Chapter 2

SYNTHESIS OF NANOPARTICLES, PREPARATION OF SAMPLES, CHARACTERIZATION TOOLS

In this chapter, we provide a discussion of the different synthesis techniques, the main synthesis method for the experiments used in the present work, and a description of the experimental procedures used for the characterization studies. It is better to understand the synthesis method used to grow the nanostructures and improve upon the precision and control we can exert over the entire range of material systems currently being researched.

2.1. SYNTHESIS TECHNIQUES

Till now, many methods have been developed to synthesize metal oxide nanostructures. Basically, they can be described as two different types: the “top-down” approaches and the “bottom-up” approaches. These two approaches developed to synthesize metal oxide.

The following objectives are considered as important while choosing technique, they are

i) The method should be reproducible,
ii) The method should produce mono dispersed nanoparticles,
iii) The surface of the particle should be defect free and
iv) The should be economical, scalable, and environment friendly.

2.1.1 Top-down Approach

This approach involves in breaking down of bulk material into nanosized structure and particle. This involves the slicing or successive cutting of bulk materials to get nanosized particle or to produce their desired structure with appropriate
properties. This technique is quite useful to produce nanosized particles on a large scale by using mechanical force. Few method under this approach are

i. Ball milling,
ii. Photo lithoigraphy,
iii. Anodizing and
iv. Plasma etching etc.

2.2 BOTTOM UP APPROACH

It involves more effective buildup of a material from the bottom: atom by atom, molecule by molecule or cluster by cluster. The major advantages of the bottom up approach lie in the production of nanostructures with less defects, more homogenous chemical composition, better control of size and shape etc. In the bottom-up approach, nano components are made from precursors in the liquid, solid, or gas phase employing either chemical or physical deposition processes that are integrated into building blocks within the final material structure. Most of the methods in bottom up synthesis are classified into liquid phase and Vapour phase synthesis. Self-assembly Brenner etal (1988) is generally regarded as the most promising means for designing and controlling the bottom-up assembly of nanometer-scale objects into structures such as sheets, tubes, wires, nanoelectronic devices and drug delivery systems. Scheme of top down and bottom up approaches for the synthesis of nano particles are shown in Figure 2.1.

![Figure 2.1 : Scheme of top down and bottom up approaches](image-url)
2.2.1 Vapour Phase Synthesis

These methods are simple, inexpensive, and operate continuously with high product yield for the fabrication of nano particles in vacuum under elevated temperatures. Some methods are

a) Physical vapour deposition

In physical vapour deposition process, vapour is created and it is deposited on a deposition substrate through a physical manner. The three most important techniques for metal oxide deposition are thermal evaporation, sputtering, and pulsed laser deposition. Each of these will be described below, but they share in common that the source material is the same as the intended depositing material and no chemical reactions occur throughout the process.

b) Thermal Evaporation Technique

Thermal evaporation is one of the most common and simple techniques of forming II-VI nanomaterials. During a basic thermal evaporation process, the substrate and source materials are placed inside a vacuum chamber. This vacuum can reach pressures as low as $10^{-9}$ torr (an ultra-high vacuum). A heating source is used to heat the source material to its vapour point or above. The condensed or powder source material is vapourized at elevated temperatures and then the resultant vapour phase(s) condenses under certain conditions (temperature, pressure, atmosphere, etc) to form a desired product along the substrate in the cooler area of the vacuum chamber.

c) Sputtering

Sputtering is a physical process whereby atoms in a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions. The ions for the sputtering process are supplied by induced plasma. A variety of specific sputtering techniques are used to modify the properties of this plasma, and thus achieve different sputtering conditions, including direct current (DC), radio-
frequency (RF), magnetron (which utilizes magnetic fields), focused ion-beam, and application of a bias voltage to the target.

d) Chemical Vapour Deposition Methods

In chemical vapour deposition (CVD) process one or more volatile precursors chemically react and/or decompose on the substrate surface to produce the desired nanomaterials. CVD processes differ from PVD in that a chemical reaction is necessary in creating the desired stoichiometry in CVD whereas in PVD the desired stoichiometry is similar to the source material. Frequently, volatile by products of the chemical reaction are produced.

