ABSTRACT

The present thesis reports the experimental investigations on synthesis and structural, optical and thermal analysis of nanoscaled transition metal oxides and their binary systems. The aim of present research was to develop thermally stable and photo-efficient phases of metal oxides by optimizing the growth parameters such as concentration of precursors, pH, annealing temperature, incorporation of dopants etc. The choice of transition metal oxides was made due to their unique and unusual structural (polymorphs) and optical characteristics, which led to their numerous applications in photocatalytic and photovoltaic devices. The bottom up, wet chemical sol-gel method was used to synthesize the proposed metal composites. It was used due to its ability to produce homogenous, uniform nanomaterials at low temperature. Also, spin coating technique was employed to prepare thin film specimens; which is considered as one of the most suitable techniques for coating of uniform thin films. The final film thickness depends on viscosity, spinning time, final speed, ramp rate, number of coatings, volume percentage of solids, and surface tension and many of these influencing factors have been optimized.

The desirable phases of zirconia (ZrO_2) and titania (TiO_2) was synthesized and stabilized to make them employable in device fabrication. The tetragonal zirconia and tetragonal titania (anatase) quantum dots were thermally stabilized by incorporating them in silica, a support matrix. The structural and optical parameters had been tailored to improve the efficiency of the metal oxide (zirconia/titania) quantum dots by varying the concentration of starting precursors of zirconia, titania and silica in the specimens. Also, annealing of specimens was performed at 650, 875 and 1100°C. The silica matrix remained amorphous after thermal treatment and act as an inert support for zirconia and titania quantum dots. The stabilities of tetragonal phase of zirconia and anatase phase of titania was found to enhance with increase in silica content. The transmission electron micrographs confirmed the formation of tetragonal zirconia and titania quantum dots embedded in silica. The EDX spectra provided the elemental mapping of specimens with peaks of zirconium (Zr) and oxygen (O), or titanium (Ti) and oxygen (O) having proportional intensities validating the formation of zirconia or titania QDs respectively. The optical band gap of zirconia QDs was found to decrease with increase in silica content while the band gap of anatase titania quantum dots was increased on increasing the concentration of silica precursor.

The blue shifting of PL emission peak as silica content increased had been observed in zirconia as well as titania quantum dots.

Also, nanoscaled binary composites namely zirconium titanates and pyrochlore rare earth titanates have been synthesized using sol-gel and spin coating techniques in powder as well as thin film forms. The Rietveld refinements, micro-structural, optical and thermal parameters of a series of zirconium titanate composites prepared by varying compositions of starting precursors were investigated. The lower values of profile parameters such as R_p, R_{wp}, R_B, R_F, χ^2 indicated that the calculated diffraction pattern is in fair agreement with observed pattern. The photoluminescence spectra show the blue shifting of emission peak at 420nm as the zirconia concentration increases. The optical band gap of zirconium titanate composites also blue shifted (3.24-3.64 eV) with decrease in crystallite size of composites. Nanoscaled pyrochlore rare earth titanates $RE_2Ti_2O_7$ (RE=Dy, Sm) were prepared by taking two compositions (0.3 and 0.5 mol) of dysprosium and samarium precursors separately. Pyrochlore structure of rare earth titanates ($Dy_2Ti_2O_7$ and $Sm_2Ti_2O_7$) was successfully developed as confirmed by XRD. The lattice constant of samarium titanate was found to be larger than that of dysprosium titanate due to larger ionic radii of Sm^{3+} ion as compared to Dy^{3+} ion. The band gap of prepared titanates was increased on increasing the concentration of rare earth precursors (Dy/Sm), while the emission peak intensity was decreased. Finally, 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.