Chapter 1

Introduction

It has been about three decades since mankind entered to the world of fascinating science of reduced dimensions what we call today **Nanoscience and Nanotechnology**. Conceptually it originated in 1959, when Richard Feynman, in his classic talk shed light on the miniaturization of materials that could offer numerous applications in the field of science and technology. Though it is worth to say researchers of 21st century have almost achieved this, still today it is the emerging area of research in physics, chemistry and materials science.

A substance can be considered as nano material when size of any of the three dimensions is reduced to nanometer scale. This scale covers a range from few nanometers to 100nm. The following chart gives idea about how small is the nanometer actually when compared to bulk as well as micron sized objects. It shows the average thickness of the human hair is in the order of 0.1mm and size of bacteria generally found in few micrometers. The diameter of DNA double helix is 2nm and radius of hydrogen atom is around 0.05nm.

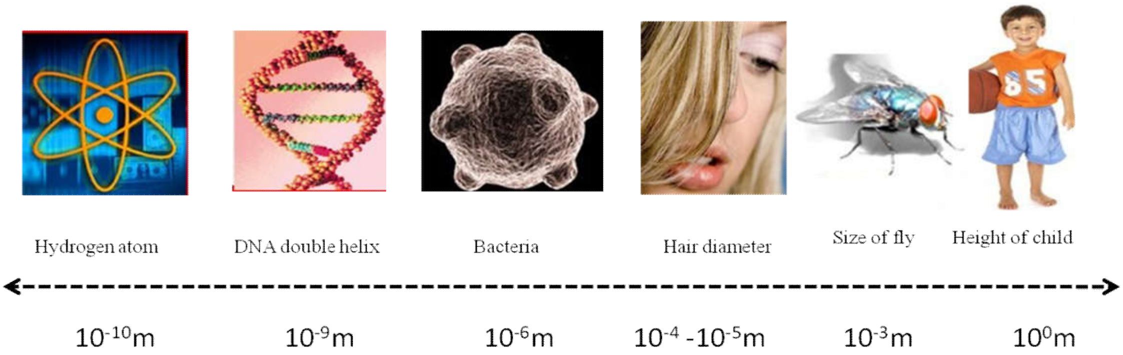

Fig.1.1 Illustration compares size of different objects ranging from 1meter to 0.1nm. (Source: http://www.azonano.com/article.aspx?ArticleID=1780)

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1.1 Fundamental of nanomaterials

The two major effects: a) large surface-to-volume ratio and b) quantum confinement become significant when size reduction occurs in materials.

a) Large surface-to-volume ratio

Many of the physical and chemical phenomena of the material are related to its free surface and often change with the number of surface atoms. As size of the matter reduced its surface area to volume ratio (SA:V) increases. Therefore smaller the size there will be large surface area and consequently material will have more number of surface atoms. It has direct effect on the reactivity of material. Surface atoms are chemically more reactive. So, nanoparticles are often used as catalysts to make the chemical reaction fast. In addition there will be large number of sites for the chemical reaction to take place on the surface.

b) Quantum effect

Quantum effect occurs when any of the dimensions of material is confined in the range of de'broglie wavelength. Here, by confinement, we mean to restrict the motion of charge carriers (electrons and holes) in a particular way, i.e., x-,y- or z- direction. Depending upon number of confined dimension, nanomaterials can be categorized in zero, one and two dimensional structures. The following table gives idea about confinement of dimensions and corresponding structure formation.

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[Table 1.1]

Nanostructures and dimensionality

No. of confined direction	Degrees of freedom	Type of structure
0	3	Bulk material
1	2	Quantum well, thin film (2D)
2	1	Quantum wire (1D)
3	0	Quantum dot, nanocrystal, colloid (0D)

As per uncertainty principle, confinement of charge carriers leads to the quantization of energy levels. As a result, unlike the continuum band in the bulk material, discrete energy levels are found in nanomaterials. Therefore, density of states as a function of dimension of the structure can be shown as below [1.1, 1.2]. Many important electrical, optical, magnetic properties arise due to this confinement of charge carriers.