2.2.2 Liquid Phase synthesis

It entails a wet chemistry route. The particle formation mechanism is the same as in the vapour phase process. While in the typically gas condensation it is not easy to control grain size and crystal shape, and furthermore its product yield is low, the wet chemistry route provide reasonable control over growth by utilizing organic ligands that act as growth confining agents. Some famous methods are colloidal chemical method, electro deposition method, sol-gel process, reversed micelles, chemical bath deposition, Hydro thermal, solvothermal and microwave irradiation technique etc.

a) Colloidal chemical method

The most common approach to the synthesis of colloidal quantum dots (QDs) is the controlled nucleation and growth of particles in a solution of chemical precursors containing the metal and the anion sources (controlled arrested precipitation). The technique of forming monodisperse colloids is very old. A common method for II-VI colloidal QD formation is to rapidly inject a solution of chemical reagents containing the group II and VI species into hot and vigorously stirred solvent containing molecules that can coordinate with the surface of the precipitated QD particles Chuskin et al (2003). Consequently, a large number of
nucleation centers are initially formed, and the coordinating ligands in the hot solvent prevent or limit particle growth via Ostwald ripening (the growth of larger particles at the expense of smaller particles to minimize the higher surface free energy associated with smaller particles).

b) Electro deposition

Electro deposition is commonly applied to generate a coating, typically metallic, on a surface by the action of reduction at the cathode. The substrate should be coated is used as a cathode and immersed into a salt solution which contains metallic ions to be deposited. The cathode attracts metallic ions under the influence of an electric field while reaching the surface of cathode, it reduced to metallic form.

c) Sol-Gel Techniques

Sol-Gel techniques incorporate the creation of inorganic networks through the formation of a colloidal suspension in a liquid (sol) and gelation of the solution to form a network in a continuous liquid phase (gel). Precursors for creating these colloids are metal/metalloid surrounded by various reactive ligands. A catalyst is used to start reaction and control pH. Sol-gel formation occurs in four stages. Hydrolysis; Condensation; Growth of particles and Agglomeration of particles.

The sol-gel process allows the fabrication of materials with a large variety of properties: ultra-fine powders, monolithic ceramics and glasses, ceramic fibers, inorganic membranes, thin film coatings and aerogels.

d) Chemical bath deposition

Chemical bath deposition (CBD) (Oberian et al 1998; Koaol et al 2014; Anuar kassim et al 2011) is one of the solution phase methods useful for the preparation of compound semiconductors from aqueous solutions. It does not require high voltage equipment, works at room temperature, and hence it is inexpensive. The
only requirement for this deposition route is an aqueous solution consisting of a few common chemicals and a substrate for the film to be deposited.

e) Solvothermal method

Solvothermal synthesis of nanoparticles provides precise control over the size, shape distribution, and crystallinity the crystallization process. The reaction process is conducted above the boiling point of the solvent and internal autogeneous pressure, and involves a hot solvent within an autoclave (sealed vessel). The process is called hydrothermal synthesis when the solvent is water.

2.3 Preparation of Pure and Ru doped Ti_{(1-x)}Sn_{x}O_{2}

Many of the above methods typically entail multiple steps involving reflux with strong acids combined with ultrasonication that take long hours or even days followed by chemical reduction of the precursor metal salts. Moreover, these methods often lack good control of particle size and morphology and large amounts of materials and energy are used. Only a few reports provide simple, efficient routes for uniform dispersion. Therefore, any new synthesis technique that helps to save time would be extremely beneficial because it would allow scientists to perform more experiments within a shorter time and testing new theories and processes could be done much faster allowing more time to expand scientific creativity Wang et al (2005). Recently, a microwave-assisted method has been widely applied in chemical reactions and synthesis of nanomaterials (Chen et al 2004; Xu et al 2007). Research has shown the method to be an attractive choice to promote reactions and is energy effective heating compared to conventional heat conduction methods (such as an oil bath) due to the direct heating of the reaction mixture Nucher et al (2004). By conventional methods, the vessel is heated and this then transfers the heat by convection. Microwave heating is more efficient in terms of the energy used, produces higher temperature homogeneity, and is considerably more rapid than conventional heat sources.
Microwave heating is a transfer of electromagnetic energy to thermal energy, and is an energy conversion phenomenon rather than the heat transfer. The electric component Stass et al (2000) of an electromagnetic field causes heating by two main mechanisms, dipolar polarization mechanism and conduction mechanism. In polarization mechanism; for a substance to generate heat when irradiated with microwaves it must possess a dipole moment, as in water molecule. A dipole is sensitive to external electric fields and will attempt to align itself with the field by rotation. The applied field provides the energy for this rotation Whittaker et al (2004). As molecules vainly attempt to follow the field, they collide with one another and heating in the sample is observed. High- and low-frequency radiation does not give rise to efficient heating: in the first case, the field oscillates too quickly for the molecules to respond; in the second case, the molecules follow the field so well that there is no random motion generated Lidstrom et al (2001). The conduction mechanism is a much stronger interaction than the dipolar mechanism with regard to the heat-generating capacity Das et al (2009). In this case, any mobile charge carriers (electrons, ions, etc.) move relatively easily through the material under the influence of the microwave’s electric field. These induced currents will cause heating in the sample due to any electrical resistance. If the sample is a metallic conductor, most of the microwave energy is reflected with relatively little energy penetrating beyond a few microns into the surface.

