CHAPTER  6

Overall Summary and Conclusions

Summary

The present thesis is mainly centered on the structural, optical, dielectric and plasmonic characterization of titania ($\text{TiO}_2$) based glasses and rheological characterization of $\text{TiO}_2$ based ceramic systems. Titania has received great attention because it is an attractive hybrid inorganic glassy system suitable to incorporate rare-earth ions. It is characterized by high thermal stability, chemical durability and mechanical strength in addition to an adjustable refractive index in a wide range. It can be fabricated in different forms by the simple technique of sol–gel processing. In general, titanium oxide is considered as a nucleating agent of crystallization in silicate glasses. However, the presence of small quantities of $\text{TiO}_2$ in other glass matrices is observed to enhance the glass forming ability and chemical durability, mechanical and insulating strengths of the glasses. Titanium dioxide is a wide band gap material that is exploited for its dielectric, photochemical, catalytic, and other properties.

In this thesis titanosilicate glasses were synthesized by sol-gel processing. Sol-gel method is quite unique due to its low processing temperature and solution mixing, enabling the production of high purity and high homogeneity of end products. Tape casting is one of the
cheapest methods to produce large TiO$_2$ ceramic sheets. Tape casting involves dispersion of inorganic ceramic powder in a liquid medium, followed by addition of organic binders and plasticizers to increase the strength and flexibility of the tapes after casting and drying.

A brief introduction of glass and ceramics, synthesis methods used for making TiO$_2$ based glass and ceramics are discussed. Sol-gel synthesis used for making TiO$_2$ based glass and tape casting synthesis used for making TiO$_2$ based ceramics are explained in detail. Sol-gel processing which is one of the major and common glass fabrication methods is discussed in detail. Tape casting processing one of the methods used for making ceramic sheets and how this method is used for making multilayer capacitors and actuators is discussed. The importance of optical spectroscopy to study the nature of glass is described. A brief discussion about dielectric spectroscopy is included. A brief outline of surface plasmon resonance of silver nanoparticles in titanosilicate glassy matrices is also given. The plasmonic coupling of metal nanoparticles with light enhances a broad range of useful optical phenomena which have tremendous potential applications in the areas of ultra-sensitive chemical and biomolecular detection and analysis.

The structural and optical characterization of silver nanocrystallites/Eu$^{3+}$: SiO$_2$-TiO$_2$ matrices synthesized through sol-gel route have been detailed. Structural characterizations were done by using EDX, XRD, FTIR, AFM and TEM measurements and optical characterizations were performed by absorption and emission spectroscopy. The TEM and XRD measurements confirmed the
presence of the nanocrystals. A broad absorption band was observed due to surface plasmon resonance of silver nanocrystals. The effect of silver nanocrystals on the emission spectrum of Eu\textsuperscript{3+} doped SiO\textsubscript{2}-TiO\textsubscript{2} matrices is discussed. An attempt has been made to explain this fluorescence enhancement by invoking phenomena such as energy transfer, asymmetric ratio, surface plasmons, surface roughness, crystallinity and grain boundary. Our analysis based on the experimental results suggests that all the phenomena except the crystallinity and grain boundary have favourable effects on the fluorescence enhancement.

The dielectric characteristics of metal/semiconductor/ rare earth doped titanosilicate glass have been included. Ag/Eu\textsuperscript{3+} and ZnO/Eu\textsuperscript{3+} doped titanosilicate glass samples were synthesized through sol-gel route. The dielectric response and the AC electrical conductivity of the samples were investigated for the frequency range 100 Hz - 2 MHz at room temperature. The dielectric characterizations include measurements involving the variation of real and imaginary part of dielectric constant as well as conductivity with frequency. The dielectric studies show low values for dielectric constant and loss at high frequencies. These characteristics for the samples suggest that the samples possess enhanced optical quality with lesser defects and these parameters are of vital importance for various nonlinear optical applications. The conductivity values were found to be of the order of $10^{-8}$ - $10^{-11}$ S/cm and the conductivity curve obeys Jonscher’s power-law dependence. The power law parameters are calculated and the values of $s$ and $\sigma_{0}$ values are comparable with the existing values.
Single semicircles are observed in the complex impedance plots of Ag/ZnO doped glass and a spike is observed at low frequencies. These semicircles reveal a single relaxation process and can be modelled by an equivalent parallel RC circuit. The spike observed at low frequencies indicates the presence of an ionic contribution to the electrical conductivity of these materials.

