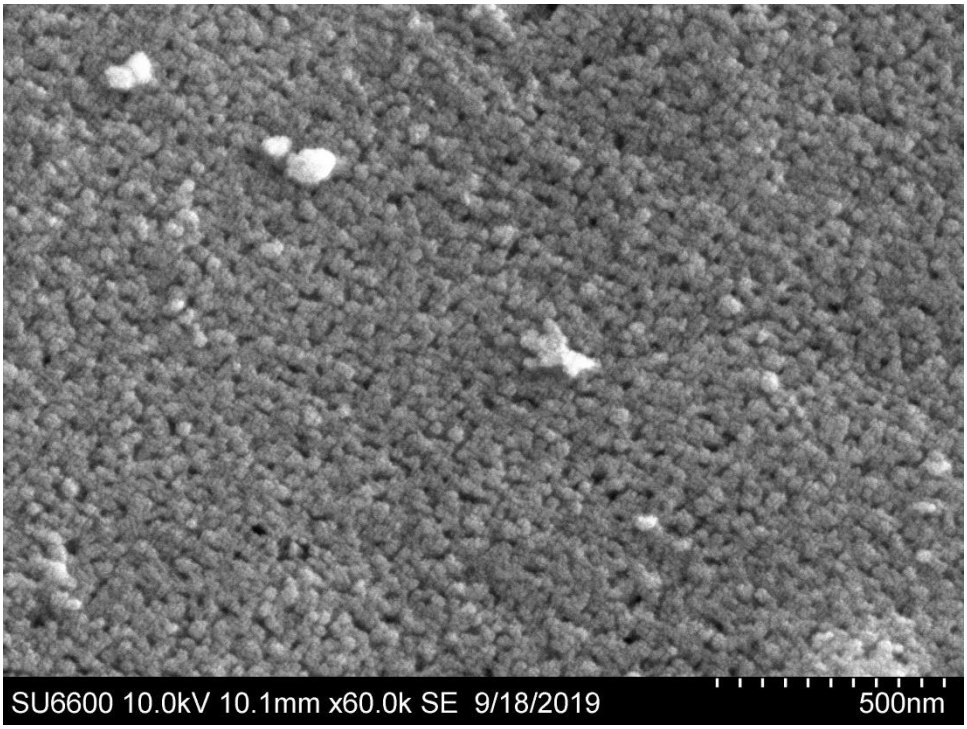

Figure 24. SEM image of Sample 9

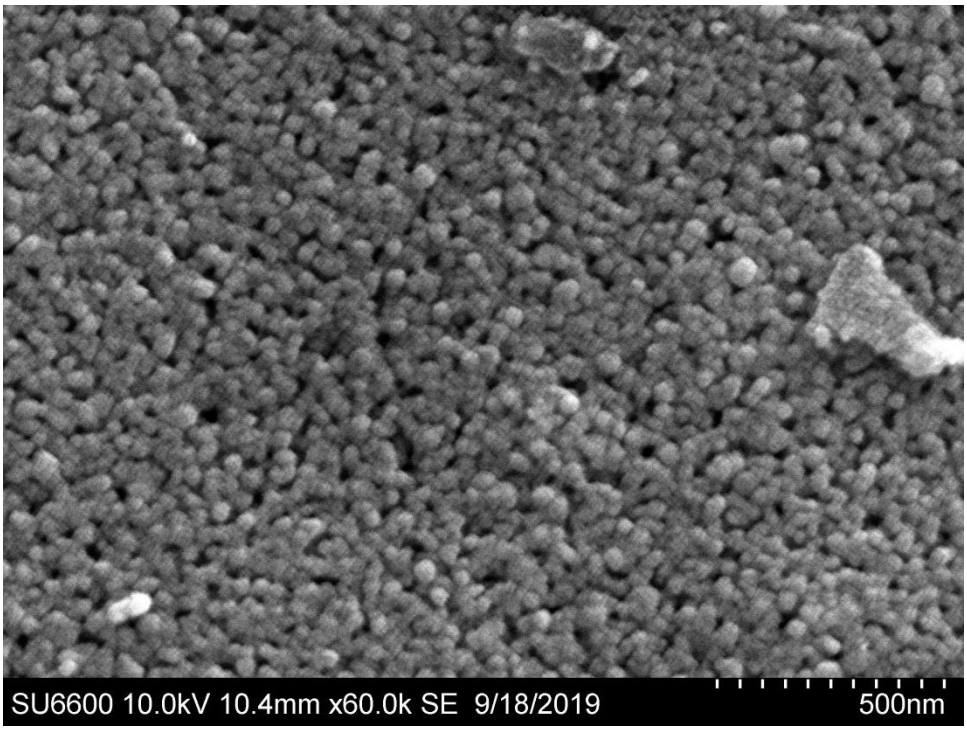

Figure 25. SEM image of Sample 10

4.2.1 Summary of Particle size results

The summary of the nanoparticle sizes obtained are as shown in table 3 below.

Sample no.	Varied condition during synthesis	Particle size	Uniform size & crystalline structure?
1	None (test)	<10 nm	No
2	Flowrate	<10 nm	No
3	Flowrate	<10 nm	No
4	Flowrate	<10 nm	No
5	Annealing temperature	50nm	Uniform size, non-crystalline
6	Annealing temperature	50nm	Yes
7	Flow rate	50nm	Yes
8	Annealing temperature	50nm	Yes
9	Annealing temperature	50nm	Yes
10	Flowrate	50nm	Yes