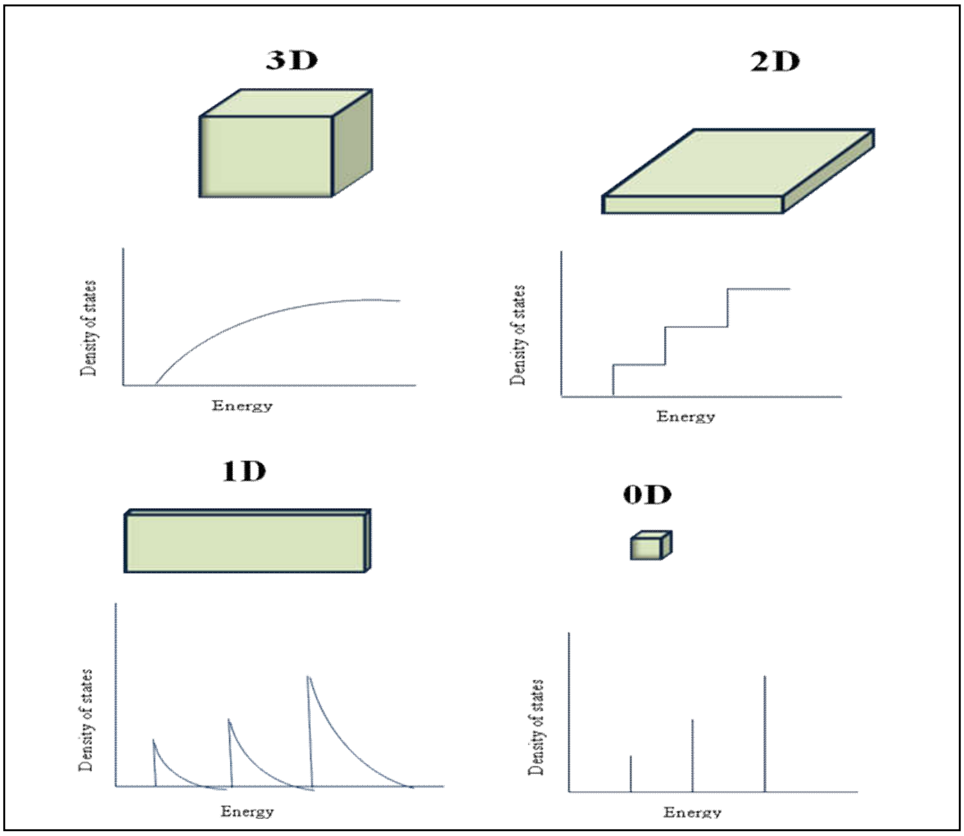


Fig. 1.2 Density of states as a function of dimension for different nanostructures

1) **Electric properties**

Discrete nature of the energy levels occurs in material due to the reduction of dimension comparable to de'broglie wavelength. The electronic structure may be modified because of the broadening of band gap. For a smaller particle, material like $PbTiO_3$ show higher value of dielectric constant. Nanomaterials with high dielectric constant are extensively used in the fabrication of components of electronic devices in order to reduce the device size [1.3].

2) Optical properties

Due to plasma oscillation of the electrons in nanoparticles, when they absorb the particular wavelength, transmit the light with different colors. The transmitted light depends on the particle size and type of material. Therefore some materials show different color when their size is reduced to nanometer scale.

