CHAPTER 1

GENERAL INTRODUCTION

1.1 Nanoscience and nanotechnology: Historical development and basic concepts

In the current era of research, a new field of interest has raised up, named to as "Nanoscience and nanotechnology" [1, 2]. Nanotechnology is a combined term attributing to each technology and science which functions on nanoscaled size; and to the scientific fundamentals and innovative properties that can be discovered and mastered while working in this range. The Nobel Prize winning physicist, Richard Feynman introduced the concept of manipulation at atomic level. Feynman proposed that "devices and materials could someday be fabricated to atomic specifications, but for this to happen, a new class of miniaturized instrumentation would be needed to manipulate and measure the properties of these small-**nano-structures**". However, the research and development in this field was not flourished until 1980's when the scanning tunneling microscope (STM) was discovered as there were limited sophisticated characterization techniques to study the unique properties of nanomaterials [3]. Following the invention of STM, extremely innovative and sophisticated characterization instruments were developed (and are still being developed) swiftly, which enabled the synthesis and analysis of nanomaterials resulting a human being's view into a real atomic world. The concepts of nanotechnology suggested by Feynman, were discussed and defined by Eric Drexler in his book "Vehicles of creation: the arrival of the nanotechnology era (1986)". From 1986 to first half of 1990s, a number of principal findings and innovations were developed, which further promoted the research in the field of nanotechnology. Since then, a great escalation of nano-technological studies and devices is in progress, the number of publications on nano-technological topics and the fabrication of smart nano-devices are multiplying day by day.

The Royal Society elucidated that "*Nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale*". The nanomaterials of sizes from 100 nm to just a few nm possess unique properties that can be extremely distinctive from their bulk forms.

The term ‘nano’ is a Greek language word whose meaning is ‘*dwarf*’. A nanometer (nm) is one thousand millionth of a meter, 10^{-9}. To exemplify the size, the width of human hair is about 40,000 nm, diameter of a virus is approximately 100 nm and the size of DNA molecule is 2nm. Ten atoms of hydrogen arranged in a straight line is equal to one nanometer. The development of new instruments and approaches has enabled scientists to tailor the matter practically atom by atom and allowed the analysis of its characteristics with a resolution in atomic range. These new devices made it possible to view the insight perceptive of the unusual structural, optical, electrical and thermal characteristics of nanomaterials facilitating their use in a wide variety of applications involving materials science, engineering, physics, chemistry and biology. The highly developed nanotechnology could fabricate smart nano-machines thousands of times more efficient, powerful and hundreds of times cheaper than today’s devices. Nanotechnology is believed to be the next industrial revolution and in future, is supposed to impact hugely on the society, economy and lives in general [4]. The technological areas in which nanotechnology is and will be used are medicine, information technology, biotechnology, energy production and storage, materials technology, manufacturing, instrumentation, environmental applications and security.

However, a few potential negative aspects of nanotechnology may affect the environment and health of users. The tailored nanoparticles can penetrate the skin, lungs and intestinal tract with unknown effects to human health as they can travel around in the body and reach for example, the brain [5]. The new modified NPs have novel properties not previously known and it is likely that these properties could cause negative impacts on ecosystems and organisms. As an example, a study led by Eva Oberdorster found that “a type of buckyball - a carbon nanoparticle that shows promise for electronic and pharmaceutical uses - can cause brain damage in fish” [6].

1.2 Nanomaterials: Synthesis, properties and applications

Nanomaterials are defined as materials with primary particles less than 100 nm in length at least in one dimension. The nanomaterials may be one dimensional (thin films), two dimensional (nanofibers, nanowires, carbon nanotubes) or three dimensional (fullerenes, quantum dots, nanocapsules, dendrimers). One can find nanoparticles (NPs) in the surrounding which are produced either naturally in volcanoes or forest fires, or pollen of flowers and can originate as soot (combustion), welding fumes and diesel exhaust etc. NPs can grow stable agglomerates or aggregates that are larger than nanosize. The agglomerates can be defined as a group of particles held together by relatively weak forces that may break apart into smaller particles upon processing. On the other hand, Aggregates are delineated as a bunch of particles held collectively by strong forces or bonds and are not easily broken apart [7]. The properties of nanomaterials change from its bulk counterpart significantly. This happens mainly due to the quantum confinement effect and/or due to the increased surface to volume ratio. Therefore preparation of nanoscaled materials with different morphologies and altered compositions, and also their analysis have been of considerable interest for fundamental studies as well as for its potential applications. Nanomaterials can retain such size dependent properties, even when the primary particles form agglomerates or aggregates. Therefore, scientific knowledge of materials composed of particles on larger size scales cannot be applied to nanomaterials and is not sufficient to predict the behavior of nanomaterials.