Table 3. Summary of Particle size

4.3 Sample purity

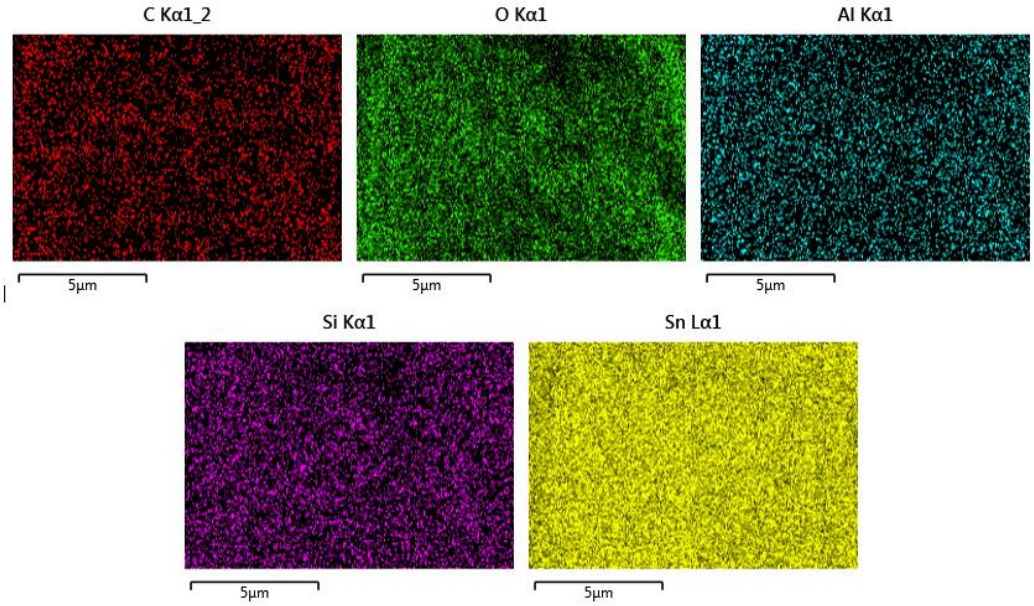

Figure 26. EDX sample composition

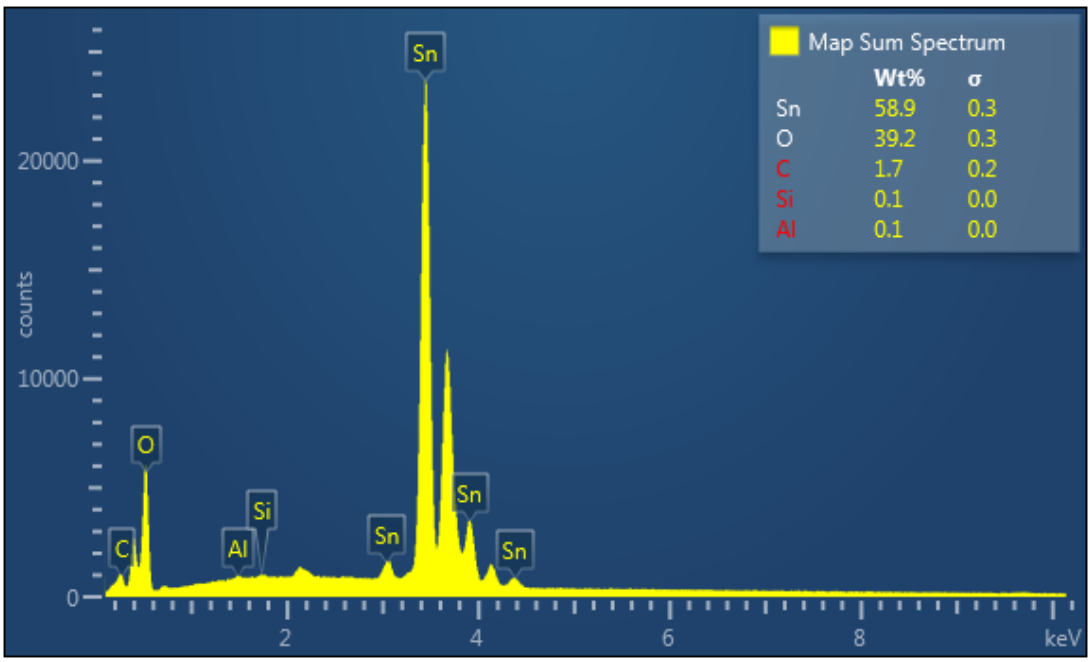

Figure 27. EDX Map Sum Spectrum

As can be seen from figures 26 and 27, the purity of the Tin oxide nanoparticle sample has been confirmed and no significant impurities have been found. The presence of Carbon, Silicon, and Aluminum impurities in small percentages may have occurred due to the synthesis environment not being perfectly clean, or the sample could have been exposed to these contents when in contact with air.

4.4 Specific heat capacity

In simple terms, DSC measures the energy absorbed and released by a sample as it is heated and cooled.

The DSC experiment was not conducted as the instrument available at SLINTEC laboratory was capable of performing DSC for the temperature range of -60 to 300 Celsius.