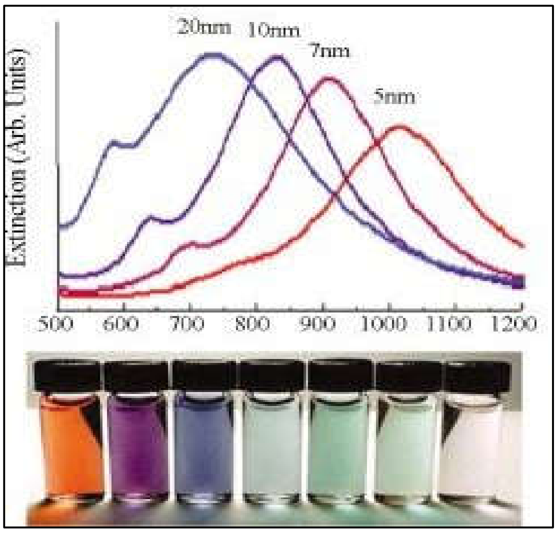


Fig. 1.3 Variation of color in gold nanoparticles [1.4]

(Source: http://www.sciencedirect.com/science/article/pii/S2090123210000056)

Gold (Au) is the well known example of this unique optical property of nanomaterials. While bulk gold material exhibits yellow color, literature shows in the range of nanometer, as particle size decreases color of gold shifts towards red from blue [1.3]. The light emitting efficiency is also improved due to miniaturization of size in some materials (like Si, Ge) as they do not emit light when found in their bulk structure [1.4].

3) Thermodynamic properties

Large surface-to-volume ratio plays the key role for the drastic change in thermodynamics at nanoscale. The thermodynamic properties of nanomaterials are based on nano thermodynamics, the theory that links macroscopic and microscopic systems by extending classical thermodynamics to nanometer scale. The variation in the melting point with particle size is the primary investigation based on this approach. The nanoparticles melt at lower temperature than the corresponding bulk material. It can be considered as a fundamental investigation for the study of phase transition and other physicochemical properties [1.5,1.6].

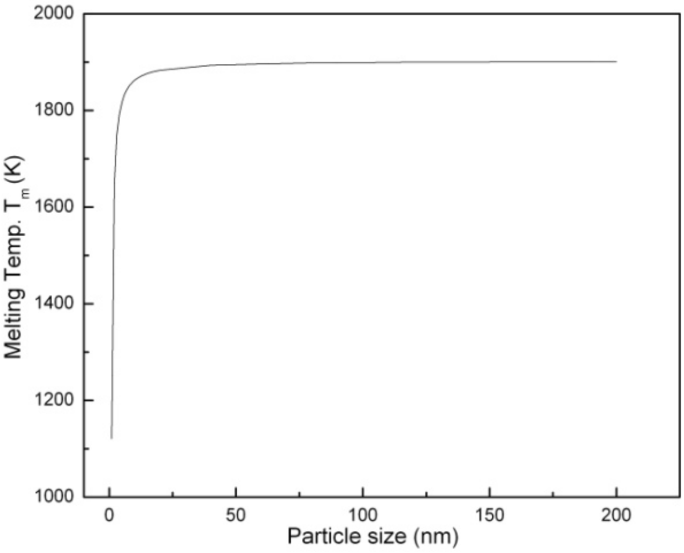


Fig.1.4 The melting temperature of Tin dioxide (SnO_2) decreases rapidly for the particle size below 5nm

The fundamental properties like specific heat and Debye temperature also vary with particle size. The specific heat is found to be increasing as diameter of particle is decreasing due to surface effect while Debye temperature decreases with decreasing particle size [1.7, 1.8].

4) Magnetic properties

In case of ferromagnetic materials, by reducing their size particles show collective behavior and act as a single domain which gets magnetized in the presence of external field. In other words, decrease in particle size leads the transformation of ferromagnetic to paramagnetic. This fact suggests reduction in Curie temperature for smaller particles [1.3].