Microwave energy is a spectrum in the same way as visible light, infrared irradiation, and UV irradiation and is delivered directly to the material through molecular interaction with the electromagnetic field. Since microwaves can penetrate the material and supply energy, heat can be generated throughout the volume of the material resulting in volumetric heating Perreux et al (2001). Additionally, the method shows acceleration in reaction rate, yield improvement, short reaction time, small particle size, narrow particle size distribution, high purity materials, and enhanced physicochemical properties (Lewis et al 1992; Shibata et al 1996). Because of these reasons, in our present study. For the first time, we made an attempt to prepare pure
and Ruthenium doped alloyed $\text{Ti}_{(1-x)}\text{Sn}_x\text{O}_2$ nanoparticles via microwave assisted solvothermal process.

2.4 EXPERIMENTAL DETAILS

2.4.1 Materials Used

Analytical reagent (AR) grade titanium tetra chloride ($\text{TiCl}_4$), stannous chloride ($\text{SnCl}_2$), urea ($\text{CO\ (NH}_2\text{)}_2$) were purchased from Sigma-Aldrich. Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) was purchased from Central Drug House (P) Ltd. These chemicals were used without additional purification for the preparation of $\text{Ti}_{(1-x)}\text{Sn}_x\text{O}_2$ nanoparticles where $x=0.0, 0.25, 0.50, 0.75$ and $1.0$. Acetone ($\text{(CH}_3\text{)}_2\text{CO}$) and double distilled water were purchased from Merck India Ltd., which was used to remove any unreacted reactants and unwanted organic byproducts present in the synthesized nanocrystalline materials.

In a typical synthesis procedure for preparation of $\text{Ti}_{(1-x)}\text{Sn}_x\text{O}_2$ (where $x = 0.0$) nanoparticles, 0.6 M $\text{CO(NH}_2\text{)}_2$ was dissolved in 50 ml ethylene glycol under vigorous stirring condition for 1 h at room temperature. Subsequently 0.2 M $\text{TiCl}_4$ solution was added in 50 ml ethylene glycol and then added slowly into the above solution. This stack solution was stirred for another 1 h at 60 °C temperature to get a clear and deep blue in colour solution. The mixed solution was transferred into a microwave container (porcelain bowl) and kept in a domestic microwave oven (LG model number LG MH2046HB operated with frequency 2.45 GHz and power 800W). Microwave irradiation was carried out at 50% of maximum power in the air about 5 min. The resultant precipitate was collected, centrifuged and washed several times with double distilled water and acetone before drying in a heating oven at 60 °C for 10 h. The final product was weighed accurately and collected as the yield. In order to prepare $\text{Ti}_{0.75}\text{Sn}_{0.25}\text{O}_2$ (where $x = 0.25$), $\text{Ti}_{0.50}\text{Sn}_{0.50}\text{O}_2$ (where $x = 0.50$), $\text{Ti}_{0.25}\text{Sn}_{0.75}\text{O}_2$ (where $x = 0.75$) and $\text{SnO}_2$ (where $x = 1.0$) the corresponding molarity of $\text{TiCl}_4$ reactant was replaced by the $\text{SnCl}_2$ precursor. The formula used to estimate the required amount of substance is given below:
\[
\text{Required substance} = \frac{M \times X \times V}{1000} \quad \text{(in gram units),}
\]

(2.1)

Where \(M\) is the molecular weight of the substance,

\(X\) is the concentration in molar units and

\(V\) is the volume of solution (in Ethylene glycol).

