Synthesis and Characterization of Co Doped SnO_2 Nanostructures

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(2015)

nanostructure materials

nanotechnology

Certificate

This is to certify that the work contained in this project entitled: "**Synthesis and Characterization of Co Doped SnO_2 Nanostructures**" has been carried out by Muhammad Ali Khilji in Laboratory of Nanoscience and Technology (LNT) under my supervision. In my opinion, this is fully adequate in the scope and quality for the thesis of MS Physics.

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DEDICATION

To

My loving Parents,

Brothers and Sister

All Great Teachers

ACKNOWLEDGEMENT

It gives me great pleasure and satisfaction to acknowledge the benefaction of the creator of the universe, **Allah Almighty**, the most kind, sympathetic and beneficent to his creature, which enables me to complete my work successfully. I offer my humblest and sincere words of thanks to his Holly **Prophet Mohammad** (P.B.U.H) who is forever a source of guidance and knowledge for humanity.

I feel great honor to express the deepest sense of appreciation to my respected supervisor **Dr. Javed Iqbal Saggu** for his inspiring guidance, skillful suggestions and keen interest during the whole period of my study. I am sure that his guidance will provide valuable source of inspiration throughout my life. I am very thankful to Mr. Tariq Jan (IIUI), Mr. Fazal Abbas (IIUI),Mr. Sibt ul Hassan(IIUI), Dr. Khalid (NINVAST), Mr. Saqib (COMSATS) and Dr. Awais (COMSATS) for their technical support during my thesis project. I am especially thankful to HEC for his support.

I am also grateful to all my friends and class fellows for giving me encouragement, appreciation and helped in completing this project.

Muhammad Ali Khilji

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Abstract

Tin dioxide (SnO_2) is an important metal oxide semiconductor having wide range of applications in electrodes of solar panel, lithium ion batteries and nano sensors. Doped and undoped Tin dioxide powders have been synthesized via easy and economical co-precipitation route using Tin chloride ($SnCl_4$) as a precursor. Prepared undoped and Co doped SnO_2 have been characterized to investigate its physical properties. Structural and morphological properties are examined by XRD, RAMAN and SEM. XRD patterns have confirmed the successful synthesis of SnO_2 with no extra peaks. The size of nanostructures is found to decrease systematically with doping content from 64.0 nm to 14.50 nm. SEM micrographs have confirmed the presence of nanostructures. RAMAN patterns have supported the results of XRD showing no extra peak. Chemical composition checked by EDS has not shown presence of any impurity in the prepared samples, while FTIR also confirmed the stretching mode of chemical bonding of rutile tetragonal structures. In addition, the band gap is significantly reduced from 3.61 eV to 2.11 eV with increase in doping. From PL results, the decrease in band gap as well as defects by doping of Co in SnO_2 are observed. The results reveal that the optical and structural properties of SnO_2 nanoparticles can easily be modulated by doping of different concentrations of Co in SnO_2 using co-precipitation method.

Chapter No. 1

Introduction

1.1 Nanotechnology

Although modern nanoscience and nanotechnology is a new field of science however nano materials have been employed from many centuries. Gold and silver particles of different sizes and morphology had been used many years ago to create different colors in the medieval churches glass windows. The actual processes involved was not well understood by the artists of that time however they modified the composition of these materials to create these beautiful works of art. Today's engineers and scientists have found a number of ways to use these materials at nanoscale. The improvement in the properties of nanomaterials such as higher strength, lighter weight, control of the light spectrum and higher chemical reactivity are more than their bulk counterpart.

1.2 History and Development of Nanotechnology

The scientific story of nanomaterials is as fallows.

- The first scientific report was on the colloidal gold particles which were synthesized by Michael Faraday in 1857.
- In 1914, Richard Zsigmondy was the first person who characterized the particle with the help of nanometer scale. Using this approach, he has made the classification based on particle size [1].

- In 1940s, fumed and precipitated silica nanoparticles were produced as a substitute for ultrafine carbon black for rubber reinforcement and sold in countries like United States and Germany.
- In 1959, the idea of nanotechnology scale was also introduced by American scientist Richard Feynman who was very inspired by this technology [2].
- The term "nanotechnology" was used first time by Norio Taniguchi at the International Conference on Precision Engineering (ICPE) in 1974 [3].
- Eric Drexler was first person who gave the idea about application of nanotechnology in "Engines of Creation", a book published in 1986 for the molecular manufacturing [4].
- Therefore in 1990, the first journal named "Nanotechnology" was published by Chris Peterson [5].
- In 1992, a book on Nano systems was published [6].

Nowadays, nanotechnology is progressing rapidly and becoming a significant part of agriculture, food, avionic technology, medicines, industry and daily life etc.

1.3 Nanomaterials

Nanomaterials have gained considerable attraction of researchers in past few years due to some specific properties which become unique at such a scale.

1. Increase in surface to volume ratio makes the nanomaterials of special importance.
2. Material with large surface area has higher chemical reactivity. For example the catalytic characteristics of gold are found to be clearly improved at nanoscale. As gold shows no

chemical reactivity in bulk and is considered as an inert element however on nanometer scale it is very reactive.

3. The physical properties can also be enhanced using nanomaterials rather than their bulk counterpart which includes electrical, physical and magnetic properties and their possible technological applications [7-9]. Such properties and applications have been studied by different researchers for different purposes and dependence of these properties on particle size has also been investigated [10-11].

1.4 Types of Nanomaterials

- Carbon based materials (fullerenes and nano tubes)
- Metal based nanomaterials
- Den trimers (providing interior cavities for other molecules)
- Composites
- Natural nanoparticles

1.5 Classification of Nanomaterials

According to Siegel, nanomaterials are of three types

1) Zero dimensional
2) One dimensional
3) Two dimensional

1.5.1 Zero Dimensional

Zero dimensional materials are the materials having all three dimensions are in nanometer range i.e. sizes $\leq$ 100nm. They are confined in all three dimensions to quantum range (1nm-

100nm) [12]. At this size a small change or disturbance in material can cause a huge effect in their physical and chemical properties like optical, electrical, magnetic and chemical reactivity.

At this level, we can describe the behavior of atoms and sub-atomic particles in accordance with quantum physics. Due to their size, they display different optical and electrical properties. The zero dimensional materials can be used in optoelectronic devices. For example

- Color Coded Quantum Dots for fast DNA testing
- Material for IR Photo detectors
- Material for Cascade Lasers

1.5.2 One Dimensional

One dimensional nanomaterials are the second class of nanomaterials in which all dimensions are in nanometer range except one which is not in nanometer range.

Figure 1.1: SEM image of nanowires [13]

Figure 1.2: TEM image of Ni doped ZnO nanorods [14]

The common thread between all of these structures is that their size (diameter) must be within 1-100 nm range and the length typically in microns (or larger) regime [15]. Nanowires, nanotubes, nanorods and nanofibers are the examples of one dimensional nanomaterials.

1.5.3 Two Dimensional

The third class of nano building blocks are the structures which extend in two dimensions in nano range i.e. they have only one dimension ≤100nm. So the structures that could possibly be with such dimension are nanosheets. Two dimensional materials include all kinds of sheets, graphene sheets, thin films and nanoporous materials. Materials exhibit unique properties at such a small scale and have variety of applications such as coatings. Such coatings are useful for enhancing the physical properties of materials [16].

1.6 Applications of Nanotechnology

Nanomaterials have gained so much attraction of researchers due to their significant physical properties. Now a day's nanotechnology is used in various fields of life such as electronics, medicine, sports and industries.

1.7 Scope of Nanotechnology

1.7.1 Medicine and Biology

Nanotechnology is playing a very vital and substantial role in our lives now a day e.g. it is used as a diagnostics tool and for treatment of hazard diseases. Cancer and other such harmful diseases are efficiently cured using this emerging field of nanotechnology [17]. Microtubule helps in diagnosis and treatment of many incurable diseases like cancer, tumors and better control of genetic diseases and other harmful diseases [18]. Nanomedicines also improve growth and other physical appearances like plastic surgery. In the field of cosmetics it provides us better tools and chemicals that are useful for our common use.

1.7.2 Physics and Electronics

Nanotechnology is of great interest in engineering as well as in material science because of its fascinating and versatile applications in the field of nanoscale electronic systems. Carbon nanotubes (CNTs) are preferred in today's modern technological applications against ordinary silica particles because of owing superpower properties with lesser energy consumption. Fabrication of CNTs in nanotechnology make it very different from their bulk counterpart because they can conduct electricity more efficiently than copper. They can also carry heat at greater rate than a diamond and is about 100 times stronger than steel [19]. Nanotechnology make it possible to fabricate the efficient, more powerful, low cost, light in weight as well as smaller size electronic devices which are the need of these days. Furthermore, this technology helped mankind to achieve memory chips with higher data storage capacity ranging up to one Tera Byte (TB) per square inch or more. Nanocrystals of cadmium selenide (CdSe) have been utilized very competently to fabricate more flexible electronic circuits.

