4.1 Introduction

Nanocomposites containing metal nanoparticles dispersed in glass matrices are focus of intense research because of their unique linear and nonlinear optical, electrical and mechanical properties [1-8]. As a result, their usage has increased immensely in various applications such as data storage systems, biosensors, waveguides, solar cells, aerospace, microelectronics etc. [9-16]. Variety of metal ions has been incorporated into glass by various methods such as low energy ion beam mixing [17], sol-gel [18], direct metal-ion implantation [19], ion-exchange [20-21], vacuum deposition [22], field-assisted ion diffusion [23] etc. Vacuum deposition and ion-exchange techniques stand apart for synthesizing metal-soda glass nanocomposites due to their inherent advantages such as high efficiency and possibility of introducing very high concentrations of metal ions into the glass matrix. Annealing of metal-composites is an equally important part of the synthesis process as it is responsible for the formation of metallic nanoparticles in the matrix in fact particles mean size, their distribution and number density are dependent on annealing temperature, duration and environment. Optimization of the crucial process parameters is always an issue of research and discussion. Once the nanoparticles are well dispersed in a matrix, the intrinsic properties of nanocomposite materials are determined by its size, shape, composition, and structure.

Present research endeavor is an effort to understand and optimize various parameters for synthesis of silver-soda glass nanocomposites and to study
remarkable changes produced in the refractive index, dielectric constant, photoluminescence spectra, surface hardness and electrical conductivity behaviour of synthesized nanocomposite as a function of post annealing temperature.

4.2 Summary

In the present research work, we have synthesized nanocomposites consisting of silver nanoparticles dispersed into a soda glass matrix by vacuum deposition technique and ion-exchange technique followed by thermal annealing in air. The effect of silver nanoparticles on structural, absorption, reflection, transmission, colour, refractive index, photoluminescence, dielectric, surface hardness and electrical conductivity behavior of soda glass has been studied. These studies have been carried out using UV-Visible Spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Photoluminescence Spectroscopy, Knoop Microhardness testing and two probe I-V measurements techniques.

Commercially available soda glass slides of dimensions 75mm×25mm×1.3mm were procured from Polar Industrial Corporation, Mumbai, India and were used as substrate material. The chemical composition of the acquired soda glass slides is (in wt%) 71.86% SiO₂, 13.30% Na₂O, 8.69% CaO, 4.15% MgO, 1.92% Al₂O₃, 0.08% Fe₂O₃. The specimens of area 2×2 cm² were cut from 1.3 mm thick optically transparent soda glass slides by using a diamond cutter. Subsequently, these samples were cleaned by acetone. Vacuum deposition and ion-exchange methods were utilized to incorporate silver in soda glass matrix. In vacuum deposition method, thin films of silver were deposited on commercially available soda glass substrates by thermal evaporation using a “VEQCO” high vacuum evaporation unit EU-300 under a vacuum of the order of 10⁻⁵ Torr in the glass vacuum chamber. Prior to the silver film deposition onto the glass substrate, surface contaminants on substrate were removed by using distilled water and acetone. Subsequently, silver wire (purity, 99.9%) was kept in a tungsten filament and was evaporated for deposition (on to glass) inside the vacuum chamber. After deposition, the source heater was turned off. The film remained under vacuum till source temperature reduced to below 100°C, to avoid the oxidation of the film. Thickness of silver films was measured by using a quartz crystal thickness monitor during deposition of films and was 2.916 kÅ. Subsequently, these silver deposited
glass samples were annealed in furnace at various temperatures from 200°C to 550°C in air for 1 hour in furnace for the growth of the nanoparticles. After the heat treatment these samples were rinsed with concentrated HNO₃ solution to remove excess silver adhering to the glass surface.