The amounts of precursor materials taken are given in Table 2.1. 5 mole \% ruthenium doped \(\text{Ti}_{(1-x)}\text{Sn}_x\text{O}_2\) samples were prepared by adding weighed amount of \(\text{RuCl}_2\) in the stack solution separately. Photograph of as prepared samples are shown in Figure 2.2.
Table 2.1: The quantity of precursor materials, mass of reactants, mass of product and the yield percentage of synthesized pure and Ru doped Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) nanoparticles

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Amount of precursors</th>
<th>*Mass of reactants</th>
<th>Mass of products</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>TiCl(_4) (ml) 2.19</td>
<td>SnCl(_2) (g) 3.604</td>
<td>G 7.398</td>
<td>g 3.135</td>
</tr>
<tr>
<td>Ti(<em>{0.75})Sn(</em>{0.25})O(_2)</td>
<td>TiCl(_4) (ml) 1.64</td>
<td>SnCl(_2) (g) 0.948</td>
<td>G 7.397</td>
<td>g 3.842</td>
</tr>
<tr>
<td>Ti(<em>{0.50})Sn(</em>{0.50})O(_2)</td>
<td>TiCl(_4) (ml) 1.10</td>
<td>SnCl(_2) (g) 1.896</td>
<td>G 7.397</td>
<td>g 4.015</td>
</tr>
<tr>
<td>Ti(<em>{0.25})Sn(</em>{0.75})O(_2)</td>
<td>TiCl(_4) (ml) 0.55</td>
<td>SnCl(_2) (g) 2.844</td>
<td>G 7.396</td>
<td>g 3.263</td>
</tr>
<tr>
<td>SnO(_2)</td>
<td>— SnCl(_2) (g) 3.792</td>
<td>CO(NH(_2))(_2) (g) 3.604</td>
<td>G 7.396</td>
<td>g 3.619</td>
</tr>
<tr>
<td>Ru doped TiO(_2)</td>
<td>TiCl(_4) (ml) 2.19</td>
<td>SnCl(_2) (g) 3.604</td>
<td>RuCl(_3) (g) 0.346</td>
<td>G 7.744</td>
</tr>
<tr>
<td>Ru doped Ti(<em>{0.75})Sn(</em>{0.25})O(_2)</td>
<td>TiCl(_4) (ml) 1.64</td>
<td>SnCl(_2) (g) 0.948</td>
<td>RuCl(_3) (g) 0.346</td>
<td>G 7.743</td>
</tr>
<tr>
<td>Ru doped Ti(<em>{0.50})Sn(</em>{0.50})O(_2)</td>
<td>TiCl(_4) (ml) 1.10</td>
<td>SnCl(_2) (g) 1.896</td>
<td>RuCl(_3) (g) 0.346</td>
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<td>G 7.742</td>
</tr>
<tr>
<td>Ru doped SnO(_2)</td>
<td>— SnCl(_2) (g) 3.792</td>
<td>CO(NH(_2))(_2) (g) 3.604</td>
<td>RuCl(_3) (g) 0.346</td>
<td>G 7.742</td>
</tr>
</tbody>
</table>
2.5 CHARACTERIZATION TECHNIQUES

Characterization includes powder X-ray diffraction (PXRD) measurements, Scanning electron microscopy (SEM) measurements, Transmission electron microscopy (TEM) measurements, Energy dispersive X-ray absorption (EDAX) analysis, optical measurements, Photoluminescence measurements and electrical measurements.

2.5.1 XRD analysis

XRD is versatile, non-destructive method that reveal detailed information about the chemical composition, crystallographic and micro structure of all types of natural and
manufactured materials. A beam of x-rays is sent into the sample and the way the beam is scattered by the atoms in the path of the x-ray is studied. The scattered x-rays constructively interfere with each other. This interference can be looked at using Bragg’s Law to determine various characteristics of the crystal or polycrystalline material. The characteristic set of d-spacing and their intensity generated in a typical X-ray scan provide ample information. When properly interpreted, by comparison with standard reference patterns and measurements, this “finger print ” allows for identification of the material. Presence of an amorphous material in the sample can be determined by occurrence of wide halo on diffraction pattern. From the X-ray powder diffraction data we can get the angle of scattering and the corresponding intensities of diffracted beams for each reflection. Lattice parameters can be obtained from this data.

In order to confirm the material of the grown crystals and to determine the particle size, powder X-ray diffraction (PXRD) data were collected for all the ten nanocrystals prepared using an automated x-ray powder diffractometer (PANalytical ) in the 2θ range of 20-80° with CuKα radiation (\(\lambda = 1.54056 \, \text{Å}\)).