1.7.3 Nanomagnetics

Nanomagnetics, the study and use of nanoscale magnetic materials is another field of investigation. The latest discovery is the electron-spin-polarized from a thin ferromagnetic film that flows reversibly can switch the magnetic orientation of the nanomagnets near by a so-called "spin transfer" opens up the prospect of new medium for the super high information storage density. This could also lead to the improvement of new components at nanoscale for high-frequency electronics. The manipulation and injection of electron spins in the semiconductor and normal metal nanostructures can lead to the further improvements in the quantum computer's elements and other "spintronic" applications.

Srinivas *et al* studied ferromagnetism in Co-doped SnO_2 (5 at. %). They found it increasing with increasing the annealing temperature [20]. Punnose *et al* also found the same behavior but few reports shows disappearance of ferromagnetism in Co doped SnO_2 nanoparticles at certain doping limits [21, 22]. Also some reports record antiferromagnetism in Co doped SnO_2 nanocrystals. In this thesis, SnO_2 and Co-doped SnO_2 nanostructures have been first synthesized with different concentrations using simple co-precipitation technique. The physical properties results are discussed in trying to find out the general behavior of doping with different concentrations.

1.7.4 Food

Nanoparticles are used to improve the growth of food and also for the preservation of food for future use. It will create a change in taste as well as helps in the protection of food and other health benefits that we get from food [23].

1.5.5 Gas Sensors

Metal oxide based gas sensors are one of the interesting field of research now a days. Very minute amount of gas vapors can be detected with higher accuracy by employing nanoscale sensors. To achieve these nanomaterials different kinds of elements have been utilized in nanotechnology. In such nano sensors little amount of gas particles is enough to alter the electrical properties of these sensing materials. SnO_2- with different metal ions doping can be used to sense the low concentrations of CO which is present in relatively low concentrations (below 50 ppm). This is toxic gas which accompanies in almost all combustion processes [24].

These nanomaterials with enhanced properties (such as hardness and melting point due to improved surface interaction between nanoparticles) at large scale can be used for gas sensing due to quantum confinement effects.

1.8 Tin Dioxide

Tin dioxide is a wide band gap semiconductor with a band gap of 3.6 eV among metal oxides. This gap is enough for variety of applications such as LED's and gas sensors. Many properties of tin dioxide can be varied easily by simple doping of many elements. Thus, use of tin dioxide is expanding day by day with many applications shifting to tin dioxide with different dopants.

- Magnetic properties can be easily tuned by doping of different magnetic impurities. Tin dioxide itself is a paramagnetic material whose domains can be easily aligned by doping with some ferromagnetic material e.g. iron, cobalt. These are typical examples which are commonly used as dopant in tin dioxide. The devices like hard disks in which weak magnetism is needed for creating high dense magnetic storage medium, otherwise it will influence neighbor magnetic storage. Tin dioxide is mostly used since 2005 for this purpose.

- Optical properties can be enhanced to some extent as desired and required. For this purpose, element with low band gap is doped to reduce the band gap. This reduction makes it useful in optoelectronic devices such as LED's etc. Normal LED in which tin dioxide used as a cathode will emit light in UV region.

1.8.1 Properties of Tin Dioxide

Some of the basic properties of tin dioxide are as follows:

Table 1.1: Properties of Tin Dioxide

Bandgap	3.6 eV	Electronic Structure of Sn	$1s^2 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^2 4p^6 4d^{10}\ 5s^2 5p^2$
Melting point	1630 °C	Electronic Structure of O	$1s^2\ 2s^2\ 2p^4$
Boiling point	2500°C	Magnetism	Paramagnetic
Molar mass	150.01 g/mol	Refractive Index	2.0006
Tin valency	2+ & 4+	Lattice constants	a=4.73 Å, b=3.18 Å
Oxygen valency	2+	Appearance	White powder
Crystalline Structure	Rutile Tetragonal	Ionic Radii of Sn	0.69 Å

1.9 Motivation

SnO_2 is very interesting material having properties that can be widely used and can be easily varied. It can be used as transparent conducting electrodes as well as in gas sensors. Doping methods are easy which can tailor the physical properties of SnO_2 to desired level. Cobalt is a ferromagnetic material and it is an interesting dopant having potential to tune the band gap of tin dioxide. Thus band gap of SnO_2 can be reduced by the doping of cobalt. In this thesis, detailed properties of undoped tin dioxide are studied and the effects of cobalt doping on the physical properties are carefully examined and discussed.

CHAPTER No. 2

SYNTHESIS OF NANOMATERIALS

2.1 Introduction

The goal of nanotechnology is to synthesize the materials which are less than 100 nm in at least one dimension. In this chapter, we will discuss different routes for the synthesis of nanomaterials which are less or equals to 100 nm in one dimension. Nanomaterials are found in variety of different morphology like nanowires, nanorods, nanoparticles etc. Top down and bottom up are two fundamental methods used for the fabrication of nanomaterials. Top down method begins with the disintegration of bulk material to desired material of nanosize. In Bottom up approach, the assembling of individual atoms, ions or molecules leads to the nanoscale materials. This method is also known as reverse of top down approach.

2.1.1 Top-Down Approach

A top down approach is a way to slash the bulk material into nano sized structures. This approach involves breaks down of big to smaller segments. The most prominent feature of this approach is that it helped us to achieve uniform morphology of the synthesized material [25]. This technique involves a variety of methodologies such as ball milling, lithography, etching and electro-spinning etc. to synthesize different nano materials with well-tuned and enhanced physical and chemical properties.

Nanofabrication is a vital tool which is playing a dominant role in advancing the field of nanotechnology. This method includes both conventional and non-conventional techniques to make nano scale materials in such a way that these are almost same as from carving smaller materials from a bulk material. The above mentioned techniques are not preferred as they are very uneconomical and time consuming for synthesizing nanostructures. Hypothetical view of top-down and bottom-up approaches are as under.

2.1.2 Bottom-Up Approach

This approach involves agglomeration of individual atoms, ions or molecules to form required nanomaterials. Hence, this approach is contrary to top down approach in which larger material is broken down into smaller fragments. This method is similar to natural way of forming crystals and amorphous particles.

This approach is comparatively easier, simpler and is more useful in synthesizing nanostructures. It is a less expensive technique and there is no wastage of material involved in this technique. This technique illuminates the contamination problems encountered during the synthesis of nanomaterials via top down approaches. It also preferred because there is no high vacuum condition is required in it.

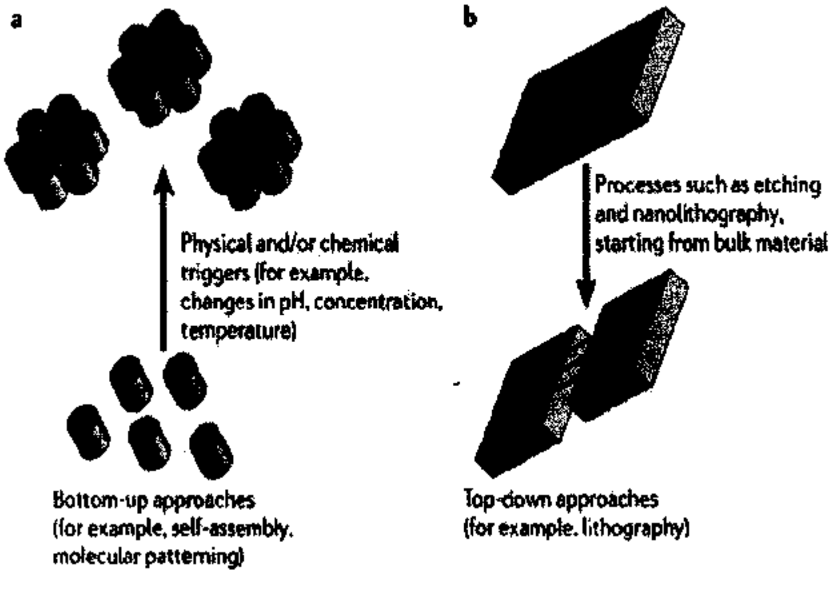

Figure 2.1: Top down and bottom up approaches [26]

2.2 Techniques for Synthesis of Nanomaterials

Following are the few techniques for the synthesis of nanomaterials:

i. **Mechanical**

   - Ball milling
   - Attrition milling
   - Mechano-chemical processing

ii. **Wet Chemistry**

   - Sol Gel
   - Colloid chemistry
   - Solvothermal/hydrothermal
   - Co-precipitations

iii. **Gas Phase Synthesis**

   - Plasma
   - Laser oblation
   - Chemical vapor synthesis

iv. **Thermal Routes**

   - Aerosol reactor
   - Self-propagating high temperature synthesis (SHS)
   - Exploding wire

v. **Others**

   - Biomimetic
   - Microwave techniques
   - Ultrasound techniques

2.3 Chemical Co-Precipitation Method

In co-precipitation method, precipitates of precursor are attained which usually are soluble under the condition employed. In this method after collecting the precipitates, unwanted nitrides and chlorides are washed using special filters or centrifuge techniques. Chemical changes play a vital role in obtaining the desired precipitates to synthesize nanomaterials.