In second method silver ion-exchanged soda glass slides were prepared by dipping soda glass slides for 1 minute in a molten salt bath of AgNO₃ and NaNO₃ (1:4 weight ratio) mixture at a temperature of 350°C. In the molten salt bath, Ag⁺–Na⁺ ion-exchange takes place. Then these silver ion-exchanged glass slides were washed with water to remove extra AgNO₃ adhering to the samples and these samples were then annealed at different temperatures from 200°C to 550°C in air for 1 hour. During annealing migration and aggregation of the silver particles takes place resulting in the formation of nanoparticles.

The UV-Visible absorption, transmission and reflection spectroscopy measurements of all the samples were carried out using Shimadzu Double Beam Double Monochromator UV-Visible Spectrophotometer (UV-2550) equipped with an Integrating Sphere Assembly ISR-240A in the wavelength range of 190 nm to 900 nm with a resolution of 0.5 nm available in our own department. We have used Hitachi “H-7500” transmission electron microscope with an operating voltage of 80 kV in order to determine the size of the silver nanoparticles embedded in soda glass matrix. Morphology of the silver-soda glass nanocomposite samples synthesize using vacuum deposition technique was studied using FE-SEM Quanta 200F. FE-SEM also included Energy Dispersive Analysis of X-rays (EDAX) assembly. SEM measurements of nanocomposite samples synthesize by ion-exchange technique were carried out using LEO 435 VP scanning electron microscope. Photoluminescence measurements of prepared nanocomposite samples were carried out using Jobin Yvon Spectroflurometer (Spex FluoroMax-3) where a Xe lamp was employed as the excitation source. Surface microhardness of the silver-soda glass nanocomposite samples were carried out at room temperature using Knoop indentation technique with a UHL microhardness tester. Electrical conductivity behavior in terms of current-voltage characteristics of silver-soda glass nanocomposite samples had been studied by Keithley 6517A Digital Electrometer.

The major outcomes of the present work are based on the results obtained from various experimental techniques used to characterize silver-soda glass
nanocomposites synthesized by vacuum deposition and ion-exchange techniques followed by thermal annealing.

The main conclusions drawn from the present studies are as follows:

1. Surface plasmon resonance (SPR) peak characteristic of silver nanoparticles was observed at ~427 nm in the optical absorption spectra of silver-soda glass nanocomposite samples synthesized by vacuum deposition method followed by thermal annealing in air at an annealing temperature of 400°C. In case of silver-soda glass nanocomposite samples synthesized by ion-exchange followed by thermal annealing in air exhibit SPR peak at ~429 nm at an annealing temperature of 200°C in the optical absorption spectra due to reduction of Ag⁺ ions to Ag⁰ atoms.

2. The size of silver nanoparticles had been found to increase with increase in annealing temperature. In case of silver-soda glass nanocomposite samples synthesized by vacuum deposition, at an annealing temperature of 400°C the size of silver nanoparticles comes out to be 4.6 nm which increased to a value of 10.0 nm at an annealing temperature of 550°C. On the other hand, for nanocomposites samples synthesized by ion-exchange, size of silver nanoparticles at an annealing temperature of 200°C had been calculated to be around 2.31 nm which increased to a value of 7.6 nm at an annealing temperature of 550°C.

3. Further the presence of silver nanoparticles inside the soda glass matrix had been confirmed by the combined analysis of scanning electron microscopy & energy dispersive analysis of X-rays (EDAX) and transmission electron microscopy study. In case of silver-soda glass nanocomposite samples synthesized by vacuum deposition, average size of the silver nanoparticles was found to be around 8±2 nm while for nanocomposite samples synthesized by ion-exchange; average size of the silver nanoparticles was observed to be 6.57±1.14 nm which is consistent with the size determined using the UV-Visible absorption spectra.

4. Improvement in the refractive indices had been observed for all the silver-soda glass nanocomposite samples. The value of refractive index increased after
incorporation of silver nanoparticles in glass from 1.52 (glass) to 1.96 (silver-soda glass nanocomposite formed at an annealing temperature of 550°C) in case of nanocomposites samples synthesized by vacuum deposition but in case of nanocomposites samples synthesized by ion-exchange, value of refractive index of silver ion-exchanged glass nanocomposite sample increased to 1.71 at the same annealing temperature of 550°C corresponding to wavelength 600 nm.