Indexing a PXRD pattern consists of the assignment of three numbers h k l (Miller indices) to each reflection. The data were indexed following the procedures of Lipson and Steeple (Lipson & Steeple 1972).

Grain or crystallite sizes of the synthesizes nanoparticles were determined by the following Debye-Scherrer’s equation

\[
D = \frac{K \lambda}{\beta \cos \theta}, \tag{2.2}
\]

where D is the mean diameter (size) of the grains, K (= 0.9) is the size factor, \(\beta\) is the full width at half maximum (in radians), \(\lambda\) is the wavelength of the X ray radiation used and 2θ is the angle at which the maximum intensity was observed. More than two
diffraction peaks were chosen wherever possible and consistency in the cluster sizes obtained from using their widths was confirmed. The lattice parameters of the synthesized nano particles were also calculated from indexed XRD pattern. Photograph of PANalytical x-ray powder diffractometer is shown in Figure 2.3

Figure 2.3 Photograph of PANalytical x-ray powder diffractometer

2.5.2 Energy Dispersive X-ray Spectroscopy

Energy Dispersive X-ray Spectroscopy (EDX) is a qualitative and quantitative X-ray microanalytical technique that can provide information on the chemical composition of a sample. To characterize the samples prepared chemically, it is necessary to determine accurately the metal atom (Ti, Sn and Ru) contents. As these samples are not soluble in water, atomic absorption spectroscopic (AAS) technique cannot be used for this. However, other techniques like energy dispersive X-ray absorption (EDAX) analysis can very well be utilized. It is an analytical technique used to estimate the composition of the prepared materials. It relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to
being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other.

To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray.

By an energy calibration of the channels in the Analyser, the collection of X-ray pulses is displayed as an energy histogram. EDAX systems are controlled by computers and are used for the basic operations of spectrum collection and peak identification. The X-ray spectra give information on the types of elements present in a specimen from the wavelength of the X-ray emitted and the elemental concentration from the intensity of the particular peak.

Energy dispersive X-ray analysis (EDX) was carried out to estimate the composition of the prepared samples using EDX-System OXFORD INCA Energy 200.

2.5.3 Field Emission scanning electron Microscopy (FESEM)

It is a modified Method of SEM. The difference between SEM and FESEM is only on their emitter type. SEM has thermionic emitter which has relative low brightness, evaporation of cathode material and thermal drift during operation. FESEM over comes these drawbacks by using Field Emission Gun (FEG); also called a cold cathode field
emitter, which does not heat the filament. FESEM images are most clearer and detail than SEM. FESEM can facilitate for Ultra-high magnification imaging.

In FESEM, the surface of a solid sample is scanned in a raster pattern with a beam of energetic electrons. The specimen and the electron beam interact in both elastic and inelastic fashion giving different types of signals. Elastic scattering events are those that do not affect the kinetic energy of the electron even when its trajectory had been affected. Inelastic scattering events are a result of the energy transfer from the electron beam to the atoms in the specimen, as result the electrons have energy loss with small trajectory deviation. Each of these signals gets specific information about topography, crystallography, surface characteristics, specimen composition.

A field-emission cathode in the electron gun provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage.

2.5.4 TEM Measurements

Transmission Electron Microscope (TEM) is a large scientific equipment that forms detailed images of extremely small objects or areas of objects by passing a beam of electrons through a very thin slice of the area of interest. TEM is used heavily in both material science/metallurgy and biological sciences. In both the cases the specimens must be very thin and should be able to withstand the high vacuum present inside the instrument. A crystalline material interacts with the electron beam mostly by diffraction rather than absorption. A length calculated bar is provided already inside the TEM picture. Using that scale one can estimate the size of the particle.
In our present study, TEM measurements were done on the selected samples using TEM facility - FEI Technai G² 300 kV, resolution 1.4 Å with 1 million magnification power.

2.5.5 UV-Vis spectral Analysis

Ultraviolet/Visible/Infrared (UV/Vis/IR) spectroscopy is a technique used to quantify the light that is absorbed and scattered by a sample. In its simplest form, a sample is placed between a light source and a photo detector, and the intensity of a beam of light is measured before and after passing through the sample. These measurements are compared at each wavelength to quantify the sample’s wavelength dependent extinction spectrum. The data is typically plotted as extinction as a function of wavelength.