2.3.1 Why Co-precipitation?

Co-precipitation is highly preferable because it is very simple and easy to handle for synthesis of nanostructures. Nanostructures of desired morphology and particle size can easily be synthesized using this technique. In this technique choice of surfactant is very significant to tune the particle size. This technique is also very fascinating because it can be employed using aqueous as well as non-aqueous mediums. A fair amount of yield of the synthesized nanomaterials can be obtained using this chemical route [27]. In our present study, we also preferred this route to synthesize undoped and Co doped SnO_2 nanostructures.

2.4 Experimental Procedure

Undoped and Co doped SnO_2 were synthesized in Laboratory of Nanoscience and Technology (LNT), Department of Physics, IIU using wet chemical/co-precipitation method. Molar ratio method was adopted to control the desired molar concentrations of dopant (Cobalt) as well as host (SnO_2). The precursors utilized for the synthesis of undoped and Co doped SnO_2 were $SnCl_4.5H_2O$ and $CoCl_2.6H_2O$. Acetic acid (CH_3COOH) was used as surfactant to control the particle size and ammonium hydroxide solution (NH_4OH) was also used to control the pH value of the solution. Moreover, ethanol was used as solvent for the precursors during the synthesis process.

3.59g of $SnO_4.5H_2O$ was added and dissolved in 100 ml ethanol to get 0.1M solution, the prepared solution was stirred at 500 rpm for about 10 minutes. Then as a surfactant, 2 ml acetic acid was added into the solution. After 10 minutes stirring, 5 ml ammonium hydroxide (NH_4OH) was also added to the solution drop by drop to adjust the required pH value of the solution. After that solution was left under a constant heating at 100 °C and stirring at 500 rpm for one hour. After an hour, the stirring was stopped and solution was allowed to cool for 30 minutes. Then the solution was centrifuged thrice with distilled water to remove the chloride ions. Finally, the synthesized solution was dried at 80 °C in the electric oven for overnight. After drying, the final product was grinded to get powder form. Finally, the samples were annealed for 4 hours in the furnace at 600 °C.

The same procedure was adopted to synthesize the doped samples. Here cobalt chloride ($CoCl_2.6H_2O$) was utilized as a precursor for doping. In this study, doping concentrations (1 %, 3 %, 5%, 7 % and 10 %) of Co was used in SnO_2 host matrix. The flow chart of whole synthesis process is given in figure 2.2.

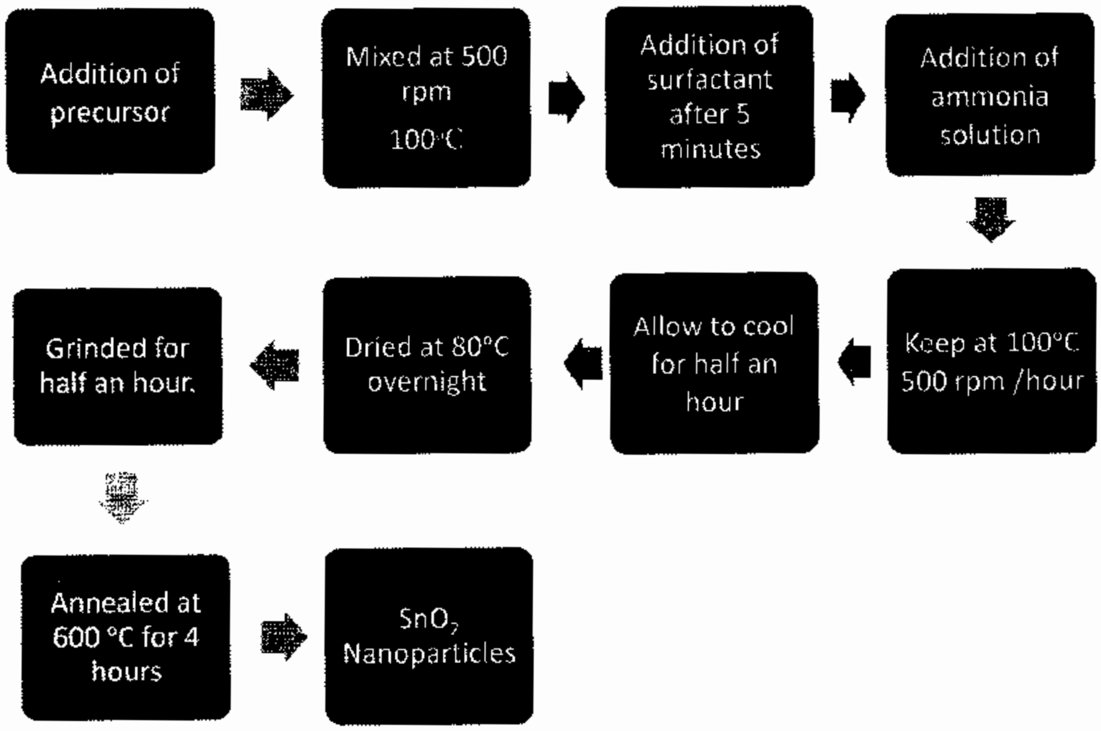

Figure 2.2: Flow chart of experimental procedure

Chapter No. 3

Characterization Techniques

In this chapter we will thoroughly discuss all the characterization techniques which we have used to characterize and analyze our synthesized samples. Followings are details of these techniques:

3.1 X-ray Diffraction (XRD)

3.1.1 Introduction

X-rays are electromagnetic radiations having wavelengths comparable to the interatomic crystal spacing and was first discovered by Sir William Roentgen in 1895 [28]. X-ray diffraction technique is useful for determining the crystallite size, crystallinity, phase's purity and their orientations. All pure crystalline materials can be determined with this technique as all the materials have their own characteristics XRD pattern as compared to each other. XRD is thought to be finger print of crystal. So, this technique is adapted in common for the identification of polycrystalline phases.

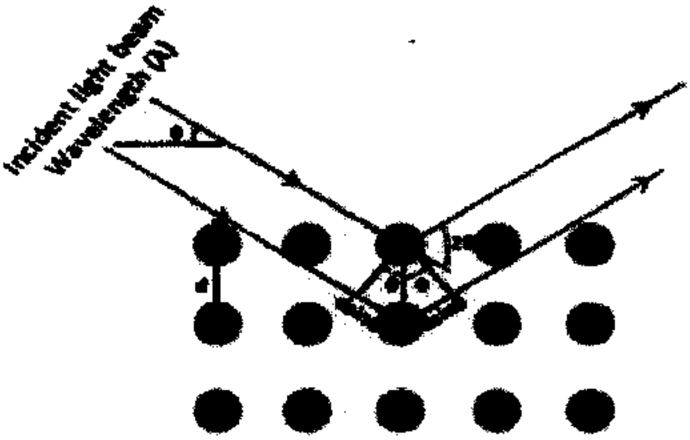

Figure 3.1: Schematic description of Bragg's Diffraction Law [29]

3.1.2 Working

During x-ray diffraction, incident x-rays beam interact with electrons in atoms and are scattered. Since, the collision of x-rays with electrons is perfectly elastic so scattered x-rays have suffer no loss of energy, momentum as well as wavelength. This scattered x-rays beam contains particular information about the sample structure, texture and phase. Diffraction peaks are observed at different angles which are different for every material. These observed characteristics peaks are based on Bragg's Law which are related to cell dimensions and are infact the finger prints of the material under observation.

3.1.3 Bragg's Law

When a crystalline material is exposed to a monochromatic beam of x-rays at a given incident angle θ then the diffraction occurs. The path difference between the different rays reflected from different parallel crystal planes differs by an integral multiple 'n' of wavelength under the condition

$$2d\sin\theta = n\lambda \quad \text{..........} 3.1$$

Where λ is the wavelength of incident x-rays, d is the inter planer spacing, θ is the Bragg's angle, n being order of diffraction.