5) Catalytic properties

Once the size of the matter approaches to sub-atomic scale, it exhibits fascinating catalytic properties resulting from large surface area of nanomaterials. The chemical activity of the catalyst to catalyze different reactions is defined by the catalytic activation energy (E_C). The value of E_C decreases with the decrease in particles' size suggests better efficiency of nanoparticles for catalysis. . In addition to particles size, there exists a remarkable impact of shape on the catalytic properties of nanomaterials. The spherical nanoparticles can act as better catalysts compared to one and two dimensional nanostructures. For a given size, tetrahedral shaped particles are catalytically the most active [1.9].

6) Mechanical properties

Hardness and strength of materials increase considerably when size is reduced to nanometer scale. Therefore nanomaterials are used to improve tribological properties.

1. 2 Different applications of nanomaterials

[Table 1.2]

Applications of nanomaterials

Type	Material	Application area
Metallic nanoparticles	Gold NPs	Biomedical application targeting cancer [1.10], Drug delivery [1.11], catalysis [1.12]
	Silver NPs	Anti-microbial agent, water purification [1.13]
	Metal nano fluid	In exchange of heat [1.14]
Semiconductors/oxides	Titanium dioxide (TiO_2)	In photocatalysis [1.15], waste water treatment [1.16], as a coating agent for paper and cosmetic products [1.17]
	Tin dioxide (SnO_2)	In gas sensors [1.18], anode material for lithium ion

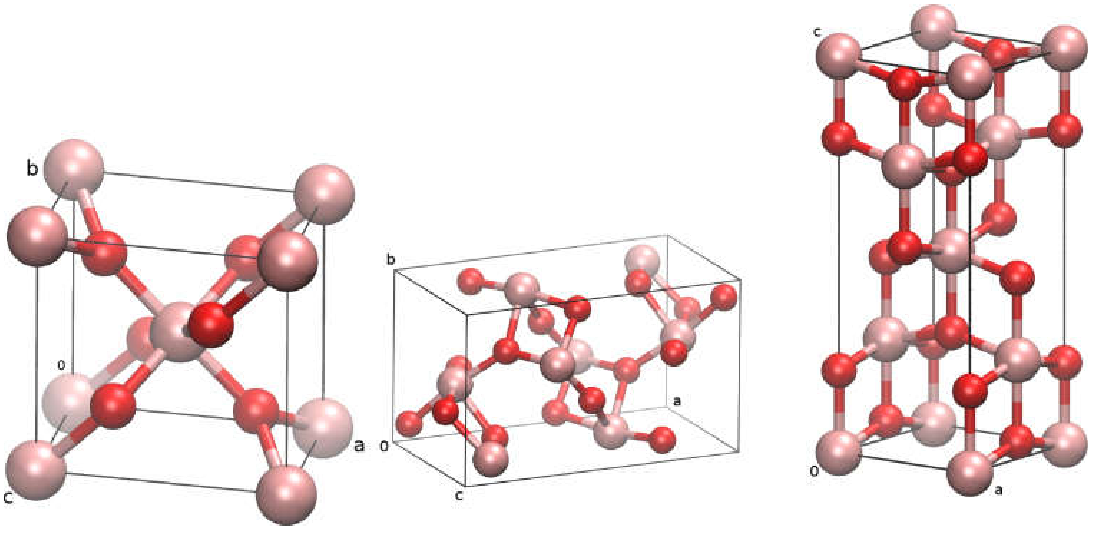
		batteries [1.19], dye - sensitized solar cells [1.20]
	Zinc oxide (ZnO)	In photonics, fabrication of Field Effect Transistor (FET),chemical and biosensors [1.21]
Carbon based nanomaterials	Fullerene	In solar cells, storage of hydrogen, diamond coating, optics and medicine.
	Carbon nano tubes (CNTs)	In lithium ion batteries, catalysis, microelectronics and solar cells
	Graphene	In optoelectronics, photovoltaic cells, energy storage and biological engineering

1.3 Nanostructured semiconducting oxides

Semiconducting oxides serve an important class of materials due to their vast area of applications in modern electronic products, optoelectronic devices, catalysis and gas sensors [1.22-1.24]. From this class, some materials like Titanium dioxides (TiO_2), Tin dioxide (SnO_2) and Zinc Oxide (ZnO) refer to wide band gap semiconductors those band gap value lies between 3-4 eV. Our research interest is focused on TiO_2 and SnO_2 because of the unique surface properties when their dimensions shrink to nanometer.