Synthesis: A number of well-developed synthesis routes, generally categorized as top-down and bottom-up approaches have been used to synthesize nanostructures [8]. The procedure of first order phase transition is followed commonly during the synthesis of nanomaterials whether the method is top-down or bottom-up. Hence it is necessary to know the basic factors of the phase transition process for growing nanomaterials with successful control over morphology and composition. In the other way, morphology and composition of nanomaterials contain information on the synthesis mechanism that it had gone through. Therefore, preparation of nanomaterials with various morphologies and compositions and investigating their properties not only reveal their technologically important applications but also help in understanding the process of phase transition in a better way. Although the phenomenon of phase transition, synthesis route, growth parameters etc. are analyzed and reported widely for several years with immense zeal, many questions are still to be answered [9].

Properties: Quantum size effect and increased surface to volume ratio of nanoparticles are the two main features why NPs exhibit unique structural, optical, electrical, magnetic, chemical and mechanical characteristics as compared to bulk form [10]? As the size of the particles decreases, the dominance of surface atoms increases gradually over the ones inside the particle. This induces the changes in individual properties of the particle and alters its interaction with other particles in the surroundings. A few properties namely high surface energy, improved absorption, electrical conductivity, are the consequences of increased relative surface area. As the high surface area is an essential aspect of efficient catalysis and structures like electrodes making them very useful for industrial applications. Not only the efficiency of products like battery improves, but also it reduces the amount of resource being used in catalytical processes and hence decreases the cost of processes. The large surface area also increases chemical reactivity of the material which is especially beneficial in the synthesis of intermixed materials like composites.

Applications: There is an extremely broad range of potential applications of nanomaterials, from electronic devices (including miniature integrated circuits, organic solar cells) to packaging films, super-hydrophobic thin films, parts of automobiles, healthcare/medicine, engineering, cosmetics, pigment coatings, etc.

1.3 Metal oxide nanomaterials

Metal oxides act as an essential component in many technological applications of different branches of science [11-16]. Due to chemical reactivity, metals could react with other elements to form a large variety of compounds e.g. carbonates, halides, oxides, hydroxides, etc. [17]. Metals can exhibit different structural geometries with metallic, semiconducting or insulating properties. The research on the synthesis and characteristics of metal oxides is growing day by day due to their applicability in numerous areas namely microelectronic circuits, photocatalysts, oxygen sensors, piezoelectric devices, solid oxide fuel cells, anti-corrosive coatings, and as electrodes. In the promising domain of nanotechnology, the aim of research is to synthesize nanostructures with application based properties using a reproducible and simplified method [18-22]. Metal oxides NPs possess exceptional physical and chemical characteristics due to high density of corner or edge surface sites at nanoscaled. The reduction in size of material influenced three major groups of properties spectacularly. The first group includes micro-structural properties such as lattice symmetry, unit cell parameters. Another prominent impact of size is related to electronic characteristics of oxide. The last major group of properties altered by size is optical parameters, such as band gap, absorption coefficient, emissivity, etc. In technological applications, metal oxides such as ZrO_2, Al_2O_3, TiO_2, SnO_2, CeO_2, ZnO, Fe_2O_3, SiO_2 and their binary systems such as CeO_2-ZrO_2, TiO_2-ZnO, CeO_2-CuO_2, SnO_2-Al_2O_3, Fe_2O_3-SiO_2, SnO_2-TiO_2, TiO_2-SiO_2 etc. are widely used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, solar cells, anticorrosion coatings, catalyst supports, absorbent, photocatalysts, electro-chromatic displays, antireflective coatings, and planar waveguides, etc.