Crystallite size is calculated using Scherer formula as [30]

$$D = \frac{k\lambda}{\beta\cos\theta} \quad \text{..........} 3.2$$

Where D is referred as crystallite size, k is the constant called shape factor, β is called full width at half maximum and θ is the Bragg's angle.

And lattice parameters by [31-32]

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad \text{.......................................} 3.3$$

Here, d is interplanar spacing, a and c being lattice constants and (hkl) are miller indices.

3.2 Morphological Investigations

3.2.1 Scanning Electron Microscope

A scanning electron microscope (SEM) is an ultramodern device which utilizes wave nature of electron beam for its scanning process to produce images of the subject under observation. The incident electron beam cooperates with electrons inside the sample thus producing various signals which contain information and knowledge about its features such as surface topography as well as composition of the sample under observation. SEM is widely used for the purpose of morphological investigations at nanoscale.

3.2.1.1 Working of SEM

Electrons are accelerated from a metal surface to the direction of sample by applying a very high positive electric potential difference. The beam is limited and concentrated in a thin focused monochromatic beam with metal bezel and magnetic lenses. When electron beam is irradiated on the sample, various kinds of signals incdluding secondary electrons, auger electrons, backscattered electrons, x-rays and cathode luminescence emitted from the sample. These signals are detected by the detector which is present in the sample chamber and connected to the computer in which computer software provides information about the given sample.

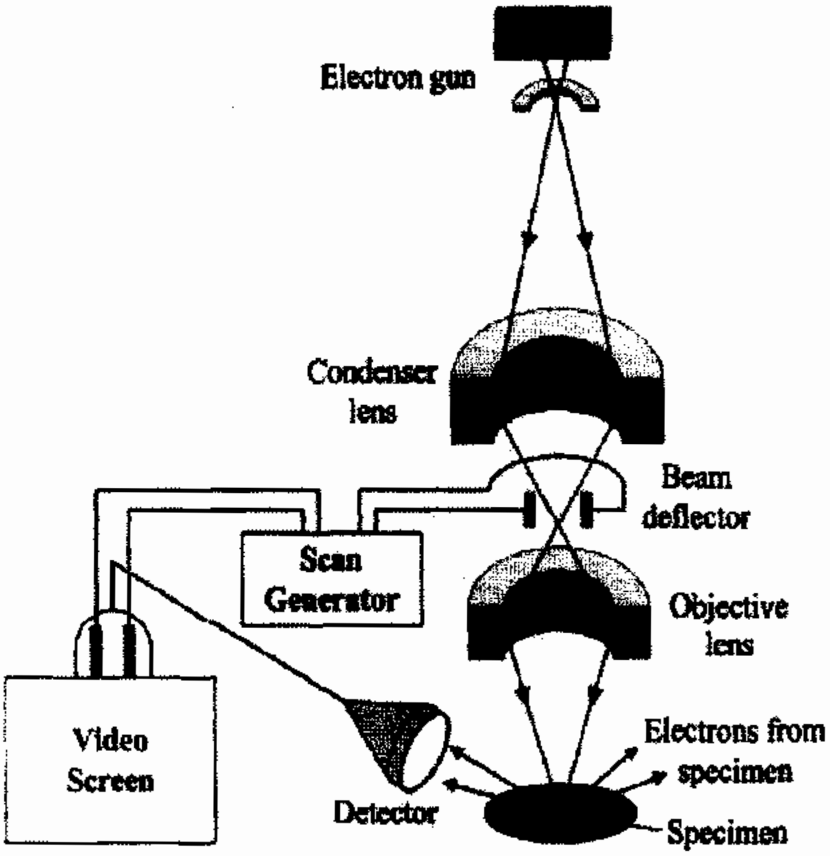

Figure3.2: Schematic diagram of SEM [33]

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

3.3.1 Introduction

Fourier transform infrared spectroscopy (FTIR) is an analytical tool for the differentiations of organic and inorganic materials. It is based on the principle of Michelson Interferometer. FTIR spectrometers are less expensive than typical spectrometer because setting of interferometers is easier than other monochromatic spectrometers. It is a useful method for the analysis of chemical bonds present in a material. Due to the diversity in the molecular vibrations of bending and stretching which react differently to different bonds to incoming radiation.

3.3.2 Working Principle of FTIR

In FTIR, infrared light beam from a polychromatic infrared source is made to incident on the splitter. A portion of incident light is refracted towards the fixed mirror and remaining half is travelled towards the movable mirror after transmitting through splitter. Hence this portion of light is transmitted through the sample and gives valuable information about the interior of the sample like its structural and arrangement of molecular components [34].

This technique involves the following steps during its analysis procedure.

- Black body is utilized to emit the infrared beam. This IR beam passes through the opening of black body where the opening monitors transfer the required energy to the sample.
- Then IR beam directly enters into the interferometer, where the spectral programming takes place. When interferogram are in a row with the IR beam then beam passes from the interferometer.
- Then beam is reflected into the sample chamber where it is turned off or "surface reflected by the sample is transmitted occurs. In this chamber, certain frequencies of energy, the unique property of the sample are absorbed.
- Finally, the beam is detected by the detector for the final measurement. These detectors are especially visible on the interferogram at the end of the signals to the computer, which sent the spectrum to the user.

3.3 Diffuse Reflectance Spectroscopy (DRS)

DRS is a non-destructive technique used to estimate the bandgap of synthesized nanomaterials. In this method, the characteristic reflection spectrum is measured by the lightgenerated medium. The primary mechanism of this technique includes scattering and absorption both of which vary with wavelength of incident radiation to produce the reflection spectrum. This spectrum provides us information related to the optical properties and structure of the medium to be measured. This is done by plotting Kebulka-Munk function against energy in eV. The formula for Kebulka-Munk function is [35]

$$F(R) = \frac{(1-R)^2}{2R} \quad \ldots\ldots 3.4$$

3.4 Photoluminescence (PL)

It is versatile, nondestructive and most sophisticated techniques for probing the electronic structure of materials. In this technique, light is fall onto a sample as a result there is photo-excitation process. This process causes electrons to transfer into allowed excited states within a material. The de-excitation of these electrons to equilibrium states gives the emission of light. This radiative process is based on the quantity of the emitted light between these two states. The schematic diagram of PL is shown in Figure 3.3.

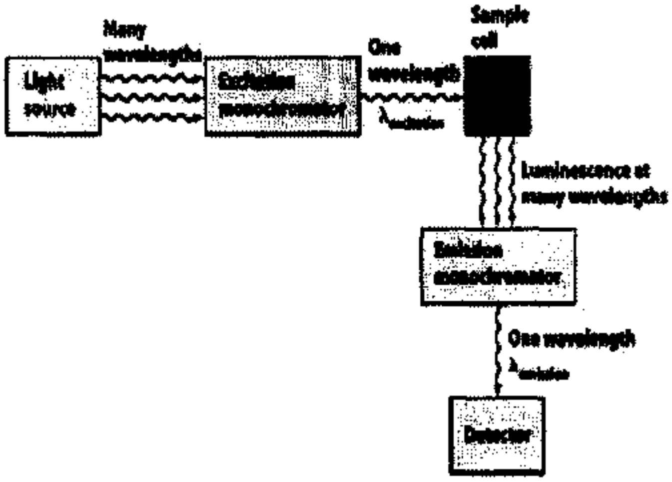

Figure 3.3: Schematic diagram of PL spectroscopy [36]

CHAPTER No. 4

RESULTS AND DISCUSSIONS

4.1 Introduction

The structural, morphological and compositional analysis of the prepared samples have been characterized by XRD, SEM and EDS. Optical reflectance have been calculated using UV spectroscopy and PL. Fourier transform infrared (FTIR) and Raman spectroscopy have been used to determine the chemical bonding and vibration modes.

4.2 Structural Analysis

In order to check the crystallinity of the prepared samples, x-ray having wavelength 1.54Å (Cu Kα) is used. The range of 2θ angle is taken from 20° to 75° with step size of 0.01. Occurrence of broad peaks confirms that all the samples are in nano range. Figure 4.1 shows no extra peaks are observed in XRD patterns which confirms the formation of undoped SnO_2 structure. The average crystallite size decreases from 65 nm to 14 nm as the dopant percent increases from 0%, 1%, 3%,5%, 7% and 10%. This is due to the fact that the Co (0.67Å) ion is smaller in size than Sn (0.69Å) ion which it replaces. The particles size have been calculated from the two major peaks i.e. (110) and (101) and then taking the average. The lattice constant 'a' and 'c' also varies as well as crystallite size with respective to varying percentages. All these values are calculated using standard Scherer's formula from the Full Width and Half Maximum (FWHM) and spacing (d) are calculated by using Bragg's Law.

$$2d\sin\theta = n\lambda \quad \ldots\ldots 4.1$$

Taking n=1 for 1st order equation 4.1 is reduced to

$$2d\sin\theta = \lambda \quad \text{.........} 4.2$$

Now by Scherer formula,

$$D = \frac{K\lambda}{\beta\cos\theta} \quad \text{.........} 4.3$$

Strain is calculated using formula

$$\text{Strain} = \frac{\beta\cos\theta}{4} \quad \text{.........} 4.4$$

Whereas λ is the wavelength of X-rays equals to 1.54 Å, β is full width at half maximum, D is crystallite size, θ is angle of reflection from inter atomic planes and K is taken as 0.89.