4.5 IR reflectance

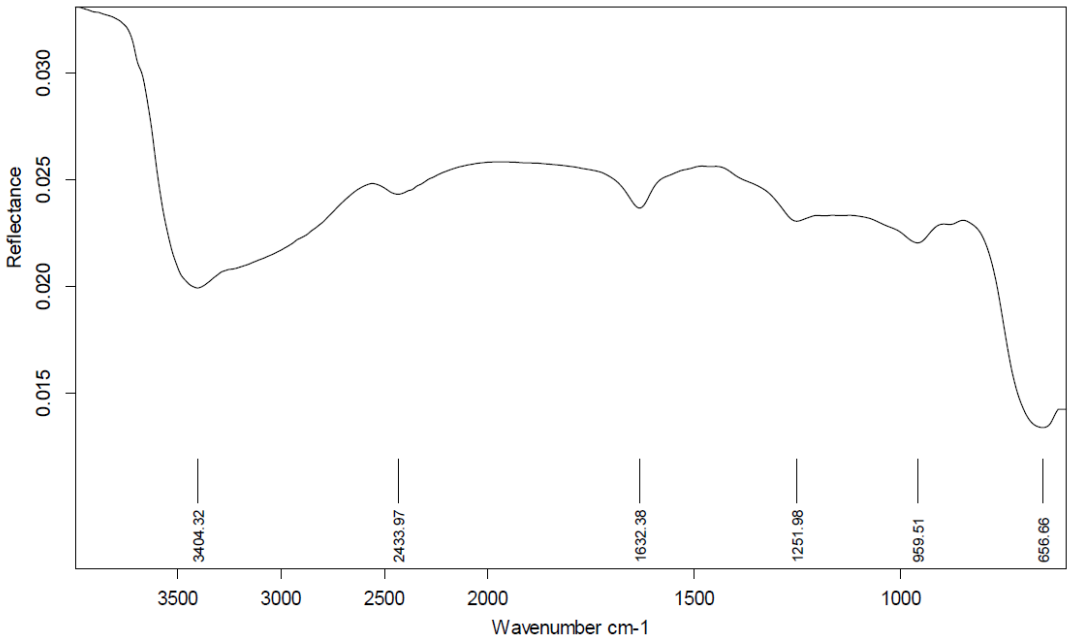

Figure 28. IR spectra for sample 1

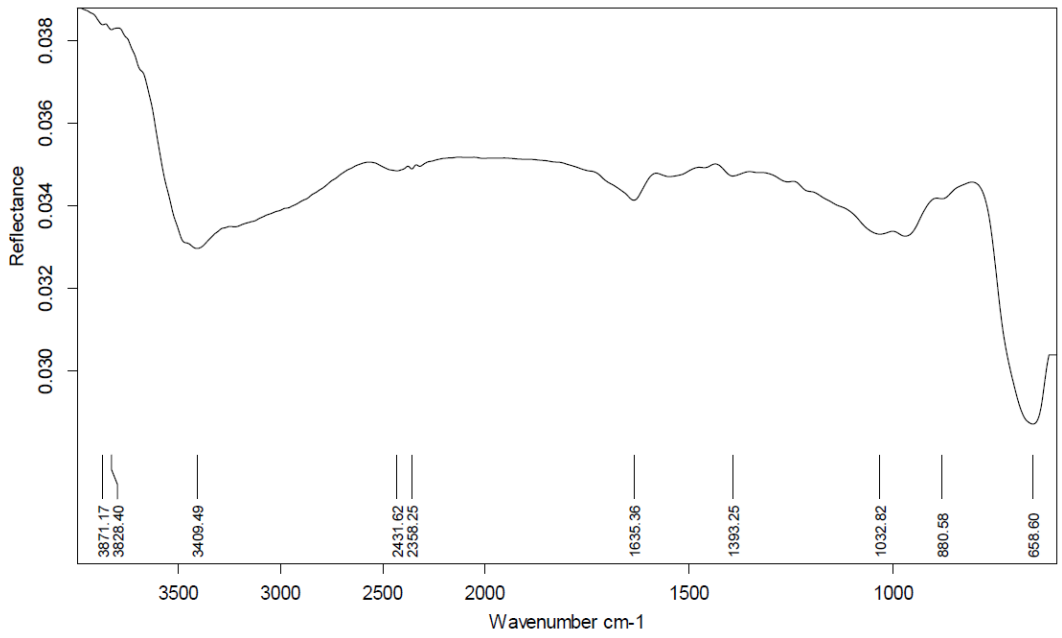

Figure 29. IR spectra for sample 2

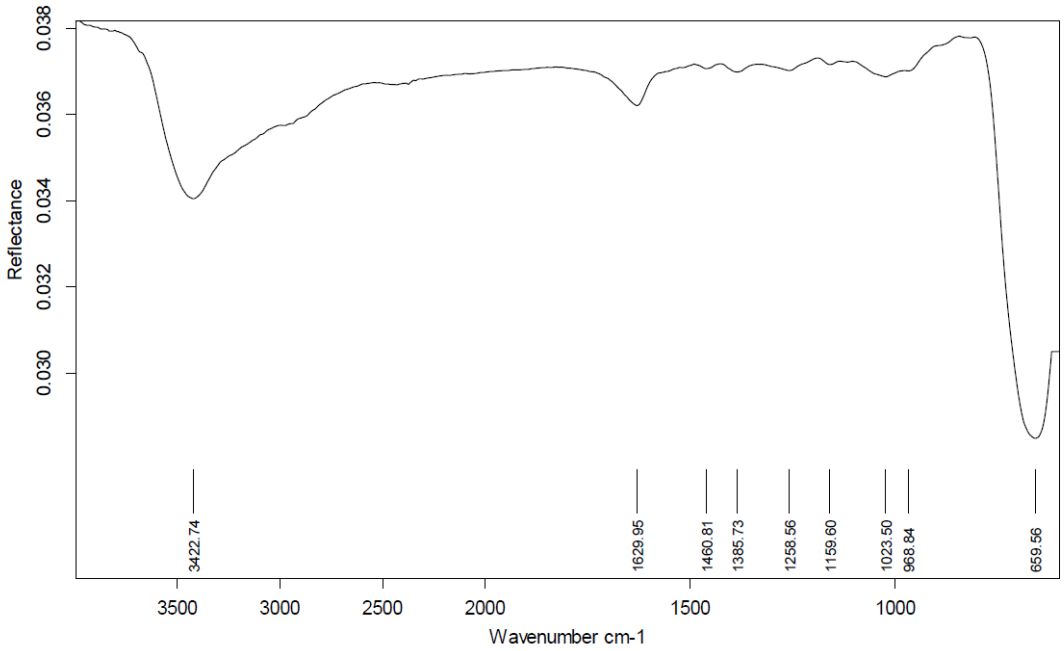

Figure 30. IR spectra for sample 3

Figure 31. IR spectra for sample 4

The IR spectrum achieved for samples 1-4 as shown in figures 28-31, respectively, show that roughly 2.5 % of incident Infrared waves are reflected by the Tin oxide nanoparticles. Which is perhaps not enough for applications such as paint coatings where in order to avoid heat gain into the building, the sample should reflect a higher IR wave intensity (percentage). Particle sizes of 400-500nm are expected to show better IR wave reflection.

5. Conclusion

The project has successfully achieved its goals of measuring and documenting the methods used for thermal and optical property measurements.

