PREFACE

The present thesis is mainly centred on the structural, optical and dielectric characterization of holmium doped silica glass matrices with and without silver nanoparticle (Ag NP) co-doping. In this thesis the silica 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. Structural characterization was carried out using techniques like Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA), X-ray diffraction (XRD) and High-resolution Transmission Electron Microscopy (HR-TEM). Optical characterization was done using absorption and emission spectroscopy. Finally the dielectric studies were carried out using impedance spectroscopy which is a very versatile electrochemical tool to characterize intrinsic electrical properties of any material and its interface. A genuine attempt has also been made in the theoretical and numerical analysis of the synthesized samples in search of surface plasmon resonance and van der Waals energy between the sol-gel produced plasmonic silver nanoparticles.

Chapter 1 begins with a brief introduction to glasses and sol-gel processing. The chemistry of sol-gel process is discussed in one of the beginning sub-sections, in this section the basic sol-gel reactions beginning from the precursor selection followed by the hydrolysis and finally the condensation reactions are discussed in detail. For a sol-gel process the processing steps hold a key role in determining the quality of end products, hence such details are also discussed by specifying each step. The
advantages of sol-gel process are numbered at the end of this section. Since we aim for the doping of rare-earths in glassy matrices, a general introduction is provided with the details of splitting of energy levels of rare earth ions. Holmium rare-earth ion is specifically introduced in this chapter with details of its electronic configurations and the energy level diagram of $\text{Ho}^{3+}$ ions. Judd-Ofelt(JO) theory and impedance spectroscopy is also discussed briefly in this chapter as a prelude to chapters 2, 3 and 4. Ag NPs were used as a co-dopant to enhance the dielectric response of rare-earth doped glassy matrices. Due to the presence of such nanoparticles, surface plasmons are exhibited in the absorption bands. Plasmonic properties of silver nanoparticles have been extensively studied for their superior performances that exceed those of other metals with a surface plasmon resonance (SPR) in the visible range like gold or copper. In the past years, a number of applications based on the SPR of AgNPs have been presented, in particular for biosensing, surface-enhanced Raman scattering and plasmon circuitry. Several of these applications take advantage of the engineering of AgNPs plasmonic response that depends on their size, shape, dielectric environment and on mutual electromagnetic interactions among particles in close proximity. In this context a brief introduction to surface plasmons and van der Waals interactions between nanoparticles is provided.

In chapter 2, $\text{Ho}^{3+}$ doped silica glasses were prepared by the sol-gel process using tetraethyl orthosilicate (TEOS), $\text{H}_2\text{O}$, $\text{HNO}_3$ and $\text{Ho(NO}_3)_3\cdot5\text{H}_2\text{O}$. The samples were characterized using TGA, FTIR spectra, HRTEM and UV-VIS absorption spectra. The TGA confirmed an almost complete removal of molecular water and the condensation of silanol groups with heat treatment. While the FTIR analysis revealed all the
vibrational modes present in the silica glass system. However, the vibrational modes corresponding to the structural defects and Si-OH bond were found to weaken with heat treatment. HRTEM confirms a cluster formation within the sol gel sample. The JO parameters and the radiative parameters were evaluated and compared with similar matrices from the optical absorption spectra. Calculated values of the JO parameters were utilized in evaluating the various radiative parameters such as electric dipole line strengths ($S_{ed}$), radiative transition probabilities ($A_{rad}$), radiative lifetimes ($\tau_{rad}$), fluorescence branching ratios ($\beta_R$) and the integrated absorption cross sections ($\sigma_a$) for stimulated emission of Ho$^{3+}$ ion. These data predict the fluorescence properties for the Ho$^{3+}$ ions in the present host. Our analysis indicates that randomly distributed three dimensional network nature of the host, clustering of Ho$^{3+}$ ions and the hydroxyl content are responsible for the weak fluorescence. The fluorescence transitions $^5F_5 \rightarrow ^5I_8$ and $^5S_2 \rightarrow ^5I_8$ are found to have the potential for optical amplification. Also asymmetry of Ho$^{3+}$ in silica glass host is found to be higher than in halide systems and lower than in oxide systems.

In chapter 3, the dielectric characteristics of Ho$^{3+}$ doped silica glasses have been carried out with the aid of complex dielectric spectroscopic investigations. This includes measurements involving the variation of real and imaginary part of dielectric constant as well as conductivity with frequency. The dielectric response and the AC electrical conductivity of the samples were investigated for the frequency range 100 Hz - 3 MHz at room temperature. The dielectric studies show low values for dielectric constant and loss at high frequencies. The characteristics of low dielectric constant and dielectric loss with high frequency for the
samples suggests that the samples possess enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications. The conductivity values were found to be of the order of $10^{-5}$ - $10^{-7}$ S/cm for Ho$^{3+}$ and the conductivity curve obeys Jonscher’s power-law dependence. The power law parameters are calculated and the values of $s$ and $\sigma_0$ are found to decrease with concentration of samples while the values of $A$ show an increasing tendency. Single semicircles are observed in the complex impedance plots of Ho$^{3+}$ doped glass and a spike is observed at low frequencies. These semicircles reveal a single relaxation process and can be modeled 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.

