ABSTRACT

The work presented in the thesis is mainly concerned with the structural, optical, dielectric and plasmonic characterization of TiO$_2$ based glass. It also includes the rheological characterisation of TiO$_2$ based ceramic composites. Recently titania (TiO$_2$) has received great attention because of its unique photocatalytic activity in the treatment of environmental contaminants. Much work has been carried out to display its promising performance in degrading a wide variety of organic and inorganic pollutants. In general, titanium oxide is considered as a nucleating agent of crystallization in silicate glasses. However, the presence of small quantities of 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 novel wide band gap material that is exploited for its dielectric, photochemical, catalytic, and other properties. TiO$_2$ as thin films and dielectric ceramic sheets are required for solar cells, photodegradation of organics in water and in air under ultraviolet illumination and for multilayer ceramic/metal composite components.

We describe the structural and spectroscopic properties of rare earth ions and metal nanoparticles incorporated in TiO$_2$ based glasses. The effect of silver nanocrystals on the emission spectrum of Eu$^{3+}$ doped SiO$_2$-TiO$_2$ matrices is discussed. An attempt has been made to explain the 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. We have also estimated the relevant parameters associated with the phenomena that affect the fluorescence emission from the Eu$^{3+}$ ions in the matrix.

The dielectric and AC conductivity studies of Ag/ZnO doped TiO$_2$ based glass systems have been carried out for the frequency range 100 Hz - 2 MHz. The conductivity variation with the Ag/ZnO dopant in the Eu$^{3+}$ doped SiO$_2$-TiO$_2$ system has been explained by correlating the presence of ionic contribution to the electrical conductivity process. Also, the frequency dependence of dielectric constant and conductivity was studied and the power law parameters were evaluated. The Cole–Cole parameters were calculated and the semicircles observed in the plots indicate a single relaxation process.

The surface plasmon resonance (SPR) of silver nanoparticles was observed in the wavelength range 300-400 nm. 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 in the present matrix. These energies are associated with the vacuum fluctuations of plasmonic modes existing in the system. A special effort has been made to study the Surface plasmon mediated excitation energy transfer (EET) between two spherical metal nanoparticles (MNP).

Finally we discuss about the TiO$_2$ ceramic sheets prepared through the tape casting techniques. The optimisation of the tape casting slurry is based on the preliminary studies of dispersion and rheological characteristics. Dispersion behaviour of TiO$_2$ in different solvent systems in combination with two different dispersants was studied and optimized for the dispersion of TiO$_2$. Based on sedimentation, viscosity and rheological characteristics, we optimized TiO$_2$ tape casting slurry composition. Sintering temperature and density of the TiO$_2$ ceramic sheets were also optimised.

**Key words:** Sol-gel processing, Fluorescence, Dielectric, Surface Plasmon, van der Waals energy, Tape Casting, Dispersion and Rheological study.