1.3.1 TiO_2 nanostructures

Both the oxides, TiO_2 and SnO_2 have identical i.e. tetragonal crystal structure but different polymorphs. TiO_2 can be crystallized in rutile, anatase of brookite structures. Among these three polymorphs, rutile and anatase have been investigated in detail by many researchers due to its easy preparation and potential industrial applications [1.25].



Rutile **Anatase** **Brookite**

Fig. 1.5 Crystal structures of three polymorphs of TiO_2 [1.26]

(Source: http://iopscience.iop.org/09538984/24/42/424206/pdf/09538984_24_42_424.pdf)

The binary metal oxides exhibit meta-stable crystal form which is different from original structure when different conditions of pressure and temperature are applied. But it is possible to have this meta-stable state at ambient condition if grain size of these materials reduces to nanometer scale [1.27]. Following table shows details of crystal structure of three polymorphs of TiO_2 [1.28, 1.29].

[Table 1.3]

Crystal structure of three polymorphs of TiO_2

Phase	Crystal structure	Lattice parameter
Rutile	tetragonal	(a = 4·5937 Å, c = 2·9587 Å) (P42/mnm)
Anatase	tetragonal	(a = 3·7845 Å, c = 9·5143 Å) (I42/amd)
Brookite	orthorhombic	(a = 5·4558 Å, b = 9·1819 Å, c = 5·1429 Å) (Pcab)

Among these three phases of TiO_2, rutile is thermodynamically stable at room temperature while anatase is kinetically stable and can be converted to rutile at higher temperature [1.30]. These polymorphic phases show considerably enhanced surface properties at nanoscale. Titania generally transforms from anatase to rutile phase at higher temperature. For bulk titania this phase transition occurs at 1473K. However temperature lowers to 673K when same material has grain size of 8nm [1.31-1.35]. Recently new polymorph of TiO_2 has been found and named as TiO_2 (B) which is in the form of nanowires and can be synthesized using solvothermal route [1.36]. In 1969, Fujushima and Honda proposed application of titanum dioxide in water catalysis [1.37]. Two basic structures of titania, rutile and anatase have different bandgap. Value of bandgap for rutile TiO_2 is 3.0 eV and 3.2 eV for anatase structure. Nanoscale anatase TiO_2 increases photocatalytic behavior due to increase in number of pores and enhancement in solid-solid interactions [1.35]. Literature shows that calcinations of nano titania at higher temperature (> 573 K) decreases its photo catalytic activity [1.38]. Cappelletti et al. observed that mixed phases of anatase-brookite composite titania has better photocatalytic activity than pure rutile phase [1.39].

1.3.2 SnO_2 nanostructures

Present research work is mainly focused on Tin dioxide (SnO_2) nano materials. Our research interest in SnO_2 is due to its electronic, chemical catalytic and sensing properties. Nano sized SnO_2 is widely used to detect sensitivity towards oxidizing and reducing gases. At ambient condition, SnO_2 exhibits rutile type tetragonal structure and it changes to $CaCl_2$ type, α-PbO_2 type and finally a pyrite (modified fluorite)-type structure when pressure is increased [1.40]. Past studies show that high pressure orthorhombic phase of SnO_2 can be synthesized when pressure is upto 15 kbar at 1073 K. But for nanometer size of SnO_2, this structure can be achieved at ambient pressure

[1.41-1.42]. It is a wide bandgap (~ 3.6 eV) semiconductor with even higher band gap at 300K. Generally tin dioxide crystallizes in cassiterite structure which has tetragonal unit cell with a space group symmetry of P42/mnm. The lattice constants are a = b = 4.731 A ° and c = 3.189 A°. In the crystal structure, tin atoms are six fold coordinated to threefold coordinated oxygen atoms as shown in below figure [1.43]. Among all the structures of