5. In case of silver-soda glass nanocomposites samples synthesized by vacuum deposition, value of dielectric constant increased from 2.4 (glass) to 3.8 (silver-soda glass nanocomposite formed at an annealing temperature of 550°C) on the other hand, for nanocomposite samples synthesized by ion-exchange, value of dielectric constant increased from 2.4 to 2.9 at the same annealing temperature of 550°C.

6. Photoluminescence spectra for silver-soda glass nanocomposite samples had been studied at an excitation wavelength of 270 nm. Drastic changes in the photoluminescence intensity due to thermal annealing of the silver deposited glass samples at room temperature had been observed. PL spectroscopy suggests that the photoluminescence spectra of silver glass nanocomposite samples was due to the presence of Ag$^+$ ions, related to electronic transitions between the 4d$^{10}$ ground state and levels of the 4d$^9$5s$^1$ Ag$^+$ configuration.

7. At excitation wavelength of 270 nm, silver deposited samples annealed at 300°C and 400°C showed a broad emission band at 365 and 367 nm respectively. Samples annealed at 500°C showed two intense broad emission bands centered at around 382 nm and 435 nm. When the annealing temperature was further increased to 550°C the two bands were shifted to 372 and 442 nm respectively, however these bands were less intense than the bands observed in the samples annealed at 500°C. The lower wavelength band emission was ascribed to spin allowed electronic transitions from the $^1$D$_2$ state to the ground $^1$S$_0$ state and the emission bands appearing at higher wavelength could be assigned to spin-forbidden transitions from $^3$D$_j$ states to $^1$S$_0$ states.
8. Knoop surface hardness for silver-soda glass nanocomposite samples synthesized by vacuum deposition method at the annealing temperature of 550°C is 2.2 times the surface hardness of soda glass at a load of 49.03 mN. In case of nanocomposites samples synthesized by ion-exchange technique, surface hardness had been found to be 1.8 times the surface hardness of soda glass at the same annealing temperature.

9. Enhancement in surface hardness is more in case of silver-soda glass nanocomposite samples synthesized by vacuum deposition as compared to such nanocomposite samples synthesized by ion-exchange technique.

10. Electrical conductivity behaviour of silver-soda glass nanocomposite samples indicates that conductivity increased after insertion of the silver nanoparticles inside the soda glass matrix and conduction occurs via tunneling mechanism.

11. DC electrical conductivity of silver-soda glass nanocomposite samples synthesized by vacuum deposition is more than that of synthesized by ion-exchange method. This may be due to the fact that size of silver nanoparticles is greater in case of nanocomposite samples synthesized by vacuum deposition.

12. The extent of improvement in refractive indices, surface hardening and dc electrical conductivity had been found to be more in case of silver-soda glass nanocomposite samples synthesized by vacuum deposition as compared to nanocomposite samples synthesized by ion-exchange method. The possible reason behind this could be the bigger size of silver nanoparticles formed using vacuum deposition method.

4.3 Future Projections

The results of the experiment reported in this thesis lead to the possibilities of further work that will be conducted in future.

- A complete study related to depth profiling of silver nanoparticles embedded in the glass matrix using Rutherford back scattering (RBS) needs to be carried out to exploit the present study in a better manner.
• A systematic study related to the dielectric behaviour of the silver-soda glass nanocomposites need to be carried out which may provide an opportunity to utilize these nanocomposite in diverse range of applications.

• On the similar pattern we will synthesize copper-soda glass nanocomposites using vacuum deposition and ion-exchange methods and characterize those using different techniques.

• On the similar pattern we will synthesize gold-soda glass nanocomposites using vacuum deposition and ion-exchange methods and characterize those using different techniques.

• Non-linear optical properties of synthesized nanocomposites will be studied extensively to exploit their potential applications in opto-electronic devices.
Chapter-4 Summary, Conclusions and Scope of the Future Work

References


Chapter-4 Summary, Conclusions and Scope of the Future Work


