Chapter VII
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Summary

This reports the “SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC PERFORMANCE OF SUBSTITUTED SPINEL, PEROVSKITE AND PYROCHLORE OXIDES”. The important findings reported in the thesis is summarized below:

In the recent years, nanosized oxides are a subject of intense research, because of their unique properties that makes them attractive, both from the scientific value of understanding their physical properties and the technological significance of enhancing the performance of the existing nanomaterials. As compared with bulk materials, nanosized materials have many special properties such as chemical activation, photocatalytic activity, semiconductivity, and optical absorption. Defect, especially oxygen vacancies is an important part of any nanostructure system that involves the chemistry. Whether the final chemistry is labeled as oxide fuel cells, photocatalysis, sensing, energy storage, synthesis of fabrication, the reaction etc. The most effective them, when transport paths through which molecules move into or out of the nanostructure materials are included as an integral part of architectural design.

The semiconductivity, photocatalytic activity and other physical properties are strongly influenced by the composition and microstructure of nanooxides, which are sensitive to the preparation methodology used in their synthesis. Several efforts have been performed in recent years to improve the quality of semiconductor oxide, spinel, perovskite and pyrochlore oxides. Low temperature synthesis yields the materials with small particle size and high surface area. They also allow stabilization of phases having cations in higher valence state and / or with metastable structure. Therefore
efforts have increased recently for the synthesis and characterization of such nanosized oxides, because of its vital technological applications.

Thus, the first part involved the synthesis of different substituted semiconductor oxides, spinel, pervoskites and pyrochlore oxides by tartarate and hydroxide precursor method. To the best our knowledge, this method has not reported in the literature. The new synthetic precursor route relies lowering of processing temperature, high purity and stoichiometric oxides. The second part involved a systematic study with respect to the structural, electrical, dielectric and photocatalytic properties to arrive at possible ionic configuration of these nanosized oxides.

In the present thesis, the author has synthesized four of substituted nanosized oxides by using tartarate and hydroxide coprecipitation method-a new precursor method. These precursors have been systematically characterized by micro analytical, infrared spectroscopy and thermal analysis (TGA and DTA) method. After characterization of these precursors are then decomposed on heating in static air at 800°C to form respective oxides. Four types of nanosized oxides such as (a) divalent and trivalent metal ion doped semiconductor oxides, (b) dual-doped spinel oxide, (c) A- and B-site cations substituted perovskite oxides, and (d) A/B-site substituted pyrochlore-type oxides are synthesized by this precursor method. These nanosized oxides are then well characterized by X-ray fluorescence spectroscopy (XRF), X-ray powder diffraction (XRD), apparent density measurements, scanning electron micrograph (SEM), infrared spectrum, direct current electrical conductivity, thermoelectric power measurements, dielectric properties and UV-visible diffuse reflectance (UV-vis-DRS) spectroscopy. The heterogeneous photocatalytic activity of Victoria blue-B and Brilliant yellow solution under sun light irradiation are also studied in the present investigation. All these studies are attempted to gain information regarding phase homogeneity, chemical activity, band gap energy and role
of substituent on structural, electrical, particle nature and photocatalytic performance of these nanosized oxides.

The above studies on individual substituted semiconducting oxides, spinel oxide, perovskite oxide and pyrochlore-type oxide are decidedly shown from the following observations.

**a) Divalent and trivalent metal ion doped semiconducting oxides**

In the first part, we have focused on the effect of doping of divalent and trivalent metal ions on the structural, electrical and photocatalytic behavior of nanosized semiconductor oxides. The undoped and doped oxides such as Bi$_2$O$_3$; Bi$_{1.9}$ Sm$_{0.038}$Cu$_{0.062}$O$_3$; Co$_3$O$_4$; Co$_{2.902}$Mn$_{0.049}$Dy$_{0.049}$O$_4$; V$_2$O$_5$; V$_{1.91}$Ni$_{0.043}$Gd$_{0.047}$O$_5$; Cu$_2$O, Cu$_{1.927}$Mn$_{0.036}$Yb$_{0.037}$O; CeO$_2$; and Ce$_{0.938}$Ni$_{0.028}$Zn$_{0.034}$O$_2$ are synthesized by tartarate and hydroxide method using their respective salt solutions.

The tartarate and hydroxide precursors are then systematically characterized microanalytical method, infrared spectroscopy and TGA/DTA analysis. A chain like polymeric octahedral structure is assigned to tartarate precursors. The obtained precursors are then decomposed on heating in static air at 650°C for 2h, cool it, reground and reheating at same temperature to convert respective doped semiconductor oxides and then investigate their structural, electrical and photocatalytic activity.