Nanoparticles have optical properties that are sensitive to size, shape, concentration, agglomeration state, and refractive index near the nanoparticle surface, which makes UV/Vis/IR spectroscopy a valuable tool for identifying, characterizing, and studying these materials.

The ultraviolet spectrum may be divided into the following regions:

a) Far (or vacuum) ultraviolet region

The region from 10-200 nm can be studied in evacuated systems and is termed as “vacuum ultraviolet”. The atmospheric absorptions below 200 nm are a blessing to all, including the spectroscopists, since it prevents the hazardous (high energy) ultraviolet radiation in the sunlight from striking the earth’s surface. In organic molecules, the maximum energy separation occurs when electrons in σ bonds are excited giving rise to absorption in the range 120-200 nm. The range is difficult to measure and is little diagnostic value.
b) **Near or Quartz ultraviolet region**

The range from 200-380 nm is the portion of the spectrum normally covered by the term ultraviolet. The atmosphere is transparent in this region and quartz optics may be used to scan from 200-380 nm. The excitation of electrons from p & d orbitals, π-orbitals and particularly π-conjugated systems occurs above 200 nm and gives rise to readily accessible and informative spectra.

c) **Visible region**

The spectral range, which is accessible with most instruments, is from 200 nm to 800 nm and this entire region is often referred to as ultraviolet spectrum although it includes the visible region (380 to 780 nm). A tungsten filament lamp is generally used for the visible region of the spectrum. Conjugation of double bonds lowers the energy required for the transitions and absorption moves to longer wavelength.

Optical absorption measurements were done at room temperature using a SHIMADZU UV-1800 PC spectrometer with a medium scan speed sampling interval 1 nm in the wavelength range 300-1100 nm. The optical bandgap calculations were done using Tauc's equation Saif ebraheem et al (2013)

\[
(\alpha h\nu) = A (h\nu - E_g)^n,
\]

where, A is a constant, \(E_g\) is the optical bandgap energy of the material and exponent n depends on the type of transition Urbach et al (1953). In this present study, for direct allowed transitions n is taken as \(\frac{1}{2}\) and \(\alpha\) is the absorption coefficient, it was determined using the relation,
\[
\alpha = \frac{2.303 \log \text{ (absorbance) }}{\text{Thickness of the sample}}.
\] (2.4)

The value of optical bandgap was calculated by extrapolating the straight line portion of \((\alpha \nu)\) vs \(\nu\) graph to \(\nu\) axis (Figure 2.4).

\[\text{Figure 2.4 Model graph for bandgap energy determination}\]

**2.5.6 Photoluminescence analysis**

Photoluminescence (PL) spectroscopy is a contactless, nondestructive method to probe the electronic structure of materials. In essence, light is directed onto a sample, where it is absorbed and where a process called photo-excitation can occur. The photo-excitation causes the material to jump to a higher electronic state, and will then release energy, (photons) as it relaxes and returns to back to a lower energy level. The emission of light, or luminescence through this process is photoluminescence, PL. Photoluminescence (PL) is thus the spontaneous emission of light from a material under optical excitation. This light can be collected and analyzed spectrally, spatially and also temporally.

In fact, PL spectroscopy gives information only on the low-lying energy levels of the investigated system. In semiconductor systems, the most common radioactive transition is between states in the conduction and valence bands, with the energy difference
being known as the band gap. During a PL spectroscopy experiment, excitation is provided by laser light with energy much larger than the optical band gap. The photo-excited carriers consist in electrons and holes, which relax toward their respective band edges and recombine by emitting light at the energy of the band gap.

The radiative transitions in semiconductors may also involve localized defects or impurity levels. In that case, the analysis of the PL spectrum leads to the identification of specific defects or impurities, and the magnitude of the PL signal allows determining their concentration.

During a PL spectroscopy experiment, excitation is provided by laser light with the energy much larger than the optical bandgap. The photo-excited carriers consist in electrons and holes, which relax towards their respective band edges and recombine by emitting light at the energy of the bandgap.

The near band edge emission band is calculated by using the following equation

\[ E_g = \frac{hc}{\lambda} \]  

(2.5) where ‘h’ is the planck’s constant \((6.624 \times 10^{-34} \text{ J s})\), ‘c’ is the velocity of light and \(\lambda\) is the emission wavelength.

In our present study the photoluminescence (PL) spectra were obtained on a Perkin Elmer LS 55 model luminescence spectrometer with a wavelength resolution of 1.0 nm at room temperature using Xe lamp source with an excitation wavelength of 30a5 nm.