1.4 Selection of the problem and Objectives

Selection of the problem:

The search and development of new/smart materials for sophisticated device fabrication is a never ending process. Although, the synthesis of metal oxides and their binaries in nanocrystalline form has experienced good progress in recent years owing to their interesting size dependent structural, electronic, magnetic, optical, dielectric and thermal properties, but there is a further scope of research in the direction of micro-structural, optical and thermal behaviour of transition metal oxides such as TiO_2, SiO_2, ZrO_2 and their binary systems TiO_2-SiO_2, ZrO_2-SiO_2 and TiO_2-ZrO_2. These metal oxides have high refractive indices, wide band gap and good insulating properties. Also, these oxides are non-toxic, biocompatible material, widely available; and show good stability in various environments. This has motivated current research regarding the synthesis and characterization of nanoscaled metal oxides and their binary systems as mentioned above, along with deriving novel properties for tremendous applications in devices such as solar cells, sensors, channel gratings, holographic gratings, photocatalysts etc. Our attention will be towards tailoring of materials properties through composition, temperature and doping etc. as per their requirement for the fabrication of devices.

Objectives:

The main objectives of the proposed research work are as follows:

1. Synthesis of nanoscaled metal oxides and their binary systems using the sol-gel technique by optimizing the growth parameters (pH, reaction temperature, reaction time, stirring rate, etc.).
2. Prepare thin film samples by using spin coating technique.

3. Study the effect of the composition of precursors and heat treatment temperature on the properties of synthesized samples.
4. Study of dopant induced changes in the properties of prepared samples.
5. Study the effect of particle/crystallite size on the properties.
6. Investigations on synthesized materials to study their structural, optical and thermal properties as:
    a. to determine the crystal structure and crystallite size using XRD.
    b. to observe the structural evolution of prepared samples using FTIR.
    c. to study morphology and microstructural properties employing SEM, TEM.
    d. to determine the optical parameters such as band gap, emission wavelength
    e. etc. by UV-visible spectroscopy and photoluminescence.
    f. to study some thermal properties with the help of TGA/DTA.

1.5 Organization of the thesis

The organization of the thesis is as follows:

Chapter 1: *General Introduction.* This section describes a general introduction to the thesis and provides a brief and general introduction to nanoscience and nanotechnology, nanomaterials and metal oxide nanomaterials with their applications in diverse fields. Finally, this chapter discusses in a brief selection of problem and objectives achieved during the term of Ph. D. programme. The objectives describe the methodology used for the synthesis of nanoscaled metal oxides and their binary system, focus areas to control growth and the characterization techniques used for studying structural, optical and thermal properties of nanomaterials prepared.

Chapter 2: *Nanoscaled Transition Metal Oxides: A Review*. This chapter provides a general literature review of the nanoscaled metal oxides and their applications. First of all, it gives a general introduction to the different kind of metal oxides. Then, the bench marking properties of metal oxide nanomaterials are described, followed by their technological applications. In the last, a literature review of current research work on metal oxides and their binary systems has been discussed.

Chapter 3: *Experimental Procedures and Analytical tools*. This chapter describes the introduction of various routes to synthesize nanomaterials in brief. The methodology/techniques used for the synthesis of powder as well as thin film samples of present work, i.e. sol-gel and spin coating, have been discussed in detail. In the next section, characterization techniques to study the structural, optical and thermal behaviour of synthesized nanomaterials have been discussed. Physical principles, advantages and applications of various instrumentation techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy with Energy dispersive X-ray spectroscopy (SEM/EDX), Transmission electron microscopy (TEM), UV-visible spectroscopy, Photoluminescence (PL) spectroscopy, Thermo gravimetric / Differential thermal analysis (TGA/DTA) etc. have been described.

Chapter 4: *Rietveld refinement, micro-structural, optical and thermal parameters of zirconium titanate composites*. This chapter discusses the methodology used for studying the structural, optical and thermal properties of nanoscaled TiO_2-ZrO_2 binary system. The results confirm the formation of zirconium titanate and the variation in properties due to a change in precursor concentration and annealing temperature.

Chapter 5: *Structural, micro-structural, optical and thermal properties of nanoscaled tetragonal zirconia quantum dots in silica*. This chapter describes the experimental details of synthesis and characterization of ZrO_2-SiO_2 binary system. Also, the structural, optical and thermal behaviors of ZrO_2-SiO_2 binary system have been discussed and modifications in properties have been found and compared with other researchers.