Table 4.1: Calculated crystallite size and lattice constants

Sample	**a=b** (Å) ±0.01	**c** (Å) ±0.01	**Crystallite Size** (nm) ±0.02	**Strain** (ε) ±0.001
Undoped SnO_2	4.75	3.17	64.20	0.135
$Co_{0.01}Sn_{0.99}O_2$	4.75	3.18	63.97	0.212
$Co_{0.03}Sn_{0.97}O_2$	4.75	3.16	53.23	0.211
$Co_{0.05}Sn_{0.95}O_2$	4.73	3.18	48.51	0.264
$Co_{0.07}Sn_{0.93}O_2$	4.73	3.18	23.66	0.280
$Co_{0.10}Sn_{0.90}O_2$	4.73	3.18	14.50	0.285

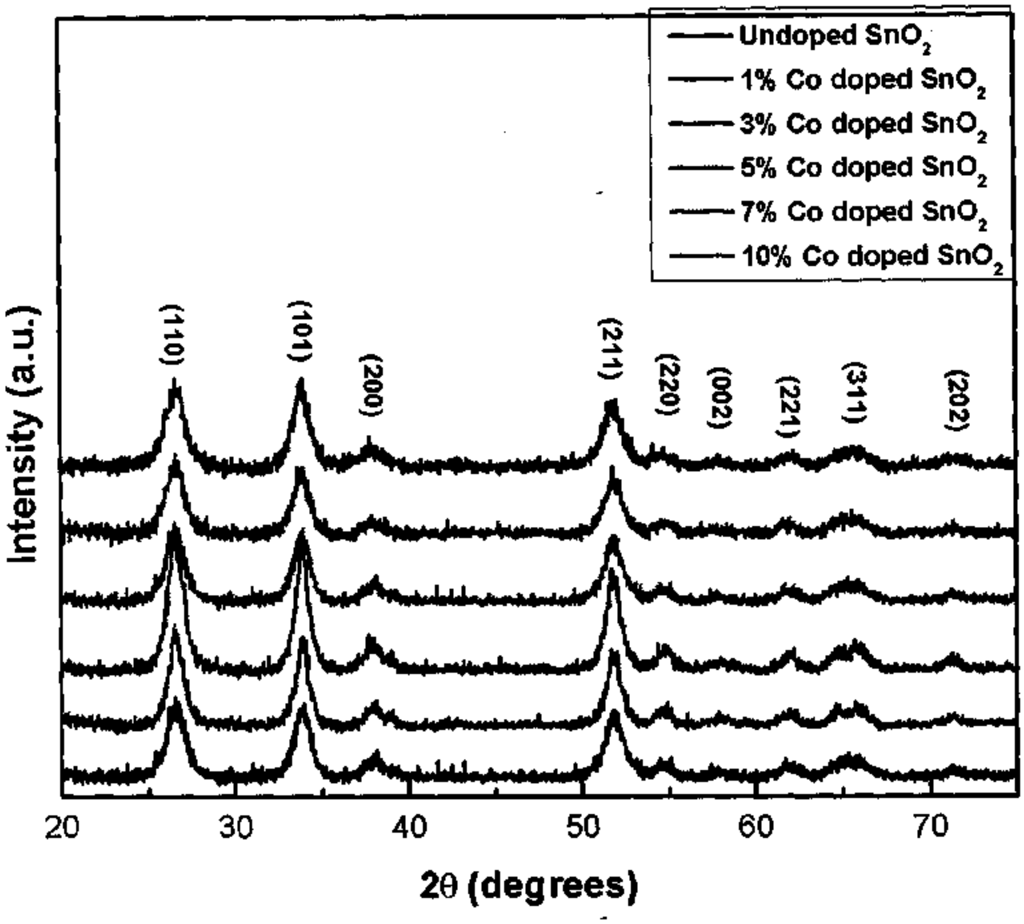

Figure 4.1: XRD patterns of undoped and Co doped SnO_2

It can be clearly observed from the XRD patterns that the Co doping has slightly shift the main diffraction peaks towards lower angles. This may be due to difference of ionic radii of dopant and host cation as mentioned above. The combined XRD patterns with no extra phase and slight peak shift confirms that Co is successfully doped in to SnO_2 host matrix.

4.3 Morphological Investigations

Scanning electron microscopy (SEM) gives us valuable information about morphology and particle size. The samples have been first coated with gold film to make it conductor for the implementation of the SEM analysis. The thickness of the coating is about 250 Å. The SEM images of undoped and Co doped SnO_2 nanostructures are given in figures 4.2 - 4.4.

Figure 4.2: SEM image of undoped SnO_2 nanostructures

Figure 4.2 shows nanoparticles morphology of SnO_2 in desired range. Particles are approximately in uniform size and some clusters are formed which are due to agglomeration. This trend of combination of particles to form larger clumps increased as doping concentration increases due to introducing magnetic material in the host matrix which cause magnetic forces become stronger and stronger with the doping level varies.

Micrographs of 1% and 3% Co doped samples are shown in figures 4.4 and 4.5 respectively.

Figure 4.3: SEM image of 1% Co doped SnO_2 nanostructures

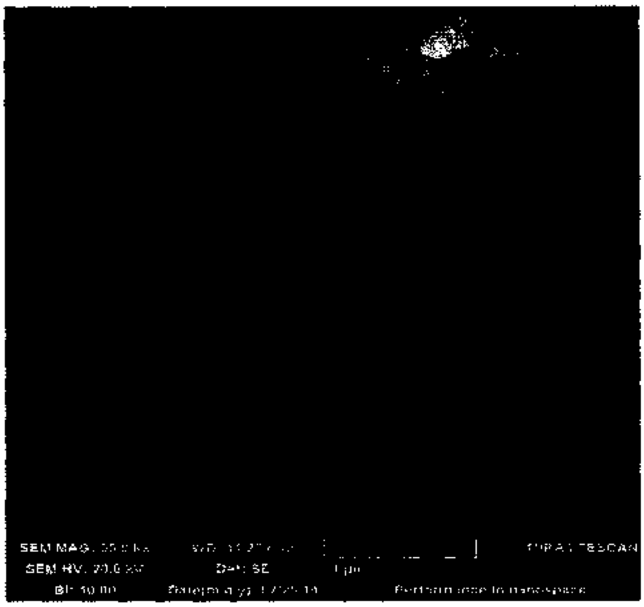

Figure 4.4: SEM image of 3% Co doped SnO_2 nanostructures

Nanostructures have been obtained as seen from SEM micrographs which are in good agreement with the results of XRD. The average particle size has been shown in table 4.2.

Table 4.2: Average particle size of SEM results

Sample	**Average particle size (nm)**
Undoped	64.00
1%	63.97
3%	53.23

4.4 Chemical Analysis

4.4.1 Energy Disperse X-ray Spectroscopy (EDS)

EDS is an analytical technique used to study chemical composition of the material. It gives information about elements in a specimen. The EDS spectra and chemical compositions of all samples are shown in figures 4.5-4.10 and tables 4.3-4.8.