The compositions of undoped and doped semiconductor oxides are determine by XRF and EDAX spectroscopy methods. The metal contents obtained with these method could be accurately quantify within ± 0.5 wt. % error. X-ray diffraction, pattern for undoped and doped semiconductor oxides possess single phased with monoclinic structure for Bi$_2$O$_3$ and its doped oxides and orthorhombic structure for V$_2$O$_5$ and its dopes oxides. A slight decrease in lattice parameter is due to a decrease of the defect concentration. The particulate properties like X-ray density, apparent
density, porosity, crystallite size and the surface area for all doped semiconductor oxides are found to great extent on the nature of precursor. The morphology and particle sizes are determined by SEM measurements, which confirmed the nanosized oxide, are formed. The infrared spectra of these semiconductor oxides reveal two absorption bands associated with the stretching and bending vibrations.

The electrical conductivity (logσ) is increased with increasing temperature for all doped semiconductor oxides. This can easily interpret in terms of increase in charge carriers (oxygen vacancies) of these compounds. i.e. hopping of small polarons from site to site. The activation energy (Ea) are calculated and found to be extrinsic surface defect migration in the whole temperature range. Thermoelectric power measurements for all compounds showed n-type semiconductor except Cu$_2$O, Co$_3$O$_4$ and their respective doped compounds have p-type semiconductivity. The variation of the dielectric constants and dielectric loss (tanδ) with increasing frequencies for all compounds exhibit space charge polarization due to the homogeneous structure as per interfacial polarization.

The band gap energy plays a critical role in deciding the photocatalytic activity of photocatalyst such as Bi$_2$O$_3$, CeO$_2$, Co$_3$O$_4$, V$_2$O$_5$, Cu$_2$O and their respective doped superconductor oxides are estimated by diffuse reflectance absorption spectrum. These oxides are sensitive to visible light and can be utilize visible light for degradating dye in solution. In the present investigation the photodegradation of Victoria blue-B and Brilliant yellow solutions by using undoped and doped semiconductor oxides under sun light are studied. The various parameters such as amount of these oxides, initial dye concentration, pH and contact time etc. have affected the percent degradation of these dyes. It is interesting noticed that the percent degradation of doped semiconductor oxides are obviously higher than that of undoped oxides. It is deduced that, doping of divalent and trivalent metal ions can introduced
new electronic state, in all semiconductor oxide to form additional interband site. The order of photocatalytic activity of undoped semiconductor oxides are CeO$_2$ > Bi$_2$O$_3$ > V$_2$O$_5$ > Cu$_2$O > Co$_3$O$_4$. The similar trends are also observed for respective doped semiconductor oxides. The pseudo first order rate constants and chemical oxygen demand (COD) showed that the photocatalytic degradation of Victoria blue-B is more rapid than that of Brilliant yellow dye, which could be ascribed to the different molecular structure of these dyes.

**b) Dual-doped spinel oxide nano particles**

In second part of the experiments is related to the structural, electrical and photocatalytic properties of dual doped spinel oxides nanoparticles synthesized by coprecipitation method. The undoped and dual doped spinel oxide such as CoAl$_2$O$_4$, Co$_{0.953}$Zn$_{0.047}$Al$_{1.95}$Fe$_{0.05}$O$_4$; CoMoO$_4$, Co$_{0.957}$Fe$_{0.043}$Mo$_{0.994}$V$_{0.046}$O; ZnRh$_2$O$_4$, Zn$_{0.949}$Bi$_{0.051}$Rh$_{1.951}$Dy$_{0.049}$O$_4$; ZnFe$_2$O$_4$, Zn$_{0.953}$Cu$_{0.047}$Fe$_{1.940}$Mn$_{0.06}$O$_4$; PrVO$_4$, Pr$_{0.952}$Gd$_{0.048}$V$_{0.956}$Ru$_{0.044}$O$_4$ are successfully synthesized by using tartarate and hydroxide precursor method. These precursors are then systematically characterized by various physico-chemical techniques and then subsequently heated at 600$^\circ$C for 4h.

The composition of these spinel oxides are checked by XRF and EDAX techniques. The X-ray diffraction pattern confirmed the cubic structure except CoMoO$_4$ and its doped oxide have monoclinic structure, while PrVO$_4$ and its doped spinel oxide have tetragonal structure. The lattice parameters of dual doped spinel oxide have slightly more value as compared to undoped spinel oxides. This can be explain based on the relative sizes of ionic radii of different dopant ions. The particulate properties like crystallite size, surface area, X-ray density, apparent density and porosity are determined. SEM images confirmed the all undoped and doped spinel oxides exhibits the nanocrystalline particles. Infrared spectra of these samples reveals two strong band at ~ 554 cm$^{-1}$(v$_1$), assigned to M-O stretching vibration of
MO$_6$ octahedral groups and another band at $\sim$484 cm$^{-1}$($v_2$), is attributed to the M-O stretching vibration of MO$_4$ tetrahedra ground of spinel oxides. While in case CoMoO$_4$ and its doped spinel oxides have three band at 910, 685 and 464 cm$^{-1}$. These bands have different vibrational modes of distorted MoO$_4$ present in CoMoO$_4$ spinel.