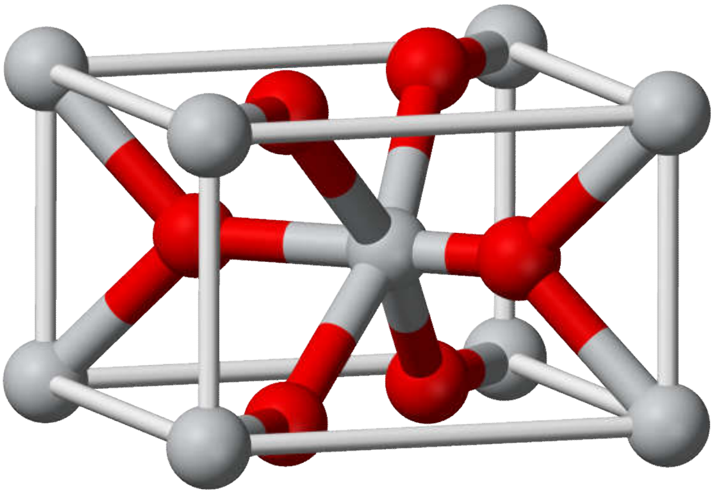


Fig. 1.6 Crystal structure of SnO_2

(Source: https://en.wikipedia.org/wiki/Cassiterite)

SnO_2, cassiterite is widely used because of its electronic and chemical properties. Surface composition of SnO_2 changes from stoichiometric surfaces with Sn^{+4} to reduced surfaces with Sn^{+2}. Changes to a reduced surface structure can the surface electronic structure of the material and hence makes SnO_2 a potential candidate for gas sensing applications [1.44]. Another interesting property proposed in literature explains surface oxygen deficiency in SnO_2 structure due to formation of energetically favorable surfaces (1 1 0) and (1 0 1) [1.45-1.47].

It is reported that physical, chemical, electronic, optical, and catalytic properties of nano SnO_2 depend on the size and shape of nanoparticles. Thereby synthesis of nano sized SnO_2 with desired size and shape has attracted intense research interest since last two decades. Past study show synthesis of SnO_2 nanomaterial with different morphology such as zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanorods, nanobelts, nanowires and nanotubes and two-dimensional (2D) nanosheets [1.48-1.58]. By choosing proper synthesis route for desired purpose one can prepare 0-D, 1-D or 2-D nanoparticles of SnO_2. For example, in spherical (0-D) nanoparticles, constituent particles are randomly arranged and do not have specific orientation so they can be used for gas sensors because of large surface area [1.59-1.62]. One dimensional structures such as nanorods, nanowires, or nanotubes of SnO_2 behave as direct electrical pathways for photo generated electrons and enhance electron transport rates. Due to this property they can be utilized in photovoltaic devices [1.63-1.65]. Two dimension structures like nanosheets and nanoplates have specific facets with large surface area and therefore they can be applied in area of catalysis, electro-catalysis and lithium-ion batteries [1.66-1.68].

Dimensionality of constituent building blocks of SnO_2 depends upon its synthesis route. Preparation method is generally solution-based and involves hydrolysis of tin precursors. There are number of parameters in synthesis route including concentration of tin precursor, pH value of aqueous solution, additives and co-solvents which can affect size and dimensionality of particles. These synthesis parameters to achieve different dimensionality are listed in below table [1.55].