In chapter 4, the effect of silver nanoparticle codoping on the dielectric properties of Ho$^{3+}$ doped silica glasses was studied. Four samples were prepared with 0.5 wt% and 1 wt% holmium concentrations, two of them were co-doped with silver (0.25wt %). The formation of silver nanocrystals was confirmed by XRD and TEM. Using the Debye-Scherrer formula the crystal size was calculated to be 20 nm and 22 nm for the sample 0.5 Ho + Ag and 1 Ho + Ag respectively. The TEM images confirm the crystallite size values obtained from XRD. One of the samples showed an icosahedral morphology of the nanocrystal formed along with spherical morphology. The dielectric studies conducted on all the samples reveal that the effect of silver co-doping has some effect on the dielectric constant, conductivity and loss tangent values over a frequency range of 10 kHz to 3 MHz. A successful tuning of the dielectric constant values can be brought
in by the silver co-doping. The sample with 1 wt% of holmium has low
dielectric constant values within the range 100 Hz to 3 MHz due to the
formation of quasimolecular structures of holmium. Such defects reduce
the hopping conduction by increasing the distance between the hopping
sites. This effect was evaded to some extent with silver codoping as a result
of the interdispersion of holmium complexes. The power-law parameters A
and s vary considerably for samples with and without silver codoping.
From the Cole-Cole plots it can be inferred that silver codoping has some
effects on the $R_b$ and $\tau$ values. From the trends and behaviour of the
samples over a frequency range from 10 kHz to 3 MHz the sample with
silver codoping could be used as a dielectric material whose dielectric
properties could be successfully tuned by controlling the doping
concentration of holmium and silver. It can be stated that suitable
geometrical structures of nanoparticles incorporated in glassy media may
open up the possibility of applications in optical energy transport devices,
dielectric optical polarizers or photonic materials.

Finally in chapter 5, we have investigated the surface plasmon
resonance of silver nanoparticles doped in silica matrix and evaluated the
van der Waals energy between AgNPs. The surface plasmon resonance of
Ag NPs were observed around 420nm. The numerical calculation of SPR
of silver nano particles with spherical morphology was done on the basis of
discrete dipole approximation method (DDA). A comparison with the
experimental spectrum confirms the validity of this method. Further, the
distinctive features of the SPR like wavelength shift and spectral
broadening are explained on the basis of highly localized plasmonic
oscillations existing in the matrix. The results show that the dielectric
parameter can be used to tune the plasmon response of AgNPs in the 350–700 nm range. We have also calculated the energy of the van der Waals interaction between two closely placed metallic nanospheres as the energy of vacuum fluctuations of all plasmonic modes existing in such system. The results obtained depend crucially on the existence of bound states of plasmons and the Van der Waals energy is found to be composed of attractive and repulsive contributions from different oscillation modes.

The work presented in the thesis has either been published in or communicated to refereed international journals, conference proceedings and presented in various seminars/symposia.

Research Papers Published in International Journals


Ag nano particles in silica glass host” Chem. Phy. Letters. [Communicated ]


Research Papers Published in Conference / Seminar Proceedings

1. **NANO2010**: “Structural and plasmonic studies of Ag nano particles in silica glass host” International conference on Nano materials and Nano technology. Centre for Nano science and Technology, K.S Rangasamy college of Technology, Tiruchengode, India


4. **NSNANO 2009**: “Effect of Triangular and Spherical Silver Nano particles on the dielectric properties of Ho\(^{3+}\) Doped Silica Glass” National Seminar on Recent Advance in Nano Science &Technology, Sree Narayana College, Kollam, Kerala (Best Paper Award in the Poster Section)

5. **NCAMDT 2008**: “Optical and Dielectric studies of Tb\(^{3+}\)/CdS nano particles doped silica xerogels” National Conference on Advanced Materials, Devices and Technologies, Sri Venkateswara University, Tirupati


8. **Photonics 2006**: “Nanocrystallization of TiO$_2$ in Titanosilicate glasses and its structural characterization” 8$^{th}$ International Conference on Optoelectronics, Fibre Optics and Photonics, University of Hyderabad, Hyderabad, Andhra Pradesh, India

9. **NLS 2006**: “Preparation and Characterization of Nd$^{3+}$ doped multilayed Sol-gel silica films with low H2O/TEOS ratio” National Laser Symposium, Raja Ramanna Centre for Advanced Technology, Indore, Madhya Pradesh, India


11. **OMTAT 2005**: “Wide UV excitation and emission of Eu$^{3+}$/ZnSe nanocrystal in silica hosts.” International conference on Optoelectronic Materials and Thin films for advanced Technology, Cochin University of Science and Technology, Kerala.

12. **NSMTMS 2005**: “optical studies of Nd$^{3+}$/K,Ag,Li in sol-gel silica matrices” National Seminar on Modern Trends in Material Science, Calicut University, Calicut, Kerala.