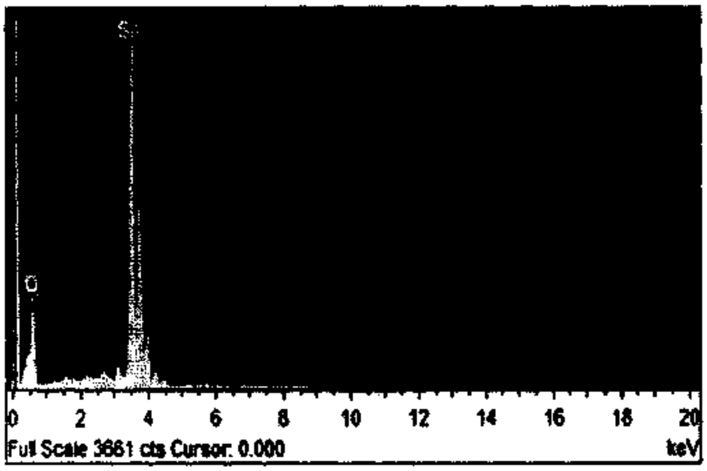

Figure 4.5: EDS spectrum of undoped SnO_2 nanostructures

Table 4.3: Compositions of elements in undoped SnO_2

Element	**Weight%**	**Atomic%**
O_K	33.06	78.56
Sn_L	66.94	21.44
Totals	100.00	100.00

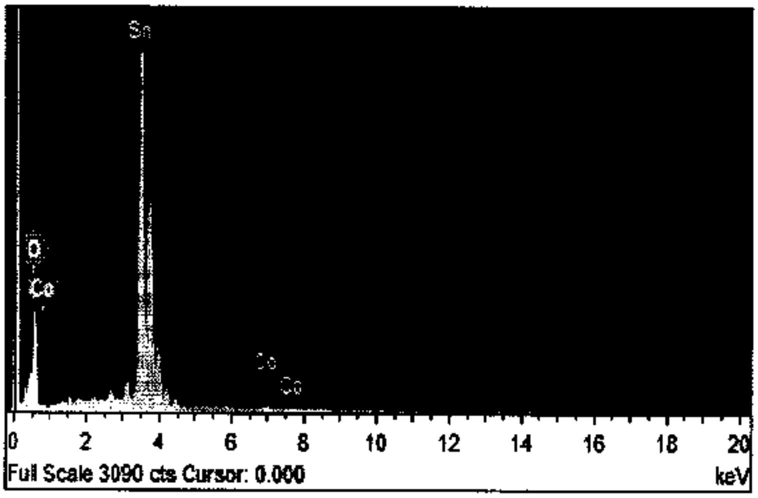

Figure 4.6: EDS spectrum of 1% Co doped SnO_2nanostructures

Table 4.4: Compositions of elements in 1% Co dope SnO_2

Element	**Weight%**	**Atomic%**
O_K	34.70	79.67
Co_K	0.39	0.24
Sn_L	64.91	20.09
Totals	100.00	100.00

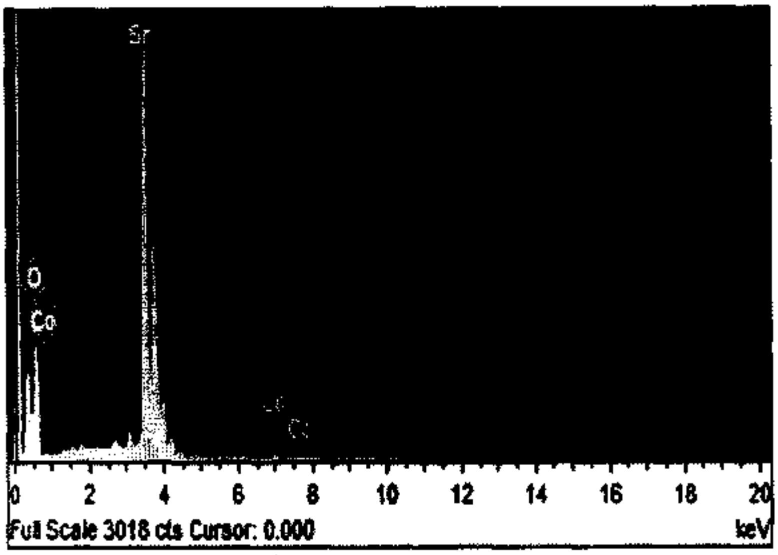

Figure 4.7: EDS spectrum of 3% Co doped SnO_2 nanostructures

Table 4.5: Compositions of elements in 3% Co doped SnO_2

Element	**Weight%**	**Atomic%**
O_K	35.04	79.81
Co_K	0.81	0.50
Sn_L	64.15	19.69
Totals	100.00	100.00

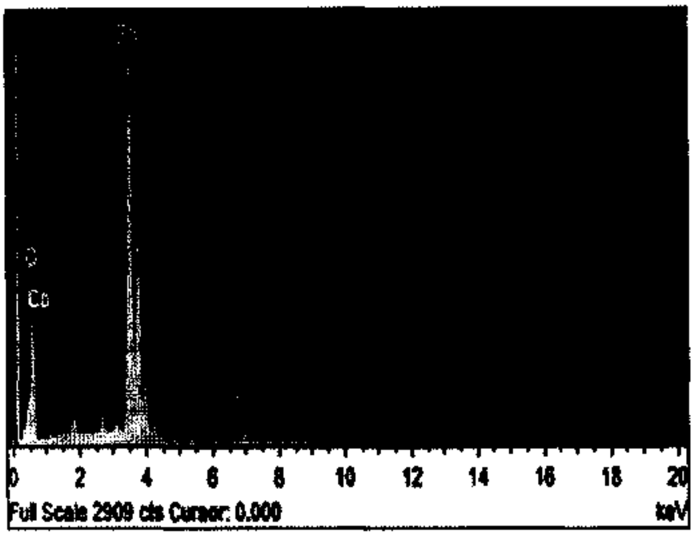

Figure 4.8: EDS spectrum of 5% Co doped SnO_2 nanostructures

Table 4.6: Compositions of elements in 5% Co doped SnO_2

Element	**Weight%**	**Atomic%**
O_K	36.64	80.67
Co_K	1.73	1.03
Sn_L	61.63	18.29
Totals	100.00	100.00

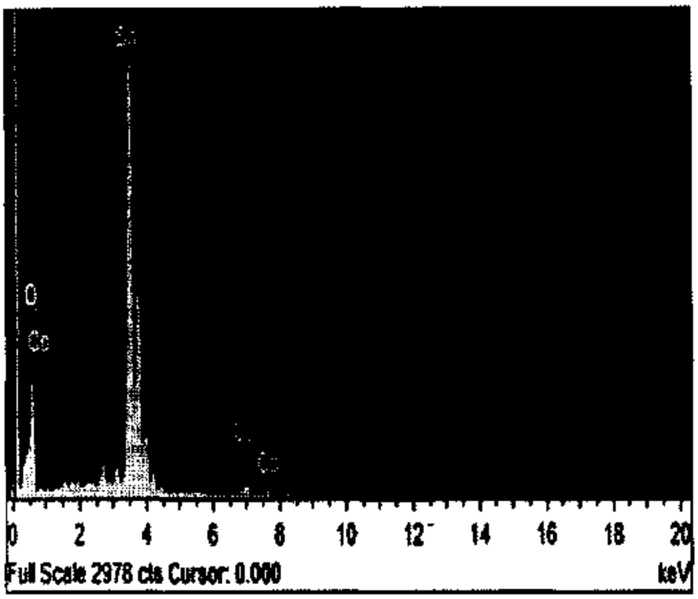

Figure 4.9: EDS of 7% Co doped SnO_2 nanostructures

Table 4.7: Compositions of elements in 7% Co doped SnO_2

Element	**Weight%**	**Atomic%**
O_K	34.52	79.11
Co_K	2.13	1.32
Sn_L	63.35	19.57
Totals	100.00	100.00

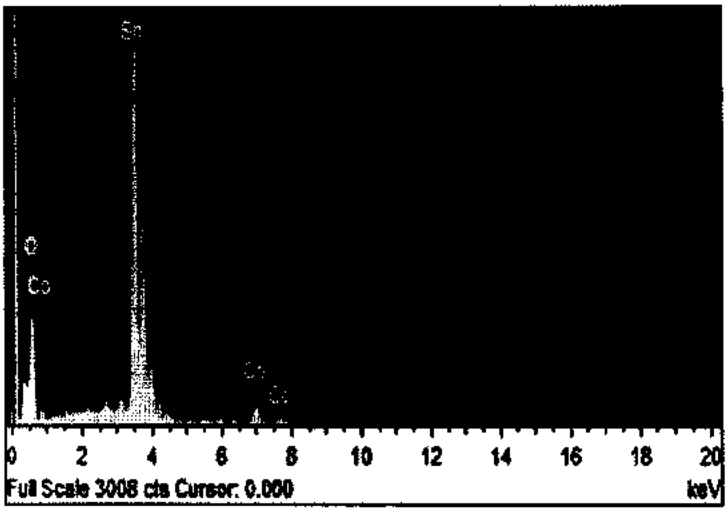

Figure 4.10: EDS spectrum of 10% Co doped SnO_2 nanostructures

Table 4.8: Compositions of elements in 10% Co doped SnO_2

Element	**Weight%**	**Atomic%**
O_K	35.32	79.40
Co_K	3.26	1.99
Sn_L	61.43	18.61
Totals	100.00	100.00

All of these EDS tables and figures depict the concentration of the components in the synthesized samples. All the elements are present in the samples. However, it is found that the present composition of elements is less then stoichiometric ratio which are used at time of reaction. This can be due to the washing, centrifugation and annealing processes. The presence of composition in final product is consistent with other elements are detected in the EDS spectrum.

