CHAPTER 8

CONCLUSIONS AND FUTURE DIRECTIONS

8.1 Conclusions

In this work, nanoscaled zirconia, titania and their binary composites namely zirconium titanates, dysprosium and samarium titanates, thermally stable and optically efficient, have been prepared via sol-gel and spin coating techniques. The structural, micro-structural, optical and thermal characteristics of prepared specimens have been studied. The general introduction of transition metal oxides, their unique properties at nanoscale and corresponding applications has been reviewed. Zirconia and titania are polymorphic in nature and can exists in different crystalline forms. Zirconia can occur in cubic, tetragonal and monoclinic phases and can also be transformed reversibly from one phase to another. The tetragonal phase of zirconia is metastable and employable in technological applications. Also, titania could possess a variety of crystal structures, the main crystalline forms are anatase, rutile and brookite. Brookite is rarely stable and has less application. Rutile phase is the most stable and abundant form of titania whereas anatase phase is highly favorable for device implementation. The current research work carried out by scientific community related to the problem of present thesis has been reviewed to understand the objectives and methodology of the research problem and the challenges that could occur during synthesis and analyzing the results of prepared specimens.

Sol-gel route and spin coating technique have been employed to synthesize powder and thin film specimens of metal oxides and their binary composites. There are a number of top-down and bottom-up approaches for the preparation of nanomaterials. Sol-gel, a bottom-up approach, is one of the most suitable synthesis route to prepare the nanomaterials with homogeneity and different morphologies. The step-wise description of sol-gel route has been discussed to enhance the knowledge about the factors involved in its mechanism. In the same way, the spin coating technique has been described including its principle, working and parameters affecting the structure, uniformity and thickness of film. The characterization of prepared specimens has been performed to study their structural, micro-structural, optical and thermal properties via complementary techniques XRD, TEM, SEM with EDX, FTIR, UV-vis, PL and TG-DTA. A brief description of all these techniques has been made.

Zirconium titanate ($ZrTiO_4$) composites have been developed via a simplified sol-gel route by varying concentration of Zr and Ti precursors. The XRD and Rietveld refinement results confirmed the development of single orthorhombic phase of $ZrTiO_4$. The values of profile parameters such as R_p, R_{wp}, R_B, R_F, χ^2 are less than 10% thereby indicating the goodness of Rietveld analysis. The increment in zirconia content decreases the degree of crystallization of zirconium titanate as observed from XRD. The blue shifting of PL emission wavelength (420 nm) has been ascribed to defect states below conduction band. The optical band gap of zirconium titanate composites has been tailored in the range 3.24-3.64 eV by controlling the crystallite size.

Also, thermally stabilized tetragonal phase of zirconia quantum dots (t-ZrO_2 QDs) in silica matrix have been successfully prepared by sol-gel protocol at low temperature. XRD analysis confirmed the formation of t-ZrO_2 QDs in silica while TEM images revealed their homogeneous dispersion and size distribution with size about 3-7nm. UV-visible and PL studies exhibited blue shift in band gap (3.65 to 5.58 eV) and red shift in emission wavelength (443 to 470 nm) of t-ZrO_2 QDs as the zirconia content increases in silica. A decrease in band gap occurred with decreasing size of the QDs that could be related with an increase of surface states of QDs.

Pyrochlore dysprosium titanates ($Dy_2Ti_2O_7$) and samarium titanates ($Sm_2Ti_2O_7$) have been synthesized to study their structural and optical behaviour altered with the concentration of rare earth precursors. XRD reveals that lattice parameters of pyrochlore titanates changes with the ionic radii of rare earth ions. FTIR exhibits characteristic absorption bands with slight variation in position and intensity depending on the rare earth ion (Dy, Sm) and its concentration. TEM images revealed almost spherical crystallites with good dispersibility and average particle size in the range 33-40 nm. The band gap decreases with increase in concentration of rare earth precursor. The values of band gap were found as 2.81 ($_{0.3mol}Dy\text{-}_{1mol}TiO_2$), 3.27 ($_{0.5mol}Dy\text{-}_{1mol}TiO_2$), 3.08 ($_{0.3mol}Sm\text{-}_{1mol}TiO_2$) and 3.55 eV ($_{0.5mol}Sm\text{-}_{1mol}TiO_2$). The prominent PL emission peak occurred at 424 nm in all prepared rare earth titanates as a result of recombination of free excitons.

The effect of composition of silica precursor on the phase and structure of titania quantum dots stabilized in silica matrix has been investigated. Anatase phase of titania QDs has been successfully stabilized in silica matrix even at higher temperature (1100°C). The rutile phase has only been developed at low concentration of silica (0.3 mol) at 1100°C. Anatase to rutile phase transformation was restrained by increasing concentration of silica (≥0.5 mol). TEM images revealed almost spherical quantum dots with uniform dispersion and size distribution in the range 2-5 nm. UV-visible studies illustrated the increase in band gap of anatase titania QDs (2.65 to 3.29 eV) as the silica content increases. A blue shift occurred in band gap with increasing size of QDs that could be related with an increase of surface states which are remarkably larger in case of QDs. The PL emission peak at 424 nm (blue emission) shifted to 400 nm (violet emission) along with significant decrease in intensity as silica content increased.

The desirable phases of metal oxides and their binary composites have been successfully prepared. The structural and optical parameters have been tailored for employing the materials in device fabrication namely oxygen sensors, solid oxide fuel cell (SOFC), photocatalysts, removal of organic dyes, dehydrogenation etc.

8.2 Future Directions

The investigations on nanoscaled metal oxides and their binary composites have enhanced the knowledge about the synthesis procedures and structural, micro-structural, optical and thermal behaviors of these materials. There is a further scope of work regarding modifications in the synthesis routes and hence in the properties of metal oxides for device fabrication. It is proposed to investigate the sensing, catalytic, opto-electronic and electrical properties of these materials.

In addition, the stabilization of pyrochlore rare earth titanates has motivated me to extend my research interest in the synthesis of a few compounds of pyrochlore family e.g. rare earth zirconates. Because these pyrochlore structure have unique and beneficial applications in the fields of photovoltaic devices, photocatalysts, water purification, radio-sensitizers, electrolytes, solid oxide fuel cells (SOFC), sensors or probes, treating of nuclear wastes.

The further work may be progressed along two directions:

1. Optimization of the growth conditions of quantum dots/composites/structures towards a particular property (e.g. photocatalytic property) and/or fabricating a particular device (e.g. sensor).
2. Investigations on more structural, optical, thermal, electrical, electronic parameters etc. required for exhaustive analysis/characterization of the present materials.

It will be a constructive step to fulfill my desire to contribute a little to the scientific community.

I would like to conclude my thesis with this phrase of Sir Winston Churchill,

"Now this is not the end. It is not even the beginning of the end.

But it is, perhaps, the end of the beginning"