[Table 1.4]

Details of tin precursor and solvent to synthesize 0-,1- and 2-D SnO_2 nanostructure [1.55,1.69-1.76]

Dimensionality	**Tin precursor**	**Additives**	**Solvents**
0 D	$SnCl_4$	D-glucose	H_2O or Ethanol
0 D	$SnCl_2$	D-glucose	H_2O
0 D	K_2SnO_3	Glucose	H_2O
0 D	K_2SnO_3	Urea, Thiourea, Ethyldiamine	H_2O or Ethanol
1 D rod	$SnCl_4$	Cetyl trimethyl ammonium bromide (CTAB)	H_2O or Ethanol
1 D cone	$SnCl_4$	Poly acrylic acid (PAA), Sodium hydroxide (NaOH)	H_2O
2 D sheet	$SnCl_2$	Urea, NaOH	H_2O or Ethanol

2 D sheet	$SnSO_4$	sodium citrate	H_2O or Alcohol

Motivated from above mentioned applications of SnO_2 and TiO_2 nanoparticles, in present work, we have studied size and dimension dependent thermodynamics properties of these nano structures at nano scale. Efforts have been made to synthesize nano sized SnO_2 and their composites to achieve enhanced mechanical and electrical properties. Specific objectives of thesis are:

i) To understand thermodynamic model based on analytical approach to calculate size dependent melting temperature and other thermo dynamical properties

ii) To calculate diffusion related parameters in nano SnO_2 particularly for nitrogen and self diffusion

iii) To estimate efficiency for catalysis in TiO_2, SnO_2 and CeO_2 nanostructure

iv) To calculate surface energy for different facets of nano sized TiO_2 and SnO_2 which gives idea about thermodynamic stability of corresponding planes

v) To prepare nano sized TiO_2

vi) To prepare SnO_2 nanoparticles characterize prepared samples X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM)

vii) To study doping effect in SnO_2

viii) To synthesize Ag-SnO_2 nanocomposites by mechanical alloying and study their density and hardness

1.4 Outline of the thesis

In Chapter 1, we introduce concept of nanomaterials and major properties like surface-to-volume ratio and quantum confinement due to size reduction. It describes variation in electrical, optical, thermodynamic and catalytic properties at nano scale. Crystal structure and synthesis conditions are explained for TiO_2 and SnO_2 nanoparticles.

In Chapter 2, using analytical modeling we have formulated theory to calculate size and shape dependent properties in semiconducting nano oxides. A theoretical description is based on nano thermodynamics. We present computational methods to estimate size dependent melting temperature, glass transition temperature, Kauzmann temperature, diffusion coefficient, catalytic activation energy, surface energy and Tolman length of nanoparticles.

In Chapter 3, we describe synthesis methods for nanoparticles. Different characterization techniques are also discussed to study structure and composition of prepared samples. Details are given for powder metallurgy method along with advantages of this method.

In Chapter 4, using theoretical modeling we present calculated results of size, dimension and shape dependent thermodynamic and other properties of SnO_2 and TiO_2 nanostructures. From calculations, we conclude that melting and glass transition temperatures of SnO_2 nanoparticles both decrease with decrease in particle size. Diffusion coefficients of self- and nitrogen diffused SnO_2 increase when size is reduced. From surface energy calculations, our results show that (112) and (110) facets of SnO_2 have maximum and minimum value of surface energy respectively for given size range. It also suggests that rutile structure of TiO_2 is more stable as compared to anatase TiO_2. Tolman length shows opposite trend than size variation in surface energy of nano structures. Comparative study of catalytic activation energy in different nano oxides shows that nano TiO_2 has maximum efficiency for catalysis. Among different shapes, tetrahedral particles can act as better catalysts.

In Chapter 5, we describe synthesis route to prepare nano sized TiO_2 and SnO_2 nanostructures using wet chemical methods. Results are given to confirm structure and chemical composition of the samples. Our XRD results show that nanoparticles of SnO_2 and TiO_2 have been successfully prepared. We have also described mechanical alloying method to prepare Ag-SnO_2 nanocomposites. Results of their density measurements and hardness measurements are given.

In Chapter 6, we summarize the present work and discuss the future scope and directions of this research work.

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