4.6 FTIR Spectroscopy

The transmittance spectra of different samples are given below in figure 4.11. There are two absorption bands at 3500 and 1674 cm^{-1} which are associated to vibration of hydroxyl groups. Shape and sizes of IR peaks clearly indicate that the Co has been incorporated into the SnO_2 host successfully. The bands exhibited in the small wavenumber region from 430 – 620 cm^{-1} are the vibrational mode of antisymmetric O–Sn–O. The absorption peaks at 473.63 cm^{-1}, 562.43 cm^{-1} and 617.22 cm^{-1} are the vibrational characteristic absorption peaks of Sn–O bond in SnO_2. The current FTIR spectra are entirely different from the spectra of microcrystalline SnO_2. These FTIR spectra clearly resemble with the standard spectra of SnO_2 nanocrystalline material [37-38].

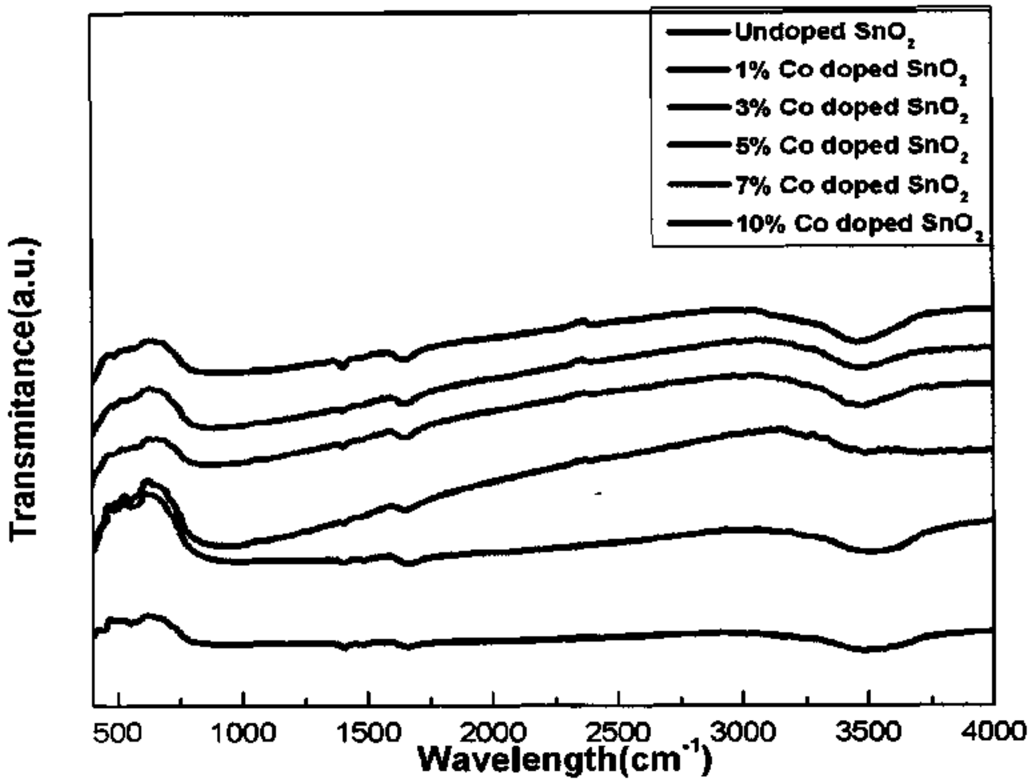

Figure 4.11: FTIR spectra of prepared samples

4.7 Raman Spectroscopy

Raman spectra of undoped and Co doped SnO_2 nanostructures are shown in figure 4.12.There are three prominent peaks at 460, 640 and 780 cm^{-1} in the Raman spectra of undoped SnO_2 sample which are linked with E_g, A_{1g} and B_{2g} modes respectively [39]. This Raman study confirm the rutile tetragonal structure of undoped SnO_2. It can be depicted from spectra that there is a decrease in the intensities of Raman peaks with cobalt doping which is associated with particle size as well as due to different types of surface defects (i.e., lattice distortion and V_o) [40]. Furthermore, it is noticed that the intensity of A_{1g} mode decreases gradually with Co doping concentration. This trend of decrease in intensity reveals that there is strong interaction between dopant and host material. There are no extra crystalline phases of CoO_2 and Sn in the spectra which confirms that dopant is well dispersed in host matrix. These results are in good agreement with above XRD and FTIR analysis.

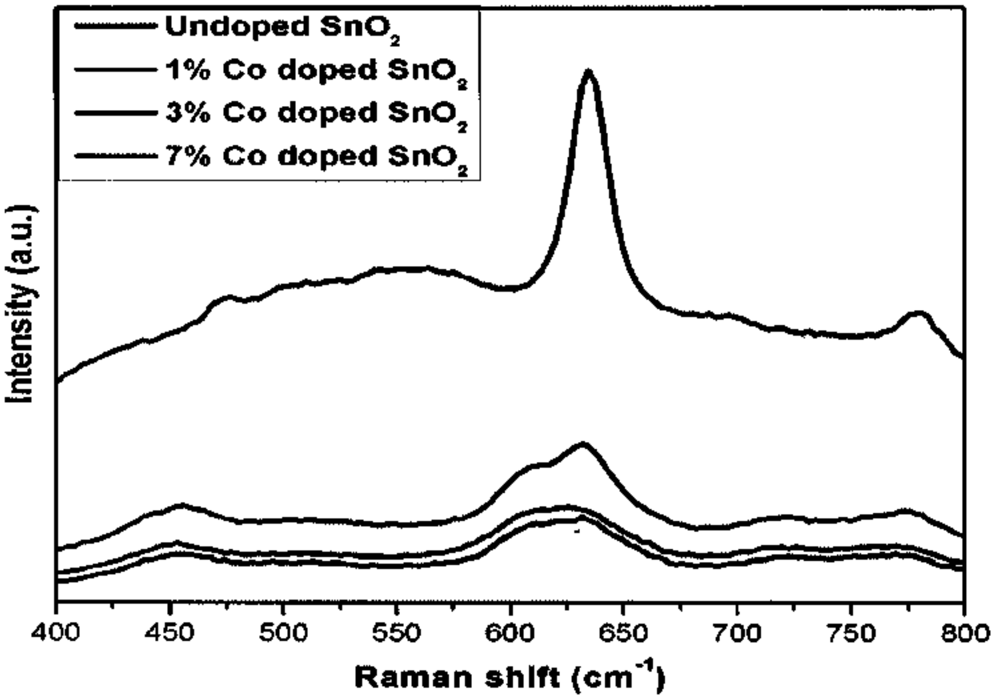

Figure 4.12: Raman spectra of synthesized samples

4.5 Ultra Violet Reflectance Spectroscopy

Ultraviolet reflectance spectroscopy is utilized to investigate the optical properties of the synthesized samples and spectra are shown in figure 4.13. The band gap is calculated using Kebulka-Munk (KM) function and is shown in figure 4.14. These results exhibit that the reflectance of undoped sample has minima at about 294 nm which attaains almost a constant trend (slightly decreasing) in the range 474-800 nm owing a band gap of 3.61 eV as also reported for thin films [41]. The observed band gap energies of as-prepared and Sn doped SnO_2 nanostructures gradually decreses from 3.61 eV to 2.24 eV and listed in table 4.9. This decline in band gap energies may be associated with impurity states created in SnO_2 nanotructures due Co doping [42].

Table 4.9: Band gap of prepared samples

Concentration	**Bandgap** (eV)
Undoped	3.61
1%	2.81
3%	3.00
5%	3.00
7%	3.30
10%	2.50

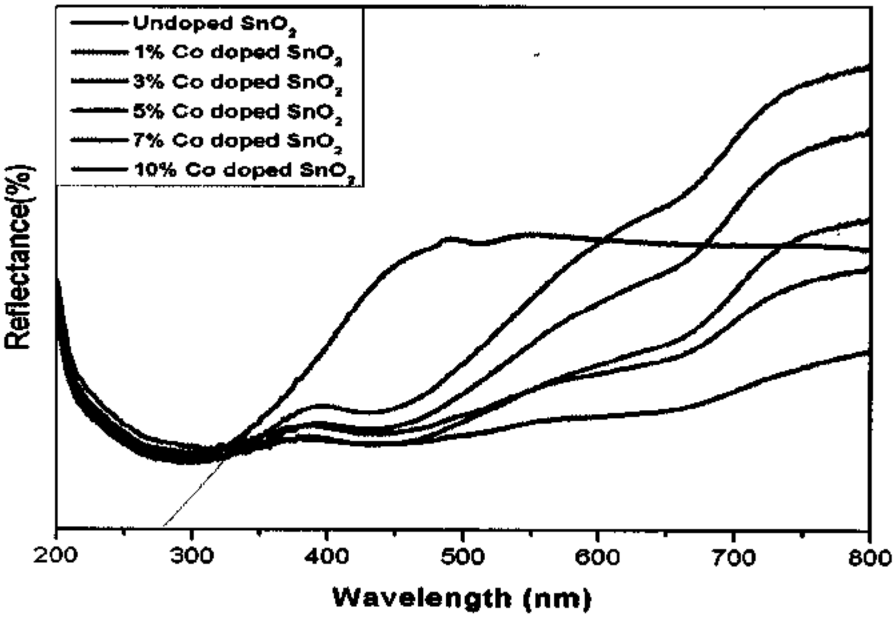

Figure 4.13 DRS scan of prepared samples

Band gap energy is calculated using Kebulka-Munk function by plotting $((1\text{-}R^2)/R^2)$ versus energy (eV) and the intercept of the linear portion of graph on energy axis gives the required energy values as mentioned in table 4.9 and shown in figure 4.14 [43].