Chapter 6: *Crystal structure, morphology and optical behaviour of nanoscaled pyrochlore rare earth titanates $RE_2Ti_2O_7$ (RE=Dy, Sm)*.This chapter describes the synthesis of pyrochlore rare earth titanates $RE_2Ti_2O_7$ by varying the concentration of rare earth metals namely Dysprosium and Samarium. The structural, optical and thermal properties of pyrochlore rare earth titanates $Dy_2Ti_2O_7$ and $Sm_2Ti_2O_7$ have been studied through a number of characterization techniques, namely XRD, FTIR, TEM, UV-vis, PL and TGA/DTA. The pyrochlore titanates are found to be suitable for many applications such as radio-sensitizers, nuclear waste treatment, organic dye removal etc.

Chapter 7: *Investigations on structural, optical and thermal aspects of nanoscaled titanium oxides stabilized in silica*. This chapter discusses systematically the synthesis, characterization and results of nanoscaled TiO_2-SiO_2 binary oxides. The structural behaviour of prepared samples has been studied through XRD, FTIR, SEM with EDX, and TEM. The phase transition of titania and stabilization of its anatase phase in silica was observed. The optical band gap of anatase titania has been modified whereas emission wavelength exhibits shifting towards shorter wavelength. The weight loss % and energy dissipation in the samples due to thermal treatment were observed through TGA/DTA analysis which reveals the crystallization stages of titania.

Chapter 8: *Conclusions and Future Directions.* This chapter concludes the research work done and the thesis. It emphasizes the research objectives achieved with self justification. Discussions on modifications in the properties of metal oxides for device fabrication have been made. Also, future directions for pursuing further research in the same field has been described in order to strengthen and enriched the work present in this thesis. In addition, I will make sincere efforts for device fabrication utilizing these materials.

References

1. N. Lane, J. Nanopar. Res. **3** (2001) 95.
2. R. F. Service, Science **290** (2000) 1526.
3. M. Ratner, D. Ratner, Nanotechnology: A gentle introduction to the next Big idea, Pearson Education Inc. (2003).
4. A. Hett, Nanotechnology: Small matter, many unknowns, Swiss Reinsurance Company (2004).
5. G. Oberdorster, Z. Sharp, V. Atudorei, A. Elder, R. Gelein, W. Kreyling, C. Cox, Inhal. Toxicol. **16** (2004) 437.
6. E. Oberdorster, Environ. Health Perspect. **112** (2004) 1058.
7. S. R. Elzey, Applications and physicochemical characterization of nanomaterials in environmental, health, and safety studies. Dissertation, University of Iowa (2010).
8. H. S. Nalwa, Handbook of nanostructured materials and nanotechnology, Academic Press (2000).
9. D. Erdemir, A. Y. Lee, A. S. Myerson, Acc. Chem. Res. **42** (2009) 621.
10. P. Holister, J. W. Weener, C. R. Vas, T. Harper, Nanoparticles: technology white papers nr. 3, Cientifica (2003).
11. C. Noguera, Physics and chemistry at oxide surfaces, Cambridge University Press (1996).
12. H. H. Kung, Transition metal oxides: surface chemistry and catalysis, Elsevier (1989).
13. V. E. Henrich, P. A. Cox, The surface chemistry of metal oxides, Cambridge University Press (1994).
14. A. F. Wells, Structural inorganic chemistry, 6th ed., Oxford University Press (1987).
15. J. A. Rodriguez, M. Fernandez-Garcia, (Eds.) Synthesis, properties and applications of oxide nanoparticles, Wiley (2007).

16. M. Fernnndez-Garcia, A. Martinez-Arias, J. C. Hanson, J. A. Rodriguez, Chem. Rev. **104** (2004) 4063.
17. R.W.G. Wyckoff, Crystal structures, 2nd ed, Wiley (1964).
18. H. Gleiter, Nanostruct. Mater. **6** (1995) 3.
19. M. Valden, X. Lai, D. W. Goodman, Science, **281** (1998) 1647.
20. J. A. Rodriguez, G. Liu, T. Jirsak, J. Hrbek, Z. Chang, J. Dvorak, A. Maiti, J. Am. Chem. Soc. **124** (2002) 5247.
21. M. Baumer, H. J. Freund, Prog. Surf. Sci. **61** (1999) 127.
22. M. L. Trudeau, J. Y. Ying, Nanostruct. Mater. **7** (1996) 245.