The temperature dependent of d.c. electrical conductivity for all undoped and dual doped spinel oxides showed definite break at about 600K. This discontinuity can be attributed to the lattice defect present and the smaller mobility of the defects, while conductivity at high temperature in the Region B corresponds to a thermally activated mobility of charge carriers. The activation energy (Ea) in the Region B is higher than the Region A for all compounds. This is based on changes of ionic distances in the spinel crystal structure. The thermoelectric power measurements for undoped and dual-doped spinel oxide showed n-type semiconductor throughout the temperature range. The dielectric constant and dielectric loss (tan$\delta$) decreases with increasing frequency. This is due to space charge polarization.

The bandgap energy (in eV) for undoped and dual-doped spinel oxide are determined by UV-vis –diffuse reflectance spectra. It is noticed that the dual-doped spinel oxides have lower band gap energy (Eg) than undoped spinel oxides. The photocatalytic degradation on Victoria blue-B and Brilliant yellow solution under sun light irradiation are found to increase on dual-doped spinel oxides. The variable studies included, the effect of pH, the amount of spinel oxides, initial dye concentration, time etc. have been evaluated. The percent degradation follows pseudo –first order kinetic. Chemical oxygen demand (COD) found to decrease after photo –oxidization reaction of these dyes.

c) **A- and B-site substituted perovskite oxides**

Third interesting set of experiments related to the influence of A- and B-site cations on the physicochemical properties of perovskite type nano oxides. The
unsubstituted and substituted perovskite oxides such as SrSnO$_3$, Sr$_{0.953}$Eu$_{0.047}$Sn$_{0.953}$Co$_{0.047}$O$_3$, SmMnO$_3$, Sm$_{0.948}$Bi$_{0.052}$Mn$_{0.963}$Cu$_{0.035}$O$_3$; NdAlO$_3$, Nd$_{0.954}$Dy$_{0.046}$Al$_{0.954}$Fe$_{0.046}$O$_3$; ZnTiO$_3$, Zn$_{0.957}$Tb$_{0.043}$Ti$_{0.966}$Zr$_{0.040}$O$_3$, are synthesized by tartrate and hydroxide precursors method and heated at 800°C. XRF and EDAX are used to confirmed the presence of metal species in the same cationic ratio as initially used for the synthesis of these perovskite oxides. X-ray diffraction pattern for all compounds have single phase perovskite with cubic structure for stannates and aluminate while, manganate has orthorhombic structure and titanate has hexagonal structure, when doping at A-site, the size differences between various ions induces local distortions and stress the structure. This is confirmed by average cationic radii at A-site $<R_A>$ and effect of mismatch factor ($\sigma^2$). The average cation size at A-site $<R_A>$ of perovskite is found to be less than 1.21 Å, which suggest the absence of cooperative long-range Jahn-Teller distortion in the compounds. Also, the mismatch factor ($\sigma^2$) are varies with the all perovskite oxides, suggest the disorder structure. The observed tolerance factor ($t$) for all compounds are found in the range of 0.760 to 0.937 which is lower than 0.95. This less tolerance factors can enhance a distortion of these pervoskite. The lattice distortion is also observed at B-site cation of pervoskite by metal-oxygen bond stretching, due to smaller ionic radii of dopants at this site. Therefore, it is concluded that as A-site doping of small cation ions, the structure changes from almost perfect cubic to less symmetric orthorhombic or hexagonal structure.

The particulate properties like X-ray density, apparent density decreases, while porosity increases for each sample perovskites. The average particle size determine from SEM image, which are found in the range of 22.14 nm to 70.19 nm, indicating the nanosized perovskite particles.
The temperature dependence the electrical conductivity for all perovskite oxide showed semiconducting behavior. The activation energy (Ea) in Region A corresponds to the charge carriers are localized on the defect center, while activation energy (Ea) in the Region B corresponds to intrinsic semiconductors for all perovskite oxides. The thermoelectric power measurement showed that all compounds are n-type semiconductivity. The variation of dielectric constant and dielectric loss (tanδ) with increasing frequencies for all perovskites suggest the dipole relaxation phenomenon.