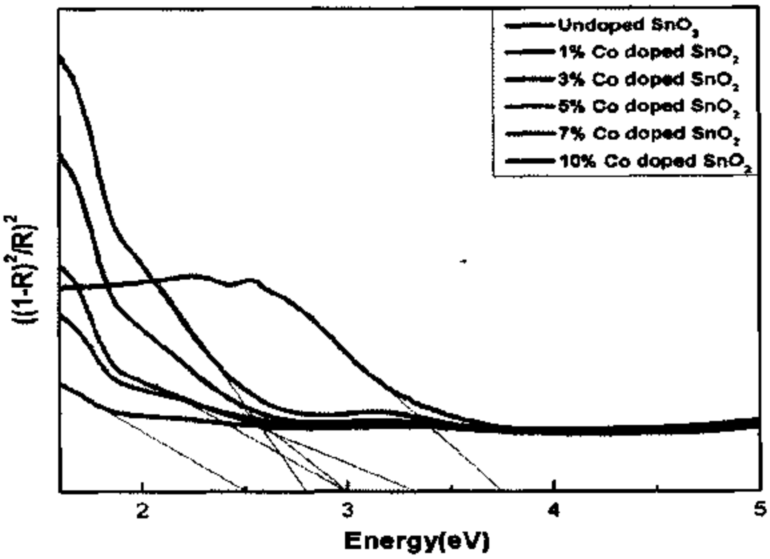

Figure 4.14: Variation of bandgap by doping concentration

4.8 Photoluminescence (PL) Spectroscopy

The PL spectra of undoped and Co doped SnO_2 samples have been carried out to investigate the inherent defects such as cation deficiency, quantum size effects and structural defects present in samples. These defects are very sensitive to different parameters such as synthesis method, types and dopant concentration, size of particle and morphology etc. PL spectra in figure 4.15 demonstrates that the prepared samples have two major transitions, one at 390-410nm and second at 540-640 nm. The first transition is assigned to near band edge transition which is almost in consistent with DRS study while the second transition is linked to the presence of large amount of defects in the sample [44]. The extra peak at 650nm in all the samples might be some of the internal instrumental perturbation in the experiment which can be removed or ignored as it not belong to any extra phase of prepared materials.

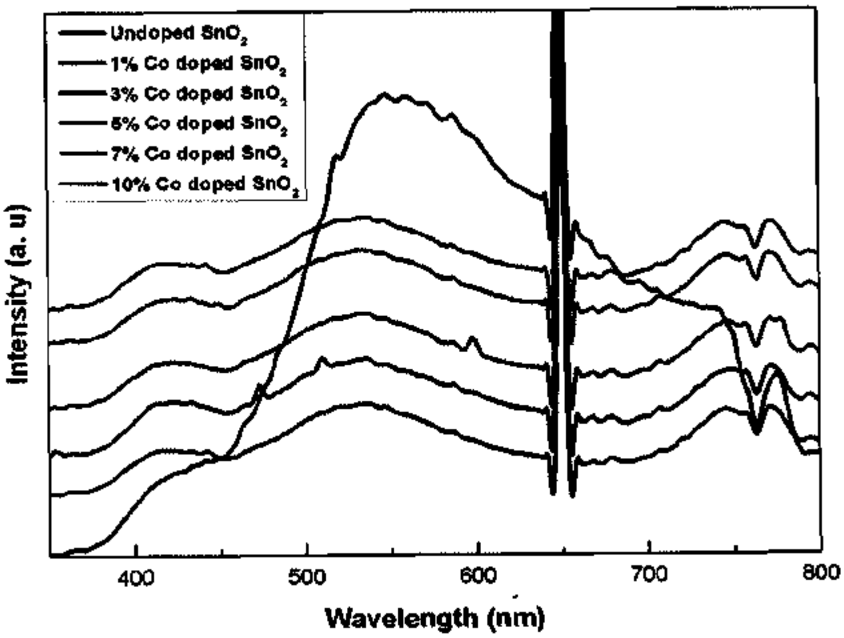

Figure 4.15: PL of undoped and Co doped SnO_2 nanostructures

CONCLUSIONS

Undoped and Cobalt doped tin dioxide nanostructures have been successfully prepared by Co-precipitation method. These prepared nanostructures have been examined by XRD, FTIR, SEM, EDS, UV, Raman and PL Spectroscopy. From the results of these characterizations, following conclusions are drawn.

- XRD patterns of undoped and Co doped SnO_2 nanostructures have confirmed the tetragonal crystal structure. The crystalline size of SnO_2 is found to decrease from 64 nm to 14 nm with the increase of cobalt concentration.
- FTIR results confirm the bonding in SnO_2 and also agrees with XRD results.
- From the results of SEM, average particle size of SnO2 nanostructures is found to be vary from 65 to 14nm with increasing the concentration of cobalt up to 10%.
- EDS patterns confirms the presence of tin, cobalt and oxygen in the samples according to the stoichiometric ratio chosen at the time of experiment.
- Raman confirms the Sn-O bonds and introduction of Co in the host material.
- The optical properties show that the bandgap is highly tailored towards lower energy values which make these prepared materials potential for solar light activated nano optoelectronics devices.

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Abstract Tin dioxide (SnO2) is an important metal oxide semiconductor having wide range of applications in electrodes of solar panel, lithium ion batteries and nano sensors. Doped and undoped Tin dioxide powders have been synthesized *via easy and economical coprecipitation route using Tin chloride (SnCl4)* as a precursor. Prepared undoped and Co doped SnO2 have been characterized to investigate its physical properties. Structural and morphological properties are examined by XRD, RAMAN and SEM. XRD patterns have confirmed the successful synthesis of SnO2 with no extra peaks. The size of nanostructures is found to decrease systematically with doping content from 64.0 nm to 14.50 nm. SEM micrographs have confirmed the presence of nanostructures. RAMAN patterns have supported the results of XRD showing no extra peak. Chemical composition checked by EDS has not shown presence of any impurity in the prepared samples, while FTIR also confirmed the stretching mode of chemical bonding of rutile tetragonal structures. In addition, the band gap is significantly reduced from 3.61 eV to 2.11 eV with increase in doping. From PL results, the decrease in band gap as well as defects by doping of Co in SnO2 are observed. The results reveal that the optical and structural properties of SnO2 nanoparticles can easily be modulated by doping of different concentrations of Co in SnO2 using coprecipitation method. Chapter No. 1 Introduction 1.1 Nanotechnology Although modern nanoscience and nanotechnology is a new field of science however nano materials have been employed from many centuries. Gold and silver particles of different sizes and morphology had been used many years ago to create different colors in the medieval churches glass windows. The actual processes involved was not well understood by the artists of that time however they modified the composition of these materials to create these beautiful works of art. Today's engineers and scientists have found a number of ways to use these materials at nanoscale. The improvement in the properties of nanomaterials such as higher strength, lighter weight, control of the light spectrum and higher chemical reactivity are more than their bulk counterpart. 1.2 History and Development of Nanotechnology The scientific story of nanomaterials is as fallows. ? The first scientific report was on the colloidal gold particles which were synthesized by Michael Faraday in 1857. ? In 1914, Richard Zsigmondy was the first person who characterized the particle with the help of nanometer scale. Using this approach, he has made the classification based on particle size [1]. ? In 1940s, fumed and precipitated silica nanoparticles were produced as a substitute for ultrafine carbon black for rubber reinforcement and sold in countries like United States and Germany. ? In 1959, the idea of nanotechnology scale was also introduced by American scientist Richard Feynman who was very inspired by this technology [2]. ? The