Several techniques such as Differential Scanning Calorimeter (DSC) experiments and UV-Visible spectroscopy were not conducted due to limitations and difficulties faced during the project. The inability to perform DSC experiments meant that none of the thermal properties could be measured which was significant for this project.

However, both methods that were not performed were documented in the literature review and results section, and this information can act as a guide for new scientists and engineers when dealing with nanomaterial selection after making property comparisons for various applications.

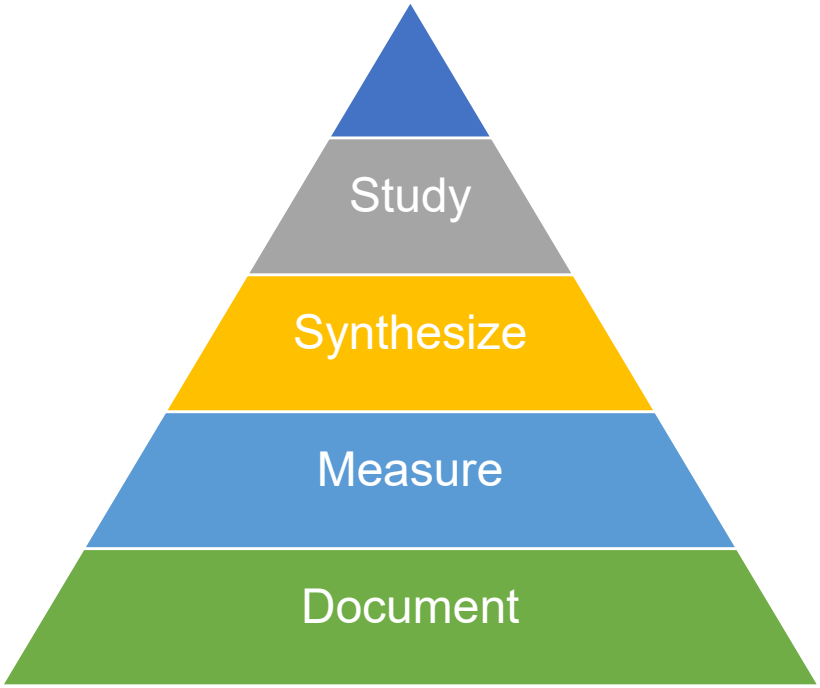

Figure 32. Goals of this project

As can be seen from the diagram above, the goals of this project were to study about nanoparticles, synthesize nanoparticles, measure certain properties and document the methods used to measure properties (that I could not be physically measure). All of these goals have been achieved and this research project can act as a quick guide for scientists and engineers involved with nanomaterial selection who need to make property measurements.

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6. Future Work

The following work can be done to extend the work done in this project:

Conduct DSC and UV-Vis spectroscopy.

Conducting DSC allows a lot more thermal property information to be gathered which will no doubt be useful as information to be included in this guide.

Synthesize a different metal oxide nanoparticle sample and try to achieve similar particle size and compare the property measurements with those obtained for Tin oxide in this project. Doing this will allow us to observer how different materials have different properties which is a criterion used in nanomaterial selection. Similarities and differences between two materials can be made further illustrating the point of measuring nanoparticle properties.

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