The investigations of surface plasmon resonance (SPR) of silver nanoparticles doped in titanosilicate matrix have been given. The surface plasmon resonance of silver nanoparticles was observed in the wavelength range 300-400nm. Numerical calculation of SPR of silver nano particles with spherical morphology was done on the basis of discrete dipole approximation (DDA) method. Distinctive features of SPR like wavelength shift and spectral broadening are explained on the basis of highly localized plasmonic oscillations existing in the matrix. The observed fluorescence spectrum fits well with the theoretically calculated one. The luminescence enhancement is attributed to the strong local electric field which increases the exciting and emitted photons coupled to SPR. Also we have made an attempt to calculate van der Waals (vdW) energy and Casimir energy between plasmonic silver nanoparticles as the energy of vacuum fluctuations of plasmonic modes. A special effort has been made to study the surface plasmon mediated excitation energy transfer (EET) between two spherical metal nanoparticles (MNP).

The optimization and dispersion behaviour of TiO$_2$ in different solvent systems in combination with two different dispersants are discussed. Based on sedimentation, viscosity and rheological
characteristics, zeotropic ethanol: xylene with a ratio of 50:50 along with 1 wt % menhaden fish oil is found to be the best solvent–dispersant combination for TiO$_2$. Tape casting slurry was optimized using polyethylene glycol 400 and benzyl butyl phthalate as plasticizers and polyvinyl butyral as the binder. Cyclohexanone was used as homogenizer. TiO$_2$ tapes were obtained by double doctor blade tape casting process and the cast tapes were dried in air at room temperature. The results show that it is possible to obtain homogenous defect free green tapes of 58.7% solid loading and green density of 55% having thickness of 90 mm. The sintering temperature of the TiO$_2$ laminated sheets was optimized at 1300°C. The experimental values of density and dielectric constant for the sheets sintered at 1300°C are in agreement with theoretical values.

**Conclusions**

Silver nanoparticles, along with europium ions, were incorporated in SiO$_2$-TiO$_2$ matrices prepared by the sol-gel route. The emission intensity of the Eu$^{3+}$ ions is greatly enhanced (around eight fold) in the presence of silver nanocrystallites. This fluorescence enhancement has been explained by invoking phenomena such as energy transfer, asymmetry ratio, surface roughness, surface plasmons and grain boundary. The experimental results show that the energy transfer from the silver nanoparticles to Eu$^{3+}$ ions is mainly responsible for fluorescence enhancement. It is also seen that the asymmetry ratio, surface plasmon resonance and more surface roughness also favour the enhancement. The experimental
observations on the fluorescence enhancement are found to be consistent with these four possible reasons existing in the literature.

Ag/ZnO nanocrystallites along with europium ions were incorporated in SiO$_2$-TiO$_2$ matrices prepared by sol-gel route. The dielectric response and the AC electrical conductivity studies of the samples with the Ag/ZnO content are performed for a frequency range of 100 Hz to 2 MHz. Our results show that with Ag doped sample the dielectric constant and AC conductivity decreased at lower frequency, but with ZnO doped sample its dielectric and conductivity value increases. At higher frequencies, the dielectric constant is found to be constant and low but AC conductivity increased rapidly. The decrease in the dielectric constant values with Ag substitution in the low frequency region is due to the effects of grain boundaries and is prominent at lower frequencies. The changes in ZnO doped sample are due to the orientational polarization and the existence of a number of oxygen vacancies and zinc interstitials. So there is a tendency of the occupied cations to be associated with the positive ion vacancies leading to dipole moments for these associated pairs. The power law parameters are determined for both the samples. The Cole-cole plots for both Ag/ZnO doped samples show a semicircle, so it can be substituted to an equivalent RC circuit.

Numerical calculation of SPR of silver nanoparticles with spherical morphology was done on the basis of discrete dipole approximation (DDA) method and compared with experimental one. Distinctive features of SPR like wavelength shift and spectral
broadening are explained on the basis of highly localized plasmonic oscillations existing in the matrix. The observed fluorescence spectrum fits well with the theoretically calculated one. The luminescence enhancement is attributed to the strong local electric field which increases the exciting and emitted photons coupled to SPR. The EET rate is found to be Forster type for long distance separation between the nanoparticles, while it is non-Forster type for short distances. The surface plasmon contribution to the Casimir energy is found to be crucial. The van der Waals energy is attractive but small with considerable contribution from both L and M modes.

The dispersion, viscosity and rheological characteristics of the tape casting slurry for TiO₂ were studied systematically at every stage of the slurry preparation. Based on these studies, a combination of 50:50 ratio of xylene–ethanol zeotropic solvent system and 1wt% MFO as the dispersant were used for achieving optimum dispersion. MFO acts as a steric dispersant and effectively disperses TiO₂ in nonaqueous medium. Using the optimized slurry with 58.7% of solid loading, which exhibits pseudo plastic behavior, visibly defect-free tapes of ~90 mm thickness and 55% green density were obtained. The sintering cycle of TiO₂ ceramics was also optimized and the properties were evaluated. The sintering temperature of the TiO₂ laminated sheets was optimized at 1300°C. The experimental values of density and dielectric constant for the sheets sintered at 1300°C are in agreement with theoretical values.