The photocatalytic degradation of Victoria blue-B and Brilliant yellow solution over the unsubstituted and substituted perovskite oxides under sun light was investigated. The processing parameters such as the initial concentration of Victoria blue–B (100 mg/L at pH =7.5) and Brilliant yellow (20 mg/L at pH= 2.5), amount of perovskite used (50mg), which also play an important role in tuning the photocatalytic activity. The percent degradation of Victoria blue-B and Brilliant yellow solution exhibits the stannate and titanate and their respective substituted compounds have higher photocatalytic performance than that of manganate and aluminate perovskite-type oxides. Pseudo-first order rate constant (k) is slightly increased in all substituted perovskite oxide. Chemical oxygen demand (COD) is used for monitoring the mineralization of above dye.

d) A/B-Site substituted pyrochlore-type nanooxides

In the last part of the experiments related to the synthesis, characterization and photocatalytic properties of A/B-Site substituted pyrochlore-type oxides. The unsubstituted and A/B-type substituted pyrochlore oxides such as Bi$_2$Ru$_2$O$_7$, Bi$_{0.953}$Dy$_{0.047}$Ru$_{1.95}$Co$_{0.05}$O$_7$, Ce$_2$Sn$_2$O$_7$, Ce$_{1.956}$Ho$_{0.044}$Sn$_{1.957}$Ni$_{0.043}$O$_7$, Sm$_2$Zr$_2$O$_7$, Sm$_{1.952}$Ti$_{0.048}$Zr$_{1.958}$Ce$_{0.042}$O$_7$, Nd$_2$Ti$_2$O$_7$, Nd$_{1.95}$Co$_{0.05}$Ti$_{1.953}$Zr$_{0.047}$O$_7$ are synthesized by tartarate and hydroxide coprecipitation method at 800°C. The compositions of the products are checked by XRF and EDAX method. X-ray diffraction pattern revealed
that the all compounds have single phasic with cubic structure except Nd$_2$Ti$_2$O$_7$ and Nd$_{1.95}$Co$_{0.05}$Ti$_{1.953}$Zr$_{0.047}$O$_7$ pyrochlorem which show a monoclinic structure. The infrared spectroscopy allows the confirmation of this structure. The pyrochlorem structure \((A_2B_2O_7)\) is also depending a cation radius ratio of A-site and B-site \((r_A^{3+}/r_B^{4+})\). As a result, it is observed that all unsubstituted and A/B-site substituted pyrochlorem was adopt a stable pyrochlorem structure with \((r_A^{3+}/r_B^{4+})\) radius ratio in the range of 1.397 to 1.867 which is greater than 1.22. This indicates that all oxides are stable pyrochlorem structure and disordered fluorite structure. The average particle size determined from, scanning electron micrograph (SEM) is in the range of 22.64 nm to 45.01 nm, which indicate all are nanosized materials. Infrared spectra of these compounds showed two strong absorption band at around 599 cm$^{-1}(\nu_1)$ and 452 cm$^{-1}(\nu_2)$ corresponds to M-O stretching vibration at B-site and M-O bond at A-site respectively in the pyrochlorem structure.

The temperature dependence of the electrical conductivity of these pyrochlores exhibit two different slope with a “break” except Bi$_2$Ru$_2$O$_7$ and Bi$_{1.953}$Dy$_{0.047}$Ru$_{1.95}$Co$_{0.05}$O$_7$ pyrochlorem oxide. This discontinuity can be attributed to hoping of defect related weakly bonded system, which is happen below the temperature range of break point and then hoping of polaron above the temperature of break point, while in case ruthenate pyrochlorem have electron-acceptor hopping in sub lattice between $M^{3+}\leftrightarrow M^{4+}$ ions at the B-site which are happen from 30 to 600°C. The thermoelectric power measurements showed p-type semiconductivity except stannate and its substituted pyrochlorem, which showed n-type semiconductivity. The decrease in dielectric constant and dielectric loss with the increase in frequency for all pyrochlorem oxides, suggest the space charge polarization, due to the presence of large grain boundary defect.
From UV-vis-diffuse reflectance spectra measured the band gap energies for all pyrochlore oxides. It was found to be in the range of 2.04 to 4.27 eV. Effect of different parameter was examined for photodegradation of Victoria blue-B (200 mg/L at pH =7.5) and Brilliant yellow (20mg/L at pH =2.5) and 50 mg pyrochlore oxide used. All pyrochlore oxide exhibit good photocatalytic activity under sun light irradiation for 120 minute. The titanate and zirconate and their respective A/B-site substituted pyrochlore showed highest photocatalytic degradation among the remaining pyrochlore oxides under investigation. This may be due to higher crystallinity and surface area. Also, titanate and zirconate have a layered structure built from slabs formed by corner-shared octahedral unit of TiO$_6$ or ZrO$_6$, which may be more favorable for the separation of e$^-$ and h$^+$ pairs generation in the catalyst during sun light irradiation.